UNIT 3

ELECTROCHEMISTRY CONCEPTS

Points to Remember

Electrochemistry may be defined as the branch of chemistry which deals with the quantitative study of inter-relationship between chemical energy and electrical energy and inter-conversion of one form into another relationships between electrical energy taking place in redox reactions.

A cell is of two types :

I. Galvanic cell

II. Electrolytic cell

In Galvanic cell, the chemical energy of a spontaneous redox reaction is converted into electrical work.

In Electrolytic cell, electrical energy is used to carry out a non-spontaneous redox reaction.

1. Conductivity (k) :

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

where R is Resistance, l/A = cell constant (G*) and ρ is resistivity.

2. Relation between k and Λ_m

$$\Lambda_m = \frac{1000 \times k}{C}$$

where Λ_m is molar conductivity, k is conductivity and C is molar concentration.

Kohlrausch's law :

(a) In general, if an electrolyte on dissociation give v_+ cations and γ_- anions, then its limiting molar conductivity (Λ^o_m) is given by

$$\Lambda^o_m = \gamma_+ \lambda^o_+ + \gamma_- \lambda^o_-$$

Here, λ^o_+ and λ^o_- are the limiting molar conductivities of cation and anion respectively and v_+ and v_- are the number of cations and anions furnished by one formula unit of the electrolyte.

(b) Degree of dissociation (α) is given by :

$$\alpha = \frac{\Lambda^{c}_{m}}{\Lambda^{o}_{m}}$$

Here, Λ^{c}_{m} = is molar conductivity at the concentration C and Λ^{o}_{m} is limiting molar conductivity of the electrolyte.

(c) Dissociation constant (K) of weak electrolyte :

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{C\left(\frac{\Lambda^{c}_{m}}{\Lambda^{o}_{m}}\right)^2}{\left(1-\frac{\Lambda_{m}}{\Lambda^{o}_{m}}\right)}$$

Dry cell :

At anode (Oxidation)

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

At cathode (Reduction)

$$2NH_4^{+} + 2MnO_2 + 2e^{-} \rightarrow 2MnO\,(OH) + 2NH_3$$

Overall $\quad Zn\,(s) + 2NH_4^{+} + 2MnO_2 \rightarrow Zn^{2+} + 2MnO\,(OH) + 2NH_3$

Mercury cell :

At anode (Oxidation)

$$Zn\,(Hg) + 2OH^{-} \rightarrow ZnO\,(s) + H_2O + 2e^{-}$$

At cathode (Reduction)

$$HgO\,(s) + H_2O + 2e^{-} \rightarrow Hg\,(l) + 2OH^{-}$$

Overall $\quad Zn\,(Hg) + HgO\,(s) \rightarrow ZnO\,(s) + Hg\,(l)$

Lead storage cell

At anode (Oxidation)

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

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

At cathode (Reduction)

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

$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4\,(s)$$

Overall

$$Pb(s) + PbO_2\ (s) + 2H_2SO_4\ (aq) \underset{\text{Recharging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_{4(s)} + 2H_2O_{(l)}$$

3. Nernst Equation for electrode reaction :

$$M^{n+}\ (aq) + ne^- \longrightarrow M(s)$$

$$E = E^\theta - \frac{2.303RT}{nF}\log\frac{1}{\left[M^{n+}\right]} = E^\theta - \frac{0.059}{n}V\log\frac{1}{\left[M^{n+}\right]}$$

The cell potential of electrochemical reaction : $aA + bB \xrightarrow{ne^-} cC + dD$ is given by :

$$E_{cell} = E^\theta{}_{cell} - \frac{2.303RT}{nF}\log\left[Q_c\right] = E^\theta - \frac{0.059}{n}V\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

4. Relation between E^θ_{cell} and equilibrium constant (K_c) :

$$E^\theta{}_{cell} = \frac{2.303RT}{nF}\log\ K_c = \frac{0.059}{n}V\log\ K_c$$

5. $\Delta G^0 = -\,nF\,E^\theta_{cell}$

where ΔG^0 = standard Gibbs energy change and nF is the number of Faradays of charge passed. E^θ_{cell} is standard cell potential.

$$\mathbf{\Delta G^0 = -\,2.303\ RT\ log\ K_c}$$

Corrosion of metals is an electrochemical phenomenon.

In corrosion, metal is oxidized by loss of electrons to oxygen and formation of oxides.

At anode (Oxidation) :

$$2Fe\ (s) \longrightarrow 2Fe^{2+} + 4e^-$$

At cathode (Reduction) :

$$O_2\ (g) + 4H^+\ (aq) + 4e^- \longrightarrow 2H_2O$$

Atmospheric oxidation :

$$2Fe^{2+}\ (aq) + 2H_2O\ (l) + \tfrac{1}{2}O_2\ (g) \longrightarrow Fe_2O_3\ (s) + 4H^+\ (aq)$$

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. What is the effect of temperature on molar conductivity ?

Ans. Molar conductivity of an electrolyte increases with increase of temperature.

Q. 2. Why is it not possible to measure single electrode potential ?

Ans. Because the half cell containing single electrode cannot exist independently, as charge cannot flow on its own in a single electrode.

Q. 3. Name the factor on which emf of a cell depends.

Ans. Emf of a cell depends on following factors :

(a) Nature of reactants

(b) Concentration of solution in two half cells

(c) Temperature

Nickel-Cadmium cell :

At anode : $Cd\ (s) + 2OH^- \underset{Recharging}{\overset{Discharging}{\rightleftharpoons}} CdO\ (s) + 2e^-$

At cathode : $2Ni(OH)_3 + 2e^- \underset{Recharging}{\overset{Discharging}{\rightleftharpoons}} 2Ni(OH)_3 + 2OH^-$

Overall : $Cd\ (s) + 2Ni(OH)_3 \underset{Recharging}{\overset{Discharging}{\rightleftharpoons}} CdO\ (s) + 2Ni(OH)_2 + H_2O$

Fuel cell :

At anode : $2H_{2(g)} + 2OH^- \rightarrow 2H_2O + 2e^-$

At cathode : $O_{2\,(g)} + 2H_2O + 4e^- \rightarrow 4OH^-$

Overall : $2H_{2\,(g)} + O_2 \rightarrow 2H_2O\ (l)$

$E^o_{cell} = 0.9V$

Q. 4. What is the effect of temperature on the electrical conductance of metal ?

Ans. Temperature increases, electrical conductance decreases.

Q. 5. What is the effect of temperature on the electrical conductance of electrolyte ?

Ans. Temperature increases, electrical conductance increases.

Q. 6. What is the relation between conductance and conductivity ?

Ans. $\Lambda_m^c = \dfrac{k}{C}$

Q. 7. What is the Debye-Huckel-Onsagar equation ?

Ans. $\Lambda_m^c = \Lambda_m^o - A\sqrt{C}$

Q. 8. Reduction potentials of 4 metals A, B, C and D are – 1.66 V, + 0.34 V, + 0.80 V and – 0.76 V. What is the order of their reducing power and reactivity ?

Ans. A > D > B > C

Q. 9. Why does a dry cell become dead even if it has not been used for a long time ?

Ans. NH_4Cl is acidic in nature. It corrodes zinc container.

Q.10. Write the overall reaction taking place in rusting.

Ans. $2Fe + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$

Q.11. Write the reaction taking place in the cell : $Al/Al^{3+} || Cu^{2+}/Cu$

Ans. $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$

Q.12. Why Na cannot be obtained by the electrolysis of aqueous NaCl solution ?

Ans. Due to low reduction potential, Na^+ ions are not reduced at cathode. Instead, H^+ are reduced and H_2 is obtained.

Q.13. What is the use of platinum foil in the hydrogen electrode ?

Ans. It is used for the in flow and out flow of electrons.

Q.14. Why Λ_m^o for CH_3COOH cannot be determined experimentally ?

Ans. Molar conductivity of weak electrolytes keeps on increasing with dilution and does not become constant even at very large dilution.

Q.15. Why is it necessary to use a salt bridge in a galvanic cell ?

Ans. To complete the inner circuit and to maintain electrical neutrality of the electrolytic solutions of the half cells.

Q.16. Why does mercury cell gives a constant voltage throughout its life ?

Ans. This is because the overall cell reaction does not have any ionic can concentration in it.

Q.17. What is the role of $ZnCl_2$ in a dry cell ?

Ans. $ZnCl_2$ combines with the NH_3 produced to form a complex salt $[Zn(NH_3)_4]^{2+}$.

Q.18. Why does the conductivity of a solution decrease with dilution ?

Ans. Conductivity of a solution is dependent on the number of ions per unit volume. On dilution, the number of ions per unit volume decreases, hence the conductivity decreases.

Q.19. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Ans. Methane and methanol.

Q.20. How does the pH of Al-NaCl solution be affected when it is electrolysed ?

Ans. When Al-NaCl solution is electrolysed, H_2 is liberated at cathode, Cl_2 at anode and NaOH is formed in the solution. Hence pH of solution increases.

Q.21. Which reference electrode is used to measure the electrode potential of other electrodes.

Ans. SHE, whose electrode potential is taken as zero.

Q.22. Out of zinc and tin, which one protects iron better even after cracks and why ?

Ans. Zinc protects better because oxidation of zinc is greater but that of tin is less than that of iron.

Q.23. Define corrosion. What is the chemical formula of rust ?

Ans. Corrosion is the slow eating away of the surface of the metal due to attack of atmospheric gases. $Fe_2O_3.xH_2O$.

Q.24. What is the EMF of the cell when the cell reaction attains equilibrium ?

Ans. Zero.

Q.25. What is the electrolyte used in a dry cell ?

Ans. A paste of NH_4Cl.

SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. How can you increase the reduction potential of an electrode for the reaction :

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

Ans. Nernst equation is :

$$E_{M^{n+}/M} = E_{M^{n+}/M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

$E_{M^{n+}/M}$ can be increased by

(a) Increase in concentration of M^{n+} ions in solution.

(b) By increasing the temperature.

Q. 2. Calculate emf of the following cell at 298 K :

$$Mg(s) + 2Ag^+(0.0001M) \rightarrow Mg^{2+}(0.130\ M) + 2Ag(s)$$

[Given : $E^{\theta}_{cell} = 3.17$ V]

Ans. $n = 2$

The Nernst equation for the cell is :

$$E = E^{\theta} - \frac{0.059}{2}\log\frac{\left[Mg^{2+}\right]}{\left[Ag^{+}\right]^2}$$

$$= 3.17 - \frac{0.059}{2}\log\frac{.130}{(.0001)^2}$$

$$= 3.17 - 0.21 = 2.96V$$

Q. 3. Suggest a way to determine the Λ_m^{o} value of water.

Ans. $\Lambda_m^{\circ}\left(H_2O\right) = \Lambda_{m\,H^+}^{\circ} + \Lambda_{m\,OH^-}^{\circ}$

It can be determine from the value of Λ_m^{o} (HCl), Λ_m^{o} (NaOH) and Λ_m^{o} (NaCl). Then,

$$\Lambda_m^{o}(H_2O) = \Lambda_m^{o}(HCl) + \Lambda_m^{o}(NaOH) - \Lambda_m^{o}(NaCl)$$

Q. 4. How much electricity in term of Faraday is required to produce 40 gram of Al from Al_2O_3 ? (Atomic mass of Al = 27 g/mol)

Ans. $$Al^{3+} + 3e^- \rightarrow Al$$

27 gram of Al require electricity = 3F

40 gram of Al require electricity = $\frac{3F}{27} \times 40$

$= 4.44$ F

Q. 5. Predict the product of electrolysis of an aqueous solution of $CuCl_2$ with an inert electrode.

Ans. $CuCl_2\,(s) + Aq \rightarrow Cu^{2+} + 2Cl^-$

$$H_2O \rightarrow H^+ + OH^-$$

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

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

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

$$Cl^- \rightarrow \tfrac{1}{2}Cl_2 + 1e^-$$

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

Q. 6. Calculate Λ_m° for $CaCl_2$ and $MgSO_4$ from the following data :

$\Lambda_{m\,(Ca^{2+})}^{\circ}$ **= 119.0, Mg^{2+} = 106.0, Cl^- = 76.3 and SO_4^{2-} = 160.05 $cm^2\ mol^{-1}$**

Ans. $$\Lambda^{\circ}_{m(CaCl_2)} = \Lambda^{\circ}_{m(Ca^{2+})} + 2\Lambda^{\circ}_{m(Cl^-)}$$

$$= 119 + (2 \times 76.3) = 271.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^{\circ}_{m(MgSO_4)} = \Lambda^{\circ}_{m(Mg^{2+})} + 2\Lambda^{\circ}_{m(SO_4{}^{2-})}$$

$$= 106 + 160 = 266 \text{ S cm}^2 \text{ mol}^{-1}$$

Q. 7. If Λ°_m for $AgNO_3$, KCl and KNO_3 are 133.4, 149.9 and 144.9 S cm^2 mol^{-1}, calculate Λ°_m for AgCl.

Ans. 138.4 S cm^2 mol^{-1}

Q. 8. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Ans. $H^+ + e^- \rightarrow \frac{1}{2}H_2 \quad n = 1$

$$E = E^{o} - \frac{0.0591}{n}\log\frac{1}{[H^+]}$$

$$E = 0 - \frac{0.0591}{1} \times pH$$

$$E = -0.0591 \times 10$$

$$E = -0.591V$$

Q. 9. If a current of 0.5 amp flows through a metallic wire for 2 hours, how many electrons would flow through the wire ?

Ans. $q = i \times t = 0.5 \times 2 \times 60 \times 60 = 3600$ C

96500 Coulombs are equal to $6.022 \times 10^{23} e^-$

So, 3600 Coulombs $= \dfrac{6.022 \times 10^{23}}{96500} \times 3600 = 2.246 \times 10^{22}$ electrons

Q.10. How much electricity is required in Coulomb for the oxidation of 1 mole of FeO to Fe_2O_3 ?

Ans. $Fe^{2+} \rightarrow Fe^{3+} + 1e^-$

So, 1F = 1 × 96500 C = 96500 C

Q.11. The conductivity of a 0.20M solution of KCl at 298K is 0.0248 S cm-1. Calculate molar conductivity.

Ans. Molar conductivity $= \dfrac{k \times 1000}{M} = \dfrac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.2 \text{ mol L}^{-1}}$

$$= 124.0 \text{ S cm}^2 \text{ mol}^{-1}$$

Q.12. Define conductivity and molar conductivity for a solution of an electrolyte.

Ans. Conductivity is defined as ease with which current flows through electrolyte. It is reciprocal of specific resistance. Molar conductivity is conductance of all the ions produced by one mole of electrolyte when electrodes are at unit distance apart and have sufficient area of cross-section to hold electrolyte.

Q.13. The resistance of conductivity cell containing 0.001M KCl solution at 298K is 1500Ω. What is the cell constant if the conductivity of 0.001M KCl solution at 298K is 0.146×10^{-3} S cm^{-1}.

Ans. Cell constant = Conductivity × Resistance

$$= 0.146 \times 10^{-3} \text{ S cm}^{-1} \times 1500\Omega = 0.219 \text{ cm}^{-1}$$

Q.14. Indicate the reactions which take place at cathode and anode in fuel cell.

Ans. At cathode : $O_2\,(g) + 2H_2O + 4e^- \longrightarrow 4OH^-\,(aq)$

At anode : $2H_2\,(g) + 4OH^-\,(aq) \longrightarrow 4H_2O + 4e^-$

The overall reaction is : $2H_2\,(g) + O_2\,(g) \longrightarrow 4H_2O\,(l)$

Q.15. Explain Kohlrausch's law of independent migration of ions.

Ans. It states that at infinite dilution, molar conductivity of an electrolyte is equal to sum of contributions due to cation as well as anion.

$$\Lambda^{\infty}_{m(Na_2SO_4)} = 2\Lambda^{\circ}_{m(Na^+)} + \Lambda^{\infty}_{m(SO_4^{2-})}$$

Q.16. Write the electrode reactions for anode and cathode in a mercury cell.

Ans. At anode : $Zn\,(amalgam) + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$

At cathode : $HgO\,(s) + H_2O\,(l) + 2e^- \longrightarrow Hg\,(l) + 2OH^-\,(aq)$

The overall reaction is : $Zn\,(amalgam) + HgO\,(s) \longrightarrow ZnO\,(s) + Hg\,(l)$

Q.17. The standard reduction potential for the Zn^{2+} (aq)/Zn (s) half cell is – 0.76V. Write the reactions occurring at the electrodes when coupled with standard hydrogen electrode (SHE).

Ans. At anode : $Zn\,(s) \longrightarrow Zn^{2+}\,(aq) + 2e^-$

At cathode : $2H^+ + 2e^- \longrightarrow H_2\,(g)$

$$Zn\,(s) + 2H^+\,(al) \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)$$

Q.18. Calculate the electrode potential of a copper wire dipped in 0.1M $CuSO_4$ solution at 25ºC. The standard electrode potential of copper is 0.34 Volt.

Ans. The electrode reaction written as reduction potential is

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad n = 2$$

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{1}{[Cu]} = 0.34 - \frac{0.0591}{2}\log\frac{1}{0.1} = 0.3104 \text{ V}$$

Q.19. Two metals A and B have reduction potential values – 0.76 V and + 0.34 V respectively. Which of these will liberate H_2 from dil. H_2SO_4 ?

Ans. Metal having higher oxidation potential will liberate H_2 from H_2SO_4. Thus, A will liberate H_2 from H_2SO_4.

Q.20. How does conc. of sulphuric acid change in lead storage battery when current is drawn from it ?

Ans. Concentration of sulphuric acid decreases.

Q.21. What type of a battery is lead storage cell ? Write the anode and cathode reaction and overall reaction occurring in a lead storage battery during discharging and recharging of cell.

Ans. It is a secondary cell.

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

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

$$Pb\,(s) + PbO_2\,(s) + 2H_2SO_4 \underset{\text{Recharging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_{4(s)} + 2H_2O\,(l)$$

Q.22. Why does the cell potential of mercury cell remain constant throughout its life ?

Ans. This is because the overall cell reaction does not involve any ion in the solution whose concentration changes during its life time.

Q.23. Why is alternating current used for measuring resistance of an electrolytic solution ?

Ans. The alternating current is used to prevent electrolysis so that the concentration of ions in the solution remains constant.

Q.24. Consider a cell given below :

$$\mathbf{Cu|Cu^{2+}\,||\,Cl^{-1}|Cl_2\,(Pt)}$$

Write the reaction that occur at anode and cathode of the cell

Ans. Anode : $Cu \rightarrow Cu^{2+} + 2e^-$

Cathode : $Cl_2 + 2e^- \rightarrow 2Cl^{-1}$

Q.25. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

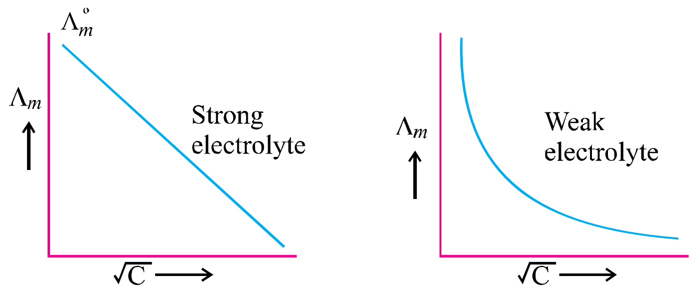
Ans. Methane and Ethane.

Q.26. E^0 values of MnO_4^-, Ce^{4+} and Cl_2 are 1.507, 1.61 and 1.358 V respectively. Arrange these in order of increasing strength as oxidizing agent.

Ans. $Cl_2 < MnO_4^- < Ce^{4+}$

Q.27. Draw a graph between Λ_m° and $\sqrt{C}$ for strong and weak electrolyte.

Ans.



Q.28. The conductivity of 0.02M solution of NaCl is 2.6×10^{-2} S cm^{-1}. What is its molar conductivity ?

Ans.

$$k = 2.6 \times 10^{-2} \text{ S cm}^{-1}$$

$$C = 0.02\text{M}$$

$$\Lambda_m = \frac{k \times 1000}{C(M)}$$

$$= \frac{2.6 \times 10^{-2} \times 1000}{0.02}$$

$$= \frac{26 \times 100}{0.02 \times 100} = \frac{26 \times 10^2}{2}$$

$$= 13 \times 10^2 \text{ S cm mol}^{-1}$$

Q.29. Give products of electrolysis of an aqueous solution of $AgNO_3$ with silver electrode.

Ans. At anode : $Ag(s) \rightarrow Ag^+ + e^-$

At cathode : $Ag^+ + e^- \rightarrow Ag(s)$

SHORT ANSWER-II TYPE QUESTIONS

Q. 1. A solution of $CuSO_4$ is electrolysed for 10 mins. with a current of 1.5 amperes. What is the mass of copper deposited at the cathode ?

Ans.

$$I = 1.5 \text{ Ampere}$$

$$\text{Time} = 10 \times 60\text{s} = 600\text{s}$$

$$Q = I \times t$$

$$= 1.5 \times 600 = 900 \text{ C}$$

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

2F amount of electricity deposit copper = 63.5 g

900 C amount of electricity deposit copper = $\dfrac{63.5 \times 900}{2 \times 96500}$

= 0.296 g

Q. 2. Depict the galvanic cell in which the reaction

$$\mathbf{Zn\ (s) + 2Ag^+ \rightarrow Zn^{2+} + 2Ag\ (s)}$$

takes place. Further show :

(a) Which of the electrode is negatively charged ?

(b) The carriers of the current in the cell.

(c) Individual reaction at each electrode.

Ans. $Zn\ (s)|Zn^{2+}\ (aq)\ ||\ Ag^+\ (aq)|Ag\ (s)$

(a) Zn electrode (anode)

(b) Ions are carriers of the current in the cell.

(c) At anode :

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

At cathode :

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

Q. 3. The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is $\mathbf{0.146 \times 10^{-3}\ S\ cm^{-1}}$?

Ans. Cell constant $= k \times R$

$= 0.146 \times 10^{-3} \times 1500$

$= 0.219\ cm^{-1}$

Q. 4. Predict the products of electrolysis in each of the following :

(a) An aqueous solution of $AgNO_3$ with platinum electrodes.

(b) An aqueous solution of $CuCl_2$ with Pt electrodes.

Ans. (a) At anode (Oxidation)

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

At cathode (Reduction)

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

(b) At anode (Oxidation)

$$Cl^- - e^- \rightarrow Cl\ (g)$$

$$Cl + Cl \rightarrow Cl_2$$

At cathode (Reduction)

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

Q. 5. The standard reduction potential for Cu^{2+}/Cu is 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1×10^{-19}.

Ans.

$$pH = 14$$

$$[H^+] = 10^{-14} \qquad \{\because pH = -\log [H^+]\}$$

$$K_w = [H^+][OH^-]$$

$$[OH^-] = \frac{k_w}{H^+} = \frac{10^{-14}}{10^{-14}} = 1$$

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

$$K_{sp} = [Cu^{2+}][OH^-]^2$$

$$1 \times 10^{-19} = [Cu^{2+}](1)^2$$

$$[Cu^{2+}] = 1 \times 10^{-19}$$

For the cell reaction,

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

$$E = E^0 - \frac{0.059}{2}\log\frac{1}{\left[Cu^{2+}\right]}$$

$$= 0.34 - \frac{0.059}{2}\log\frac{1}{1\times10^{-19}}$$

$$= 0.34 - \frac{0.059}{2}\times 19 = -0.22\ V$$

Q. 6. Determine the values of equilibrium constant K_c and ΔG^θ for the following reaction :

$$\mathbf{Ni\ (s) + 2Ag^+\ (aq) \rightarrow Ni^{2+}\ (aq) + 2Ag\ (s) \qquad E^\theta = 1.05\ V}$$

Ans.

$$\Delta G^\theta = -nFE^\theta_{cell}$$

$$n = 2,\ E^\theta_{cell} = 1.05\ V$$

$$F = 96500\ C\ mol^{-1}$$

$$\Delta G^\theta = -2 \times 1.05 \times 96500$$

$$= -202.650\ kJ$$

$$\Delta G^\theta = -RT \ln K_c$$

$$\ln K_c = -\frac{\Delta G^\theta}{RT} = \frac{-202.650 \times 10^3}{8.314 \times 298}$$

$$K_c = 3.32 \times 10^{35}$$

Q. 7. The K_{sp} for AgCl at 298 K is 1.0×10^{-10}. Calculate the electrode potential for Ag^+/Ag electrode immersed in 1.0M KCl solution. Given $E^\theta_{Ag^+/Ag} = 0.80$ V.

Ans. $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$

$$K_{sp} = [Ag^+][Cl^-]$$

$$[Cl^-] = 1.0 \text{ M}$$

$$[Ag^+] = \frac{k_{sp}}{[Cl^-]} = \frac{1 \times 10^{-10}}{1} = 1 \times 10^{-10} \text{ M}$$

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

$$E = E^\theta - \frac{0.059}{1} \log \frac{1}{[Ag^+]}$$

$$= 0.80 - \frac{0.059}{1} \log \frac{1}{10^{-10}}$$

$$= 0.80 - 0.059 \times 10 = 0.21 \text{ V}$$

Q. 8. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500ºC. The free energy change for the decomposition reaction :

$$\mathbf{\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2 \text{ is } \Delta G = +960 \text{ kJ, F} = 96500 \text{ C mol}^{-1}.}$$

Ans.

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$$

$$n = \frac{6 \times 2}{3} = 4e^-$$

$$\Delta G = -nFE$$

$$\Delta G = 960 \times 10^3 \text{ J}, n = 4, F = 96500 \text{ C mol}^{-1}$$

$$960 \times 10^3 = -4 \times 96500 \times E$$

$$E = -2.487 \text{ V}$$

Minimum potential difference needed to reduce $Al_2O_3 = -2.487$ V.

Q. 9. Two electrolytic cells containing silver nitrate solution and copper sulphate solution are connected in series. A steady current of 2.5 amp was passed through them till 1.078 g of Ag were deposited. How long did the current flow ? What weight of copper will be deposited ? (Ag = 107.8 u, Cu = 63.5 u)

Ans.

$$w = z \times i \times t$$

$$t = \frac{w}{z \times i}$$

$$t = \frac{1.078 \times 1 \times 96500}{107.8 \times 2.5} = 386 \text{ seconds}$$

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

$$w = \frac{63.5}{2 \times 96500} \times 2.5 \times 386 = 0.3175 \text{ gram}$$

Q.10. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 amp for 20 minutes. What mass of the nickel will be deposited at the cathode ? (Ni = 58.7 u)

Ans.

$$w = z \times i \times t$$

$$z = \frac{58.7}{2 \times 96500}$$

$$w = 1.825 \text{ gram}$$

Q.11. The cell in which the following reaction occurs :

$$\mathbf{2Fe^{3+}\,(aq) + 2I^{-}\,(aq) \rightarrow 2Fe^{2+}\,(aq) + I_2\,(s) \text{ has } E^0_{cell} = 0.236\ V.}$$

Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Ans.

$$n = 2$$

$$\Delta G^o = -nFE^0_{cell} = -2 \times 96500 \times 0.236\ J = -45.55\ kJ/mol$$

$$\Delta G^o = -2.303\ RT \log K_c$$

$$\log K_c = \frac{\Delta G^o}{-2.303RT} = \frac{45.55 \times 10^3}{2.303 \times 8.314 \times 298} = 7.983$$

$$K_c = \text{antilog}\,(7.983) = 9.616 \times 10^7$$

Q.12. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given Λ^o (H^+) = 349.6 S cm^2 mol^{-1}, Λ^o ($HCOO^-$) = 54.6 S cm^2 mol^{-1}.

Ans. $\Lambda^o_m\,(HCOOH) = \Lambda^o_m\,(H^+) + \Lambda^o_m\,(HCOO^-)$

$= 349.6 + 54.6\ S\ cm^2\ mol^{-1} = 404.2\ S\ cm^2\ mol^{-1}$

$\Lambda^o_m = 46.1\ S\ cm^2\ mol^{-1}$

$HCOOH \rightleftharpoons HCOO^- + H^+$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{46.1}{404.2} = 0.114$$

Initial conc.	$C\ mol\ L^{-1}$	0	0
At equil.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025\times(0.114)^2}{1-0.114}$$

$$= 3.67\times10^{-4}$$

Q.13. Calculate the standard cell potentials of galvanic cells in which the following reaction take place :

$$\mathbf{2Cr\,(s) + 3Cd^{2+}\,(aq) \rightarrow 2Cr^{3+}\,(aq) + 3Cd\,(s)}$$

Also calculate ΔG^o and equilibrium constant of the reaction.

Ans. $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

$= -0.40 - (-0.74) = 0.34\ V$

$\Delta G^o = -nFE^0_{cell} = -6\times96500\times0.34 = -196860$

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

$-\Delta G^o = 2.303\ RT\log K_c$

$196860 = 2.303\times8.314\times298\log K_c$

Or $\log K_c = 34.5014$

$K_c = \text{antilog}\ 34.5014 = 3.192\times10^{34}$

Q.14. Calculate the potential of the following cell Sn^{4+} (1.5 M) + Zn $\rightarrow$ Sn^{2+} (0.5 M) + Zn^{2+} (2M).

Given : $E^0_{Sn^{4+}/Sn^{2+}} = 0.13V,\ E^0_{Zn^{2+}/Zn} = -0.76V$

Will the cell potential $\uparrow$ or $\downarrow$ if the concentration of Sn^{4+} is increased ?

Ans.
$$E_{cell} = E^\theta_{cell} - \frac{0.0591}{n}\log\frac{[Sn^{2+}][Zn^{2+}]}{[Sn^{4+}][Zn]}$$

$$= 0.89 - \frac{0.0591}{2}\log\frac{0.5\times2}{1.5\times1}$$

$$= 0.89 - \frac{0.0591}{2}\log\frac{1}{1.5}$$

$$= 0.895 \text{ V}$$

On increasing the concentration of Sn^{4+}, EMF of the cell will increase.

Q.15. E° (Cu^{2+}/Cu) and E° (Ag^+/Ag) is + 0.337 V and + 0.799 V respectively. Make a cell whose EMF is +ve. If the concentration of Cu2+ is 0.01M and E_{cell} at 25°C is zero, calculate the concentration of Ag^+.

Ans. Cu is more reactive than silver, so that the cell is as Cu/Cu^{2+} (0.01M) || Ag^+(C)/Ag or cell reaction

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{\left[Cu^{2+}\right]\left[Ag\right]^2}{\left[Cu\right]\left[Ag^+\right]^2}$$

$$= E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{(0.01)\times 1^2}{1\times\left[Ag^+\right]^2}$$

Or $\quad [Ag^+] = 1.47 \times 10^{-9}$ M

Q.16. Calculate the potential of the cell at 298 K :

Cd/Cd^{2+} (0.1M) || H^+ (0.2M)/Pt, H_2 (0.5 atm)

Given E° for Cd^{2+}/Cd = – 0.403 V, R = 8.314 J^{-1} mol^{-1}, F = 96500 C mol^{-1}.

Ans. The cell reaction is Cd + $2H^+$ (0.2M) $\rightarrow$ Cd^{2+} (0.1M) + H_2 (0.5 atm)

$$E^{\circ}_{cell} = 0 - (-0.403) = +0.403 \text{ V}$$

$$E_{cell} = 0.403 - \frac{2.303RT}{nF}\log\frac{\left[Cd^{2+}\right]\times P_{H_2}}{\left[Cd\right]\left[H^+\right]^2}$$

$$= 0.403 - \frac{2.303\times 8.314\times 298}{2\times 96500}\log\frac{0.1\times 0.5}{(0.2)^2}$$

$$E_{cell} = 0.403 - 0.003 = 0.40 \text{ V}$$

Q.17. The electrical resistance of a column of 0.05M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

Ans. Diameter = 1 cm, radius = 0.5 cm

Area $= \pi r^2 = 3.14 \times (0.5)^2 = 0.785$ cm2

$$\rho = \frac{R \times A}{l} = \frac{5.55 \times 10^3 \times 0.785}{50}$$

$$= 87.135 \text{ ohm cm}$$

$$\text{Conductivity (k)} = \frac{1}{\rho} = \frac{1}{87.135} = 0.01148 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$= 0.01148 \text{ ohm cm}$$

$$\text{Molar conductivity } \Lambda_m^c = \frac{K \times 1000}{M} = \frac{0.01148 \times 1000}{0.05}$$

Q.18. The measured resistance of a conductance cell containing 7.5 × 10^{-3} M solution of KCl at 25ºC was 1005 ohms. Calculate (a) specific conductance, (b) molar conductance of the solution.

Ans. 1.247×10^{-3} S cm^{-1}, 165.83 S cm^2 mol^{-1}

Q.19. Conductivity of saturated solution of $BaSO_4$ at 315 K is 3.648 × 10^{-6} ohm^{-1} cm^{-1} and that of water is 1.25 × 10^{-6} ohm^{-1} cm^{-1}. Ionic conductance of Ba^{2+} and SO_4^{2-} are 110 and 136.6 ohm^{-1} cm^2 mol^{-1} respectively. Calculate the solubility of $BaSO_4$ in g/L.

Ans. $$\Lambda^o_m (BaSO_4) = \Lambda^o_m Ba^{2+} + \Lambda^o_m SO_4^{2-} = 110 + 136.6 = 246.6 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$K_{BaSO4} = K_{BaSO4} \text{ (solution)} - K_{water} = 3.648 \times 10^{-6} - 1.25 \times 10^{-6}$$

$$= 2.398 \times 10^{-6} \text{ S cm}^{-1}$$

$$\Lambda_m^c = \frac{K \times 1000}{\text{Solubility}} = \frac{2.398 \times 10^{-6} \times 1000}{246.6} = 9.72 \times 10^{-6} \text{ mol/L}$$

$$= 9.72 \times 10^{-6} \times 233 = 2.26 \times 10^{-3} \text{ g/L}$$

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Conductivity of 0.00241M acetic acid is 7.896 × 10^{-5} S cm^{-1}. Calculate its molar conductivity and if Λ^o_m for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant ?

Ans. $$\Lambda^o_m = \frac{k \times 1000}{M}$$

$$= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.00241 \text{ mol L}^{-1}}$$

$$= 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{32.76}{390.5} = 8.39 \times 10^{-2}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.00241 \times \left(8.39 \times 10^{-2}\right)^2}{1 - 8.39 \times 10^{-2}}$$

$$= 1.86 \times 10^{-5}$$

Q. 2. Three electrolytic cells A, B, C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively all connected in series. A steady current of 1.5 amperes was passed through then until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow ? What mass of copper and of zinc were deposited ?

Ans. $$Ag^+ + e^- \rightarrow Ag\ (s)$$

108 g of silver is deposited by 96500 C.

$$1.45 \text{ g silver is deposited by} = \frac{96500 \times 1.45}{108}$$

$$= 1295.6 \text{ C}$$

$$Q = I \times t$$

$$1295.6 = 1.5 \times t$$

$$t = \frac{1295.6}{1.5} = 863 \text{ s}$$

In cell A, the electrode reaction is

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

$$\text{2F of electricity deposit Zn} = 65.3 \text{ g}$$

$$\text{1295.6 of electricity deposit Zn} = \frac{65.3 \times 1295.6}{2 \times 96500}$$

$$= 0.438 \text{ g}$$

In cell C, the electrode reaction is

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

$$\text{2F of electricity deposit Cu} = 63.5 \text{ g}$$

$$\text{1295.6 of electricity deposit Cu} = \frac{63.5 \times 1295.6}{2 \times 96500}$$

$$= 0.426 \text{ g}$$

Q. 3. (a) Define Kohlraush's law.

(b) Suggest a way to determine the Λ^o_m for CH_3COOH.

(c) The Λ^o_m for sodium acetate, HCl, NaCl are 91.0, 425.9 and 126.4 S cm^2 mol^{-1} respectively at 298 K. Calculate Λ^o_m for CH_3COOH.

Ans. (a) The molar conductivity at a infinite dilution for a given salt can be expressed as the sum of the individual contribution from the ions of electrolyte.

$$E = 0.36 - \frac{0.059}{2}\log\frac{0.004}{0.2}$$

$$= 0.36 - \frac{0.059}{2}\log 2\times10^{-3}$$

$$= 0.36 - \frac{0.059}{2}(-2.6990)$$

$$= 0.36 + 0.08 = 0.44 \text{ V}$$

(b) $\Lambda^o\ CH_3COOH = ?$

$$\Lambda^o\ CH_3COO^- + \Lambda^o\ H^+ = \Lambda^o\ CH_3COO^- + \Lambda^o\ Na^+ + \Lambda^o\ H^+ + \Lambda^o\ Cl^- - \Lambda^o\ Na^+ - \Lambda^o\ Cl^- \quad ...(i)$$

$$\Lambda^o_m\ CH_3COOH = \Lambda^o\ CH_3COONa + \Lambda^o\ HCl - \Lambda^o\ NaCl$$

(c) $\Lambda^o_m\ CH_3COOH = \Lambda^o\ CH_3COONa + \Lambda^o\ HCl - \Lambda^o\ NaCl$

$$= 91.0 + 425.9 - 126.4$$

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

Q. 4. (a) Define weak and strong electrolytes.

(b) The E^θ values corresponding to the following two reduction electrode processes are :

(i) $Cu^+/Cu = 0.52$ V (ii) $Cu^{2+}/Cu^+ = 0.16$ V

Formulate the galvanic cell for their combination. Calculate the cell potential and ΔG^o for the cell reaction.

Ans. (a) **Weak electrolyte :** The substance which partially ionized in solution is known as weak electrolyte. Example : NH_4OH.

Strong electrolyte : The substance which completely ionized in solution is known as strong electrolyte. Example : NaCl.

(b)

$$Cu^+ + e^- \rightarrow Cu$$

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

Overall cell reaction : $2Cu^+ \rightarrow Cu + Cu^{2+}$

$$Cu^{+}/Cu^{2+}||Cu^{+}/Cu$$

$$E^{\theta}_{cell} = 0.52 - 0.16 = 0.36 \text{ V}$$

$$\Delta G^{o} = -nFE^{\theta}_{cell}$$

$$= -1 \times 96500 \times 0.36$$

$$= -34740 \text{ J mol}^{-1}$$

Q. 5. (a) Give anode and cathode reaction of mercury cell.

(b) Calculate emf of the cell for the cell reaction at 25°C for the cell :

$$\mathbf{Zn/Zn^{2+}\ (0.0004M)\ ||\ Cd^{2+}\ (.2M)/Cd\ (s)}$$

Given : $E^{o}_{cell} = 0.36$ V

Ans. (a) At anode : $Zn + 2OH^{-} \rightarrow ZnO + 2e^{-} + H_2O$

At cathode : $HgO\ (s) + H2O + 2e^{-} \rightarrow Hg\ (l) + 2OH^{-}$

(b) $Zn + Cd^{2+} \rightarrow Zn^{2+} + Cd$

$$n = 2$$

According to Nernst equation :

$$E_{cell} = E^{\circ}_{cell} - \frac{0.059}{n} \log \frac{[Zn^{2+}]}{[Cd^{2+}]}$$

VALUE BASED QUESTIONS (4 Marks)

Q. 1. People are advised to limit the use of fossil fuels resulting in Green House Effect leading to a global rise in temperature of earth. Hydrogen provides an ideal alternative in fuel cells.

(a) Write electrode reactions in H_2-O_2 fuel cells.

(b) Can we use CH_4 in place of H_2 ? If yes, then write the electrode reaction at anode.

(c) How is green house effect reduced by the use of fuel cells ?

(d) Write the values associated with preference to fuel cells.

Q. 2. In Apollo space programs, H_2-O_2 fuel cell was used.

(a) Explain why fuel cell is preferred in space programme.

(b) Mention the values associated with the decision of using fuel cells.

(c) Can we use the fuel cells in automobiles ?

(d) How can we increase efficiency of fuel cells ?

Q. 3. Ira, a student of science, went with her father to buy a battery for their invertor and camera. They found two types of batteries, one a lead storage and other a Ni-Cd storage battery. Later was more expensive but lighter in weight. Ira insisted to purchase costlier Ni-Cd battery.

(a) In your opinion, why Ira insisted for Ni-Cd battery ? Give reasons.

(b) Write the values associated with above decision.

(c) Write overall cell reaction during the discharge.

(d) Can this cell be sealed unlike lead storage cell ?

Q. 4. Shyam bought a dry cell which was very old. He puts it in torch. The torch did not glow. He found that the cell was dead.

(a) Why did this happen ?

(b) Write the overall cell reaction during discharge.

(c) What value did you derive from it ?

(d) Why is dry cell not rechargeable ?

Q. 5. Sakshi, a student of Chemistry of class XII, found that some kitchenwares made of iron or copper were galvanized. Sakshi told her mother not to use these cookwares and advised her mother to get them plated with tin instead of zinc.

(a) Why Sakshi was against using the cookwares plated with zinc ?

(b) What would happen if cookwares plated with zinc were used in kitchen ?

(c) Can the cookwares be plated with tin ?

(d) What values are associated with the advice of Sakshi ?

(e) What would happen if the tin plating on cookwares made of copper or iron is broken ?