Unit - 3

ELECTROCHEMISTRY

VSA QUESTIONS (1 - MARK QUESTIONS)

1. What is a galvanic cell?
2. Give the cell representation for Daniell Cell.
3. Mention the purpose of salt-bridge placed between two half-cells of a galvanic cell?
4. Give the condition for Daniell Cell in which there is no flow of electrons or current.
5. How is electrode potential different from cell potential?
6. Can you store zinc sulphate solution in a copper container? Give suitable reason. ($E^{\theta}Zn^{2+}/Zn$ = – 01.76V, E^{θ} Cu^{2+}/Cu = 0.34v)
7. How does electrochemical series help us in predicting whether a redox reaction is feasible or not?
8. Write Nernst equation for the electrode reaction. $M^{n+}_{(aq)} + ne^{-} \rightarrow M_{(s)}$ at 298 K and 1 bar pressure.
10. List the two factors that influence the value of cell potential of a galvanic cell.
11. How is equilibrium constant of a reaction related to standard cell potential?
12. Write the relation between E^{θ}cell and equilibrium constant (K) of cell reaction.
13. Define cell constant. Write the SI unit of cell constant.
14 How does specific conductance or conductivity of electrolytic solution vary with temperature?
15. What is the SI unit of (i) Conductance; (ii) Conductivity.
16. Represent a concentration cell with a suitable example.

17. State one difference between a primary battery and secondary battery.

*18. Galvanized iron does not corrode even if the coating of zinc is broken. Explain why?

(Given : $\left(E^{\theta}\ Fe^{2+}/_{Fe} = -0.44V;\ E^{\theta}Zn^{2+}/_{Zn} = -0.76V\right)$

19. Write the unit of Faraday constant.

*20. Write the name of a chemical substance which is used to prevent corrosion.

[**Ans. :** Bisphenol]

21. Show is the direction of flow of electrons in the following cell :

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

22. Rusting of iron becomes quicker in saline water?

*23. Two metals A and B have reduction potential values of – 0.25V and 0.80V respectively. Which of these will liberate hydrogen gas from dilute H_2SO_4?

24. Express the relation between conductivity and molar conductivity.

25. Name the cell which was used in Apollo space programme.

26. How many faradays are required to oxidise 1 mole of H_2O to O_2.

[**Ans. :** 2F]

SA (I) TYPE QUESTIONS (2 - MARK QUESTIONS)

1. List two points of difference between metallic conductance and electrolytic conductance.

2. List two points of difference between electrochemical cell and electrolytic cell.

3. List two factors which affect the conductivity of ionic solutions.

4. A conventional method of representing a Daniel cell is :

   $Zn\ (s)\ |\ Zn^{2+}\ (1M)\ ||\ Cu^{2+}\ (1M)\ |\ Cu\ (s)$.

   (i) Draw a diagram of the cell and mark anode and cathode as current is drawn from the cell.

   (ii) Write the reactions taking place at the cathode and the anode during the operation of Daniel cell.

*5. Suggest a method to determine the Λ°_{m} value of water.

6. Write the cell reaction which occur in the lead storage battery (a) when the battery is in use (b) when the battery is on charging.

7. Why absolute value of electrode potential cannot be determined?

8. Account for the fact that when chlorine is passed through a fluoride solution, no reaction takes place. $\left(\text{Given } E^{\theta}\ F_2 \,/\, 2F^- = 2.87V;\ E^{\theta}_{Cl_2/2Cl^-}\ Cl_2 \,/\, 2Cl^- = 1.36V\right)$

9. Copper does not dissolve in HCl (*aq*) but dissolves in HNO_3 (aq) producing Cu^{2+} ions. Explain the difference in behaviour.

   [Given $E^{\theta}_{Cu^{2+}/Cu^-} = 0.34V$; $E^{\theta}_{Cl_2/2Cl^-} = 1.36V$ and $NO_3^- + 4H^+\ 3e^- \rightarrow$ NO (g) + $2H_2O$, $E^{\theta}_{NO_3^-/NO} = 0.97V$]

10. Explain the following observations :
    (a) The product of electrolysis of molten NaCl are sodium metal and chlorine gas.
    (b) The product of electrolysis of aqueous sodium chloride solution are NaOH, Cl_2 and H_2.

11. What are fuel cells? Describe the principle and overall reaction involved in the working of hydrogen–oxygen fuel cell or $CH_3OH - O_2$ fuel cell.

12. Explain the meaning of the terms
    (a) Ionic mobility. (b) Overvoltage.

*13. Some standard reduction potential are as given below :

Half Cell	E^{θ} Value
F_2/F^-	2.9V
Ag^+/Ag	0.8V
Cu^+/Cu	0.5V
Fe^{2+}/Fe	–0.4V
Na^+/Na	–2.7V
K^+/K	–2.9V

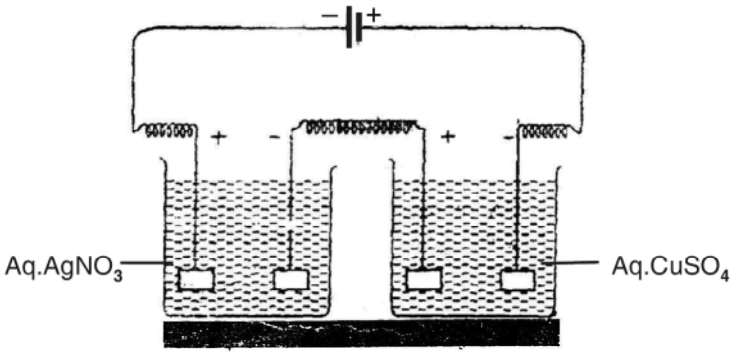
    (a) Arrange oxidising agents in order of increasing strength.
    (b) Which of these oxidising agents will oxidise Cu to Cu^+ under standard conditions?

14. Account for the following observations :

(a) In a dry cell, the build up of ammonia around the carbon cathode should disrupt the electric current, but in practice this does not happen.

(b) Ordinary dry cells are not rechargeable.

*15. The following figure shows two electrolytic cells connected in series.



(a) How much electricity is required for the reduction of 1 mole of Ag^+ ions to Ag?

(b) If three faradays of electricity is passed through these cells, what is the ratio of cations Ag^+ and Cu^{2+} deposited on cathodes?

[**Ans. :** (a) 1F, (b) 2:1]

16. You are aquainted with the construction and working of a lead storage battery. Give the plausible reasons for these facts.

(a) There is only a single compartment unlike other electrochemical cells which have two compartments

(b) Addition of water is necessary from time to time for maintenance

SA (II) TYPE QUESTIONS (3 - MARK QUESTIONS)

1. Using the standard electrode potential, predict the reaction, If any that occurs between the following :

   (a) $Fe^{3+}(aq)$ and $I^{-}(aq)$, $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77V$; $E^{\circ}_{I_2/2I^{-}} = 0.54V$

   (b) $Fe^{3+}(aq)$ and $Br^{-}(aq)$, $E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77V$; $E^{\circ}_{Br_2/2Br^{-}} = 1.07V$

   (c) $Ag^{+}(aq)$ and $Cu(s)$, $E^{\circ}_{Cu^{2+}/Cu} = 0.34V$; $E^{\circ}_{Ag^{+}/Ag} = 0.8V$

2. 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?

3. Describe the composition of anode and cathode in a mercury cell. Write the electrode reactions for this cell. Why does it provide constant voltage throughout its life?

4. Give reasons for :

   (a) For a weak electrolyte, its molar conductivity of dilute solution increases as the concentration of solution is decreased.

   (b) Molar conductivity of a strong electrolyte like KCl decreases almost linearly while increasing concentration?

   (c) It is not easy to determine Λ°_{m} of a weak electrolyte by extrapolation of $\sqrt{c}$ υs Λ_m curves?

5. (a) Write the mechanism of the corrosion of metals.

   (b) How is underground iron pipe is protected from corrosion?

6. Formulate the galvanic cell in which the following reaction takes place :

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

   State

   (a) Which one of its electrodes is negatively charged?

   (b) The reaction taking place at each of its electrode.

   (c) The direction of current within this cell.

*7. The standard reduction potentials are as given below :–

Half Cell	E° Value
$Zn(OH)_2/Zn$	– 1.245 V
$Mg(OH)_2/Mg$	– 2.690 V
$Fe(OH)_2/Fe$	– 0.877 V
$Fe(OH)_3/Fe$	– 2.30 V

Under standard conditions :

(a) Which is the strongest reducing agent?

(b) Which reducing agent could reduce $Zn(OH)_2$ to Zn?

(c) Which reducing agent could reduce $Fe(OH)_2$ to Fe?

LONG ANSWER TYPE QUESTIONS (5 MARKS)

1. (a) Explain with example the terms weak and strong electrolytes.

(b) Calculate the emf of the cell

$$Mg\,|Mg^{2+}(0.001M\,\|Cu^{2+}(0.001M)\,|Cu$$

$$E^{\varnothing}_{Cu^{2+}/Cu} = 0.34V; E^{\varnothing}_{Mg^{2+}/Mg} = -2.375V$$

[**Ans. :** 2.651 V]

2. (a) Explain Kohlrausch law of independent migration of ions. Mention two applications of this law.

(b) The conductivity of 0.001M CH_3COOH is 4.95×10^{-5} Scm^{-1}. Calculate its dissociation constant. Given for acetic acid Λ°_m is 390.5 S cm^2 mol^{-1}. [**Ans. :** = 0.126]

3. (i) Define molar conductivity. Draw the plots showing the variation of molar conductivity for strong and weak electrolyte with square root of concentation.

(ii) Resistance of a solution (A) is 50 ohm and that of solution (B) is 100 ohm, both solutions being taken in the same conductivity cell, if equal volumes of solutions (A) and (B) are mixed, what will be the resistance of the mixture, using the same cell? Assume that there is no increase in the degree of dissociation of (A) and (B) on mixing. [**Ans. :** 66.66 ohm]

[**Hint. :** k = Conductivity, y = Cell constant]

$k_1 = \frac{1}{50}\, y,\ k_2 = \frac{1}{100}\, y$: and specific conductance of mixture is given by

$$= \frac{k_1 + k_2}{2}$$

$$\frac{k_1 + k_2}{2} = \frac{1}{R} \times y,\ \frac{1}{2}\left[\frac{y}{50} + \frac{y}{100}\right] = \frac{1}{R} \times y \Rightarrow R = 66.66 \text{ ohm}$$

4. (a) State Faraday's first and second laws of electrolysis.

   (b) Silver is deposited on a metallic vessel of surface area 800 cm^2 by passing current of 0.2 ampere for 3 hours. Calculate the thickness of silver deposited.

   (Density of silver = 10.47 g cm^{-3}, Molar atomic mass of silver = 107.924 g mol^{-1}] [**Ans. :** 2.9×10^{-4} cm]

5. (a) Draw the diagram of standard hydrogen electrode. Write the electrode reaction.

   (b) Calculate the equilibrium constant for the reaction :

   $Fe^{2+} + Ce^{4+} \rightleftharpoons Ce^{3+} + Fe^{3+}$

   Given $E^{\varnothing}_{Ce^{4+}/Ce^{3+}} = 1.44V; E^{\varnothing}_{Fe^{3+}/Fe^{2+}} = 0.68V$

   [**Ans. :** 7.6×10^{12}]

NUMERICAL PROBLEMS

*1. The emf of the following cells are:

$Ag\,|Ag^+(1M\,\|\,Cu^{2+}(1M)\,|Cu,\ E^{\varnothing} = 0.46V$

$Zn\,|Zn^{2+}(1M\,\|\,Cu^{2+}(1M)\,|Cu,\ E^{\varnothing} = 1.1V$

Calculate emf of the cell :

$An\,(s)\,|Zn^{2+}(1M\,\|\,Ag^{2+}(1M)\,|Ag\,(s)$

2. For concentration cell

$$Cu\,(s)\,|\,Cu^{2+}\,(0.01M\,\|\,Cu^{2+}\,(0.1M)\,|\,Cu\,(s)$$

(a) Calculate the cell potential.

(b) Will the cell generate emf when concentration becomes equal?

[**Ans. :** (a) 0.295V, (b) No.]

3. Calculate the equilibrium constant for the reaction at 25°C.

$$Cu(s) + 2Ag^{+}\,(aq) \rightleftharpoons Cu^{2+}\,(aq) + 2Ag\,(s)$$

The standard cell potential for the reaction at 25°C is 0.46V.

[Given R = 8.314 JK^{-1} mol^{-1}] [**Ans. :** 4.0×10^{15}]

4. Calculate $\Delta G°$ for the reaction.

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

$$E^{\oslash}_{Cu^{2+}/Cu} = +0.34\,V;\ E^{\oslash}_{Fe^{2+}/Fe} = -0.44\,V$$ [**Ans. :** –150, 540 kJ]

6. Write the Nernst equation and calculate the emf of the following cell at 298K.

$$Cu(s)\ |\ Cu^{2+}\ (0.130M)\ ||\ Ag+\ (10^{-2}\ M)\ |\ Ag(s)$$

Given $E^{\oslash}_{Cu^{2+}/Cu} = +0.34\,V;\ E^{\oslash}_{Ag^{+}/Ag} = +0.80\,V$ [**Ans. :** 0.37V]

7. A zinc rod is dipped in 0.1M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298K. Calculate the electrode potential

$\left(E^{\oslash}_{Zn^{2+}/Zn} = -0.76\,V\right)$. [**Ans. :** –0.7902V]

8. For the electrode Pt, H_2 (1 atm) | $H^{+}_{(aq)}$ (*xM*), the reduction electrode potential at 25°C is – 0.34V. Write the electrode reaction and calculate the value of x. and the pH of solution.

[**Ans. :** $x = 1.807 \times 10^{-6}$, pH = 5.743]

9. For what concentration of Ag^{+} (aq) will the emf of the given cell be zero at 25°C if concentration of Cu^{2+} (aq) is 0.1M?

Given $E^{\varnothing}_{Ag^+/Ag} = 0.80\,V$; $E^{\varnothing}_{Cu^{2+}/Cu} = +0.34\,V$.

Cell : Cu (s) | Cu^{2+} (aq) || Ag^+ (aq) | Ag(s) [**Ans. :** 5.3×10^{-9}]

10. Zinc granules are added in excess to 500 mL of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of Zn^{2+} | Zn and Ni^{2+} | Ni are –0.75 V and – 0.24 V respectively, find out the concentration of Ni^{2+} in solution at equilibrium.

[**Ans. :** 5.88×10^{-18}M]

11. The molar conductivity of 0.1M CH_3COOH solution is 4.6 S cm^2 mol^{-1}. Calculate the conductivity and resistivity of the solution.

[**Ans. :** .00046 S cm^{-1}, 2174 Ω cm]

12. The molar conductivities of NH^+_4 ion and Cl^- ion are 73.5 S cm^2 mol^{-1} and 76.255 cm^2 mol^{-1} respectively. The specific conductivity of 0.1 M NH_4Cl is 1.288×10^{-2} S cm^{-1}. Calculate the dissociation constant of NH_4Cl.

[**Ans. :** 7.396×10^{-2}]

13. Molar conductivity at infinite dilution for NH_4Cl, NaOH and NaCl solution at 298K are respectively 129.8, 218.4 and 108.9 Scm^2 mol^{-1} and m for 10^{-2} M solution of NH_4OH is 9.33 S cm^2 mol^{-1}. Calculate the degree of dissociation of NH_4OH. [**Ans. :** 0.039]

14. Write the Nernst equation and emf of the following cell at 298 K; Pt(s)/ $Br_2(l)$| Br^-(0.010M) || H^+(0.030M) | H_2(g) (0.9 bar) | Pt(s). $E^{\varnothing}\,Br_2 / Br^- / Pt = 1.09V$.

[**Ans. :** –1.297V]

15. In the button cells widely used in watches and other derices, the following reaction takes place :

$Zn(s) + Ag_2O\,(s) + H_2O\,(l) \rightarrow Zn^{2+}\,(ag) + 2Ag(s) + 2OH^-(aq)$

Determine $\Delta_r G^{\varnothing}$ and $E^{\varnothing}$ for the reaction.

Given $E^{\varnothing}_{Zn^{2+}/Zn} = -0.76V$; $E^{\varnothing}_{Ag^+/Ag} = 0.8V$

[**Ans.:** –301.08 kJ / mol., $E^{\theta}_{cell} = 1.56V$]