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UNIT—3

ELECTROCHEMISTRY

1 MARK QUESTIONS

- Q. 1. Which solution will allow greater conductance of electricity, 1 M NaCl at 293 K or 1 M NaCl at 323 K and why?
- Ans. 1 M NaCl at 323 K as the ionic mobilities increase with increase in temperature.
- Q. 2. What does the negative value of E° cell indicate?
- **Ans.** ΔG will be positive, the cell will not work.
- Q. 3. Why is the equilibrium constant K, related to only E°_{cell} and not E_{cell} ?
- **Ans.** This is because E_{cell} is zero at equilibrium.
- Q. 4. What is the sign of ΔG for an electrolytic cell?
- Ans. Positive.
- Q. 5. Rusting of iron is quicker in saline water than in ordinary water. Why is it so?
- **Ans.** In saline water, NaCl helps water to dissociate into H⁺ and OH⁻. Greater the number of H⁺, quicker will be rusting of Iron.
- Q. 6. What would happen if the protective tin coating over an iron bucket is broken in some places?
- Ans. Iron will corrode faster as the oxidation potential of Fe is higher than that of tin.
- Q. 7. Can a nickel spatula be used to stir a solution of Copper Sulphate? Justify your answer.

$$(E^{\circ}_{Ni^2+/Ni} = -0.25 \text{ V}$$
 $E^{\circ}_{Cu^2+/Cu} = 0.34 \text{ V})$





- **Ans.** Reduction potential of Ni is less than Cu. Ni will replace the Cu from CuSO₄. Thus Ni spatula cannot be used to stir a solution of CuSO₄.
- Q. 8. Which out of 0.1 M HCl and 0.1 M NaCl, do you expect have greater Λ^{∞} and why?
- **Ans.** 0.1 M HCl will have greater Λ_{m}^{∞} because H⁺ (aq) being smaller in size than Na⁺ (aq) and have greater mobility.
- Q. 9. Three iron sheets have been coated separately with three metals A, B, C whose standard electrode potentials are given below:

A B C Iron
$$E^{\circ}_{value} - 0.46 \, V - 0.66 \, V - 0.20 \, V - 0.44$$

Identify in which rusting will take place faster when coating is damaged.

- **Ans.** Rusting of iron will take place when coated with metal C as it is placed above iron more than other metal.
- Q. 10. Which will have greater molar conductivity? Solution containing 1 mol KCl in 200 cc or 1 mol of KCl in 500 cc.

Ans. 1 mol of KCl in 500 cc.

2 MARKS QUESTIONS

- Q. 1. (a) How will the value of E_{cell} change in an electrochemical cell involving the following reaction of the concentration of Ag⁺ (aq) is increased ?
 - (b) What will be e. m. f. when the cell reaches equilibrium :

Mg (s) + 2 Ag⁺ (aq)
$$\longrightarrow$$
 Mg²⁺ (aq) + Ag (s)

Ans. (a)
$$E_{cell} = E_{cell}^{\circ} - \frac{0.059}{2} \log \frac{Mg^{2+}}{Ag^{+}}$$

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As the concentration of [Ag $^+$] ion increases, E_{cell} increases.

- (b) e.m.f. = 0
- Q. 2. (a) In a cell reaction, the equilibrium constant K is less than one. Is E° for the cell positive or negative?
 - (b) What will be the value of K of $E_{cell}^{\circ} = 0$?

Ans. For a cell
$$E^{\circ} = \frac{0.0591}{n} \log K$$

$$K < 0 \Rightarrow \log K < 0$$

Then E° will be negative.

(b) If
$$E_{cell}^{\circ} = 9$$
 then $0 = \frac{0.0591}{n} \log K$

$$log K = 0 \Rightarrow K = 1$$

Q. 3. Knowing that:

$$Cu^{2+}$$
 (aq) + 2 e⁻ \longrightarrow Cu (s) E° = + 0.34 V

2 Ag⁺ (aq) + 2 e⁻
$$\longrightarrow$$
 2 Ag (s) E° = + 0.80 V

Reason out whether, 1 M $AgNO_3$ solution can be stored in Copper Vessel or 1 M $CuSO_4$ solution in Silver Vessel.

Ans. A solution of an electrolyte can be stored in a particular vessel only in case there is no chemical reaction taking place with the material of the vessel.

Cu is a strong reducing agent and can lose electrons to Ag⁺ as E° of Cu is less than that of Cu. So AgNO₃ cannot be kept in Copper Vessel.

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CuSO₄ solution can be stored in Ag Vessel as no chemical reaction will take place as Ag is placed above Cu in the activity series and Ag is less reactive than Copper.

- Q. 4. What is the number of electrons in one Coloumb of electricity?
- **Ans.** Charge on one mole of electrons = 1 F = 96500 C

96500 C of Charge is present on electrons = 6.022 x 10²³

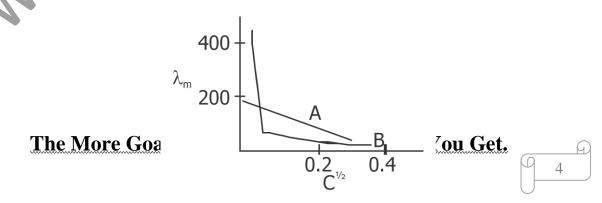
∴ 1 C of Charge is present on electrons =
$$\frac{6.022 \times 10^{23}}{96500 \text{ C}}$$
 × 1 C

$$= 6.24 \times 10^{18}$$

- Q. 5. Which of the following pairs will have greater conduction and why?
 - (a) Copper wire at 25 °C and Copper wire at 50 °C.
 - (b) 0.1 M acetic acid solution or 1 M acetic acid solution?
- **Ans.** (a) Copper wire at 25 °C because with increase in temperature metallic conduction decreases due to vibration of kernels.
 - (b) 0.1 M acetic acid solution because with dilution degree of dissosciation increases and hence no. of ions.

3 MARKS QUESTIONS

- Q. 1. The following curve is obtained when molar conductivity (λ_m) is plotted against the square root of concentration for 2 electrolytes A and B.
 - (a) What can you say about the nature of the two electroyltes A and B?
 - (b) How do you account for the increase in molar conductivity $\lambda_{_m}$ for the electrolytes A and B on dilution ?







- **Ans.** (a) A is a strong electrolyte and B is a weak electrolyte.
 - (b) Molar conductivity of a strong electrolyte (A) increases with dilution as ionic mobility increases. In a weak electrolyte molar conductivity increases steeply with dilution as degree of dissociation increases and hence no. of ions increases.
- Q. 2. Iron and nickel are used to make electrochemical cell by using a salt bridge to join a half cell containing 1 M Fe²⁺ (aq) in which a strip of iron has been immersed to a second half cell which contains 1 M Ni²⁺ (aq) in which a strip of Ni has been immersed? A voltmeter is connected between the two metal strips:

$$E^{\circ}_{Fe^{2}+/Fe} = -0.44 \text{ V}$$
 $E^{\circ}_{Ni^{2}+/Ni} = -0.25 \text{ V}$

- (a) Write the name of the cathode and anode.
- (b) Write the half reactions involved?
- (c) What would be the effect on the Voltmeter reading if Fe²⁺ concentration were increased?

Ans. (a) Anode: Fe

Cathode: Ni

- (b) Reaction at anode : Fe \longrightarrow Fe²⁺ + 2 e⁻ Reaction at cathode : Ni²⁺ + 2 e⁻ \longrightarrow Ni
- (c) Voltmeter reading decreases.
- Q. 3. Consider the electrochemical cell:

Zn (s) / Zn²⁺ (aq) // Cu²⁺ (aq) / Cu. It has an electrical potential of 1.1 V when concentration of Zn²⁺ and Cu²⁺ ions is unity.

State the direction of flow of electrones and also specify if Zinc and Copper are deposited or dissolved at their respective electrodes. When:

- (a) an external opposite potential of 0.8 V is applied.
- (b) an external opposite potential of 1.1 V is applied.

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- (c) an external opposite potential of 1.4 V is applied.
- Ans. (a) Electrons flow from Zn rod to Cu rod.

 Zinc dissolved and Copper gets deposited.
 - (b) No flow of electrons and current.No change observed at Zinc and Copper electrodes (system is at equilibrium).
 - (c) Electrons flow from Cu rod to Zn rod.Zinc is deposited and Copper gets dissolved.
- Q. 4. Given that:

$$CO^{3+} + e^{-} \longrightarrow CO^{2+}$$
 $E^{\circ} = 1.82 \text{ V}$
2 H₂O \longrightarrow O₂ + 4 H⁺ +4 e⁻ $E^{\circ} = -1.23 \text{ V}$

Explain why CO3+ is not stable in aqueous solution?

Ans. The E° can be calculated as:

4 [CO³⁺ + e⁻
$$\longrightarrow$$
 CO²⁺] E° = 1.82 V
2 H₂O \longrightarrow O₂ + 4 H⁺ +4 e⁻ E° = -1.23 V

Cell reaction : 4 CO³⁺ + 2 $H_2O \longrightarrow CO^{2+} O_2 + 4 H^+$

 $E_{cell}^{\circ} = 1.82 \text{ V} - (-1.23 \text{ V}) = 3.05 \text{ V}$

Since E°_{cell} is positive, the cell reaction is spontaneous. CO^{3+} iron will take part in the reaction and hence unstable in aqueous solution.

Q. 5. For the reaction:

$$Ag^+ + Hg \longrightarrow Ag + Hg_2^{2+}$$

 $E^{\circ} = 0.80 \text{ V}$ $E^{\circ} = 0.79 \text{ V}$

Predict the direction in which the reaction will proceed if :

 $[Ag^+] = 10^{-1} \text{ mol/h } [Hg^{2+}] = 10^{-3} \text{ mol/h}$

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Ans. Cell reaction is:

$$2 \text{ Ag}^{+} + 2 \text{ Hg} \longrightarrow 2 \text{ Hg} + \text{Hg}_{2}^{2+}$$

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

$$= (0.80 \text{ V} - 0.79 \text{ V}) - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-1}}^{2}$$

$$= 0.01 \text{ V} - \frac{0.0591}{2} (-1) = 0.01 + 0.0295$$

$$= 0.0395 \text{ V}$$

Since $E_{\text{\tiny cell}}$ is positive, the reaction will be spontaneous in the forward direction.