CHAPTER - 13 **ELECTROCHEMISTRY**

SYNOPSIS

1. Electrolytes and Electrolysis

A substance which decomposes as a result of the passage of electric current is called an **electrolyte** and phenomenon of decomposition by electricity is called **electrolysis**.

- 2. Electrolytic cell: The apparatus used to carry out electrolysis is known as electrolytic cell.
- 3. Faradays Laws of Electrolysis

I) First Law: The amount of the substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through an electrolyte.

$$W\alpha 1\times t=1\times t\times z=Q\times z$$

I = Current strength in amp., t = time in secs., Q = Quantity of charge (coulombs)

Z is a constant known as Electrochemical equivalent

When I = I amp., t = I sec. then Q = 1 coulomb, then w = z. Thus electrochemical equivalent is the amount of the substance deposited or liberated by 1 ampere current passing for 1 second (i.e. 1 coulomb, 1 \times t = Q)

II Second Law: When the same quantity of electricity is passed through different electrolytes, the amounts of the products obtained at the electrodes are directly proportional to their chemical equivalents or equivalent weights. Thus

4. One Faraday: $E\alpha Z$; $E = FZ \cdot F = Known$ as Faraday

One Faraday is the quantity of charge carried by one mole of electrons.

IF =
$$1.6023 \times 10^{-19} \times 6.023 \times 10^{23} = 96500$$
 Coulombs

5. Amount of the substance m liberated or deposited at an electrode

$$m = \frac{Eq. wt of the Sub. \times 1 \times t}{96500} = \frac{Eq. wt \times Q}{96500}$$

6. Comparison of Electrolytic and Metallic conductors

Metallic conduction	Electrolytic conductor
1) due to movement of electrons	due to movement of ions
2) No transfer of matter	there is transfer of matter
3) No change in chemical property	there is chemical change

4) decreases with increase of temperature

increases with increase of temperature

- Factors affecting electrolytic conduction: Inter ionic attraction, viscosity, temperature, solvation of ions etc.
- Ohm's Law: The potential difference across the conductor is directly proportional to the current flowing through it.

Potential difference α current

 $V \alpha 1$; V = RI; where R is a constant known as resistance of the conductor

 $R = \frac{V}{I}$ units. Law is applicable to metallic as well as electrolytic conductors. R is expressed in Ohms. It

is also designated as Ω .

9. Resistance (R): It offers obstruction to the passage of electric current. It is directly proportional to the length (I) and inversely proportional to the area of cross section (a) of the conductor.

$$R \alpha \frac{l}{a} = \rho \times \frac{l}{a}$$
 where ρ is constant, called **resistivity or specific resistance**

when l = 1cm and a = 1cm² then $\rho = R$

10. Specific Resistance (ρ): The resistance offered by 1cm³ of the conductor is known as specific resistance. Units of $\rho = \frac{Ra}{I} = \frac{Ohm \times cm^2}{cm} = Ohm \, cm \, or \, \Omega \, cm$

 Conductance (C): It is ease of flow of electric current through the conductor and reciprocal of resistance R.

$$C = \frac{1}{R}$$
 units ohm⁻¹, mhos or Ω^{-1}

12. Specific Conductivity $(\kappa \text{ kappa})$: It is the reciprocal of specific resistance

$$\kappa = \frac{1}{\rho} = \frac{l}{R_a} = C \times \frac{l}{a} = C \times \text{cell constant} \left(\frac{l}{a} = \text{cell constant}\right)$$

Hence specific conductivity $\kappa(Kappa) = conductance \times cell constant$

Units
$$\kappa = Ohm^{-1} cm^{-1} = \Omega^{-1} cm^{-1} (\Omega^{-1} = S \text{ Seimens})$$

- 13. Effect of dilution on conductance: The number of current carrying particles or ions per ml decreases on dilution and specific conductivity, being the conductance of one centimetre cube of solution, decreases with dilution.
- **14.** Cell constant and its determination: The quantity $\frac{l}{a}$ is known as cell constant. Its direct measurement is very difficult. It is measured by using standard solution of KCl whose conductivity is known at specific conductance of KCl solutions.

Hence cell constant =
$$\frac{\text{specific conductance}}{\text{measured conductance}}$$

- **15.** Equivalent conductivity (\land_{eq}): The conductivity of all the ions produced when 1gram equivalent of an electrolyte is dissolved in V ml of solution is known as equivalent conductivity.
- 16. Relation between equivalent conductivity (\land_m) and specific conductivity (κ)

$$\lambda_{\rm eq} = \kappa \times V = \kappa.\frac{1000}{N} \text{ where V is the volume in cm}^3 \text{ or mI containing 1g eq. of the electrolyte}$$

- 17. Units of equivalent conductivity: Ohm-1 cm2 eq-1
- 18. Effect of dilution on equivalent conductivity: Since the degree of dissociation of the electrolyte increases with dilution, the equivalent conductivity also increases. The increase is more in case of weak electrolytes than strong electrolytes.

The equivalent conductivity increases and specific conductivity decreases

- 19. Molar Conductivity (Am): The conductivity of all the ions produced when 1 mole of an electrolyte is dissolved in V ml of solution is known as molar conductivity.
- 20. Relation between Molar conductivity (A_m) and specific conductivity (χ):

$$\land_{_{m}} = \kappa. V = \kappa \frac{1000}{M} \text{ where V is the volume in cm}^{_{3}} \text{ or mI containing 1 mole of the electrolyte}$$

Units of molar conductivity (Am): ohm-1 cm2 mol-1

Effect of dilution on Molar conductivity: Since the degree of dissociation of electrolyte increases with dilution, \wedge_m also increases but less in case of strong electrolytes and more in case of weak electrolytes.

- 21. Debye Huckel Onsagar equation: Relation between molar conductivity \wedge_m at a particular concentration and molar conductivity at infinite dilution \wedge_m^∞ is given by $\wedge_m^c = \wedge_m^\infty$ $b\sqrt{C}$ where b is constant. It depends upon nature of solvent and temperature.
- 22. Degree of dissociation (α): For weak electrolytes is given by

$$\alpha = \frac{\bigwedge_{m}^{c}}{\bigwedge_{m}^{\infty}} = \frac{\text{Molar conductivity at a given concentration}}{\text{Molar conductivity at infinite dilution}}$$

Kohlrausch's law: At infinite dilution the molar conductivity of an electrolyte is the sum of the ionic conductivities of the cations and anions. e.g. for A_xB_y.

$$\wedge_{m}^{\infty} (A_{x}B_{y}) = x\lambda_{+}^{\infty} + y\lambda_{-}^{\infty}$$

24. Nernst Equation for Electrode Potential: The relationship between the concentration of ions and electrode potential is given by Nernst equation.

$$M^{n+} + ne^- \rightarrow M$$

$$E = E^{0} + \frac{2.303RT}{nF} log[M^{n+}] = E^{0} + \frac{.059}{n} log[M^{n+}]$$

25. Nernst equation for cell potential: Consider a general cell reaction involving n electrons

$$aA + bB \rightarrow cC + dD$$

$$E = E^{0} + \frac{2.303RT}{nF} log \frac{[A][B]}{[C][D]}$$

26. Nernst equation and equilibrium constant (K_c): When E_{cell} drops to zero the concentration of ions will be equilibrium concentrations. We have for general cell reaction.

$$aA + bB \rightleftharpoons cC + dD$$

$$E_{cell}^{0} = \frac{2.303RT}{nF} \log K_{c}$$

According to Gibbs and Helmholtz, the decrease of free energy (ΔG) of the reaction occurring in the cell is equal to electrical energy

Hence $-\Delta G = nFE =$ Electrical work done

The standard free energy and E_{cell}^0 are related as $\Delta G^0 = -nFE_{cell}^0$

- 27. Relationship between free energy change and equilibrium constant : $\Delta G^0 = -2.303RT \log K_c$
- 28. Concentration Cells: They are of two types
 - (I) Electrode Concentration Cells: Two electrodes of different concentrations are dipped in the same solution of electrolyte e.g.

Pt,
$$H_2(pH_1 = p_1) |H^*| H_2(pH_2 = p_2)$$
 Pt where $p_1 > p_2$

$$E_{cell} = \frac{2.303RT}{nF} log \frac{p_1}{p_2}$$

(II) Electrolyte concentration cells: Electrodes are the same but electrolyte solutions have different concentrations eg.

$$Zn, Zn^{++}(c_1) \parallel Zn^{++}(c_2); Zn$$
 where $c_2 > c_1$

$$E_{cell} = \frac{2.303}{nF} RT \log \frac{c_2}{c_1} = \frac{0.0591}{n} \log \frac{c_2}{c_1}$$

- 29. Some commercial cells and their types: They are broadly classified into two groups.
 - (I) Primary cells: They cannot be recharged and used again/ Examples are
 - (a) Dry cell or Leclanche cell: Particulars are

Anode - Zinc Container

Cathode - graphite rod surrounded by MnO2 powder

Electrolyte - paste of NH₄CI + ZnCI₉

Cathode Reaction: MnO₂ + NH₄ + e⁻ → MnO(OH) + NH₃

Anode reaction : $Zn - 2e^- \longrightarrow Zn^{2+}$

Overall reaction : $Zn^{2+} + 2NH_3 \rightarrow \left[Zn(NH_3)_2\right]^{2+}$

Cell potential: 1.25 to 1.5 V

(II) Secondary cells: Can be recharged and can be used again and again. Examples

(a) Lead Storage battery :

Anode - Spongy lead

Cathode - grid of lead packed with PbO₂

Electrolyte - 38% H₂SO₄ by mass

Anode Reaction : $Pb + SO_4^- \rightarrow PbSO_4 + 2e^-$

Cathode Reaction: $PbO_2 + SO_4^- + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O_4$

Net Reaction: $Pb + PbO_2 + 4H^+ + 2SO_4^- \rightarrow 2PbSO_4 + 2H_2O$

When recharged, the cell reactions are reversed

30. Fuel Cells: They convert chemical energy into electrical energy. The reactants are continuously fed and products are removed.

(a) Hydrogen-Oxygen-Fuel Cell: Electrodes - made of porous graphite impregnated with catalyst (Pt, Ag or a metal oxide).

Electrolyte: Aqueous solution of KOH or NaOH

Oxygen and hydrogen are continuously fed into the cell.

Oxidation Half-cell Reaction: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Reduction Half-cell Reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Net Reaction: $2H_2 + O_2 \rightarrow 2H_2O$

EMF of the cell: 1 volt

31. Corrosion: Slow formation of undesirable compounds such as oxides, sulphides or carbonates at the surface of metals by reaction with moisture and other atmospheric gases is known as corrosion.

Factors affecting corrosion :

(I) Reactivity of metals

(II) Presence of moisture and atmospheric gases like CO2, SO2 etc

(III) Presence of impurities

(IV) Strains in the metal

(V) Presence of electrolyte

32. Prevention of corrosion:

- (I) Barrier protection: By painting, coating, electroplating
- (II) Sacrificial protection: By galvanization, Sheraridising
- (III) Electrical protection
- (IV) Use of anti-rust compounds

PART-I (JEE MAIN)

SECTION-I- Straight objective type questions

- Which of the following statements is true for the Daniell cell? 1.
 - 1) Electrons flow from copper electrode to zinc electrode
 - 2) Current flows from zinc electrode to copper electrode
 - 3) Cations move towards copper electrode
 - 4) Cations move towards zinc electrode
- 2. The standard reduction potential for two half reactions are given below

$$Zn^{2+} + 2e^{-} \longrightarrow Zn$$
; $E^{0} = -0.76 \text{ V}$

$$Fe^{2+} + 2e^{-} \longrightarrow Fe$$
; $E^{0} = -0.44 \text{ V}$

The emf for the cell reaction, $Fe^{2+} + Zn \rightarrow Zn^{2+} + Fe$ is

$$2) + 0.32 V$$

- Consider the reaction, $Zn(s)+Cl_2(1 \text{ atm}) \rightarrow Zn^{2+}(aq)+2Cl^{-}(aq)$. E^0_{cell} for this cell is 2.12 V. To 3. increase the cell potential,
 - 1) [Zn] should be decreased
- 2) [Zn2+] should be decreased
- 3) [C]⁻] should be increased
- 4) P_{Cl_2} should be decreased
- **Assertion:** For a cell reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, at equilibrium, voltmeter gives 4. zero reading.

Reason: At the equilibrium, there is no change in the concentration of Cu^{2+} and Zn^{2+} ions. Choose the correct option:

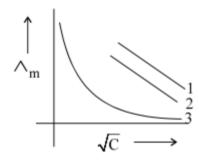
- 1) Both assertion and reason are true and reason is the correct explanation of assertion.
- Both assertion and reason are true but reason is not the correct explanation of assertion.
- 3) Assertion is true but reason is false.
- 4) Assertion is false but reason is true.
- 5. For a cell reaction involving a two-electron transfer, the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be

1)
$$1 \times 10^{-10}$$

2)
$$29.5 \times 10^{-2}$$
 3) 10

4)
$$1 \times 10^{10}$$

A graph of molar conductivity of three electrolytes (NaCl, HCl, NH₄OH) is plotted against √C. Identify 6. the electrolytes (C = molar concentration)



- 1
- 2

3

- 1) NaCl
- **HCI**
- NH,OH

- 2) NH,OH
- NaCl
- **HCI**

- 3) HCI
- NaCl
- NH₄OH

- 4) NH,OH
- **HCI**

- NaCl
- 7. Following limiting molar conductivities are given as

$$\wedge_{m(H_2SO_4)}^o = x Scm^2 mol^{-1}$$

$$\wedge_{m(K,SO_4)}^o = y Scm^2 mol^{-1}$$

$$\wedge_{m(CH_3COOK)}^{o} = zScm^2mol^{-1}$$

 $\Lambda_{\rm m}^{0}$ (in S cm²mol⁻¹) for CH₃COOH will be

2)
$$x + y - z$$

4)
$$\frac{(x-y)}{2} + z$$

8. The correct expression for dissociation constant of acetic acid in terms of molar conductivity is (C = molar concentration)

1)
$$K_a = \frac{C \wedge_m^2}{\wedge_m^0 - \wedge_m}$$

$$\text{1) } K_{a} = \frac{C \wedge_{m}^{2}}{\wedge_{m}^{0} - \wedge_{m}} \qquad \text{2) } K_{a} = \frac{C \left(\wedge_{m}^{0} \right)^{2}}{\wedge_{m} \left(\wedge_{m}^{0} - \wedge_{m} \right)} \text{ 3) } K_{a} = \frac{C \wedge_{m}^{2}}{\wedge_{m}^{0} \left(\wedge_{m}^{0} - \wedge_{m} \right)} \text{ 4) } K_{a} = \frac{C \left(\wedge_{m}^{0} \right)^{2}}{\wedge_{m} - \wedge_{m}^{0}}$$

Three faraday of electricity are passed through molten $\mathrm{Al_2O_3}$, aqueous solution of $\mathrm{CuSO_4}$ and 9. molten NaCl taken in different electrolytic cells. The amount of Al, Cu and Na deposited at the cathodes will be in the ratio of

1) 1 mole: 2 mole: 3 mole

2) 3 mole: 2 mole: 1 mole

3) 1 mole: 1.5 mole: 3 mole

4) 1.5 mole: 2 mole: 3 mole

10. On electrolysis, in which of the following, O₂ would not be liberated at the anode? 2) aqueous AgNO, solution with Pt electrodes 1) dilute H₂SO₄ with Pt electrodes 3) aqueous CuCl₂ solution with Pt electrodes 4) aqueous CuSO₄ with Pt electrodes 11. In a dry cell, at cathode, the oxidation state of manganese decreases from +x to +y. The value of x and y are respectively 2) 6, 3 3) 4, 3 4) 3, 2 1) 4, 2 12. When lead storage battery is charged 1) Lead dioxide dissolves Sulphuric acid is regenerated 3) The lead electrode becomes coated with lead sulphate 4) The amount of sulphuric acid decreases **SECTION-II - Numerical Type Questions** EMF of the following cell at 298 K in V is $x \times 10^{-2}$. 13. Zn|Zn²⁺ (0.1 M)||Ag+ (0.01 M)|Ag. The value of x is Given: $E_{Zn^{2+}/Zn}^0 = -0.76V$, $E_{Ag^{+}/Ag}^0 = 0.80 \text{ V}$, $\frac{2.303 \text{ RT}}{F} = 0.059$ Given that the standard electrode potential of Cu²*/Cu and Cu⁺/Cu are 0.34 V and 0.522 V respectively. 14. The standard potential of Cu²⁺/Cu⁺ is × 10⁻² V 15. The resistance of conductivity cell containing 0.01 M KCl solution at 298 K is 1750Ω . If the conductivity of 0.01 M KCl solution at 298 K in 0.152 × 10⁻³ S cm⁻¹, then the cell constant of the conductivity cell is × 10⁻³ cm⁻¹ The potential of a hydrogen electrode decreases by $x \times 10^{-2}$ V, when its solution initially at pH = 0 is 16. neutralised to pH = 7. The value of x is Given: $\frac{2.303 \text{ RT}}{F} = 0.059$, $P_{H_2} = 1 \text{ bar}$ PART-II (JEE ADVANCED) Section-III - Only one option correct type The specific conductance of a saturated solution of AgCl is 3.4 x 10-6 S cm-1 at 25°C. If $\lambda(Ag^+) = 62.3 \text{ Scm}^2\text{mol}^{-1}$ and $\lambda(Cl^-) = 67.7 \text{ Scm}^2\text{mol}^{-1}$, solubility of AgCl at 25°C will be A) 2.6 x 10⁻⁵ M B) 1.7 x 10⁻⁵ M C) 3.7 x 10⁻⁵ M D) $3.7 \times 10^{-3} M$ When a concentrated solution of an electrolyte is diluted: 18. A) its specific conductance decreases but equivalent conductance increases B) its specific conductance increases but equivalent conductance decreases

C) both specific conductance and equivalent conductance increases

D) both specific conductance and equivalent conductance decreases

- 19. The emf of the cell $Pt(s)|H_2(g, 1 \text{ atm})|HA(0.01 \text{ M})||HCl(1M)|H_2(g, 1 \text{ atm})|Pt(s)$ is 0.295 V. Dissociation constant of the acid HA would be
 - A) 1 × 10-4
- B) 1 × 10-6
- C) 1×10^{-8}
- D) 1 × 10-5
- 20. When a certain aqueous solution was electrolysed with Pt electrodes, the pH of the solution was found not to change. The solution would be that of:
 - A) AgNO₃
- B) NaCl
- C) CuSO₄
- D) KNO_a
- 21. If reduction potential of Cu²*/Cu couple is 0.1335 V in a saturated solution of Cu(OH)₂, the pH of solution will be (Given : Standard reduction potential of Cu²*/Cu couple is 0.34 V; K_{sp} of Cu(OH)₂ is 1×10⁻¹⁹)
 - A) 6

B) 8

- C) 12
- D) 11

Section IV - One or more option correct type

- 22. A blue colour can be observed in the solution when:
 - A) Cu electrode is placed in AgNO₃ solution
 - B) Cu electrode is placed in ZnSO, solution
 - C) Cu electrode is placed in dil HNO,
 - D) Cu electrode is placed in NiSO, solution
- 23. Equal quantity of electricity is passed through three electrolytic cells containing aqueous solutions of FeSO₄, Fe₂(SO₄)₃ and Fe(NO₃)₃ respectively. Regarding the electrolytic process, which of the following is/are correct? (Assume that only iron is reduced at the cathode).
 - A) The amount of iron deposited in three cases are equal
 - B) The amount of iron deposited in Fe₂(SO₄)₃ and Fe(NO₃)₃ are equal
 - C) Same gas is evolved at anode in all three cases
 - D) Amount of iron deposited in Fe₂(SO₄)₃ is double that in case of Fe(NO₃)₃
- 24. Select the correct relation(s) from the following

A)
$$\Delta S^0 = \left(\frac{\partial E^0}{\partial T}\right)_P \times nF$$

B)
$$\Delta S^0 = -\left(\frac{\partial E^0}{\partial T}\right)_n \times nF$$

C)
$$\left(\frac{\partial E^{0}}{\partial T}\right)_{P} = \left(\frac{\partial \Delta S^{0}}{\partial T}\right)_{P}$$

D)
$$E^0 = -\frac{\Delta H^0}{nF} + T \left(\frac{\partial E^0}{\partial T} \right)_P$$

25. Which of the following statements is/are correct?

(Use:
$$E^{0}_{\text{Cu}^{2+}|\text{Cu}}=0.34~V,~E^{0}_{\text{Sn}^{2+}/\text{Sn}}=\text{-}0.14~V$$
 and and $E^{0}_{\text{H}^{+}/\text{H}_{2}}=0.0~V$)

- A) Cu2+ ions can be reduced by H2
- B) Cu can be oxidized by H*
- C) Sn2+ ions can be reduced by H₂
- D) Sn can be oxidized by H*

- 26. 2 amperes of current is passed for 16 min and 5 seconds through 1000 ml of 2 molar aqueous solution of CuSO₄ using Pt electrodes. Then
 - A) 1.204 × 10²² electrons are passed through the cell
 - B) 0.635 g of Cu is deposited at cathode
 - C) 1.204 × 10²³ electrons are passed through the cell
 - D) 1.27 g of Cu is deposited at cathode

Section V - Numerical type questions

- 27. Conductivity of 0.02 M KCl at 25°C is 4 x 10⁻³ ohm⁻¹ cm⁻¹. The resistance of this solution at 25° when measured with a particular cell was 200 ohms. The resistance of 0.01 M CuSO₄ at 25°C measured with the same cell was 8 x 10³ ohms. What is molar conductivity of the copper sulphate solution (in ohm⁻¹ cm² mol⁻¹) at 25°C?
- 28. The cell potential for $Zn |Zn_{(aq)}^{2+}| Sn^{x+}| Sn$ is 0.801 V at 298 K. The reaction quotient for the reaction is 10^{-2} . The number of electrons involved in the given electrochemical cell reaction is _____

(given
$$E_{Zn^{2+}/Zn}^0 = -0.763V$$
 $E_{Sn^{x+}/Sn}^0 = +0.008V & \frac{2.303 \, RT}{F} = 0.06V$)

Section-VI - Matrix match type

29. Matcth the following

Column-I (Reduction process)

- I) 1 mole of MnO- to Mn2+
- II) 1 mole of Cr₂O₂²⁻ to Cr³⁺
- III) 1 mole of Sn4+ to Sn2+
- IV) 1 mole of Al3+ to Al
- A) $I \rightarrow R$; $II \rightarrow O$; $III \rightarrow P$; $IV \rightarrow O$
- C) $I \rightarrow R$: $II \rightarrow S$: $III \rightarrow P$: $IV \rightarrow O$

Column-II (Charge required)

- P) 193000 C
- Q) 289500 C
- R) 482500 C
- S) 579000 C
- B) $I \rightarrow P$; $II \rightarrow O$; $III \rightarrow R$; $IV \rightarrow S$
- D) I \rightarrow P; II \rightarrow S; III \rightarrow R; IV \rightarrow S

Match the following

Column-I (Cell)

- Pt |H₂(0.1 bar)|H⁴(0.1M)||H⁴(1M)|H₂(1 bar)|Pt
- II) Ag|AgCl|KCl (0.1 M)||Ag*(0.01M)|Ag
- III) Cu|Cu²⁺(0.1M)||Cu²⁺(0.01M)|Cu
- IV) Pt|Cl₂(1 bar)|HCl(0.1M)||NaCl(0.1M)| Cl₂(1bar)|Pt
- A) $I \rightarrow PR$; $II \rightarrow PQR$; $III \rightarrow PS$; $IV \rightarrow S$
- B) I \rightarrow PQR; II \rightarrow PQR; III \rightarrow PS; IV \rightarrow PS
- C) I \rightarrow PO; II \rightarrow PO; III \rightarrow PS; IV \rightarrow S
- D) I \rightarrow POR; II \rightarrow O; III \rightarrow PS; IV \rightarrow PS

Column-II (Feature)

- P) Concentration cell
- $Q) E_{col} > 0$
- R) $E_{cell}^0 = 0$ but cell is working
- S) Non working condition