2

Electrochemistry

Fastrack Revision

- **Electrochemistry:** Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.
- **Electrochemical Cells**
  - Potential difference between the electrode and the electrolyte is called electrode potential.
  - The potential difference between the two electrodes of a galvanic cell is called cell potential and is measured in volts.
  - Electromotive force (emf) of the cell is the difference between the electrode potentials (reduction potentials) of the cathode and anode.
- **Electromotive Force (emf) of Galvanic Cell**

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

- **Nernst Equation**
  - For the electrode reaction, $M^{n+}(aq) + ne^- \longrightarrow M(s)$, the electrode potential is given by,

$$E = E^{\circ} - \frac{RT}{nF}\log_e \frac{1}{[M^{n+}]}$$

$$= E^{\circ} - \frac{0.0591}{n}\log_{10} \frac{1}{[M^{n+}]} \quad \text{(at 298 K)}$$

  - For concentration cell, emf at 298 K is given by

$$E = \frac{2.303}{nF}\log\frac{C_2}{C_1} \qquad [\because C_2 > C_1]$$

  - To calculate electrode potential of a cell:

$$aA + bB \xrightarrow{ne^-} xX + yY$$

$$E = E^{\circ} - \frac{0.0591}{n}\log\frac{[X]^x[Y]^y}{[A]^a[B]^b}$$

Knowledge BOOSTER

If two electrodes of the same metal are dipped separately into two solutions of the same electrolyte having different concentrations and the solutions are connected through salt bridge, such cells are known as concentration cells e.g., Cu^+ concentration cell.

  - For a cell at equilibrium, $E^{\circ}_{\text{cell}} = \frac{0.0591}{n}\log_{10} K$
- **Relation between Gibbs' Energy of the Reaction and emf of the Cell**

$$\Delta_r G = -nFE_{(\text{cell})}$$

where, nF = amount of charge passed

- **Relation of Gibbs' Free Energy with Equilibrium Constant**

$$\Delta_r G^{\circ} = -2.303\,RT\log K_c$$

- **Conductance of Electrolytic Solutions**
  - Resistance is the property of a substance to obstruct the flow of charge.
  - It is directly proportional to the length (l) and inversely proportional to its area of cross-section (A).

$$R = \rho\frac{l}{A}$$

where, ρ = resistivity or specific resistance.

  - The SI unit of resistivity is ohm metre (Ωm) or ohm cm (Ω cm).

Knowledge BOOSTER

IUPAC recommends using resistivity over specific resistance.

  - Conductance is the ease with which current flows through a conductor.
  - Conductance, $C = \frac{1}{R}$, where R = resistance
  - Unit of C is ohm^{-1} (or Ω^{-1}) or mho or siemens (S).
- **Specific Conductivity**
  - Specific conductivity, $\kappa = C \times \frac{l}{a}$ where, $\frac{l}{a}$ = cell constant
  - Unit of κ is $\text{ohm}^{-1}\ \text{cm}^{-1}$ or Sm^{-1}.

Knowledge BOOSTER

The substances which have very large conductivity are known as conductors e.g., metals and their alloys, non-metals like carbon black and some organic polymers are also conductors.

- **Equivalent Conductivity**
  - Equivalent conductivity, $\Lambda_{eq} = \frac{\kappa \times 1000}{\text{Normality}}$
  - Unit of Λ_{eq} is $\text{ohm}^{-1}\ \text{cm}^2$ equivalent or siemens m^{-2} equivalent^{-1}.
- **Molar Conductivity**
  - Molar conductivity, $\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$
  - Unit of Λ_m is $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ or siemens $\text{m}^2\ \text{mol}^{-1}$.
- **Kohlrausch Law (of independent migration of ions)**
  - According to the law, limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

$$\Lambda^{\infty}_m = \lambda^{\infty}_{c^+} + \lambda^{\infty}_{a^-}$$

where, $\lambda^{\infty}_{c^+}$ = molar conductivity of cations,

$\lambda^{\infty}_{a^-}$ = molar conductivity of anions.

- For an electrolyte A_xB_y,

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

$$\Lambda^{\infty}_m (A_xB_y) = x\lambda^{\infty}_{(A^{y+})} + y\lambda^{\infty}_{(B^{x-})}$$

- Degree of dissociation of weak electrolytes,

$$\alpha = \frac{\Lambda^c_m}{\Lambda^{\circ}_m}$$

- Dissociation constant of weak electrolytes,

$$K = \frac{c\alpha^2}{1-\alpha} = \frac{c(\Lambda^c_m)^2}{\Lambda^{\circ}_m(\Lambda^{\circ}_m - \Lambda^c_m)}$$

where, Λ^c_m = molar conductivity at concentration 'c'

Λ°_m = limiting molar conductivity

- **Electrolytic Cells:** The cell which converts electrical energy to chemical energy is known as electrolytic cell.
- **Faraday's First Law of Electrolysis:** The amount of chemical reaction which occurs at any electrode during electrolysis by passing current is proportional to the quantity of electricity passing through the electrolyte (in solution or in molten state).

  Thus, W gram amount of the substance gets deposited on passing Q coulomb of electricity

  $$W \propto Q \quad \text{or} \quad W = ZQ \quad \text{or} \quad W = Zit$$

  where, Q = quantity of electricity, i = current (A), t = time (sec), Z = constant of proportionality called electrochemical equivalent.
- **Faraday's Second Law of Electrolysis:** The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights,

  i.e., $$\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3} = \ldots\ldots$$

  where, W_1 is the mass of substance deposited and E_1 is its equivalent weight and so on.
- **Dry Cell:** It consists of a zinc container which acts as anode and cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of NH_4Cl and $ZnCl_2$.

Knowledge BOOSTER

Dry cell has a potential of about 1.5 V.

- **Mercury Cell:** It consists of Zn-Hg amalgam as anode. The cathode is a paste of mercuric oxide (HgO) and carbon powder. The electrolyte is a paste of KOH and ZnO. The cell constant is 1.35V approx. and remains constant during its life.

Knowledge BOOSTER

Mercury cell has a potential of 1.35 V.

- **Lead Storage Battery:** It consists of a lead anode and a grid of lead packed with lead dioxide as cathode. A 38% solution of sulphuric acid acts as the electrolyte. When the battery is in use (discharging), the cell reactions are:

  At anode:

  $$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

  At cathode:

  $$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

  During charging, the reactions are reversed.
- **Fuel Cells:** They are galvanic cells. They are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol directly into electrical energy. *e.g.*, hydrogen-oxygen cell.
- **Corrosion:** It is basically an electrochemical phenomenon in which a metal oxide or other salt of the metal forms a coating on the metal surface, *e.g.*, rusting of iron, in which the following reactions take place:

  At anode:

  $$2Fe(s) \longrightarrow 2Fe^{2+}(aq) + 4e^- \qquad \text{(Oxidation)}$$

  At cathode:

  $$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \qquad \text{(Reduction)}$$
- **Methods used for Preventing Corrosion:** Some of the methods are:
  - Covering the surface with paint or by some chemicals e.g. bisphenol.
  - Covering the surface by other metals such as Sn, Zn, etc., that are inert or react to save the object.
  - Providing a sacrificial electrode of another metal like Mg, Zn, etc., which corrodes itself but saves the metal surface.

Practice Exercise

Multiple Choice Questions

Q 1. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called: *(NCERT EXEMPLAR)*

a. cell potential

b. cell emf

c. potential difference

d. cell voltage

Q 2. The correct representation of cell reaction

$$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag \text{ is:}$$

a. $Ag \mid Ag^+ \parallel Zn \mid Zn^{2+}$

b. $Zn \mid Zn^{2+} \parallel Ag \mid Ag^+$

c. $2Ag \mid Ag^+ \parallel Zn \mid Zn^{2+}$

d. None of the above

Q 3. The standard oxidation electrode potential of four metals A, B, C and D are $+1.5$ V, -2.0 V, $+0.84$ V and -0.36 V respectively. The order of increasing reactivity of these metals is:

a. $A < B < C < D$ b. $D < C < B < A$

c. $A < C < D < B$ d. $B < C < D < A$

Q 4. The standard reduction potential of elements A, B, C and D are respectively -2.90, $+1.50$, -0.74 and $+0.34$ V. Among these the strongest oxidising agent is:

a. A b. B c. C d. D

Q 5. The standard reduction potential (E°_{red}) values of A, B and C are $+0.68$ V, -2.54 V and -0.50 V respectively. The order of their reducing power is:

a. $A > B > C$ b. $A > C > B$

c. $C > B > A$ d. $B > C > A$

Q 6. $CuSO_4$ is not stored in aluminium bottle because:

a. Cu gets oxidised b. Cu^{2+} gets reduced

c. Al gets reduced d. $CuSO_4$ gets decomposed

Q 7. Following four colourless solutions of salts have been kept in different test tubes and a copper strip was dipped in each. Which solution will turn blue in the end?

a. $Zn(NO_3)_2$ b. $Cd(NO_3)_2$

c. $AgNO_3$ d. $Pb(NO_3)_2$

Q 8. The correct cell to represent the following reaction is: *(CBSE 2023)*

$$Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$$

a. $2Ag \mid Ag^+ \parallel Zn \mid Zn^{2+}$ b. $Ag^+ \mid Ag \parallel Zn^{2+} \mid Zn$

c. $Ag \mid Ag^+ \parallel Zn \mid Zn^{2+}$ d. $Zn \mid Zn^{2+} \parallel Ag^+ \mid Ag$

Q 9. $Ag^+(aq) + e^- \longrightarrow Ag(s)$; $E^\circ = +0.80$ V

$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$; $E^\circ = -0.44$ V

Find the E°_{cell} for:

$Fe(s) + 2Ag^+(aq) \longrightarrow Fe^{2+}(aq) + 2Ag(s)$ *(CBSE 2023)*

a. 1.6 V b. -1.16 V c. 2.04 V d. 1.24 V

Q 10. ΔG and E°_{cell} for a spontaneous reaction will be: *(CBSE 2023)*

a. positive, negative b. negative, negative

c. negative, positive d. positive, positive

Q 11. Which of the following solutions will have the highest conductivity at 298 K? *(CBSE SQP 2023-24)*

a. 0.01 M HCl solution

b. 0.1 M HCl solution

c. 0.01 M CH_3COOH solution

d. 0.1 M CH_3COOH solution

Q 12. Which of the following solutions of KCl will have the highest value of molar conductivity? *(CBSE 2023)*

a. 0.01 M b. 1 M c. 0.5 M d. 0.1 M

Q 13. Kohlrausch gave the following relation for strong electrolyte:

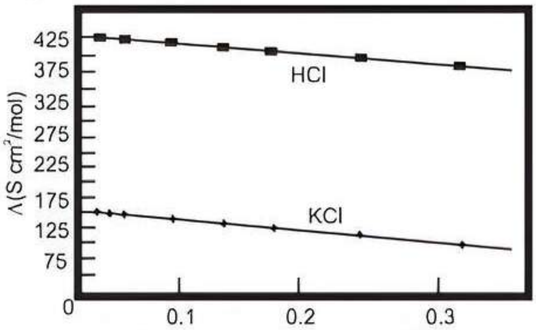
$$\Lambda = \Lambda_o - A\sqrt{C}$$

Which of the following equality holds true? *(CBSE 2023)*

a. $\Lambda = \Lambda_o$ as $C \longrightarrow \sqrt{A}$ b. $\Lambda = \Lambda_o$ as $C \longrightarrow 0$

c. $\Lambda = \Lambda_o$ as $C \longrightarrow \infty$ d. $\Lambda = \Lambda_o$ as $C \longrightarrow 1$

Q 14. The molar conductivity of CH_3COOH at infinite dilution is 390 S cm^2/mol. Using the graph and given information, the molar conductivity of CH_3COOK will be: *(CBSE SQP 2022-23)*



a. 100 S cm^2/mol b. 115 S cm^2/mol

c. 150 S cm^2/mol d. 125 S cm^2/mol

Q 15. How many Faradays are required to reduce 1 mol of MnO_4^- to Mn^{2+}? *(CBSE 2023)*

a. 4 b. 3 c. 6 d. 5

Q 16. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is: *(NCERT EXEMPLAR)*

a. 1F b. 6F c. 3F d. 2F

Q 17. The cathode reaction during the charging of a lead storage battery leads to the: *(CBSE 2023)*

a. formation of $PbSO_4$

b. reduction of Pb^{2+} to Pb^{4+}

c. formation of PbO_2 and Pb

d. deposition of Pb at the anode

Q 18. When a lead storage battery is charged, then:

a. PbO_2 dissolves

b. $PbSO_4$ gets deposited on lead electrode

c. H_2SO_4 regenerates

d. quantity of acid reduces

Q 19. The net reaction occurring in hydrogen-oxygen fuel cell is:

a. $2H_2(g) + 4\,OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

b. $O_2(g) + 2H_2O(l) \longrightarrow 2e^- + 4OH^-(aq)$

c. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

d. None of the above

Q 20. Corrosion of iron is: *(CBSE 2023)*

a. a decomposition process

b. a photochemical process

c. an electrochemical process

d. a reduction process

Assertion & Reason Type Questions

Directions (Q. Nos. 21-32): *Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:*

a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).

c. Assertion (A) is true but Reason (R) is false.

d. Assertion (A) is false but Reason (R) is true.

Q 21. **Assertion (A):** Cu is less reactive than hydrogen.

Reason (R): $E^\circ_{Cu^{2+}/Cu}$ is negative. *(NCERT EXEMPLAR)*

Q 22. **Assertion(A):** E_{Cell} should have a positive value for the cell to function.

Reason (R): $E_{cathode} < E_{anode}$ *(NCERT EXEMPLAR)*

Q 23. **Assertion (A):** $E^\circ_{Cu^{2+}/Cu}$ is positive (+0.34 V).

Reason (R): Copper has high $\Delta_a H^\circ$ and low $\Delta_{hyd} H^\circ$. *(CBSE 2023)*

Q 24. **Assertion (A):** Conductivity of all electrolytes decreases on dilution.

Reason (R): On dilution number of ions per unit volume decreases. *(NCERT EXEMPLAR)*

Q 25. **Assertion (A):** Conductivity decreases with decrease in concentration of electrolyte.

Reason (R): Number of ions per unit volume that carry the current in a solution decreases on dilution. *(CBSE 2023)*

Q 26. **Assertion (A):** Molar conductivity decreases with increase in concentration.

Reason (R): When concentration approaches zero, the molar conductivity is known as limiting molar conductivity. *(CBSE 2023)*

Q 27. **Assertion (A):** Λ_m for weak electrolytes shows a sharp decrease when the electrolytic solution is diluted.

Reason (R): For weak electrolytes, degree of dissociation increases with dilution of solution. *(CBSE 2023)*

Q 28. **Assertion (A):** Limiting molar conductivity (Λ°_m) is obtained by the extrapolation of the Λ_m *versus* $C^{1/2}$ curve of strong electrolyte.

Reason (R): Λ°_m for weak electrolytes is obtained by using Kohlrausch's law. *(CBSE 2023)*

Q 29. **Assertion (A):** Mercury cell does not give steady potential.

Reason (R): In the cell reaction, ions are not involved in solution. *(NCERT EXEMPLAR)*

Q 30. **Assertion (A):** Electrolysis of NaCl solution gives chlorine at anode instead of O_2.

Reason (R): Formation of oxygen at anode requires overvoltage. *(NCERT EXEMPLAR)*

Q 31. **Assertion (A):** For measuring resistance of an ionic solution, an AC source is used.

Reason (R): Concentration of ionic solution will change if DC source is used. *(NCERT EXEMPLAR)*

Q 32. **Assertion (A):** During electrolysis of aqueous copper sulphate solution using copper electrodes hydrogen gas is released at the cathode.

Reason (R): The electrode potential of Cu^{2+}/Cu is greater than that of H^+/H_2. *(CBSE SQP 2023-24)*

Answers

1. (b) cell emf
2. (d) Correct representation is:

$$Zn \mid Zn^{2+} \parallel Ag^+ \mid Ag$$

3. (c) $A < C < D < B$
4. (b) B
5. (d) $B > C > A$

More is the reducing potential, more is the power to get itself reduced or lesser is the reducing power.

6. (b) Cu^{2+} gets reduced

Al is more reactive than Cu, *i.e.*, Cu^{2+} gets reduced.

7. (c) $AgNO_3$

$AgNO_3$ will turn blue in the end.

8. (d) $Zn \mid Zn^{2+} \parallel Ag^+ \mid Ag$
9. (d) 1.24V

Given, $E^\circ_{cathode} = +0.80$ V and $E^\circ_{anode} = -0.44$ V

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= 0.80 - (-0.44) \text{ V} \\ &= 1.24 \text{ V} \end{aligned}$$

10. (c) negative, positive

For a spontaneous reaction, $\Delta G < 0$ and $E^\circ_{cell} > 0$

$\Delta G = -nFE_{cell}$

$\therefore$ ΔG and E°_{cell} will have opposite signs.

11. (b) 0.1 M HCl solution

0.1 M HCl solution will have the highest conductivity at 298K because conductivity is higher for strong electrolyte and it decreases with dilution.

12. (a) 0.01 M

0.01 M KCl solution will have the highest value of molar conductivity under similar conditions.

13. (b) $\Lambda = \Lambda_0$ as $C \to 0$

Given, $\Lambda = \Lambda_0 - A\sqrt{C}$

When $C \to \sqrt{A}$, we have $\Lambda = \Lambda_0 - A\sqrt{\sqrt{A}}$

When $C \to 0$, we have $\Lambda = \Lambda_0 - A\sqrt{0}$

$= \Lambda_0$

So, this equality holds true.

14. (b) 115 S cm^2/mol

Given: $\Lambda^\circ_{CH_3COOH} = 390$ S cm^2/mol

$\Lambda^\circ_{KCl} = 150$

Scm^2/mol (from graph).

$\Lambda^\circ_{HCl} = 425$ S cm^2/mol (from graph)

Using formula,

$$\begin{aligned} \Lambda^\circ_{CH_3COOK} &= \Lambda^\circ_{CH_3COOH} + \Lambda^\circ_{KCl} - \Lambda^\circ_{HCl} \\ &= 390 + 150 - 425 \\ &= 115 \text{ S cm}^2\text{/mol} \end{aligned}$$

15. (d) $MnO_4^- + 5e^- \longrightarrow Mn^{2+}$

Oxidation number of Mn in MnO_4^- is +7.

Oxidation number of Mn in Mn^{2+} is +2.

Change in oxidation number = 7 − 2 = 5.

$\therefore$ 5 Faradays are required to reduce 1 mol of MnO_4^- to Mn^{2+}.

16. (c) The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is equal to the number of electrons required to convert Al_2O_3 to Al.

$$Al^{3+}(aq) \xrightarrow{+3e^-} Al(s)$$

Hence, 3F charge is required.

17. (b) reduction of Pb^{2+} to Pb^{4+}

18. (c) H_2SO_4 regenerates

19. (c) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

20. (c) an electrochemical process

Corrosion of iron is an electrochemical process because in it, metals lose electrons and oxygen accepts them. Thus, there is conversion of a metal into its compounds, by continuous interaction with atmospheric air and water vapour.

21. (c) Reason is false because $E^\circ_{Cu^{2+}/Cu} = +0.34$ volt, *i.e.*, positive.

22. (c) $E_{cell} = E_{cathode} - E_{anode}$

We know that E_{cell} should have a positive value. This is true only when $E_{cathode} > E_{anode}$

Hence, Reason (R) is false.

23. (a) $E^\circ_{Cu^{2+}/Cu}$ is positive because of high atomisation enthalpy and low hydration enthalpy of copper.

Also, the high energy to transform Cu(*s*) to $Cu^{2+}(aq)$ is not balanced by hydration enthalpy. Hence, Reason (R) is the correct explanation of Assertion (A).

24. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

25. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

26. (b) Molar conductivity decreases with increase in concentration. Hence, Assertion (A) is true.

In limiting molar conductivity, the concentration of the electrolyte approaches zero. So, Reason (R) is true, but Reason (R) is not the correct explanation of Assertion (A).

27. (d) Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted because on adding excess water to increase the dilution, the degree of dissociation increases leading to increase in the number of ions in the solution.

Hence, Reason (R) is true but Assertion (A) is false.

28. (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).

29. (d) Assertion (A) is false but Reason (R) is true.

30. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

31. (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

32. (d) During electrolysis, Cu will deposit at cathode. Hence, Assertion (A) is false but Reason (R) is true.

Case Study Based Questions

Case Study 1

Molar conductivity of a solution is the conductance of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and large cross-sectional area, so as to contain the electrolyte. In other words, molar conductivity is the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. It is denoted by Λ_m.

The molar conductivity is related to conductivity as:

$$\Lambda_m = \kappa \times V = \frac{1000}{C} \times \kappa = \kappa \times \frac{1000}{\text{Molarity}}$$

Unity of Λ_m (molar conductivity) shall be $ohm^{-1}\ cm^{-1} mol^{-1}$ or $Scm^2\ mol^{-1}$.

Thus, knowing molar concentration (*C*) and conductivity (κ), Λ_m can be calculated. Λ_m° is called molar conductivity at infinite dilution. The molar conductivity of strong electrolytes is found to vary with concentration according to the equation,

$$\Lambda_m^C = \Lambda_m^\circ - A\sqrt{C}$$

This equation is called Debye-Huckel Onsager equation.

Here, *A* is constant depending upon the type of electrolyte taken and nature of solvent and temperature.

Read the given passage carefully and give the answer of the following questions:

Q 1. If conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}, the molar conductivity of the solution shall be (in S cm^{-1} mol^{-1})

a. 3.276 b. 0.3276
c. 32.76 d. 327.6

Q 2. Molar conductivity of a solution is $1.26 \times 10^2\ \Omega^{-1}\ cm^2\ mol^{-1}$. Its molarity is 0.01. Its specific conductivity will be:

a. 1.26×10^{-9} b. 1.26×10^{-3}
c. 1.26×10^{-4} d. 12.6×10^{-3}

Q 3. The increase in molar conductivity of HCl with dilution is due to:

a. increase in self-ionisation of water
b. hydrolysis of HCl
c. decrease in self-ionisation of water
d. decrease in interionic forces

Q 4. Which of the following is wrong about molar conductivity?

a. The solution contains Avogadro number of molecules of the electrolyte.
b. It is the product of specific conductivity and volume of solution in cc containing 1 mole of electrolyte.
c. Its units are $ohm^{-1}\ cm^2\ mol^{-1}$.
d. Its value for 1 M NaCl is same as that of 1 M glucose solution.

Answers

1. (c) 32.76

2. (b) 1.26×10^{-3}

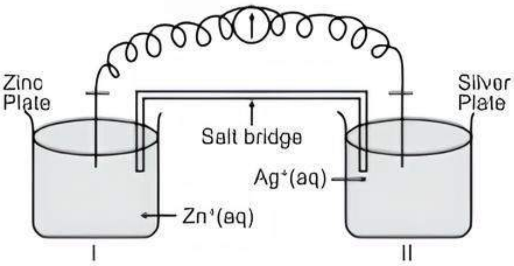
3. (d) decrease in interionic forces

4. (d) Its value for 1 M NaCl is same as that of 1 M glucose solution

Case Study 2

Oxidation-reduction reactions are commonly known as redox reactions. They involve transfer of electrons from one species to another. In a spontaneous reaction, energy is released which can be used to do useful work. The reaction is split into two half reactions. Two different containers are used and a wire is used to drive the electrons from one side to the other and a Voltaic/Galvanic cell is created. It is an electrochemical cell that uses spontaneous redox reactions to generate electricity. A salt bridge also connects to the half cells. The reading of the voltmeter gives the cell voltage or cell potential or electromotive force. If E°_{cell} is positive, the reaction is spontaneous and if it is negative, the reaction is non-spontaneous and is referred to as electrolytic cell. Electrolysis refers to the decomposition of a substance by an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+}. This was first formulated by Faraday in the form of laws of electrolysis.

The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. Conductivity is represented by κ and it depends upon nature and concentration of electrolyte, temperature etc. A more common term molar conductivity of a solution at a given concentration is conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. Limiting molar conductivity of weak electrolytes cannot be obtained graphically.



Read the given passage carefully and give the answer of the following questions:

(CBSE 2022 Term-2)

Q 1. Is silver plate the anode or cathode? What will happen if the salt bridge is removed?

Q 2. When does electrochemical cell behaves like an electrolytic cell?

Q 3. (i) What will happen to the concentration of Zn^{2+}, and Ag^+ when $E_{cell} = 0$?

(ii) Why does conductivity of a solution decreases with dilution?

OR

The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution.

Answers

1. Silver plate is the cathode. No current will flow and the voltage will drop to zero if the salt bridge is removed.
2. An electrochemical cell behaves like an electrolytic cell when $E_{ext} > E_{cell}$.
3. (i) When $E_{cell} = 0$ (equilibrium is reached), concentration of Zn^{2+} and Ag^+ ions will not change.
   (ii) The number of ions per unit volume that carry the current in a solution decreases on dilution. Hence, conductivity decreases.

OR

We know that, $\Lambda_m = \dfrac{1000 \times \text{Conductivity}}{\text{Molarity}}$

$$\Rightarrow \quad \text{Conductivity} = \frac{\Lambda_m \times \text{Molarity}}{1000}$$

$$= \frac{138.9 \times 1.5}{1000} = 0.208 \text{ S cm}^{-1}.$$

Case Study 3

The lead-acid battery represents the oldest rechargeable battery technology. Lead acid batteries can be found in a wide variety of applications including small-scale power storage such as UPS systems, ignition power sources for automobiles, along with large, grid-scale power systems. The spongy lead act as the anode and lead dioxide as the cathode. Aqueous sulphuric acid is used as an electrolyte. The half-reactions during discharging of lead storage cells are:

Anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$

$\longrightarrow PbSO_4(s) + 2H_2O$

There is no safe way of disposal and these batteries end-up in landfills. Lead and sulphuric acid are extremely hazardous and pollute soil, water as well as air. Irrespective of the environmental challenges it poses, lead-acid batteries have remained an important source of energy.

Designing green and sustainable battery systems as alternatives to conventional means remains relevant. Fuel cells are seen as the future source of energy. Hydrogen is considered a green fuel. Problem with fuel cells at present is the storage of hydrogen. Currently, ammonia and methanol are being used as a source of hydrogen for fuel cell. These are obtained industrially, so add to the environmental issues.

If the problem of storage of hydrogen is overcome, is it still a 'green fuel'? Despite being the most abundant element in the Universe, hydrogen does not exist on its own so needs to be extracted from the water using electrolysis or separated from carbon fossil fuels. Both of these processes require a significant amount of energy which is currently more than that gained from the hydrogen itself. In addition, this extraction typically requires the use of fossil fuels. More research is being conducted in this field to solve these problems. Despite the problem of no good means to extract Hydrogen, it is a uniquely abundant and renewable source of energy, perfect for our future zero-carbon needs.

Read the given passage carefully and give the answer of the following questions:

(CBSE SQP 2023-24)

Q 1. How many coulombs have been transferred from anode to cathode in order to consume one mole of sulphuric acid during the discharging of lead storage cell?

Q 2. How much work can be extracted by using lead storage cell if each cell delivers about 2.0 V of voltage? (1F = 96500 C).

Q 3. Do you agree with the statement "Hydrogen is a green fuel." Give your comments for and against this statement and justify your views.

OR

Imagine you are a member of an agency funding scientific research. Which of the following projects will you fund and why?

(i) Safe recycling of lead batteries

(ii) Extraction of hydrogen

Answers

1. 2 mole e^- (or $2F$) have been transferred from anode to cathode to consume 2 mol of H_2SO_4 therefore, one mole H_2SO_4 requires one Faraday of electricity or 96500 coulombs.
2. We have $W_{max} = -nFE^\circ = -2 \times 96500 \times 2.0 = 386000$ J of work can be extracted using lead storage cell when the cell is in use.
3. Yes. Hydrogen is a fuel that on combustion gives water as a by product. There are no carbon emissions and no pollutions caused.

   However, at present the means to obtain hydrogen are electrolysis of water which use electricity obtained from fossil fuels and increase carbon emissions.

   In spite of the problems faced today in the extraction of hydrogen, we cannot disagree on the fact that hydrogen is a clean source of energy. Further research can help in finding solutions and green ways like using solar energy for extraction of hydrogen.

   No. It is true that hydrogen is fuel that on combustion gives water as a by product. There are no carbon emissions and no pollutions caused.

   However, at present the means to obtain hydrogen are electrolysis of water which use electricity obtained from fossil fuels and increase carbon emissions.

   Hydrogen is no doubt a green fuel, but the process of extraction is not green as of today. At present, looking at the process of extraction, hydrogen is not a green fuel.

   OR

   Both answers will be treated as correct.

   (i) Lead batteries are currently the most important and widely used batteries. These are rechargeable. The problem is waste management which needs research and awareness. Currently, these are being thrown into landfills and there is no safe method of disposal or recycling. Research into safer method of disposal will reduce the pollution and health hazards caused to a great extent.

   (ii) Fuel cell is a clean source of energy. Hydrogen undergoes combustion to produce water. The need of the hour is green fuel and hydrogen is a clean fuel. The current problem is obtaining hydrogen. Research that goes into this area will help solve the problem of pollution and will be a sustainable solution.

Very Short Answer Type Questions

Q 1. Why are alkali metals strong reducing agents?

Ans. All alkali metals occupy lowest position in the electrochemical series because the values of their standard electrode potential are more negative. Thus, these have strong tendency to form cation by losing electron(s) and hence, act as strong reducing agents.

Q 2. Although aluminium is placed below hydrogen in the electrochemical series but it is stable in air and water. Why?

Ans. This is because of the formation of an inert layer of its oxide which prevents aluminium from spontaneous reaction.

Q 3. Why is silver nitrate solution kept in coloured bottles? *(CBSE 2016)*

Ans. Silver nitrate gets decomposed in the presence of sunlight. To prevent its decomposition by sunlight, it is kept in coloured bottles.

$$2AgNO_3(s) \xrightarrow{\text{Sunlight}} 2Ag\downarrow + 2NO_2\uparrow + O_2\uparrow$$

Q 4. $HgCl_2$ and $SnCl_2$ cannot exist together in an aqueous solution. Explain with reason.

Ans. $HgCl_2$ and $SnCl_2$ can not exist together in an aqueous solution because they react with each other.

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_2$$

Q 5. Explain why hydrogen is released at anode when melted calcium hydride is electrolysed.

Ans. Melted calcium hydride contains negatively charged hydrogen or hydrogen in the form of hydride ion.

$$Ca^{2+}\ (H)_2^-$$

Thus, when calcium hydride is electrolysed, hydrogen (H_2) is released at anode.

Q 6. Write Nernst equation of electrode potential and explain the symbols used in it.

Ans. For an electrode reaction.

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

The Nernst equation is $E = E^\circ + \frac{2.303RT}{nF}\log[M^{n+}]$

where, E = electrode potential E° = standard electrode potential, n = number of electrons involved in the electrode reaction, R = gas constant, T = absolute temperature, F = Faraday.

Q 7. Can Br^- be oxidised into bromine by Fe^{3+} ion?

$$(E^\circ_{Fe^{3+}/Fe^{2+}} = 0.771\text{ V}, E^\circ_{Br_2/Br^-} = 1.09\text{ V})$$

Ans. No, because, the E°_{cell} obtained by the reaction of Fe^{3+} and Br^- ions is negative.

$$\begin{array}{ll} 2Br^- \longrightarrow Br_2 + 2e^-, & E^\circ = -1.09\text{ V} \\ 2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}, & E^\circ = +0.77\text{ V} \\ \hline 2Fe^{3+} + 2Br^- \longrightarrow 2Fe^{2+} + Br_2, & E^\circ = -0.32\text{ V} \end{array}$$

Q 8. Using the E° values of A and B, predict which is better for coating the surface of iron $[E^\circ_{(Fe^{2+}/Fe)} = -0.44\text{ V}]$ to prevent corrosion and why?

$$E^\circ_{(A^{2+}/A)} = -2.37\text{ V} ; E^\circ_{(B^{2+}/B)} = -0.14\text{ V}$$

(CBSE 2016)

Ans. Metals of lower electrode potential value when connected with iron protect it from oxidation and prevent corrosion. Hence, coating of metal. A having lower electrode potential will be better than B which has higher $E^\circ_{(B^{2+}/B)} = -0.14$ V.

Q 9. Define corrosion.

Ans. The process in which metals react with substances present in the atmosphere (like CO_2, H_2S, H_2O etc.) and form a layer of their compounds on its surface is called corrosion.

Example: Formation of $Fe_2O_3 \cdot x\,H_2O$ at iron surface.

Q 10. Out of zinc and tin, whose coating is better to protect iron objects? *(CBSE 2020)*

Ans. Zn is a better choice.

Short Answer Type-I Questions

Q 1. Explain strong and weak electrolytes with examples.

Ans. Strong Electrolytes: The substances which have the ability to dissociate completely or almost completely are called strong electrolytes *e.g.*, NaCl, HCl, KCl, NaOH, HNO_3, H_2SO_4 etc.

Weak Electrolytes: The substances which undergo only partial dissociation or very less ionisation are called weak electrolytes *e.g.*, H_2CO_3, $ZnCl_2$, CH_3COOH etc.

Q 2. Is the following reaction possible? Explain with reason.

$$Fe(s) + H_2SO_4(aq) \longrightarrow FeSO_4 + H_2\uparrow$$

Ans. In the reaction $Fe(s) + H_2SO_4(aq) \longrightarrow FeSO_4 + H_2\uparrow$ atoms of Fe (which is placed below hydrogen in the electrochemical series or standard electrode potential of Fe is more negative than H) are able to give electrons. Hence, Fe displaces H_2 from H_2SO_4. Thus, this reaction is possible.

Q 3. Zinc metal can displace copper from copper sulphate solution but gold cannot. Explain with reason.

Ans. In electrochemical series, Zn is placed below Cu *i.e.*, standard electrode potential E° value of Zn is more negative than that of Cu, so Zn can displace, Cu from $CuSO_4$ solution. Contrary to this, gold (Au) is placed above copper in electrochemical series, so it can not displace Cu from $CuSO_4$ solution.

Q 4. HgO decomposes on heating but MgO does not. Explain with reason.

Ans. The oxides of the elements which are placed above Cu in the electrochemical series or which have standard reduction potential less than + 0.34 V, get decomposed on heating. Since Hg is placed above Cu whereas Mg is placed below it, so HgO gets decomposed on heating but MgO does not.

$$2HgO(s) \xrightarrow{\Delta} 2Hg + O_2\uparrow$$

$$MgO(s) \xrightarrow{\Delta} \text{No effect}$$

Q 5. Explain half-cell with example.

Ans. When a metallic electrode is dipped into an electrolyte solution, an equilibrium develops between metallic electrode and metal ions. This assembly is called half cell.

Example: When a rod of zinc metal (*i.e.*, electrode) is dipped into the zinc sulphate solution (solution of metal salt *i.e.*, electrolyte) the ions of zinc metal (electrode) try to move into the solution. After losing two electrons, the metal electrode becomes positively charged. This assembly works as a half-cell.

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

Q 6. One of zinc and copper does not displace hydrogen gas from acids. Why?

OR

Zinc reacts with dilute hydrochloric acid but copper does not. Explain with reason.

Ans. Since, the standard reduction potential of zinc is higher (negative value) as compared to that of hydrogen. So, it displaces hydrogen from the dilute acids.

$$Zn(s) + \underset{\text{(dilute)}}{2HCl} \longrightarrow ZnCl_2 + H_2\uparrow$$

The standard reduction potential of copper is lower (negative value) than that of hydrogen, so it can not displace hydrogen from dilute acids.

$$Cu(s) + HCl(aq) \longrightarrow \text{No reaction.}$$

Q 7. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? *(CBSE 2023)*

Ans. Kohlrausch Law: To calculate the molar conductivity (at infinite dilution) of weak electrolytes, Kohlrausch gave a law, called Kohlrausch law. According to this law, at infinite dilution, the molar conductivity of an electrolyte can be represented as the sum of ionic molar conductivities of its all the cations and anions of the electrolyte.

Decrease of Conductivity on Dilution: The conductivity basically changes with the change in the concentration of the given electrolyte. During dilution, the number of ions present per unit volume carrying the current tends to decrease. This results in a decrease in the conductivity of the electrolytic solution.

Q 8. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298K. Calculate the electrode potential.

$$\left[E^\circ_{(Zn^{2+}/Zn)} = -0.76\ \text{V}\right]$$

Sol. The electrode reaction written at reduction reaction is,

$$Zn^{2+} + 2e^- \longrightarrow Zn \qquad (n = 2)$$

Applying Nernst equation, we get

$$E^\circ_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} - \frac{0.0591}{2}\log\frac{1}{[Zn^{2+}]}$$

As 0.1 M $ZnSO_4$ solution is 95% dissociated, this means that in the solution,

$$[Zn^{2+}] = \frac{95}{100} \times 0.1 = 0.095\ \text{M}$$

$$\therefore\ E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2}\log\frac{1}{0.095}$$

$$= -0.76 - 0.02955\,(3 - 1.9777)$$

$$= -\underline{0.79021\ \text{V}}$$

Q 9. In a galvanic cell, the following cell reaction occurs:

$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)\ E^\circ_{cell} = +1.56\ \text{V}$

(i) Is the direction of flow of electrons from zinc to silver or silver to zinc?

(ii) How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions?

(CBSE 2017)

Ans.

TiP

Be specific while writing answers. Avoid unnecessary explanations.

(i) The direction of flow of electrons is from zinc to silver.

(ii) Concentration of Zn^{2+} ions will increase and Ag^+ ions will decrease when the cell functions.

Q 10. Following reactions may occur at cathode and anode during electrolysis of aqueous sodium chloride. What products will be held at anode and cathode? Use given E° values to justify your answer.

Cathode: $Na^+(aq) + e^- \rightarrow Na(s),\quad E^\circ = -2.71\ \text{V}$

$$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g),\ E^\circ = 0.00\ \text{V}$$

Anode: $Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^-,\ E^\circ = +1.36\ \text{V}$

$$2H_2O(aq) \rightarrow O_2(g) + 4H^+ + 4e^-,\quad E^\circ = +1.23\ \text{V}$$

(CBSE 2019)

Ans. **At cathode:** $H_2(g)$ is produced due to greater E° value of H^+ ion.

At anode: $Cl_2(g)$ is produced due to over voltage of oxygen.

Q 11. Find out the EMF of the cell Zn / Zn^{2+} (1 M) || Co^{2+} / CO (1 M)| Co. For this cell E° values for Zn^{2+} / Zn and Co^{2+} are −0.76 V and + 0.28 V respectively and their concentrations are 1 molar.

Sol. Given,

$$E^\circ_{Zn^{2+}/Zn} = -0.76\ \text{V},$$

$$E^\circ_{Co^{2+}/Co} = +0.28\ \text{V}$$

For the cell, Zn | Zn^{2+} (1 M) || Co^{2+} (1 M) | Co the half-cell reactions are as follows:

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

$$\underline{Co^{2+} + 2e^- \longrightarrow Co}$$

$$\underline{Zn + Co^{2+} \longrightarrow Zn^{2+}\ Co;\ n = 2}$$

From Nernst equation,

$$E_{cell}(\text{EMF}) = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Co^{2+}]}$$

$$= (E^\circ_{Co^{2+}/Co} - E^\circ_{Zn^{2+}/Zn}) - \frac{0.0591}{2}\log\frac{1}{1}$$

$$= [0.28 - (-0.76)] - 0$$

$$= 0.28 + 0.76 = \underline{1.04\ \text{V}}.$$

COMMON ERROR

Students tend to overlook or incorrectly copy the data.

Q 12. A cell is constructed between copper and silver

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

If the two half-cells are working under standard condition, then calculate the emf of the cell.

$$E^\circ_{Cu^{2+}/Cu} = +0.34\ \text{V},\ E^\circ_{Ag^+/Ag} = +0.80\ \text{V}$$

Sol. In standard conditions, E_{cell} is called E° cell and for this cell,

$$E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu}$$

$$= 0.80 - (+0.34)\ \text{V} = \underline{+0.46\ \text{V}}$$

Q 13. The standard electrode potential of Daniell cell is 1.1 V. Calculate the standard Gibbs energy for the following reaction:

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

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

Sol. The half-cell reactions of the Daniell cell are as follows:

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

$$\underline{Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)}$$

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

Standard Gibbs energy, $\Delta_r G^\circ = -nF\,E^\circ_{cell}$

$$= -2\ \text{mol} \times (96500\ \text{C mol}^{-1}) \times (1.1\ \text{V})$$

$$= -212300\ \text{C-V} = 212300\ \text{J} = \underline{-212.3\ \text{kJ}}$$

Q 14. Calculate the potential of hydrogen electrode in contact with a solution, pH of which is 10. *(NCERT INTEXT)*

Sol. For hydrogen electrode

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2$$

From Nernst equation,

$$E_{H^{\circ},\frac{1}{2}H_2} = E^{\circ}_{H^+,\frac{1}{2}H_2} - \frac{0.0591}{n}\log\frac{1}{[H^+]}$$

$$= 0 - \frac{0.0591}{1}\log\frac{1}{10^{-10}}$$

$$[\because pH = 10;\ H^+ = 1 \times 10^{-pH} = 10^{-10}\ M]$$

$$= -\,0.0591 \times 10 = -\,0.591\ V.$$

Q 15. The electrical resistance of a column of 0.05mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate the conductivity. *(CBSE 2023)*

Sol. Given, length of column, $l = 50$ cm

Diameter of column = 1 cm

Radius = 0.5 cm

Electrical resistance of column,

$$R = 5.55 \times 10^3 \text{ ohm}$$

We know that, resistivity, $\rho = \frac{AR}{l}$

$$\rho = \frac{(\pi r^2) \times R}{l}$$

$$= \frac{3.14 \times (0.5)^2 \times 5.55 \times 10^3}{50}$$

$$= \frac{0.785 \times 5.55 \times 10^3}{50}$$

$$= 87.135\ \Omega\ cm$$

Conductivity, $\kappa = \frac{1}{\rho}$

$$= \frac{1}{87.135\ \Omega\ cm}$$

$$= 0.01147\ Scm^{-1}$$

Hence, the required conductivity is $0.01147\ Scm^{-1}$.

Q 16. Define molar conductivity for the solution of an electrolyte. How does it vary with concentration?

Ans. Molar conductivity of a solution at a given concentration is defined as the conductance of the electrolytic solution kept between the electrodes of a conductivity cell at unit distance but having area of cross-section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte.

Molar conductivity increases with decrease in concentration because total volume *V* of solution containing one mole of electrolyte also increases.

Q 17. The resistance and conductivity of a conductivity cell containing 0.001 M KCl solution of 298K are 1200 Ω and 1.5×10^{-4} S cm^{-1}. Calculate its cell constant and molar conductivity. *(CBSE 2022 Term-2)*

Sol. Cell constant = Conductivity × Resistance

$$= 1.5 \times 10^{-4} \times 1200$$

$$= 0.18\ cm^{-1}$$

$$\text{Molar conductivity } (\Lambda_m) = \frac{1000 \times \text{Conductivity}}{\text{Molarity}}$$

$$= \frac{1000 \times 1.5 \times 10^{-4}}{0.001}$$

$$= 150\ cm^2 mol^{-1}.$$

Q 18. The conductivity of 0.001 M acetic acid is 7.8×10^{-5} S cm^{-1}. Calculate its degree of dissociation if Λ°_m for acetic acid is 390 S cm^2 mol^{-1}. *(CBSE 2022 Term-2)*

Sol. $$\text{Molar conductivity } (\Lambda_m) = \frac{1000 \times \text{Conductivity}}{\text{Molarity}}$$

$$= \frac{1000 \times 7.8 \times 10^{-5}}{0.001}$$

$$= 78\ S\ cm^2 mol^{-1}.$$

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m}{\Lambda^{\circ}_m} = \frac{78}{390} = 0.2$$

Q 19. (i) Why on dilution the Λ_m of CH_3COOH increases very fast, while that of CH_3COONa increases gradually?

(ii) What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell? *(CBSE 2022 Term-2)*

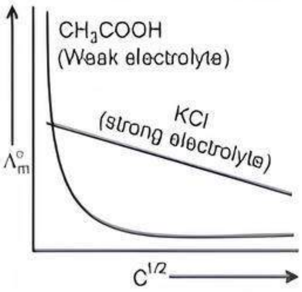
Ans. (i) In case of CH_3COOH which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation resulting in drastic increase in Λ_m.

In the case of CH_3COONa which is a strong electrolyte, the number of ions remains the same but the inter-ionic attraction decreases resulting in gradual increase in Λ_m.

(ii) If external potential applied becomes greater than E°_{cell} of electrochemical cell, the reaction gets reversed. It now functions as an electrolytic cell.

Q 20. With the help of a graph explain why it is not possible to determine Λ°_m for a weak electrolyte by extrapolating the molar conductivity (Λ_m) *versus* $C^{1/2}$ curve as for strong electrolyte. *(CBSE 2023)*

Ans. Weak electrolytes have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation and consequently, the number of ions in total volume of solution that contains 1 mole of electrolyte. On dilution, Λ_m increases steeply especially near lower concentrations. Hence, Λ°_m cannot be obtained by extrapolation of Λ_m to zero



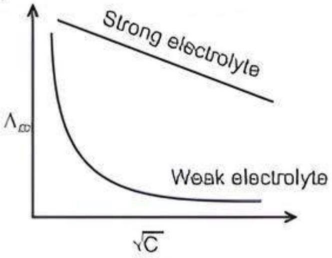
concentration as for strong electrolyte. For strong electrolytes, Λ_m increases slowly with dilution and is represented by $\Lambda_m = \Lambda_m^\circ - AC^{1/2}$

On plotting Λ_m against $C^{1/2}$, a straight line is obtained with intercept equal to Λ_m° and slope equal to $-A$.

Q 21. On diluting two electrolytes *A* and *B*, the Λ_m of *A* increases 25 times while that of '*B*' increases by 1.5 times. Which of the two electrolytes is strong? Justify your answer graphically. *(CBSE 2023)*

Ans. *B* is a strong electrolyte. The molar conductivity increases slowly with dilution as there is no increase in number of ions on dilution as strong electrolytes are completely dissociated.

The graph can be shown as follows:



Q 22. Write a short note on electrolytic cell.

Ans. The cell which converts electrical energy into chemical energy is called electrolytic cell. In it, anode is positive terminal and cathode is negative terminal. Electricity is given by external sources like battery or some other sources. In this cell, both the electrodes are dipped in the same electrolytic solution filled in a vessel. Here no salt bridge or porous pot is used. *e.g.*, when electricity is passed using two electrodes in the solution of $ZnCl_2$, it gets decomposed. Here, oxidation takes place at anode and reduction takes place at cathode in the following manner:

$$ZnCl_2(aq) \rightleftharpoons \underset{\text{cathode}}{Zn(s)} + \underset{\text{anode}}{Cl_2(g)}$$

i.e., $ZnCl_2(aq) \rightleftharpoons + Zn^{2+}(aq) + 2Cl^-(aq)$

At anode: $2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-$ (oxidation)

At cathode: $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$ (reduction)

TiP

Electrical energy is used to carry out non-spontaneous chemical reactions.

Q 23. Write the Faraday's first law of electrolysis. *(CBSE 2015)*

Ans. According to Faraday's first law, when electricity is passed through the solution of an electrolyte, the amount of substance deposited at any of the electrode is directly proportional to the quantity of electricity passed through the electrolyte (solution or melt). *i.e.*,

$\Rightarrow$ $W \propto Q \Rightarrow W = Z \times Q \Rightarrow W = Z \times I \times t$

where, Q = charge (in coulomb), I = current (in ampere)

t = time (in second) and Z = electrochemical equivalent.

Q 24. Give the Faraday's second law of electrolysis.

TiP

Write the law as stated. Stick to the statement as the marks are allotted to that only.

Ans. According to Faraday's second law, the amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their equivalent weights, *i.e.*,

$$W_1 \propto E_1 \text{ and } W_2 \propto E_2$$

$$\therefore \quad \frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3} = \ldots$$

where $W_1, W_2, W_3 \ldots$ are masses of substances 1, 2, 3, ... respectively and E_1, E_2, E_3 are their respective equivalent weights.

Q 25. Write the name of the cell which is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell. *(CBSE 2017)*

Ans. Mercury cell is generally used in hearing aids.

Reactions in Mercury Cell:

At anode:

$$Zn(s) + 2OH^- \longrightarrow ZnO(s) + H_2O(l) + 2e^-$$

At cathode:

$$HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-$$

Overall reaction:

$$Zn(s) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

COMMON ERROR

Students often make mistake in writing electrode reactions for different cells.

Q 26. Write the name of the cell which is generally used in transistors. Write the reactions taking place at the anode and the cathode of this cell. *(CBSE 2017)*

Ans. Leclanche cell is commonly used in transistors. The electrode reactions of Leclanche cell can be written as:

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

At cathode: $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

NH_3 produced in the reaction at cathode forms a complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$.

Q 27. Give reasons:

(i) Mercury cell delivers a constant potential during its life time.

(ii) In the experimental determination of electrolytic conductance, Direct Current (DC) is not used. *(CBSE 2023)*

Ans. (i) This is because the overall reaction in mercury cell does not involve any ion in solution whose concentration can change during its life time.

(ii) This is due to the following reasons:

(a) On using DC, electrolysis will occur and the concentration of the solution will change with time.

(b) Using DC will polarise the electrodes and electrolyte leading to an error in measured conductivity.

Q 28. Define fuel cell with an example. What advantages do the fuel cells have over primary and secondary batteries? *(CBSE 2023)*

Ans. Fuel Cell: The galvanic cells which are designed to convert the energy of combustion of fuels like hydrogen, methane etc. directly into electrical energy are called fuel cells. These cells are 70%, more efficient as compared to thermal plants and are pollution free *e.g.*, Hydrogen-oxygen fuel cell.

Fuel cells have the following advantages over primary and secondary batteries:

(i) Fuel cells run continuously as long as the reactants are supplied and products are removed continuously.

(ii) Fuel cells convert the energy of combustion of fuels into electrical energy and are highly efficient.

Q 29. Name the cell which:

(i) was used in Apollo Space programme.

(ii) is used in automobiles and inverters.

(iii) is suitable for hearing aids and watches.

(iv) does not give a steady potential and is used in transistors. *(CBSE 2023)*

Ans. (i) Fuel cell

(ii) Lead storage battery

(iii) Mercury cell

(iv) Dry cell or Leclanche cell

Q 30. Write the name of the cell which is generally used in inverters. Write the reactions taking place at the anode and the cathode of this cell. *(CBSE 2017)*

Ans. Lead storage battery is used in inverters. In this, the anode is made of spongy lead and the cathode is a grid of lead packed with lead dioxide. The electrolyte used is H_2SO_4 (38% by mass).

At anode:

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

At cathode:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s)$$
$$2H_2O(l)$$

The overall cell reaction:

$$Pb(s) + PbO_2(s) + H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

On recharging the battery, the reaction is reversed

$$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$$

TiP

Lead storage battery is a secondary cell which can be recharged by passing direct current through it.

Q 31. Corrosion is an electrochemical phenomenon. The oxygen in moist air reacts as follows:

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq).$$

Write down the possible reactions for corrosion of zinc occurring at anode, cathode and overall reaction to form a white layer of zinc hydroxide. *(CBSE SQP 2022-23)*

Ans. The possible reactions for corrosion of zinc occurring at anode and cathode and overall reaction to form a white layer of zinc hydroxide are as shown:

Anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Overall: $2Zn(s) + O_2(g) + 2H_2O(l) \longrightarrow 2Zn^{2+}(aq) + 4OH^-(aq)$

$2Zn(s) + O_2(g) + 2H_2O(l) \longrightarrow 2Zn(OH)_2(ppt)$

Q 32. Using $E°$ values of X and Y given below, predict which is better for coating the surface of iron to prevent corrosion and why? *(CBSE 2023)*

Given: $E^\circ_{X^{2+}/X} = -2.36\text{ V}$

$E^\circ_{Y^{2+}/Y} = -0.14\text{ V}$

$E^\circ_{Fe^{2+}/Fe} = -0.44\text{ V}$

Ans. The oxidation potentials of elements is important to be considered here because corrosion is a phenomenon of oxidation of iron. Element having higher oxidation potential than Fe oxidises faster than iron preventing its corrosion.

The oxidation potential of X is higher than iron so it can be used for coating the surface of iron in order to prevent corrosion.

Short Answer Type-II Questions

Q 1. What is redox potential? Explain.

Ans. The potential difference developed in the equilibrium between metal and ions of the solution, when oxidation and reduction reactions take place in the cell is called redox potential.

Example: $\underset{\text{Oxidising agent}}{Ox} + ne^- \longrightarrow \underset{\text{Reducing agent}}{Red}$

If the potential of the cell is E, then concentration of oxidising agent (Ox) and concentration of reducing agent (Red) at 25° are related as:

$$E = E^\circ + \frac{0.0591}{n}\log_{10}\frac{(Ox)}{(Red)}$$

or

$$E = E^\circ - \frac{0.0591}{n}\log_{10}\frac{(Red)}{(Ox)}$$

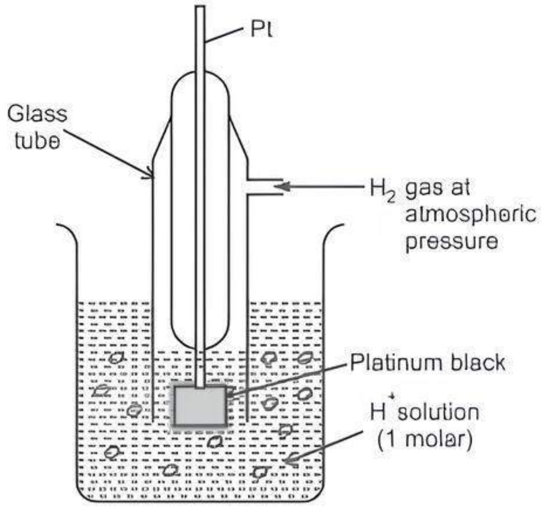
Here, E° = Redox potential, n = number of electrons accepted by oxidising agent (Ox). By accepting them, the oxidising agent gets converted into its reducing agent form (Red). Above equation is called Nernst equation, *e.g.*,

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

$$E = E^\circ - \frac{0.0591}{n}\log_{10}[M^{n+}]$$

Q 2. Describe standard hydrogen electrode along with the figure and write an application of it.

Ans. Standard Hydrogen Electrode: The standard hydrogen electrode consists of a platinum electrode coated with a layer of platinum black. To make this electrode, a thin plate of platinum metal is dipped in chloroplatinic acid and then AC current is passed. Due to this, it is coated by a layer of platinum black.



Standard hydrogen electrode

This plate is surrounded by a glass plate (as shown in the fig.). which contains an opening at the upper side for the passage of hydrogen gas at one atmospheric pressure and another opening at the lower side to release rest of the hydrogen gas. This electrode is dipped in a 1M solution of hydrogen ion (*i.e.*, 1.0M HCl). In this solution, at atmospheric pressure, some of the pure hydrogen gas gets adsorbed over the platinum surface and the remaining gets dissolved in one molar solution of the acid. Thus, an equilibrium develops between the hydrogen gas adsorbed over platinum electrode and hydrogen ions present in the solution.

$$H_2 \rightleftharpoons 2H^+(aq) + 2e^-$$

It can also be expressed in the following manner:

$$\underset{p = 1\text{ atmosphere } (a = 1.0M)}{H_2(g), Pt \mid H^+(aq)} \quad \text{or} \quad \underset{p = 1\text{ atmosphere } (a = 1.0M)}{Pt \mid H_2(g) \mid H^+(aq)}$$

The electrode potential of Standard Hydrogen Electrode (SHE) is taken as zero (0.0000 V).

TiPS

- *The value of the oxidation potential of the same cell reaction will be the same with the sign reversed.*
- *Sometimes metals like Pt or gold are used as inert electrodes.*

Applications: It is used to calculate standard electrode potential of an electrode. For this, a galvanic cell is constructed by using the electrode (electrode potential of which is to be calculated) and a standard hydrogen electrode and the cell potential (or emf) is calculated. This emf is the standard electrode potential of that electrode with respect to hydrogen.

Q 3. Calculate the emf of the following cell at 298 K:

$Fe(s) \mid Fe^{2+}$ (0.001 M $\parallel H^+$ (0.01 M) + $H_2(g)$ (1 bar) | Pt(s)

Given that $E^\circ_{cell} = +0.44$ V

[log 2 = 0.3010 log 3 = 0.4771 log 10 = 1]

(CBSE 2022 Term-2)

Sol. The cell reaction is

$$Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)$$

$\therefore n = 2$

According to Nernst equation, at 298 K.

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Fe^{2+}]}{[H^+]^2}$$

$$= 0.44 - \frac{0.0591}{2}\log\frac{(0.001)}{(0.01)^2}$$

$$= 0.44 - 0.02955\log(10)$$

$$= 0.44 - 0.02955 = \underline{0.41045\text{ V}}.$$

Q 4. Write the Nernst equation and calculate the emf of the following cell at 298 K:

$Zn \mid Zn^{2+}$ (0.001 M) $\parallel H^+$ (0.01 M) | $H_2(g)$ (1 bar) | Pt (s)

Given: $E^\circ_{Zn^{2+}/Zn} = -0.76$ V

$E^\circ_{H^+/H_2} = 0.00$ V [log 10 = 1]

(CBSE 2023, 2022 Term-2)

Sol. $E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{Zn^{2+}/Zn} = 0 - (-0.76) = 0.76$ V

Cell reaction is:

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

$\therefore n = 2$

Nernst equation is: $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n}\log\dfrac{[Zn^{2+}]}{[H^+]^2}$

$$= 0.76 - \frac{0.0591}{2}\log\frac{(0.001)}{(0.01)^2}$$

$$= 0.76 - 0.02955\log 10$$

$$= 0.76 - 0.02955 = \underline{0.73045\text{ V}}$$

Q 5. Calculate Δ_rG° and log K_C for the following cell:

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

Given that $E^\circ_{cell} = 1.05$ V, IF = 96,500 C mol^{-1}

(CBSE 2022 Term-2)

Sol. Here, $n = 2$

We know that, $\Delta_rG^\circ = -nF\,E^\circ_{cell}$

$$= -2 \times 96500 \times 1.05$$

$$= -202650\text{ J/mol}$$

$$= -202.650\text{ kJ/mol}$$

Also, $E^\circ_{cell} = \dfrac{0.0591}{n}\log K_C$

$$\Rightarrow \quad \log k_c = \frac{E^\circ_{cell} \times n}{0.0591} = \frac{1.05 \times 2}{0.0591} = \underline{35.53}$$

Q 6. Calculate the emf of the following cell. Also predict, which electrode is positive terminal and which one is negative terminal. Write the half-cell reaction and overall reaction occurring in the cell.

$Ni \mid Ni^{2+}$ (0.1 M) $\parallel Ag^+$ (0.1M) | Ag

$E^\circ_{Ni^{2+}/Ni} = -0.25$ V and $E^\circ_{Ag^+/Ag} = +0.80$ V

Sol.

TiP

Do more practice of numericals based on Nernst equation.

For the cell

$$Ni \mid Ni^{2+}\ (0.01\text{ M}) \parallel Ag^+\ (0.1M) \mid Ag$$

the half-cell reactions are as follows:

At anode (at negative terminal):

(i) $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$ (oxidation)

At cathode (at positive terminal):

(ii)

$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$ (reduction)

Cell reaction : $Ni(s) + 2Ag^+(aq) \rightleftharpoons Ni^{2+}(aq) + 2Ag(s)$

$$\underline{\text{Standard emf of cell } (E^\circ_{\text{cell}}) = [E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}]}$$
$$= E^\circ_{Ag^+/Ag} - E^\circ_{Ni^{2+}/Ni}$$
$$= 0.80 - (-0.25)\text{ V} = 1.05\text{ V}$$

From Nernst equation,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log_{10}\frac{[Ni^{2+}(aq)]}{[Ag^+(aq)]^2}$$

where, $n = 2$, $E^\circ_{\text{cell}} = 1.05$ V

$[Ni^{2+}(aq)] = 0.1$ M and $[Ag^+(aq)] = 0.1$ M

$$\text{emf of the cell } (E_{\text{cell}}) = 1.05 - \frac{0.0591}{2}\log_{10}\frac{0.1}{(0.1)^2}$$
$$= 1.05 - \frac{0.0591}{2}\log_{10}10$$
$$= 1.05 - \frac{0.0591}{2} \times 1$$
$$= (1.05 - 0.0295)\text{ V} = \underline{1.0205\text{ V}}.$$

Q 7. The cell in which the following reaction occurs $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$ has $E^\circ_{\text{cell}} = 0.236$ V at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction. *(NCERT INTEXT)*

Sol. The two half-cell reactions are as follows:

$$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$$
$$2I^- \longrightarrow I_2 + 2e^-$$

Thus, for this reaction, $n = 2$

$$\underline{\Delta_r G^\circ = -nFE_{\text{cell}}}$$
$$= -(2\text{mol}) \times (96500\text{ C mol}^{-1}) \times (0.236\text{ V})$$
$$= -45548\text{ C-V or J}$$
$$= -45.55\text{ kJ}$$

Further, $\underline{\Delta_r G^\circ = -2.303\, RT \log k_c}$

or $$\log k_c = \frac{-\Delta_r G^\circ}{2.303\, RT}$$
$$= \frac{+45.55\text{ kJ}}{2.303 \times 8.314 \times 10^{-3}\text{ kJ K}^{-1} \times 298\text{ K}}$$
$$= 7.983$$

and $k_c = \text{Antilog }(7.983) = 9.616 \times 10^7$

Thus, the standard Gibbs energy of the cell is $\underline{-45.55\text{ kJ}}$ and its equilibrium constant is $\underline{9.616 \times 10^7}$.

Q 8. Calculate the emf of the following cell at 25°C:

$Al(s) \mid Al^{3+}(0.001\text{ M}) \parallel (0.1)\, Ni^{2+} \mid Ni(s)$

Given: $E^\circ_{(Ni^{2+}/Ni)} = -0.25$ V

$E^\circ_{(Al^{3+}/Al)} = -1.66$ V

[log 2 = 0.3010, log 3 = 0.4771]

(CBSE 2023, 19)

Sol. Given, $E^\circ_{(Ni^{2+}/Ni)} = -0.25$ V

$E^\circ_{(Al^{3+}/Al)} = -1.66$ V

$$\underline{E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}}$$

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

According to the cell reaction, $n = 6$

Now, using Nernst equation,

$$\underline{E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[Al^{3+}]^2}{[Ni^{2+}]^3}}$$

Putting values, we get

$$E_{\text{cell}} = 1.41 - \frac{0.0591}{6}\log\frac{(10^{-3})^2}{(10^{-1})^3}$$
$$= 1.41 - \frac{0.0591}{6}(\log(10^{-6}) - \log(10^{-3}))$$
$$= 1.41 - \frac{0.0591}{6}(-6\log 10 + 3\log 10)$$
$$= 1.41 - \frac{0.0591}{6}(-6+3)$$
$$= 1.41 - \frac{0.0591}{6}(-3) = 1.41 + \frac{0.0591}{2}$$
$$= \underline{1.4395\text{ V}}.$$

COMMON ERROR

Students tend to forget mentioning the formula and start the calculations or do not mention the units. Marks are allotted for formulas and units too.

Q 9. (i) The cell in which the following reaction occurs:

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$

has $^{\circ}_{\text{cell}}$ = 0.236V at 298K. Calculate the standard Gibbs energy of the cell reaction. (Given: 1F = 96,500 C mol^{-1})

(ii) How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours? (Given: 1F = 96,500 C mol^{-1}) *(CBSE 2017)*

Sol. (i) Standard Gibbs free energy is given by the following expressions:

$$\Delta_r G^\circ = -nFE^\circ_{\text{Cell}}$$

where, n = number of moles of electrons transferred,

F = Faraday's constant = 96,500 C mol^{-1},

E°_{cell} = cell constant.

Two half-reactions for the given redox reaction can be written as:

$$2Fe^{3+}(aq) + 2e^- \longrightarrow 2Fe^{2+}(aq)$$
$$2I^-(aq) \longrightarrow I_2(s) + 2e^-$$

2 moles of electrons are involved in the reaction, hence $n = 2$

Therefore, by substituting all the values in eq. (i), we get

$$\Delta_r G^\circ = -(2\text{mol}) \times (96500\text{ C mol}^{-1}) \times (0.236\text{ V})$$
$$= -45548\text{ J}$$
$$\Delta_r G^\circ = \underline{-45.55\text{ kJ}}$$

(ii) Given, current $(I) = 0.5$ A, time $(t) = 2$h

Quantity of charge (Q) passed $= i \times t$

$$= (0.5\text{ A}) \times (2\text{h})$$
$$= (0.5\text{A}) \times (2 \times 60 \times 60\text{ s})$$
$$= 3600\text{ C}$$

Again, $Q = ne^-$

where, n = number of electrons

e^- = charge on electron

$$\therefore\ n = \frac{Q}{e^-} = \frac{3600\text{C}}{1.6 \times 10^{-19}\text{C}} = 2250 \times 10^{19}$$

Thus, number of electrons = $\underline{2.250 \times 10^{22}}$

Q 10. (i) Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of $AgNO_3$ for 15 minutes. (Given: Molar mass of Ag = 108 g mol^{-1}, 1F = 96500 C mol^{-1})

(ii) Define fuel cell. *(CBSE 2017)*

Sol. (i) Given, current $(I) = 2$A, time $(t) = 15$ min

Quantity of electricity passed will be Q

$$= I \times t = 2 \times 15 \times 60 = 1800\text{ C}$$

Electrolysis of $AgNO_3$

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

Atomic mass of Ag = 108 g mol^{-1}

As, 96500 C deposit 108 g of Ag

$$\therefore\ 1800\text{ C will deposit} = \frac{108 \times 1800}{96500}\text{ g of Ag}$$
$$= \underline{2.014\text{ g of Ag}}$$

TiP

To find out the mass of Ag deposited at cathode, we first need to find the quantity of electricity passed using Faraday's law.

(ii) Fuel Cell: The galvanic cells in which chemical energy of combustion of fuels like hydrogen, methane etc. is converted into electrical energy are called fuel cells.

Q 11. (i) Why does the blue colour of aqueous solution of $CuSO_4$ disappear slowly when an iron rod is kept into it? Explain.

(ii) Iron displaces copper from copper sulphate solution but platinum does not displace copper. Why?

Ans. (i) In electrochemical series, Fe is placed below Cu, *i.e.*, its E° is more negative than E°_{Cu}. So, it displaces copper (Cu) from the $CuSO_4$ solution. Due to this, the blue colour of the solution disappears slowly.

$$CuSO_4(aq) + Fe(s) \longrightarrow FeSO_4(aq) + Cu(s)\downarrow$$

(ii) Standard electrode potential of Fe is more negative as compared to that of Cu. So, Fe can displace Cu from $CuSO_4$ solution.

$$CuSO_4(aq) + Fe(s) \longrightarrow FeSO_4(aq) + Cu(s)\downarrow$$

On the other hand, electrode potential of Pt is less negative or more positive as compared to Cu. Hence, Pt cannot displace Cu from $CuSO_4$ solution.

Q 12. Define conductivity and describe the relationship between conductivity and resistance.

Ans. Conductivity: The inverse of resistivity is called the conductivity or specific conductance. The conductance of an electrolytic solution placed between the electrodes having area of cross-section one cm^2 and which are one cm apart from each other is called conductivity or specific conductance. It is represented by the Greek letter κ (kappa). Its SI units is Sm^{-1} but quite often, it is expressed in Scm^{-1}.

Relationship between Conductivity and Resistance: We know that the electrical resistance of any object is directly proportional to its length l and inversely proportional to its area of cross-section A *i.e.*,

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho\frac{l}{A} \qquad \ldots(1)$$

Here, the constant of proportionality ρ (rho) is called resistivity.

So, resistivity $\rho = \dfrac{RA}{l}$

Further, conductivity $\propto \dfrac{1}{\text{resistivity}}$

$$\kappa = \frac{1}{\rho} = \frac{l}{RA} \quad \text{or} \quad \kappa = \frac{1}{R} \times \frac{l}{A} = \frac{1}{R} \times G$$

Here, $\dfrac{l}{A}$ or G is called cell constant.

So, conductivity $= \dfrac{1}{\text{resistivity}} \times$ cell constant.

Q 13. State Kohlrausch law for the independent migration of ions. Mention the application of the law. *(CBSE 2015)*

Ans. Kohlrausch Law: To calculate the molar conductivity (at infinite dilution) of weak electrolytes, Kohlrausch gave a law, called Kohlrausch law. According to this law, at infinite dilution, the molar conductivity of an electrolyte can be represented as the sum of ionic molar conductivities of its all the cations and anions of the electrolyte."

Application of Kohlrausch Law: An important application of Kohlrausch law is the calculation of molar conductivity of weak electrolyte at infinite dilution. For example, at infinite dilution, the value of molar conductivity (Λ^∞_m) of acetic acid is calculated using the molar conductivities of strong electrolytes like hydrochloric acid (HCl), sodium acetate (CH_3COONa) and sodium chloride (NaCl). Suppose the values of molar conductivities of these electrolytes are x, y and z respectively, then according to Kohlrausch law,

$$\Lambda^\infty_{m\,(CH_3COOH)} = \lambda^\infty_{(CH_3COO^-)} + \lambda^\infty_{(H^+)}$$

$$\Lambda^\infty_{m\,(HCl)} = x = \lambda^\infty_{(H^+)} + \lambda^\infty_{(Cl^-)} \qquad \ldots(1)$$

$$\Lambda^\infty_{m\,(CH_3COONa)} = y = \lambda^\infty_{(CH_3COO^-)} + \lambda^\infty_{(Na^+)} \qquad \ldots(2)$$

$$\Lambda^\infty_{m\,(NaCl)} = z = \lambda^\infty_{(Na^+)} + \lambda^\infty_{(Cl^-)} \qquad \ldots(3)$$

On subtracting eq. (3) from the sum of eqs. (1) and (2), we get

$$\Lambda^{\infty}_{m\,(HCl)} + \Lambda^{\infty}_{m\,(CH_3COONa)} - \Lambda^{\infty}_{m\,(NaCl)}$$

$$= \lambda^{\infty}_{m(CH_3COO^-)} + \lambda^{\infty}_{m\,(H^+)}$$

$$\Re^{\infty}_{m\,(CH_3COOH)} \quad \hat{O} \quad -$$

Then, the value of $\Lambda^{\infty}_{m\,(CH_3COOH)}$ can be calculated by substituting the values of x, y and z.

Q 14. 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 $= \lambda^{\circ}_{(H^+)} = 349.6$ S cm^2 mol^{-1}

and $= \lambda^{\circ}_{(HCOO^-)} = 54.6$ S cm^2 mol^{-1}) *(NCERT INTEXT)*

Sol. $$\Lambda^{\circ}_{m\,(HCOOH)} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{HCOO^-} = 349.6 + 54.6$$

$$= 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

Given, $\Lambda_{m\,(HCOOH)} = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$

∴ Degree of dissociation,

$$\alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m} = \frac{46.1 \text{ S cm}^2 \text{ mol}^{-1}}{404.2 \text{ S cm}^2 \text{ mol}^{-1}}$$

$$= \underline{0.114 \text{ or } 11.4\%}$$

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

Initial concentration c mol L^{-1} 0 0

Concentration at equilibrium $c(1-\alpha)$ $c\alpha$ $c\alpha$

$$k_\alpha = \frac{c\alpha . c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$= \frac{0.025 \times (0.114)^2}{(1-0.114)} = \underline{3.67 \times 10^{-4}}$$

Q 15. (i) Can we construct an electrochemical cell with two half-cells composed of $ZnSO_4$ solution and zinc electrodes? Explain your answer.

(ii) Calculate the λ°_m for Cl^- ion from the data given below:

$$\Lambda^{\circ}_{m\,(MgCl_2)} = 258.6 \text{ Scm}^2 \text{ mol}^{-1}$$

and $\lambda^{\circ}_{m\,Mg^{2+}} = 106 \text{ Scm}^2 \text{ mol}^{-1}$

(iii) The cell constant of a conductivity cell is 0.146 cm^{-1}. What is the conductivity of 0.01M solution of an electrolyte at 298 K, if the resistance of the cell is 1000 ohm?

(CBSE SQP 2023-24)

Ans. (i) Yes, if the concentration of $ZnSO_4$ in the two half cell is different, the electrode potential will be different making the cell possible.

(ii) We have, $\Lambda^{\circ}_{m\,(MgCl_2)} = \lambda^{\circ}_{m\,(Mg^{2+})} + 2\lambda^{\circ}_{m\,(Cl^-)}$

$$258.6 = 106 + 2\lambda^{\circ}_{m\,(Cl^-)}$$

$$\lambda^{\circ}_{m\,(Cl^-)} = \underline{76.3 \text{ Scm}^2 \text{ mol}^{-1}}$$

(iii) We know that cell constant,

$$G^{\circ} = k \times R$$

$$k = G^{\circ}/R$$

$$= 0.146/1000$$

$$= 1.46 \times 10^{-4} \text{ Scm}^{-1}$$

Hence, the conductivity is $\underline{1.46 \times 10^{-4} \text{ Scm}^{-1}}$.

Q 16. The electrical resistance of a column of 0.05 M KOH solution of diameter 1 cm and length 45.5 cm is 4.55 × 10^3 ohm. Calculate its molar conductivity.

(CBSE 2017)

Sol. Given, concentration of KOH (M) = 0.05 M

diameter = 1 cm; radius (r) = $\frac{1}{2}$ cm,
length (l) = 45.5 cm

electrical resistance (R) = 4.55 × 10^3 ohm.

$$\text{Area of the column } (A) = \pi r^2 = 3.14 \times \left(\frac{1}{2}\right)^2 = \frac{3.14}{4}$$

$$= 0.785 \text{ cm}^2$$

$$\text{Resistivity, } \quad \rho = \frac{RA}{l} = \frac{4.55 \times 10^3 \Omega \times 0.785 \text{ S cm}^2}{45.5}$$

$$= 78.5 \ \Omega \text{ cm}$$

$$\text{Conductivity, } \kappa = \frac{1}{\rho} = \frac{1}{78.5 \ \Omega \text{ cm}} = 0.0127 \text{ S cm}^{-1}$$

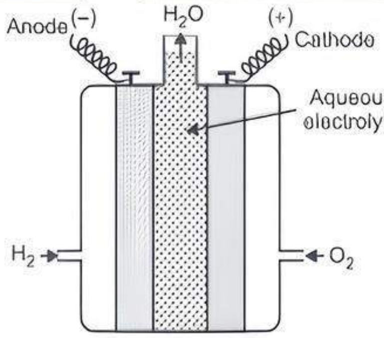
$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa \times 1000}{M}$$

$$= \frac{0.0127 \times 1000}{0.05}$$

$$= \underline{254.77 \text{ S cm}^2 \text{mol}^{-1}}$$

Q 17. What are fuel cells? Describe the hydrogen-oxygen fuel cell in brief.

Ans. Fuel Cells: The galvanic cells which are designed to convert the energy of combustion of fuels like hydrogen, methane etc. directly into electrical energy are called fuel cells. These cells are 70% more efficient as compared to thermal plants and are pollution free *e.g.*, Hydrogen-oxygen fuel cell.



Fuel cell using H_2 and O_2 to produce electricity

Hydrogen-oxygen fuel cell: In this cell, hydrogen and oxygen gases are bubbled through porous carbon electrodes into concentrated aqueous NaOH solution. Catalysts such as finely divided Pt or Pd metals are incorporated into the electrodes for raising the rate of electrode reaction.

The electrode reaction are as follows:

At cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

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

Overall cell reaction is

$$2H_2(g) + O_{2(g)} \rightarrow 2H_2O(l)$$

The water vapours produced during the reaction are condensed and can be used for drinking purpose.

The cell runs continuously as long as the reactants are supplied.

TiP

Fuel cells are pollution free, efficient upto 70% and never become dead due to continuous supply of fuel.

Q 18. What are primary cells? Describe dry cell in short.

Ans. Primary Cells: These are the cells in which the reaction occurs only once and after use over a period of time, the cell becomes dead and cannot be reused again *e.g.*, dry cell (or Leclanche cell).

Dry Cell: It is also called Leclanche cell. This cell contains a zinc container, which also acts as anode and a carbon (graphite) rod surrounded by powdered MnO_2 and carbon or charcoal, which acts as cathode. The space between the electrodes is filled by a moist paste of ammonium chloride NH_4Cl and zinc chloride $ZnCl_2$.

The electrode reactions are as follows:

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

At cathode: $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

Ammonia formed during the reaction forms a complex with Zn^{2+} to give $[Zn(NH_3)_4]^{2+}$. The cell generates a potential of nearly 1.5 V.

Q 19. Distinguish between electrolytic cell and galvanic cell.

Ans. Difference between electrolytic cell and galvanic cell:

S. No.	Basis of Difference	Electrolytic cell	Galvanic cell
(i)	Energy conversion	In this cell, electrical energy is converted into chemical energy.	In this cell, chemical energy is converted into electrical energy.
(ii)	Anode polarity	In it, anode is the positive terminal.	In it, anode is the negative terminal.
(iii)	Cathode polarity	Here, cathode is the negative terminal.	Here, cathode is the positive terminal.
(iv)	External source of electrical energy	It is necessary to use a battery or any other source of electrical energy in its external circuit.	No need of using external source of electrical energy in it.
(v)	Position of electrodes	Both the electrodes are dipped in an electrolyte solution present in the same vessel.	Here two electrodes are dipped in separate vessels having solutions of different electrolytes.
(vi)	Salt bridge	Here, salt bridge or porous vessel is not used.	Here, salt bridge or porous vessel is used.

Q 20. Explain how rusting of iron is envisaged as setting up of an electrochemical cell. *(NCERT INTEXT)*

Ans. Mechanism of Corrosion (rusting of iron): Rusting of iron is an electrochemical process. It results in the formation of an electrochemical substance at the iron surface. Drops of water containing CO_2 and O_2 form a layer over the iron surface. Dissolved CO_2 increases the conductivity of water and hence, it acts as electrolyte solution.

$$CO_2 + H_2O \rightleftharpoons 2H^+ + CO_3^{2-}$$

Iron atoms act as anode and take part in reduction half-reaction. Thus, a small electrochemical cell sets up at the iron surface.

In acidic medium, following chemical reactions takes place during rusting of iron.

At anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ (oxidation)

At cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ (reduction)

Atmospheric oxidation:

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

This Fe_2O_3 gets hydrolysed to form red brown powder of rust ($Fe_2O_3 \cdot xH_2O$).

Long Answer Type Questions

Q 1. (i) Write the cell reaction and calculate the emf of the following cell at 298 K:

$Sn(s) \mid Sn^{2+}(0.004\ M) \parallel H^+\ (0.020\ M) \mid H_2\ (g)$ (1 bar) $\mid Pt\ (s)$

(Given: $E^\circ_{Sn^{2+}/Sn} = -0.14$ V)

(ii) Give reasons:

(a) On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.

(b) Conductivity of CH_3COOH decreases on dilution. *(CBSE 2018)*

Sol. (i) $Sn(s) \mid Sn^{2+}\ (0.004\ M) \parallel H^+\ (0.020\ M) \mid H_2(g)$ (1 bar) $\mid Pt(s)$

Cell reaction is

$$Sn + 2H^+(0.020M) \longrightarrow Sn^{2+}(0.004\ M) + H_2(1\ bar)$$

$$E^\circ_{cell} = E^\circ_{\left(H^+,\frac{1}{2}H_2\right)} - E^\circ_{(Sn^{2+}/Sn)}$$

$$= 0 - (-0.14\ V) = 0 + 0.14\ V = 0.14\ V$$

For calculation of emf, we apply Nernst equation:

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{(Sn^{2+}) \times p_{H_2}}{(H^+)^2}$$

$$= 0.14 - \frac{0.0591}{2}\log\frac{(0.004) \times 1}{(0.020)^2}$$

$$= 0.14 - \frac{0.0591}{2}\log\frac{0.004}{0.0004}$$

$$= 0.14 - \frac{0.0591}{2}\log 10 = 0.14 - \frac{0.0591}{2}$$

$$= \underline{0.11\ V}$$

COMMON ERROR

Clarify your calculation with suitable steps. Missing steps leads to marks deduction.

(ii) (a) From standard oxidation potential, it is clear that oxygen gas should be evolved at anode but its rate of evolution is very low. In order to increase this, we have to increase the voltage of external battery. Because of which chloride ions get oxidised easily and Cl_2 gas is evolved at anode.

TiP

Conductivity decreases with decrease in concentration for all electrolytes (weak or strong) as the number of ions per unit volume that carry the current in a solution decreases on dilution.

(b) On dilution, number of CH_3COOH ions per unit volume decreases.

Hence, conductivity decreases.

Note: Conductivity decreases with decrease in concentration for all electrolytes (weak or strong) as the number of ions per unit volume that carry the current in a solution decreases on dilution.

Q 2. (i) Molar conductivity of substance '*A*' is 5.9×10^3 S/m and '*B*' is 1×10^{-16} S/m. Which of the two is most likely to be copper metal and why?

(ii) What is the quantity of electricity in Coulombs required to produce 4.8 g of Mg from molten $MgCl_2$? How much Ca will be produced if the same amount of electricity was passed through molten $CaCl_2$? (Atomic mass of Mg = 24u, atomic mass of Ca = 40 u).

(iii) What is the standard free energy change for the following reaction at room temperature? Is the reaction spontaneous?

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

(CBSE SQP 2022-23)

Ans. (i) Since metals are conductors so, they have high value of conductivity. Here, the molar conductivity of substance *A* is more than that of *B*, so *A* is most likely to be copper metal.

(ii) $$Mg^{2+} + 2e^- \longrightarrow Mg$$

1 mole of magnesium ions gains two moles of electrons or 2*F* to form 1 mole of Mg.

1 mole of Mg = 24 g Mg

i.e. 24 g Mg requires 2F electricity

4.8 g Mg requires 2 × 4.8/24 = 0.4

$F = 0.4 \times 96500 = 38600$ C

Hence, 38600 C of electricity is required to produce 4.8 g of Mg.

$$Ca^{2+} + 2e^- \longrightarrow Ca$$

2*F* electricity is required to produce 1 mole = 40 g Ca

1.4 F electricity will produce 8 g Ca

Hence, 8 g of Ca will be produced.

(iii) Given reaction is:

$Sn(s) + 2Cu^{2+}(aq) \longrightarrow Sn^{2+}(aq) + 2Cu^{2+}(s)$

We have, F = 96500 C, $n = 2$

At anode:

$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$; $E^\circ_{anode} = -0.14$ V

At cathode:

$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$; $E^\circ_{cathode} = -0.15$ V

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= 0.15 - (-0.14) = 0.29 \text{ V}$$

Standard free energy change, $\Delta G_0 = -nFE^\circ_{cell}$

$$= -2 \times 96500 \times 0.29 = \underline{55970 \text{ J/mol}}$$

If the Gibbs free energy for a process is negative, the process is spontaneous but if the Gibbs Free Energy is positive, the process is non-spontaneous. In the given case, the Gibbs Free Energy is positive so, the reaction is non-spontaneous.

Q 3. (i) Conductivity of 2×10^{-3} M methanoic acid is 8×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation if Λ°_m for methanoic acid is 404 Scm^2 mol^{-1}.

(ii) Calculate the $\Delta_r G^\circ$ and log K_c for the given reaction at 298 K:

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

Given: $E^\circ_{(Ni^{2+}/Ni)} = -0.25$ V, $E^\circ_{(Ag^+/Ag)} = +0.80$ V

1F = 96500 C mol^{-1} *(CBSE 2023)*

Sol. (i) Given, conductivity $(\kappa) = 8 \times 10^{-5}$ Scm^{-1}

Concentration $(C) = 2 \times 10^{-3}$ M

We know that, molar conductivity (Λ_m)

$$= \frac{1000 \times \text{conductivity}\,(\kappa)}{\text{concentration}\,(C)}$$

$$\Lambda_m = \frac{1000 \times 8 \times 10^{-5}}{\hat{0} \times \ ^{-3}}$$

$$= 40 \text{ S cm}^2 \text{ mol}^{-1}$$

Also, $\Lambda^\circ_m = 404$ S cm^2 mol^{-1}

Degree of dissociation, $\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{40}{404} = \underline{0.099}$

or, $\alpha = \underline{9.9\%}$

(ii) Given, $E^\circ_{(Ni^{2+}/Ni)} = -0.25$ V, $E^\circ_{(Ag^+/Ag)} = +0.80$ V

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

or, $$E^\circ_{cell} = E^\circ_{(Ag^+/Ag)} - E^\circ_{(Ni^{2+}/Ni)}$$
$$= 0.80 - (-0.25) = 1.05 \text{ V}$$

For the reaction,

$$n = 2$$
$$\Delta_r G^\circ = -nFE^\circ_{cell}$$
$$= -2 \times 96500 \text{ C mol}^{-1} \times 1.05 \text{ V}$$
$$= -\underline{202.650 \text{ kJ}}$$

Further, $\Delta_r G^\circ = -2.303\, RT \log k_c$

or, $$\log K_C = \frac{-\Delta_r G^\circ}{2.303\, RT}$$

$$= -\frac{(-202.650 \text{ kJ})}{2.303 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \times 298 \text{ K}}$$

$$= \underline{35.5}$$

Thus, the value of $\Delta_r G^\circ$ is calculated as $-\underline{202.650 \text{ kJ}}$ and that of log K_C is $\underline{35.5}$.

Q 4. (i) The molar conductivities of NH_4^+ and Cl^- ion are 73.8 S cm^2 mol^{-1} and 76.2 S cm^2 mol^{-1} respectively. The conductivity of 0.1 M NH_4Cl is 1.29×10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation.

(ii) Calculate the half-cell potential at 298 K for the reaction

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

If $[Zn^{2+}] = 0.1$ M and $E^\circ_{(Zn^{2+}/Zn)} = -0.76$ V

(CBSE 2023)

Sol. (i) Given, conductivity $(\kappa) = 1.29 \times 10^{-2}\ S\ cm^{-1}$

$$\text{Concentration } (C) = 0.1\ M$$

$$\text{Molar conductivity } (\Lambda_m) = \frac{1000 \times \kappa}{C}$$

$$= \frac{1000 \times 1.29 \times 10^{-2}}{0.1}$$

$$= \underline{129\ S\ cm^2\ mol^{-1}}$$

$$\Lambda^\circ_{(NH_4Cl)} = \Lambda^\circ_{(NH_4^+)} + \Lambda^\circ_{(Cl^-)}$$

$$= (73.8 + 76.2)\ S\ cm^2\ mol^{-1}$$

$$= 150\ S\ cm^2\ mol^{-1}$$

Degree of dissociation,

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{129}{150} = \underline{0.86}$$

or, $\alpha = \underline{86\%}$

(ii) The electrode reaction is

$$Zn^{2+} + 2e^- \longrightarrow Zn \text{ where } n = 2$$

Applying Nernst equation,

$$E_{(Zn^{2+}/Zn)} = E^\circ_{(Zn^{2+}/Zn)} - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$$

$$= -0.76 - \frac{0.0591}{2} \log \frac{1}{0.1}$$

$$= -0.76 - 0.02955 = -0.78955\ V$$

Hence, the half-cell potential is $-\underline{0.78955\ V}$.

Q 5. (i) State Kohlrausch's law of independent migration of ions. Write an expression for the limiting molar conductivity of acetic acid according to Kohlrausch's law.

(ii) Calculate the maximum work and log k_c for the given reaction at 298 K:

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

Given: $E^\circ_{Ni^{2+}/Ni} = -0.25$ V, $E^\circ_{Ag^+/Ag} = +0.80$ V

1 F = 96500 C mol^{-1} *(CBSE 2023)*

Ans. (i) **Kohlrausch law of independent migration of ions:**

To calculate the molar conductivity (at infinite dilution) of weak electrolytes, Kohlrausch gave a law, called Kohlrausch law. According to this law, at infinite dilution, the molar conductivity of an electrolyte can be represented as the sum of ionic molar conductivities of its all the cations and anions of the electrolyte."

According to Kohlrausch law, the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. The limiting molar conductivity of acetic acid can be represented by the following expression:

$$\Lambda^\circ_{m(CH_3COOH)} = \lambda^\circ_{(CH_3COO^-)} + \lambda^\circ_{H^+}$$

(ii) Given, $E^\circ_{(Ni^{2+}/Ni)} = -0.25$ V, $E^\circ_{(Ag^+/Ag)} = +0.80$ V

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

or, $$E^\circ_{cell} = E^\circ_{(Ag^+/Ag)} - E^\circ_{(Ni^{2+}/Ni)}$$

$$= 0.80 - (-0.25) = 1.05\ V$$

For the reaction,

$$n = 2$$

$$\Delta_r G^\circ = -nFE^\circ_{cell}$$

$$= -2 \times 96500\ C\ mol^{-1} \times 1.05\ V$$

$$= \underline{-202.650\ kJ}$$

Further, $\Delta_r G^\circ = -2.303\ RT \log k_c$

or, $$\log k_c = \frac{-\Delta_r G^\circ}{2.303\ RT}$$

$$= -\frac{(-202.650\ kJ)}{2.303 \times 8.314 \times 10^{-3}\ kJ\ K^{-1} \times 298\ K}$$

$$= \underline{35.5}$$

Hence, the maximum work is $\underline{-202.650\ kJ}$ and that of $\log k_c$ is 35.5.

Q 6. (i) State Faraday's first law of electrolysis. How much charge, in terms of Faraday, is required for the reduction of 1 mol Cu^{2+} to Cu?

(ii) Calculate emf of the following cell at 298 K for

Mg (*s*) | Mg^{2+} (0.1 *M*) || Cu^{2+} (0.01 *M*) | Cu (*s*)

[E°_{cell} = + 2.71 V, 1 F = 96500 C mol^{-1}, log 10 = 1] *(CBSE 2023)*

Ans. (i) **Faraday's first law of electrolysis:**

According to Faraday's first law, when electricity is passed through the solution of an electrolyte, the amount of substance deposited at any of the electrode is directly proportional to the quantity of electricity passed through the electrolyte (solution or melt). *i.e.*,

$$\Rightarrow \quad W \propto Q \Rightarrow W = Z \times Q$$

$$\underline{W = Z \times I \times t}$$

where, Q = charge (in coulomb), I = current (in ampere)

t = time (in second) and Z = electrochemical equivalent.

The electrode reaction will be

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

Here, one mole of Cu^{2+} require 2 mole of electrons.

Charge on one electron = 1.6021×10^{-19}C

Charge on one mole of electrons

$$= N_A \times 1.6021 \times 10^{-19}C$$

$$= 6.02 \times 10^{23}\ mol^{-1} \times 1.6021 \times 10^{-19}C$$

$$= 96487\ C\ mol^{-1}$$

$$= 1\ F\ (\text{Faraday})$$

Hence, 2F charge is required for the reduction of 1 mol Cu^{2+} to Cu because one mole of Cu^{2+} require 2 mole of electrons *i.e.*, 2F charge.

(ii) For the cell,

$Mg(s) \mid Mg^{2+}(0.1\ M) \parallel Cu^{2+}(0.01\ M) \mid Cu(s)$, the half-cell reaction are as follows:

$$Mg \longrightarrow Mg^{2+} + 2e^-$$

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

$$Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu$$

$n = 2$ (number of electrons involved)

From Nernst equation,

$$\text{emf}(E_{cell}) = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$= \left[[E^{\circ}_{(Cu^{2+}/Cu)}] - E^{\circ}_{(Mg^{2+}/Mg)}\right] - \frac{0.0591}{2}\log\frac{0.1}{0.01}$$

$$= +2.71 - \frac{0.0591}{2}\log 10$$

$$= +2.71 - 0.02955$$

$$= \underline{2.68045\ V}$$

Hence, emf of the cell is <u>2.68045 V.</u>

Q 7. (i) Why does the cell voltage of a mercury cell remain constant during its lifetime?

(ii) Write the reaction occurring at anode and cathode and the products of electrolysis of *aq*. KCl.

(iii) What is the pH of HCl solution when the hydrogen gas electrode shows a potential of –0.59 V at standard temperature and pressure?

(CBSE SQP 2022-23)

Ans. (i) The cell voltage of a mercury cell remains constant during its lifetime as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

(ii) The reaction occurring at anode and cathode and the products of electrolysis of *aq*. KCl are as under:

Electrolysis of aq. KCl: $KCl(aq) \rightarrow K^+(aq) + Cl^-(aq)$

At cathode: $H_2O(l) + e^- \rightarrow 1/2\ H_2(g) + OH^-(aq)$

At anode: $Cl^-(aq) \rightarrow 1/2\ Cl_2(aq) + e^-$

Net reaction: $KCl(aq) + H_2O(l) \rightarrow K^+(aq) + OH^-(aq) + 1/2\ H_2(g) + 1/2\ Cl_2(g)$

(iii) Given, potential of hydrogen gas electrode $= -0.59$ V

Electrode reaction: $H^+ + e^- \longrightarrow 0.5\ H_2$

Applying Nernst equation,

$$E_{(H^+/H_2)} = E^{\circ}_{(H^+/H_2)} - \frac{0.059}{n}\log\frac{[H_2]^{1/2}}{[H^+]}$$

$$E^{\circ}_{(H^+/H_2)} = 0\ V \Rightarrow \quad E_{(H^+/H_2)} = -0.59\ V$$

$$n = 1$$

$$[H_2] = 1\ \text{bar}$$

$$-0.59 = 0 - 0.059(-\log[H^+])$$

$$-0.59 = -0.059\ pH$$

So, the pH of HCl solution is <u>10.</u>

Q 8. (i) For the reaction:

$2AgCl(s) + H_2(g)\ (1\ atm) \longrightarrow 2Ag(s) + 2H^+\ (0.1\ M) + 2Cl^-\ (0.1\ M), \Delta G^{\circ} = -43600$ J at 25°C.

Calculate the emf of the cell. $[\log 10^{-n} = -n]$

(ii) Define fuel cell and write its two advantages.

(CBSE 2023, 18)

Ans. (i) Gibbs energy of reaction is

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

Given, $\Delta G^{\circ} = -43600$ J, $n = 2$, $E^{\circ}_{cell} = ?$

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

Putting the values in the formula, we get

$$-43600\ J = -2 \times 96500 \times E^{\circ}_{cell}$$

$$E^{\circ}_{cell} = \left(\frac{43600}{2 \times 96500}\right)V$$

$$E^{\circ}_{cell} = 0.22\ V$$

Now using Nernst equation,

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\left[\frac{[H^+]^2[Cl^-]^2}{H_2(g)}\right]$$

Putting values, we get

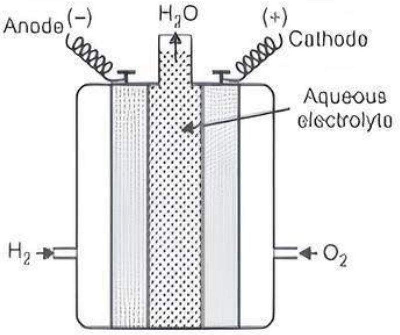
$$E_{cell} = 0.22 - \frac{0.0591}{2}\log\left[\frac{(0.1)^2(0.1)^2}{1}\right] \quad (\because n = 2)$$

$$= 0.22 - \frac{0.0591}{2}\log(10^{-4})$$

$$E_{cell} = 0.22 - \frac{0.0591}{2}(-4)$$

$$= \underline{0.3382\ V.}$$

(ii) Fuel cell is a galvanic cell in which chemical energy from combustion of fuels is converted into electrical energy. In this type of galvanic cells, reactants are continuously feed to the electrodes, which react to produce electricity and products thus formed are continuously removed. Fuel cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol etc. directly into electrical energy are highly efficient (70%) when compared to efficiency of thermal power plants (40%).



Fuel cell

The two advantages of fuel cell are:

(a) Fuel cells are pollution free.

(b) They never become dead due to continuous supply of fuel.

Q 9. Briefly describe lead storage battery. Write the reaction occurring at its anode and cathode.

Ans. Lead storage battery is a secondary cell and it is an example of commercial cell.

It can be recharged by passing current through it in the opposite direction so that it can be used again. It can undergo a large number of discharging and charging cycles. Its description is as follows:

Lead storage cell contains a Pb anode. The various plates of cathode and anode are arranged in alternating order and a porous plastic or fiber glass sheet is fitted in between them. All these plates are dipped in acid (dilute H_2SO_4 38% and density 1.30 g/cm^3) which is filled in a hard rubber or plastic vessel and acts as electrolyte.

At the time of discharging or when battery is generating electricity, the following reactions are used:

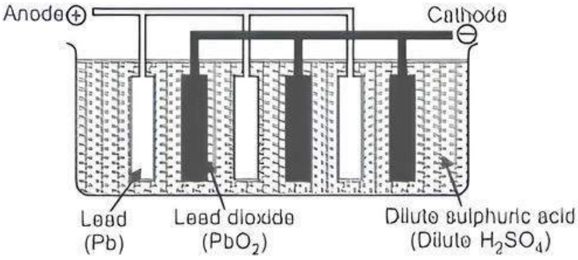
At anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

At cathode:

$$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

Net cell reaction:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$



Lead storage battery

This cell is used in automobiles and inverters. Each such cell generates 2V electricity so by combining 3 or 6 cells in series, 6-12 volt electricity can be generated.

Q 10. (i) Calculate $\Delta G°$ for the reaction

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

Given: $E°$ for $Zn^{2+}/Zn = -0.76$ V and

$E°$ for $Cu^{2+}/Cu = +0.34$ V

$R = 8.314$ JK^{-1} mol^{-1}

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

(ii) Give two advantages of fuel cells. *(CBSE 2020)*

Sol. (i) $E°_{cell} = E°_{cathode} - E°_{anode}$

$$= E°_{Cu^{2+}|Cu} - E°_{Zn^{2+}|Zn}$$

$$= +0.34\ V - (-0.76\ V)$$

$$= 1.10\ V$$

We know that, $\Delta G° = -nE°_{cell}F$

$$= -2 \times 1.10\ V \times 96500\ C\ mol^{-1}$$

$$= -212300\ J\ mol^{-1}$$

$$= -212.3\ kJ\ mol^{-1}$$

(ii) Advantages of Fuel Cells:

(a) They are pollution free.

(b) They are highly efficient.

Q 11. (i) Out of the following pairs, predict with reason which pair will allow greater conduction of electricity:

(a) Silver wire at 30°C or silver wire at 60°C.

(b) 0.1 M CH_3COOH solution or 1 M CH_3COOH solution.

(c) KCl solution at 20°C or KCl solution at 50°C.

(ii) Give two points of differences between electrochemical and electrolytic cells.

(CBSE 2020)

Ans. (i) (a) Silver wire at 30°C, because as temperature decreases, resistance decreases so conduction increases.

(b) 0.1 M CH_3COOH; because on dilution degree of ionisation increases hence conduction increases.

(c) KCl solution at 50°C; because at high temperature mobility of ions increases and hence conduction increases.

(ii) Difference between electrochemical and electrolytic cells:

S. No.	Basis of Difference	Electrochemical Cell	Electrolytic Cell
1.	Electrode polarity	Anode– negative Cathode– positive	Anode–positive Cathode–negative
2.	Energy conservation	It converts chemical energy to electrical energy.	It converts electrical energy to chemical energy.

Chapter Test

Multiple Choice Questions

Q 1. Match the Column I with Column II and mark the appropriate choice.

Column I	Column II
(A) Kohlrausch's law	(i) $\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$
(B) Molar conductivity	(ii) $K_a = \frac{c\alpha^2}{1-\alpha}$
(C) Degree of dissociation	(iii) $\Lambda^\circ_m = \Lambda^\circ_c + \Lambda^\circ_a$
(D) Dissociation constant	(iv) $\Lambda_m = \frac{\kappa}{c}$

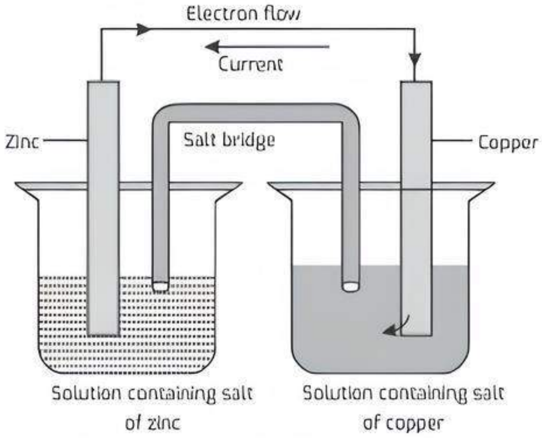
a. (A) → (iii), (B) → (iv), (C) → (i), (D) → (ii)

b. (A) → (i), (B) → (ii), (C) → (iii), (D) → (iv)

c. (A) → (iv), (B) → (i), (C) → (ii), (D) → (iii)

d. (A) → (ii), (B) → (iii), (C) → (iv), (D) → (i)

Q 2. Which of the following statements is correct about the given Daniell cell:



a. This cell converts the electrical energy liberated during the redox reaction to chemical energy.

b. This cell has an electrical potential greater than 1.1 V when concentration of Zn^{2+} and Cu^{2+} ions is unity (1 mol dm^{-3}).

c. In this cell, copper is acting as cathode and zinc is acting as anode.

d. Redox reaction occurring in this cell is

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

Q 3. E° values of three metals are listed below:

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s);\ E^\circ = -0.76V$

$Fe^{2+}(aq) + 2e^- \rightarrow 2Fe(s);\ E^\circ = -0.44V$

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s);\ E^\circ = -0.14V$

Which of the following statements are correct on the basis of the above information?

(i) Zinc will be corroded in preference to iron if zinc coating is broken on the surface.

(ii) If iron is coated with tin and the coating is broken on the surface then iron will be corroded.

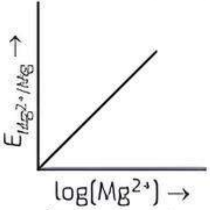
(iii) Zinc is more reactive than iron but tin is less reactive than iron.

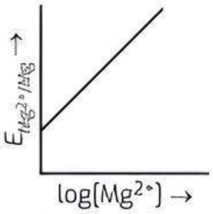
a. (i) and (ii)
b. (ii) and (iii)
c. (i), (ii) and (iii)
d. (i) and (iii)

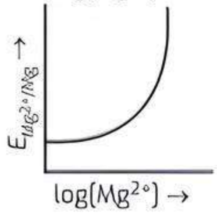
Q 4. Electrode potential for Mg electrode varies according to the equation.

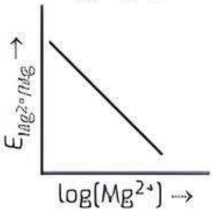
$$E_{(Mg^{2+})|Mg} = E^\circ_{Mg^{2+}|Mg} - \frac{0.059}{2}\log\frac{1}{[Mg^{2+}]}$$

The graph of $E_{Mg^{2+}|Mg}$ vs log $[Mg^{2+}]$ is:

a. 

b. 

c. 

d. 

Assertion and Reason Type Questions

Directions (Q. Nos. 5-6): *Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:*

a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).

c. Assertion (A) is true but Reason (R) is false.

d. Assertion (A) is false but Reason (R) is true.

Q 5. **Assertion (A):** Current stops flowing when $E_{cell} = 0$.
Reason (R): Equilibrium of the cell reaction is attained.

Q 6. **Assertion (A):** $E_{Ag^+/Ag}$ increases with increase in concentration of Ag^+ ions.
Reason (R): $E_{Ag^+/Ag}$ has a positive value.

Case Study Based Question

Q 7. A lead storage battery is the most important type of secondary cell having a lead anode and a grid of lead packed with PbO_2 as cathode. A 38%

solution of sulphuric acid is used as electrolyte. (Density = 1.294 g mL^{-1}) The battery holds 3.5 L of the acid. During the discharge of the battery, the density of H_2SO_4 falls to 1.139 g mL^{-1}. (20% H_2SO_4 by mass).

Read the given passage carefully and give the answer of the following questions:

(i) Write the reaction taking place at the cathode when the battery is in use.

(ii) How much electricity in terms of Faraday is required to carry out the reduction of one mole of PbO_2?

(iii) What is the molarity of sulphuric acid before discharge?

OR

Write the products of electrolysis when dilute sulphuric acid is electrolysed using Platinum electrodes.

Very Short Answer Type Questions

Q 8. What is the necessity to use a salt bridge in a galvanic cell?

Q 9. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch's law.

Short Answer Type-I Questions

Q 10. (i) On the basis of standard electrode potential values stated for acid solutions, predict whether Ti^{4+} species may be used to oxidise Fe (II) to Fe (III).

$Ti^{4+} + e^- \longrightarrow Ti^{3+}$ $E^\circ = +0.01$ V

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $E^\circ = +0.77$ V

(ii) Based on the data arrange Fe^{2+}, Mn^{2+} and Cr^{2+} in the increasing order of stability of +2 oxidation state.

$E^\circ_{Cr^{3+}/Cr^{2+}} = -0.4V$, $E^\circ_{Mn^{3+}/Mn^{2+}} = +1.5V$, $E^\circ_{Fe^{3+}/Fe^{2+}} = +0.8V$.

Q 11. What type of battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it.

Q 12. Why on dilution the Λ_m of CH_3COOH increases drastically while that of CH_3COONa increases gradually?

Short Answer Type-II Questions

Q 13. A galvanic cell consists of a metallic zinc plate immersed in 0.1 M $Zn(NO_3)_2$ solution and metallic plate of lead in 0.02 M $Pb(NO_3)_2$ solution. Calculate the emf of the cell. Write the chemical equation for the electrode reactions and represent the cell.

(Given: $E^\circ_{Zn^{2+}/Zn} = -0.76$ V, $E^\circ_{Pb^{2+}/Pb} = -0.13$ V)

Q 14. When a certain conductance cell is filled with 0.1 M KCl, it has a resistance of 85 ohm at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration. [Specific conductance of 0.1 M KCl = 1.29×10^2 ohm^{-1} cm^{-1}].

Q 15. (i) Write two advantages of H_2-O_2 fuel cell over ordinary cell.

(ii) Equilibrium constant (K_c) for the given cell reaction is 10. Calculate E°_{cell}.

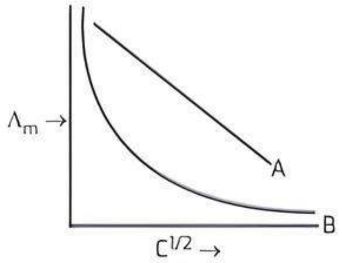
$$A(s) + B^{2+}(aq) \rightleftharpoons A^{2+}(aq) + B(s)$$

Long Answer Type Questions

Q 16. (i) A steady current of 2 A was passed through two electrolytic cells *X* and *Y* connected in series containing electrolytes $FeSO_4$ and $ZnSO_4$ until 2.8 g of Fe deposited at the cathode of cell *X*. How long did the current flow? Calculate the mass of Zn deposited at the cathode of cell *Y*.

(Molar mass : Fe = 56 g mol^{-1} Zn = 65.3 g mol^{-1}, 1F = 96500 C mol^{-1})

(ii) In the plot of molar conductivity (Λ_m) vs square root of concentration ($C^{1/2}$), following curves are obtained for two electrolytes *A* and *B*.



Answer the following:

(a) Predict the nature of electrolytes *A* and *B*.

(b) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes *A* and *B*?

Q 17. (i) What is limiting molar conductivity? Why is there steep rise in the molar conductivity of weak electrolyte on dilution?

(ii) Calculate the emf of the following cell at 298 K:

$Mg(s) | Mg^{2+} (0.1 M) || Cu^{2+} (1.0 \times 10^{-3} M) | Cu(s)$

(Given, $E^\circ_{cell} = 2.71$ V)