

ELECTRO-CHEMISTRY

Welcome to the Electrochemistry Revision Module tailored for CBSE - 12th (Chemistry) students. This module offers a comprehensive review of electrochemical principles, including redox reactions, electrochemical cells, and electrolysis, crucial for success in the CBSE examination.

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Prepare effectively for your CBSE Class 12th Chemistry exams with our Electrochemistry Revision Module. Let's embark on a journey to master this fascinating branch of chemistry!

OFFLINE-ONLINE LEARNING ACADEMY

The Success Destination





- **Comprehensive Coverage:** This module covers all essential concepts of electrochemistry, ensuring thorough preparation for exams and assessments.
- **Clear Explanation:** Concepts are explained clearly and concisely, supported by illustrative examples and diagrams to facilitate learning.
- **Practice-oriented Approach:** Ample practice questions, numerical exercises, and mock tests enable students to apply their knowledge and reinforce their understanding of electrochemistry.

KEY - FEATURES

- **Redox Reactions:** Explore the fundamentals of redox reactions, understanding oxidation, reduction, and the assignment of oxidation states. Learn how to balance redox equations and identify oxidizing and reducing agents.
- **Electrochemical Cells:** Study the structure and functioning of electrochemical cells, including galvanic cells and electrolytic cells. Explore the components of a cell, such as electrodes, electrolytes, and the salt bridge, and understand how they contribute to cell operation.
- **Cell Potential and EMF:** Delve into the concept of cell potential and electromotive force (EMF), learning how to calculate standard electrode potentials and cell potentials using the Nernst equation. Understand the factors affecting cell potential and its significance in predicting cell spontaneity.
- **Electrochemical Series:** Investigate the electrochemical series and its role in predicting the feasibility of redox reactions. Analyze the relative reactivity of metals and non-metals based on their standard electrode potentials.
- **Faraday's Laws and Electrolysis:** Learn about Faraday's laws of electrolysis, elucidating the quantitative relationship between the amount of substance deposited or liberated during electrolysis and the quantity of electric charge passed through the electrolyte.
- **Applications of Electrochemistry:** Explore the practical applications of electrochemistry in various fields, including electroplating, corrosion prevention, energy storage (batteries), and electrochemical sensors. Understand the technological advancements enabled by electrochemical processes.
- **Environmental and Industrial Impacts:** Examine the environmental and industrial implications of electrochemical processes, including their role in wastewater treatment, metal extraction, and the production of chemicals and materials. Explore sustainable practices and challenges in electrochemical industries.



REVISION MODULE



ELECTRO



Syllabus

- Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis.



Learning Outcomes

- Analyse redox reactions and interprets data for prediction of EMF of cell.
- Calculate EMF of cell from Nerst equation.
- Analyse factors for variations of conductivity of cell with concentration.
- Understand Kohlrausch's Law and apply in calculations of electrolysis.

Revision Notes

Electrolytic Conductivity, Electrolytes and Kohlrausch's Law

- **Electrochemistry** is the branch of chemistry which deals with the study of the production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to result in non-spontaneous chemical transformations.
- **Electrolytic conduction:** The flow of electric current through an electrolytic solution is called electrolytic conduction.
- **Electrolyte:** A substance that dissociates in solution to produce ions and hence conducts electricity in dissolved state or molten state.
Weak electrolyte – H_2CO_3 , CH_3COOH , HCN , MgCl_2
Strong electrolyte – NaCl , HCl , NaOH
- **Degree of ionisation:** It is the ratio of number of ions produced to the total number of molecules in electrolyte.
- **Resistance** is defined as the property of given 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).

$$R \propto \frac{l}{A} \quad \text{or; } R = \rho \frac{l}{A}$$

ρ = Resistivity or specific resistance.

- **Resistivity:** If a solution is placed in between two parallel electrodes having cross sectional area ' A ' and distance ' l ' apart, then

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

where ρ = resistivity and its SI unit is Ohm-m also Ohm-cm is used as a unit.

- **Conductance:** The ease with which the current flows through a conductor is called conductance. It is reciprocal of resistance. *i.e.*,

$$C = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$$

The SI unit of conductance is **Siemens (S)**.

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

$$1S = 1 \text{ Ohm}^{-1} = 1 \Omega^{-1}$$

- **Conductivity:** It is reciprocal of resistivity and is denoted by κ (Greek Kappa).

$$\kappa = C \times \frac{l}{A}$$

where C = Conductance of the solution

l = Distance or length

A = Area of cross section

Its SI unit is $S \text{ m}^{-1}$. Also expressed as $S \text{ cm}^{-1}$.

It depends upon the:

- (i) Nature of the material,
 - (ii) Temperature,
 - (iii) The number of valence electrons per atom or size of the ions produced and their solvation (electrolytes)
- **Metallic conductance** is the electrical conductance in metals that occurs due to the movement of electrons. It depends upon the:
- (i) Nature and structure of the metal,
 - (ii) Number of valence electrons per atom,
 - (iii) Temperature
- **Electrolytic or ionic conductance** is the conductance of electricity that occurs due to ions present in the solution. It depends upon the:
- (i) Nature of electrolyte or interionic attractions,
 - (ii) Solvation of ions,
 - (iii) Nature of solvent and its viscosity,
 - (iv) Temperature
- **Cell constant (G):** It is the ratio of distance between electrodes to the cross-sectional area between electrodes.

$$\text{Cell constant (G)} = \frac{l}{A} = \kappa \text{ in cm}^{-1} \text{ or m}^{-1}$$

It depends on the:

- (i) Distance between the electrodes
 - (ii) Area of cross section
- The resistance of electrolytic solution is determined by wheatstone bridge method where R_2 is resistance of electrolyte solution. A null point detected by P detector such that,

$$\text{Unknown } R_2 = \frac{R_1 R_4}{R_3}$$

- **Molar conductivity:** It is defined as the conducting power of all the ions produced by one gram mole of an electrolyte in a solution. It is denoted by Λ_m .

$$\Lambda_m = \frac{\kappa}{C} \times 1000 \text{ S cm}^2 \text{ mol}^{-1}$$

where κ = Conductivity

C = Concentration of solution.

SI unit of molar conductivity is $S \text{ m}^2 \text{ mol}^{-1}$.

- **Debye Huckel Onsager equation:** It is applicable for strong electrolyte:

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

where Λ° = Limiting molar conductivity, Λ_m = Molar conductivity, A = Constant and C = Concentration of solution.

- **Kohlrausch's law of independent migration of ions:** According to this law, limiting molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of contributions from its individual ions. If the molar conductivity of the cations is denoted by λ_+^∞ and that of the anions by λ_-^∞ then the law of independent migration of ions is:

$$\Lambda_m^\infty = v^+ \lambda_+^\infty + v^- \lambda_-^\infty \text{ or } \Lambda_m^\circ = v^+ \lambda_+^\circ + v^- \lambda_-^\circ$$

Applications of Kohlrausch's law

- (i) Calculation of molar conductivities of weak electrolyte at infinite dilution.
- (ii) Calculation of degree of dissociation (α) of weak electrolytes:

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m}{\Lambda_m^\circ}$$

- (iii) Determination of dissociation constant (K) of weak electrolytes:

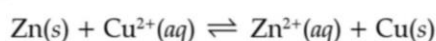
$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{C\Lambda_m^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)}$$

- (iv) Determination of solubility of sparingly soluble salts:

$$\text{Solubility} = \frac{\kappa \times 1000}{\Lambda_m^\circ}$$

Redox Reactions and Electrochemical Cells, Electrode Potential and Nernst Equation

- **Redox reaction:** A chemical reaction in which oxidation and reduction both processes take place simultaneously is known as redox reaction. Oxidation is a process in which any substance loses one or more electrons while reduction is the process in which one or more electrons are gained by another substance.
- **Galvanic cell:** A device in which the redox reaction is carried indirectly and chemical energy is converted to electrical energy. It is also called galvanic cell or voltaic cell.
- **Redox couple:** It is defined as having together the oxidised and reduced form of a substance taking part in an oxidation or reduction half reaction.
- **Galvanic cell or Voltaic cell:** It consists of two metallic electrodes dipped in electrolytic solutions. Electrical energy is produced as a result of chemical reaction which takes place in this cell.
- **Daniell cell:** It is a type of galvanic cell which consist of two electrodes (Zn and Cu) in contact with the solution of its own ion i.e., ZnSO_4 and CuSO_4 respectively.



Cell is represented as,



- **Salt Bridge and its function:** It is an inverted U-shaped glass tube which contains a suitable salt in the form of a thick paste made in agar-agar. It performs following functions:
 - (i) It completes inner cell circuit.
 - (ii) It prevents transference of electrolyte from one half-cell to the other.
 - (iii) It maintains the electrical neutrality of the electrolytes in the two half-cells.
- **Electrode Potential:** It is the potential developed by the electrode with respect to the standard reference electrode. By convention, the reference electrode is standard hydrogen electrode which have a potential of zero volt.
- **Standard Electrode Potential:** Electrode potential at 25°C , 1 bar pressure and 1 M solution is known as standard electrode potential (E°). The standard electrode potential of any electrode can be measured by connecting it to Standard Hydrogen Electrode (SHE). SHE has a standard potential at all temperatures. It consists of a platinum foil coated with platinum black dipped into an aqueous solution in which the $\text{H}^+ = 1 \text{ M}$ at 25°C and 1 bar pressure. The potential difference between the two electrodes of a galvanic cell is called the cell potential (measured in volts). It is also called the emf of the cell when no current is flowing through the circuit.
- **EMF of the cell:** It is the sum of electric potential differences produced by separation of charges that occur at each phase boundary in the cell.

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

In terms of standard oxidation electrode potential:

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

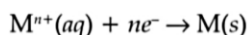
where

E°_{cathode} = standard electrode potential of cathode

and

E°_{anode} = standard electrode potential of anode

- **Standard oxidation potential:** It is the potential difference when given electrode is in contact with its ions having 1 molar concentration, undergoes oxidation when coupled with standard hydrogen electrode.
- **Electrochemical series:** It is the arrangement of the element in order of their increasing electrode potential values. The series has been established by measuring the potential of various electrodes occurs SHE.
- **Nernst equation:** If the concentration of species in the electrode reaction is not equal to 1 M, then we use Nernst equation. For a general electrode,

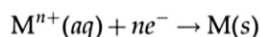


the Nernst equation can be written as

$$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}]}$$

where E° = Standard electrode potential, R = Gas constant ($8.31 \text{ JK}^{-1} \text{ mol}^{-1}$), T = Temperature (K), n = Number of moles of electrons and F = Faraday (96500 C).

For a cell, the electrode potential for any concentration of ions using electrode reactions is



At equilibrium,

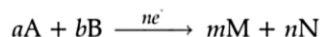
$$E^\circ_{\text{cell}} = \frac{0.059}{n} \log K_c$$

Where,

K_c = Equilibrium constant

$$K_c = \frac{[M(s)]}{[M^{n+}]}$$

For the general electrochemical cell with the net reaction,



the Nernst equation at 298 K can be written as

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

where

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

- **Gibbs energy:**

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

For cell reaction to be spontaneous, ΔG must be negative,

Calculations of $\Delta_r G^\circ$ and $\Delta_r G$:

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

and

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

We also know that, Gibbs energy change is equal to the useful work done.

For cell reaction to be spontaneous, ΔG must be negative.

$$\Delta G^\circ = -2.303 RT \log K$$

Electrolysis, Law of Electrolysis, Batteries, Fuel Cells and Corrosion

- **Electrolysis** is the process of decomposition of an electrolyte when electric current is passed through either its aqueous solution or molten (fused) state. This process takes place in electrolytic cell.
- **Faraday's first law of electrolysis:** The amount of chemical reaction which occurs at any electrode during electrolysis is proportional to the quantity of electricity passed through the electrolyte.

$m = Z \times I \times t$, where Z = Electrochemical equivalent

- **Faraday's second law of electrolysis:** Amount of various substances liberated by the same quantity of electricity passed through the electrolytic solution is proportional to their chemical equivalent weights.

$$\frac{w_1}{E_1} = \frac{w_2}{E_2}$$

- **Products of electrolysis depend on**
(i) Physical state of material.
(ii) Types of electrode being used.
➤ Battery is a combination of galvanic cells in series and used as a source of electrical energy.

Types of batteries:

- (i) Primary batteries are non-chargeable batteries such as Leclanche cell and Dry cell.
(ii) Secondary batteries are chargeable cells involving reversible reaction. Example, Lead storage battery and Nickel-cadmium cells.
➤ **Dry cell (Leclanche cell):** The anode consists of a zinc container and the cathode is a graphite electrode surrounded by powdered MnO_2 and C. The space is filled with paste of NH_4Cl and ZnCl_2 .

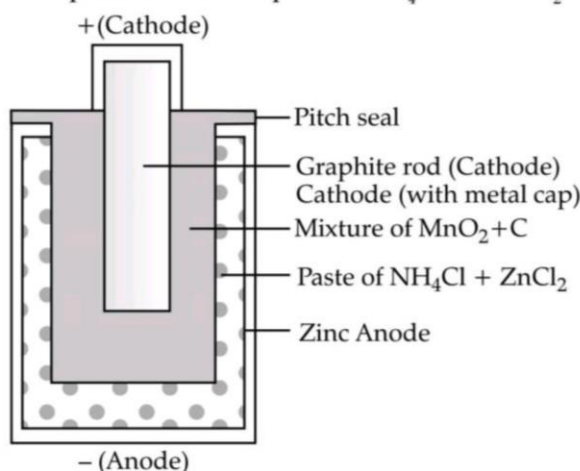


Fig 1: Dry cell

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

At cathode: $\text{MnO}_2(\text{s}) + \text{NH}_4^+(\text{aq}) + 2\text{e}^- \rightarrow \text{MnO(OH)} + \text{NH}_3$

The net reaction: $\text{Zn} + \text{NH}_4^+(\text{aq}) + \text{MnO}_2 \rightarrow \text{Zn}^{2+} + \text{MnO(OH)} + \text{NH}_3$

- **Lead storage battery:**

Anode - Spongy lead

Cathode - Lead packed with Lead dioxide

Electrolyte - Aqueous solution of H_2SO_4 (38%)

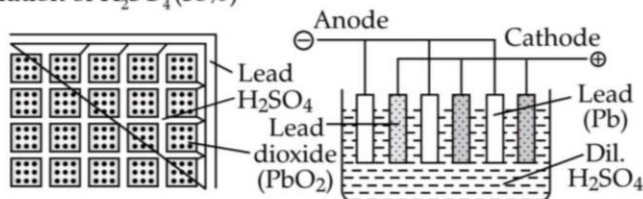


Fig 2: Lead storage battery

Discharge reaction of cell:

At anode: Following reaction takes place at anode

$\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$

Reaction at cathode: PbO_2 filled in lead grid gets reduced to Pb^{2+} ions which combines with SO_4^{2-} ions to form $\text{PbSO}_4(\text{s})$.

Complete cathode reaction is as follows:

$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

Complete cell reaction: $\text{Pb(s)} + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

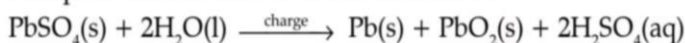
Recharge reaction of cell: It changes the direction of electrode reaction. PbSO_4 accumulated at cathode gets reduced to Pb.

At cathode: $\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightarrow \text{Pb(s)} + \text{SO}_4^{2-}(\text{aq})$

At anode: PbSO_4 gets oxidised to PbO_2

$\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^-$

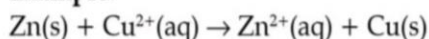
Complete cell reaction would be as follows:



➤ **Conventions for representing the galvanic cell:**

- (i) Double vertical line is used for salt bridge. Left hand side of the double line is anode and the cathode is on the right hand side.
- (ii) A single vertical line is used to separate metal and the electrolytic solution.
- (iii) If there is no metallic surface involved, we write Pt.

Example:



- **Fuel cells:** Electrical cells that are designated to convert the energy from the combustion of fuels such as hydrogen, carbon monoxide or methane directly into electrical energy are called fuel cells.

In the cell:

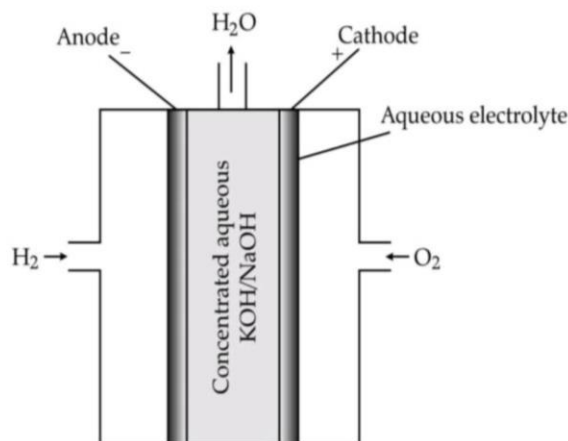
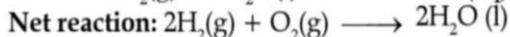
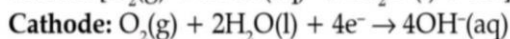
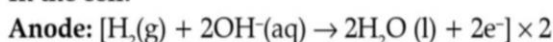
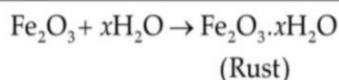
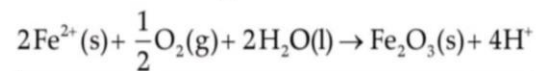
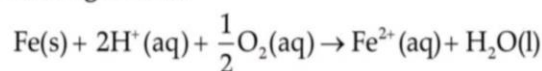


Fig 3: Fuel cell using H₂ and O₂ produces electricity

- **Corrosion:** The process of slow conversion of metals into their undesirable compounds (usually oxide) by reaction with moisture and other gases present in the atmosphere.

Rusting of iron:



Prevention of Corrosion:

- (i) **Barrier protection:** By covering the surface with paint or a thin film of grease or by electroplating.
- (ii) **Sacrificial protection:** By galvanization.
- (iii) Alloying.

Know the Terms

- **Superconductors:** Materials with a zero resistance.
- **Limiting molar conductivity:** Molar conductivity when concentration approaches zero.
- **Electrolyte:** Substance that dissociates into electrically conducting ions.
- **Over voltage:** It is the difference between the potential required for the evolution of a gas and its standard reduction potential.

Know the Formulae

- $\text{Current (I)} = \frac{\text{Potential difference (V)}}{\text{Resistance (R)}}$
- $\text{Resistance (R)} = \rho \frac{l}{A}$
- $\text{Conductance (C)} = \kappa \frac{A}{l}$
- $\text{Specific conductivity } (\kappa) = C \times \frac{l}{A} = \frac{\text{Cell constant}}{R}$
- $\text{Cell constant (G*)} = \frac{l}{A}$
- For strong electrolyte, $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$
 $\Lambda^\circ = \nu_+ \Lambda_+^\circ + \nu_- \Lambda_-^\circ$
- $\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^\circ}$
- $K = \frac{C\alpha^2}{(1-\alpha)} = \frac{C(\Lambda_m^c)^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m^c)}$
- $\text{Solubility} = \frac{\kappa \times 1000}{\Lambda_m^\circ}$
- $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$
- $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$
- **Nernst equation:**

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303 RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ at } 298 \text{ K}$$
- $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$
- $\Delta_r G^\circ = -2.303 RT \log K_c$
- $Q = It$
- $m = ZIt$



(A) OBJECTIVE QUESTIONS

1 Mark Each



Stand Alone MCQs

Q. 1. Debye-Huckel Onsager equation for strong electrolytes:

$$\Lambda = \Lambda_\infty - A\sqrt{C}$$

Which of the following equality holds?

(A) $\Lambda = \Lambda_\infty$ as $C \rightarrow \sqrt{A}$ (B) $\Lambda = \Lambda_\infty$ as $C \rightarrow \infty$

(C) $\Lambda = \Lambda_\infty$ as $C \rightarrow 0$ (D) $\Lambda = \Lambda_\infty$ as $C \rightarrow 1$

[A] [CBSE Delhi Set-II 2020]

Ans. Option (C) is correct.

Explanation: At infinite dilution, concentration approaches to zero and molar conductivity at infinite dilution is Λ_∞ . When $C \rightarrow 0$
 Then $\Lambda = \Lambda_\infty$

Q. 2. Which of the following option will be the limiting molar conductivity of CH_3COOH if the limiting molar conductivity of CH_3COONa is $91 \text{ Scm}^2\text{mol}^{-1}$? Limiting molar conductivity for individual ions are given in the following table.

S.No	Ions	limiting molar conductivity / $\text{Scm}^2\text{mol}^{-1}$
1	H^+	349.6
2	Na^+	50.1
3	K^+	73.5
4	OH^-	199.1

- (A) $350 \text{ Scm}^2\text{mol}^{-1}$ (B) $375.3 \text{ Scm}^2\text{mol}^{-1}$
(C) $390.5 \text{ Scm}^2\text{mol}^{-1}$ (D) $340.4 \text{ Scm}^2\text{mol}^{-1}$

[CBSE SQP 2020-21]

Ans. Option (C) is correct.

Explanation: The limiting molar conductivity (Λ_m°) for strong and weak electrolyte can be determined by using Kohlrausch's law which states that "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."

$$\begin{aligned}\Lambda_{\text{CH}_3\text{COONa}} &= \Lambda_{\text{CH}_3\text{COO}^-} + \Lambda_{\text{Na}^+} \\ 91 \text{ Scm}^2\text{mol}^{-1} &= \Lambda_{\text{CH}_3\text{COO}^-} + 50.1 \text{ Scm}^2\text{mol}^{-1} \\ \Rightarrow \Lambda_{\text{CH}_3\text{COO}^-} &= 40.9 \text{ Scm}^2\text{mol}^{-1} \\ \text{For acetic acid,} \\ \Lambda_{\text{CH}_3\text{COOH}} &= \Lambda_{\text{CH}_3\text{COO}^-} + \Lambda_{\text{H}^+} \\ &= 40.9 \text{ Scm}^2\text{mol}^{-1} + 349.6 \text{ Scm}^2\text{mol}^{-1} \\ &= 390.5 \text{ Scm}^2\text{mol}^{-1}\end{aligned}$$

Q. 3. Which of the statements about solutions of electrolytes is not correct?

- (A) Conductivity of solution depends upon size of ions.
(B) Conductivity depends upon viscosity of solution.
(C) Conductivity does not depend upon solvation of ions present in solution.
(D) Conductivity of solution increases with temperature.

[R]

Ans. Option (C) is correct.

Explanation: Conductivity depends upon the nature of the solute added, size of the ions produced, nature of solvent, viscosity of solvent and solvation of ions present in solution. Greater the solvation of ions of an electrolyte, lesser will be the electrical conductivity of the solution.

Q. 4. When 0.1 mol $\text{CoCl}_3(\text{NH}_3)_5$ is treated with excess of AgNO_3 , 0.2 mol of AgCl are obtained. The conductivity of solution will correspond to:

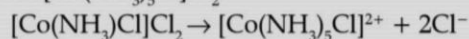
- (A) 1: 3 electrolyte (B) 1: 2 electrolyte
(C) 1: 1 electrolyte (D) 3: 1 electrolyte

[A]

Ans. Option (B) is correct.

Explanation: When 0.1 mole of $\text{CoCl}_3(\text{NH}_3)_5$ was reacted with excess of AgNO_3 , we get 0.2 moles of AgCl . As, 1 mol AgNO_3 can give only 1 mole AgCl . In the given reaction 1 mol $\text{Co}(\text{NH}_3)_5\text{Cl}_3$ will

give 2 mol Cl^- ions, when 2Cl^- are not in coordinate sphere of complex. Thus, the formula for complex has to be $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.



Therefore, the conductivity of the solution will be 1: 2 electrolyte.

Q. 5. The cell constant of a conductivity cell _____.

- (A) Changes with change of electrolyte.
(B) Changes with change of concentration of electrolyte.
(C) Changes with temperature of electrolyte.
(D) Remains constant for a cell.

Ans. Option (D) is correct.

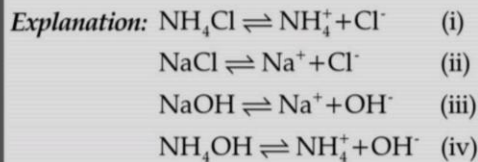
Explanation: The cell constant of a conductivity cell is directly proportional to distance between two conductive plates and inversely proportional to the cross section area. Thus, it remains constant for a particular cell.

Q. 6. $\Lambda_m^\circ [\text{NH}_4\text{OH}]$ is equal to _____.

- (A) $\Lambda_m^\circ [\text{NH}_4\text{OH}] + \Lambda_m^\circ [\text{NH}_4\text{Cl}] - \Lambda_m^\circ [\text{HCl}]$
(B) $\Lambda_m^\circ [\text{NH}_4\text{Cl}] + \Lambda_m^\circ [\text{NaOH}] - \Lambda_m^\circ [\text{NaCl}]$
(C) $\Lambda_m^\circ [\text{NH}_4\text{Cl}] + \Lambda_m^\circ [\text{NaCl}] - \Lambda_m^\circ [\text{NaOH}]$
(D) $\Lambda_m^\circ [\text{NaOH}] + \Lambda_m^\circ [\text{NaCl}] - \Lambda_m^\circ [\text{NH}_4\text{Cl}]$

[U]

Ans. Option (B) is correct.



To get equation (iv)

$$\Lambda_m^\circ (\text{NH}_4\text{Cl}) + \Lambda_m^\circ (\text{NaOH}) - \Lambda_m^\circ (\text{NaCl}) = \Lambda_m^\circ (\text{NH}_4\text{OH})$$

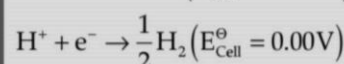
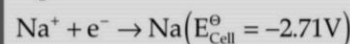
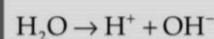
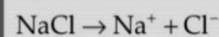
Q. 7. In the electrolysis of aqueous sodium chloride solution which of the half cell reaction will occur at anode?

- (A) $\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s}); E_{\text{Cell}}^\ominus = 2.71 \text{ V}$
(B) $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-; E_{\text{Cell}}^\ominus = 1.23 \text{ V}$
(C) $\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2(\text{g}); E_{\text{Cell}}^\ominus = 0.00 \text{ V}$
(D) $\text{Cl}^-(\text{aq}) \rightarrow \frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^-; E_{\text{Cell}}^\ominus = 1.36 \text{ V}$

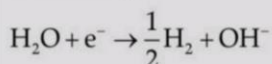
[U]

Ans. Option (D) is correct.

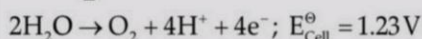
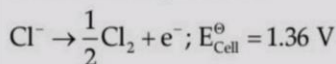
Explanation: During electrolysis



At cathode,



At anode, two reactions are possible where lower of E° is preferred



But due to slow oxidation process of O_2 it needs high voltage. Thus, Cl_2 will form rather than O_2 as preference.

AI Q. 8. Which of the following statement is correct?

- (A) E_{Cell} and $\Delta_r G$ of cell reaction both extensive properties.
(B) E_{Cell} and $\Delta_r G$ of cell reaction both intensive properties.
(C) E_{Cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property.
(D) E_{Cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property. **[R]**

Ans. Option (C) is correct.

Explanation: E_{cell} is an intensive property and it does not depend upon number of particles but $\Delta_r G$ of the cell reaction is an extensive property because this depends upon number of particles.

Q. 9. An electrochemical cell behaves like an electrolytic cell when:

- (A) $E_{\text{cell}} = E_{\text{external}}$ (B) $E_{\text{cell}} = 0$
(C) $E_{\text{external}} > E_{\text{cell}}$ (D) $E_{\text{external}} < E_{\text{cell}}$

[R] [CBSE O.D. Set-II 2020]

Ans. Option (C) is correct.

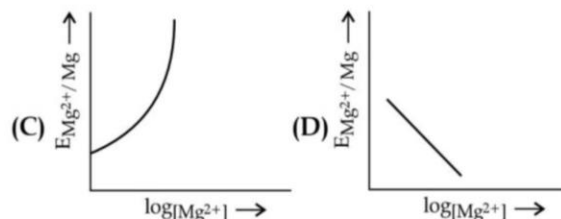
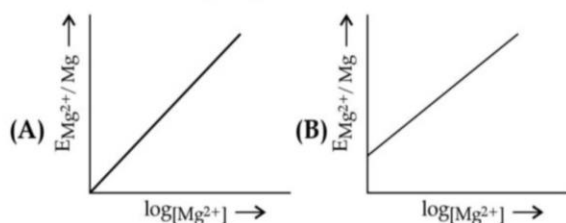
Explanation: If an external opposite potential is applied on the electrochemical cell, the reaction continues to take place till the opposite voltage reaches the value 1.1 V. At this stage, no current flows through the cell and if there is any further increase in the external potential (E_{external}), then reaction starts functioning in opposite direction i.e., an electrochemical cell behaves like an electrolytic cell.

$$E_{\text{external}} > E_{\text{cell}}$$

AI Q. 10. Electrode potential for Mg electrode varies according to the equation:

$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^\circ - \frac{0.059}{2} \log \frac{1}{[\text{Mg}^{2+}]}$$

The graph of $E_{\text{Mg}^{2+}/\text{Mg}}$ vs $\log [\text{Mg}^{2+}]$ is:



Ans. Option (B) is correct.

Explanation:

$$E_{\text{Mg}^{2+}/\text{Mg}} = E_{\text{Mg}^{2+}/\text{Mg}}^\circ + \frac{0.059}{2} \log [\text{Mg}^{2+}]$$

Compare this equation with the equation of straight line $y = mx + c$.

The graph of $E_{\text{Mg}^{2+}/\text{Mg}}$ vs $\log [\text{Mg}^{2+}]$ is a straight line with a positive slope and intercept $E_{\text{Mg}^{2+}/\text{Mg}}^\circ$.

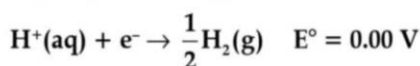
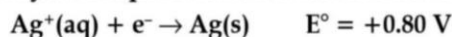
Q. 11. In an electrochemical process, a salt bridge is used:

- (A) as a reducing agent
(B) as an oxidizing agent
(C) to complete the circuit so that current can flow
(D) None of these **[R]**

Ans. Option (C) is correct.

Explanation: In an electrochemical cell, a salt bridge is used to keep solution electrically neutral and allow the flow of ions from one cell to another so that reaction can not stop, otherwise due to accumulation of ions on cathode and anode can stop reactions.

Q. 12. Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution:



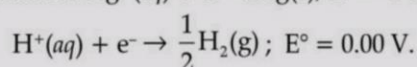
On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode? **[A]**

- (A) $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) \quad E^\circ = +0.80 \text{ V}$
(B) $\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2(\text{g}) \quad E^\circ = 0.00 \text{ V}$

- (C) Both reactions are feasible
(D) None of these above **[U]**

Ans. Option (A) is correct.

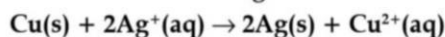
Explanation: $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}); E^\circ = +0.80 \text{ V}$



On the basis of their standard reduction potential (E°) values, cathode reaction is given by the one with higher E° values.

Thus, $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$ reaction will be more feasible at cathode.

Q. 13. Consider the following reaction:



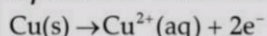
Depict the galvanic cell in which the given reaction takes place.

- (A) $\text{Cu}^{2+}(\text{aq}) | \text{Cu(s)} || \text{Ag}^+(\text{aq}) | \text{Ag(s)}$
 (B) $\text{Cu(s)} | \text{Cu}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag(s)}$
 (C) $\text{Ag}^+(\text{aq}) | \text{Ag(s)} || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$
 (D) $\text{Ag(s)} | \text{Ag}^+(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu(s)}$

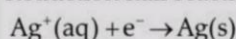
[A]

Ans. Option (B) is correct.

Explanation: Oxidation half reaction



Reduction half reaction



Anode salt Cathode
(Oxidation) bridge (Reduction)

Q. 14. Which of the following statements is not correct ?

- (A) Copper liberates hydrogen from acids.
 (B) In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine.
 (C) Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution.
 (D) Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution.

[A]

Ans. Option (A) is correct.

Explanation: Copper does not liberate hydrogen from acids because copper lies below hydrogen in electrochemical series. So, copper does not have sufficient electrode potential to liberate elemental hydrogen from compounds in which oxidation state of hydrogen is +1.

Q. 15. Calculate the emf of the following cell at 298 K:



[Given $E^\circ_{\text{cell}} = 2.71 \text{ V}$]

- (A) 1.426 V (B) 2.503 V
 (C) 2.651 V (D) 1.8 V

[U]

Ans. Option (C) is correct.

Explanation:

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} \\ &= 2.71 \text{ V} - \frac{0.059}{2} \log \frac{0.1}{0.001} \\ &= 2.71 \text{ V} - \frac{0.059}{2} \log 10^2 \\ E_{\text{cell}} &= 2.651 \text{ V} \end{aligned}$$

Q. 16. Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidising power.

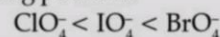
Ion	ClO_4^-	IO_4^-	BrO_4^-
Reduction potential E°/V	$E^\circ = 1.19\text{V}$	$E^\circ = 1.65\text{V}$	$E^\circ = 1.74\text{V}$

- (A) $\text{ClO}_4^- > \text{IO}_4^- > \text{BrO}_4^-$ (B) $\text{IO}_4^- > \text{BrO}_4^- > \text{ClO}_4^-$
 (C) $\text{BrO}_4^- > \text{IO}_4^- > \text{ClO}_4^-$ (D) $\text{BrO}_4^- > \text{ClO}_4^- > \text{IO}_4^-$

[A]

Ans. Option (C) is correct.

Explanation: Higher the reduction potential, higher is its tendency to get reduced. Hence, the order of oxidising power is:



Q. 17. Using the data given below find strongest reduction agent.

$$E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}, E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$$

$$E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}, E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$$

- (A) Cl^- (B) Cr
 (C) Cr^{3+} (D) Mn^{2+}

[A]

Ans. Option (B) is correct.

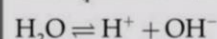
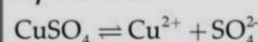
Explanation: The negative value of standard reduction potential for Cr^{3+} to Cr means that the redox couple is a stronger reducing agent.

Q. 18. What will happen during the electrolysis of aqueous solution of CuSO_4 by using platinum electrodes?

- (A) Copper will deposit at cathode.
 (B) Copper will deposit at anode.
 (C) Oxygen will be released at anode.
 (D) Copper will dissolve at anode.

Ans. Option (A) and (C) are correct.

Explanation:

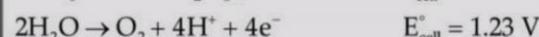


At cathode,



This reaction where copper metal is deposited at cathode will take place due to higher reduction potential.

At anode,



The reaction with lower value of E° will be preferred at anode, hence O_2 is released at anode.

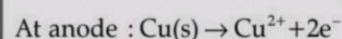
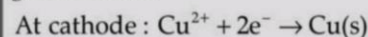
Q. 19. What will happen during the electrolysis of aqueous solution of CuSO_4 in the presence of Cu electrodes?

- (A) Copper will deposit at cathode
 (B) Copper will dissolve at anode
 (C) Oxygen will be released at anode
 (D) Copper will deposit at anode

[U]

Ans. Option (A) and (B) are correct.

Explanation: Electrolysis of CuSO_4 can be represented by two half-cell reactions these occurring at cathode and anode, respectively, as given below :



On dissolution of CuSO_4 in water will dissociate as Cu^{2+} , SO_4^{2-} , H^+ , OH^- .

At anode, SO_4^{2-} and OH^- are stable to exist on their own, so these do not oxidise. Thus, Cu on anode oxidise to form Cu^{+2} ion and dissolve anode gradually. At cathode, Cu^{+2} ion is reduced rather H^+ because of higher potential of copper.

Thus, in above reaction Cu will deposit at cathode while copper will dissolve at anode. Hence, (A) and (B) are the correct options.

Q. 20. Conductivity κ , is equal to _____.

- (A) \wedge_m (B) $\frac{G^*}{R}$
(C) $\frac{l}{A}$ (D) All of the above **A**

Ans. Option (B) is correct.

Explanation: $\kappa = \frac{1}{R} \cdot \frac{l}{A}$ or $\frac{G^*}{R}$



Assertion and Reason Based MCQs

Directions: In the following questions, a statement of Assertion (A) is followed by a statement of Reason (R). Mark the correct choice as:

- (A) Both (A) and (R) are true, and (R) is the correct explanation of (A).
(B) Both (A) and (R) are true, but (R) is not the correct explanation of (A).
(C) (A) is true, but (R) is false.
(D) (A) is false, but (R) is true.

Q. 1. **Assertion (A):** Conductivity of an electrolyte increases with decrease in concentration.

Reason (R): Number of ions per unit volume decreases on dilution.

Ans. Option (D) is correct.

Explanation: Conductivity of an electrolyte decreases with decrease in concentration because of ions per unit volume decreases on dilution. Molar-conductivity of electrolyte increase with decrease in concentration as total volume of solution of 1 mole electrolyte increase.

Q. 2. **Assertion (A):** \wedge_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

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

Ans. Option (A) is correct.

Explanation: Weak electrolytes dissociate partially in concentrated solution. On dilution, their degree of dissociation increases hence, their \wedge_m increases sharply.

Q. 3. **Assertion (A):** Electrolytic conduction increases with increase in temperature.

Reason (R): Increase in temperature cause the electronic movement more rapid.

Ans. Option (C) is correct.

Explanation: As the temperature of electrolytic solution is increased, the degree of ionisation increases, that ions carry charges. This results in the increase of electrical conductance of electrolytic solutions.

Q. 4. **Assertion (A):** Molar conductivity of an ionic solution depends on temperature.

Reason (R): Molar conductivity of an ionic solution depends on the concentration of electrolytes in the solution.

Ans. Option (B) is correct.

Explanation: Molar conductivity of an ionic solution depends on the temperature as well as on the concentration of the electrolytes in the solution. Therefore, on increase in temperature, molar conductivity increases whereas molar conductivity decrease on increase in concentration.

Q. 5. **Assertion (A):** E_{cell} should have a positive value for the cell to function.

Reason (R): $E_{\text{cathode}} < E_{\text{anode}}$

Ans. Option (C) is correct.

Explanation: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$
To have positive value of E_{cell} , E_{cathode} should be greater than E_{anode} .

Q. 6. **Assertion (A):** Cu is less reactive than hydrogen.

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

Ans. Option (C) is correct.

Explanation: Cu is less reactive than hydrogen because $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ is positive.

Q. 7. **Assertion (A):** Copper sulphate can be stored in zinc vessel.

Reason (R): Zinc is more reactive than copper.

Ans. Option (D) is correct.

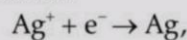
Explanation: Zinc will get dissolved in CuSO_4 solution, since, zinc is more reactive than copper.

Q. 8. **Assertion (A):** $E_{\text{Ag}^+/\text{Ag}}$ increases with increase in concentration of Ag^+ ions.

Reason (R): $E_{\text{Ag}^+/\text{Ag}}$ has a positive value.

Ans. Option (B) is correct.

Explanation:



$$E_{\text{Ag}^+/\text{Ag}} = E^\circ_{\text{Ag}^+/\text{Ag}} - \frac{RT}{nF} \ln \frac{1}{[\text{Ag}^+]}$$

On increasing $[\text{Ag}^+]$, $E_{\text{Ag}^+/\text{Ag}}$ will increase and it has a positive value.

Q. 9. **Assertion (A):** Electrolysis of NaCl solution gives chlorine at anode instead of O_2 .

Reason (R): Formation of oxygen at anode requires over voltage.

Ans. Option (A) is correct.

Explanation: Formation of oxygen has lower value of E° than formation of chlorine even then it is not formed because of kinetically slow oxidation of O_2 it requires over voltage.



Case-based MCQs

I. Read the passage given below and answer the following questions: (1×4 = 4)

The cell constant is usually determined by measuring the resistance of the cell containing a solution whose conductivity is already known. For this purpose, we generally use KCl solutions whose conductivity is known accurately at various concentrations and at different temperatures. Consider the resistance of a conductivity cell filled with 0.1 M KCl solution is 200 Ω. If the resistance of the same cell when filled with 0.02 M KCl solution is 420 Ω.

(Conductivity of 0.1 M KCl solution is 1.29 S m⁻¹.)

The following questions are multiple choice questions. Choose the most appropriate answer:

Q. 1. What is the conductivity of 0.02 M KCl solution ?

- (A) 0.452 S m⁻¹ (B) 0.215 S m⁻¹
(C) 0.614 S m⁻¹ (D) 0.433 S m⁻¹

Ans. Option (C) is correct.

Explanation: Conductivity of 0.02 mol L⁻¹ KCl Solution = Cell constant/resistance i.e., $k = \frac{G^*}{R}$

$$= \frac{258}{420}$$

$$= 0.614 \text{ S m}^{-1}$$

Q. 2. What will happen to the conductivity of the cell with the dilution ?

- (A) First decreases then increases
(B) Increases
(C) First increases then decreases
(D) Decreases

Ans. Option (D) is correct.

Explanation: The conductivity decreases with dilution because on dilution number of ions per unit volume that are charge carriers decreases.

Q. 3. The cell constant of a conductivity cell _____.

- (A) Changes with change of electrolyte.
(B) Changes with change of concentration of electrolyte.
(C) Changes with temperature of electrolyte.
(D) Remains constant for a cell.

Ans. Option (D) is correct.

Explanation: The cell constant of a conductivity cell remains constant for a cell as it only depends on distance between the electrodes and their cross-section area.

Q. 4. SI unit for conductivity of a solution is:

- (A) S m⁻¹ (B) S m² mol⁻¹
(C) mol cm⁻³ (D) S cm² mol⁻¹

Ans. Option (A) is correct.

Explanation: SI unit for conductivity of a solution is S m⁻¹ as conductivity is reciprocal of resistivity

$$\text{where } \kappa = \frac{l}{A}$$

$$\text{unit of } \kappa = \text{S} \frac{(\text{m})}{(\text{m}^2)}$$

$$\kappa = \text{S m}^{-1}$$

Q. 5. Which of the following is not true?

The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to:

- (A) size of the ions in which they dissociate
(B) concentration of ions
(C) charge of the ions in which they dissociate
(D) is independent of ions movement under a potential gradient

Ans. Option (D) is correct.

Explanation: The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to size and charge of the ions in which they dissociate, concentration of ions, ease with which the ions move under a potential gradient.

II. Read the passage given below and answer the following questions:

A galvanic cell consists of a metallic zinc plate immersed in 0.1 M Zn(NO₃)₂ solution and metallic plate of lead in 0.02 M Pb(NO₃)₂ solution.

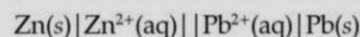
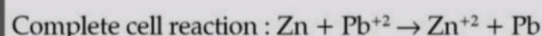
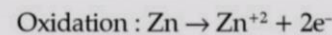
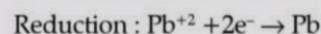
The following questions are multiple choice questions. Choose the most appropriate answer:

Q. 1. How will the cell be represented ?

- (A) Zn(s) | Zn²⁺(aq) || Pb²⁺(aq) | Pb(s)
(B) Zn²⁺(s) | Zn(aq) || Pb²⁺(aq) | Pb(s)
(C) Pb²⁺(aq) | Pb(s) || Zn²⁺(s) | Zn(aq)
(D) Pb(s) | Pb²⁺(aq) || Zn²⁺(s) | Zn(aq)

Ans. Option (A) is correct.

Explanation: In galvanic cells, redox reaction that start from left corner follow:



Q. 2. Calculate the emf of the cell.

- (A) 6.01 V (B) 0.412 V
(C) 0.609 V (D) 4.12 V

Ans. Option (C) is correct.

Explanation: According to Nernst equation:

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

$$E_{\text{cell}} = [-0.13 - (-0.76)] - \frac{0.0591}{2} \log \frac{0.1}{0.02}$$

$$= 0.63 - 0.02955 \times \log 5$$

$$= 0.63 - 0.02955 \times 0.6990$$

$$= 0.63 - 0.0206 = 0.6094 \text{ V}$$

Commonly Made Errors

- The cell representation is given incorrectly by many candidates.
- The calculation of emf of the cell by using Nernst equation is incorrect, in some cases.
- Students forget the $E^\circ_{\text{Pb}^{2+}/\text{Pb}}$ and $E^\circ_{\text{Zn}^{2+}/\text{Zn}}$ sometimes.

Answering Tip

- Do more practice of cell representation and numerical based on Nernst equation.
- Keep memorising standard reduction potential values in reactivity series.

Q. 3. What product is obtained at cathode ?

- (A) Zn (B) Pb
(C) Zn^{2+} (D) Pb^{2+}

Ans. Option (B) is correct.

Explanation:

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

Cathode reaction: $\text{Pb}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Pb(s)}$

Q. 4. Which of the following statement is not correct about an inert electrode in a cell ?

- (A) It does not participate in the cell reaction.
(B) It provides surface either for oxidation or for reduction reaction.
(C) It provides surface for conduction of electrons.
(D) It provides surface for redox reaction.

Ans. Option (D) is correct.

Explanation: Inert electrode does not participate in redox reaction and acts only as source or sink for electrons. It provides surface either for oxidation or for reduction reaction.

III. Read the passage given below and answer the following questions:

Products of electrolysis depend on the nature of material being electrolysed and the type of electrodes being used. If the electrode is inert (e.g., platinum or gold), it does not participate in the chemical reaction and acts only as source or sink for electrons. On the other hand, if the electrode is reactive, it participates in the electrode reaction. Thus, the products of electrolysis may be different for reactive and inert electrodes.

Aqueous copper sulphate solution and aqueous silver nitrate solution are electrolysed by 1 ampere current for 10 minutes in separate electrolytic cells. In these questions, a statement of assertion followed by a statement of reason. Choose the correct answer out of the following choices:

- (A) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(B) Assertion and reason both are correct statements but reason is NOT correct explanation for assertion.

(C) Assertion is correct statement but reason is wrong statement.

(D) Assertion is wrong statement but reason is correct statement.

Q. 1. **Assertion (A):** The mass of copper and silver, deposited on the cathode are same.

Reason (R): Copper and silver have different equivalent masses.

Ans. Option (D) is correct.

Explanation: According to Faraday's second law of electrolysis the amount of different substance liberated when same quantity of electricity passes through electrolytic solutions is directly proportional to equivalent weight.

$$W = ItE/96500$$

$$= 1 \times 10 \times 60 \times 31.8/96500 \text{ for copper.}$$

It will be different for silver since the equivalent weight of silver is different.

Q. 2. **Assertion (A):** At equilibrium condition $E_{\text{cell}} = 0$ or $\Delta_r G = 0$.

Reason (R): E_{cell} is zero when both electrodes of the cell are of the same metal.

Ans. Option (B) is correct.

Explanation:

At equilibrium, condition of $E_{\text{cell}} = 0$, $\Delta_r G = 0$ because E_{cathode} become equal to E_{anode} .

Q. 3. **Assertion (A):** The negative sign in the expression $E_{\text{Zn}^{2+}/\text{Zn}} = -0.76\text{V}$ means Zn^{2+} cannot be oxidised to Zn.

Reason (R): Zn is more reactive than hydrogen and Zn will be oxidised and H^+ will get reduced.

Ans. Option (A) is correct.

Explanation: It shows that the reduced form of (Zn) is not stable. It is difficult to reduce Zn^{2+} to Zn. Rather the reverse reaction i.e., Zn can get oxidised to Zn^{2+} and H^+ will get reduced as it is stabler among both the reduced species.

Q. 4. **Assertion (A):** In a galvanic cell, chemical energy is converted into electrical energy.

Reason (R): Redox reactions provide the chemical energy to the cell.

Ans. Option (A) is correct.

Explanation: The redox reactions provide the chemical energy to the galvanic cell which is converted into electrical energy.

Q. 5. **Assertion (A):** Zinc sulphate cannot be stored in copper vessel.

Reason (R): Zinc is more reactive than copper.

Ans. Option (D) is correct.

Explanation: Zinc sulphate cannot be stored in copper vessel as zinc is more reactive than copper. Thus, no effect will be observed as no reaction is occurred.

✓ **(B) SUBJECTIVE QUESTIONS**



Short Answer Type Questions-I

(2 Marks Each)

Q. 1. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is

$39.05 \text{ S cm}^2 \text{ mol}^{-1}$. Given $\Lambda^\circ_{(\text{H}^+)} = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\Lambda^\circ_{(\text{CH}_3\text{COO}^-)} = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$.

[A] [CBSE Delhi Set-1, 2, 3 2017]

Ans. $\Lambda^\circ_{\text{CH}_3\text{COOH}} = \Lambda^\circ_{\text{CH}_3\text{COO}^-} + \Lambda^\circ_{\text{H}^+}$ [½]

$$= 40.9 + 349.6 = 390.5 \text{ S cm}^2 \text{ mol}^{-1} \quad [½]$$

$$\text{Now, } \alpha = \Lambda_m / \Lambda^\circ_m \quad [½]$$

$$= 39.05 / 390.5 = 0.1 \quad [½]$$

[CBSE Marking Scheme 2017]

Commonly Made Error

- Students tend to forget specifically mentioning the formula and start the calculations or do not mention all the steps or specific units.

Answering Tip

- Write the working formula in each step followed by value assignment for each entity. Give appropriate unit along with the answer.

[AI] Q. 2. The conductivity of a 0.01 M solution of acetic acid at 298 K is $1.65 \times 10^{-4} \text{ S cm}^{-1}$.

Calculate molar conductivity (Λ_m) of the solution. [A] [CBSE Comptt. Delhi/OD 2018]

Ans. $\Lambda_m = \frac{1000\kappa}{C}$ [½]

$$\Lambda_m = \frac{1.65 \times 10^{-4} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.01 \text{ mol L}^{-1}} \quad [½]$$

$$= 16.5 \text{ S cm}^2 \text{ mol}^{-1} \quad [1]$$

[CBSE Marking Scheme 2018]

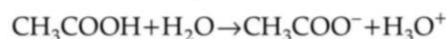
Q. 3. The conductivity of 10^{-3} mol/L acetic acid at 25°C is $4.1 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its degree of dissociation if Λ°_m for acetic acid at 25°C is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$. [A] [O.E.B.]

$$\begin{aligned} \text{Ans. } \Lambda_m &= \frac{1000\kappa}{C} \\ \Lambda_m &= \frac{1000 \text{ cm}^3 \text{ L}^{-1} \times 4.1 \times 10^{-5} \text{ S cm}^{-1}}{10^{-3} \text{ mol L}^{-1}} \\ &= 41 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \alpha &= \frac{\Lambda_m}{\Lambda^\circ_m} \\ \alpha &= \frac{41}{390.5} = 0.105 \end{aligned}$$

Q. 4. Why on dilution the Λ_m of CH_3COOH increases drastically, while that of CH_3COONa increases gradually? [U] [O.E.B.]

Ans. In case of CH_3COOH which is a weak electrolyte, the number of ions increases 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 .

Q. 5. Solutions of two electrolytes 'A' and 'B' are diluted. The limiting molar conductivity of 'B' increases 1.5 times while that of 'A' increases 25 times. Which of the two is a strong electrolyte?

Justify your answer.

[A] [O.E.B.]

Ans. 'B' is a strong electrolyte.

B is a strong electrolyte which is completely dissociated into ions, but on dilution interionic forces overcome and ions are free to move. So there is slight increase in molar conductivity on dilution.

Q. 6. The resistivity of a 0.8M solution of electrolyte is $5 \times 10^{-3} \Omega \text{ cm}$. Calculate its molar conductivity.

[A] [O.E.B.]

Ans. Resistivity (ρ) = $5 \times 10^{-3} \Omega \text{ cm}$
Conductivity of solution (κ)

$$= \frac{1}{\text{Resistivity}}$$

$$= \frac{1}{5 \times 10^{-3} \Omega \text{ cm}}$$

$$= 0.2 \times 10^3 \Omega^{-1} \text{ cm}^{-1}$$

$$= 200 \Omega^{-1} \text{ cm}^{-1}$$

Molar conductivity

$$\Lambda_m = \frac{1000 \times \kappa}{M}$$

$$= \frac{1000 \times 200}{0.8} = 2.5 \times 10^5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

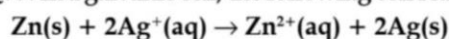
Commonly Made Error

- Some students get confused in conductivity and molar conductivity and calculate conductivity rather than molar conductivity.

Answering Tip

- Learn and understand the difference between conductivity and molar conductivity and also formula for their calculation.

[AI] Q. 7. In a galvanic cell, the following cell reaction occurs:



$$E^\circ_{\text{cell}} = +1.56 \text{ V}$$

(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?

[A&E] [CBSE Foreign Set-1, 2, 3 2017]

- Ans. (i) Zinc to silver [1]
 (ii) Concentration of Zn^{2+} ions will increase and Ag^+ ions will decrease. [1]
 [CBSE Marking Scheme 2017]

Q. 8. Calculate the emf of the following cell at 298 K



[Given: $E^\circ_{\text{cell}} = +0.30\text{ V}$] [O.E.B.]

Ans. $2\text{Cr(s)} + 3\text{Fe}^{2+}(\text{aq}) \rightarrow 3\text{Fe(s)} + 2\text{Cr}^{3+}(\text{aq})$ [A]
 Where, $n = 6$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

$$E_{\text{cell}} = 0.30\text{ V} - \frac{0.059}{6} \text{ V} \log \frac{[10^{-1}]^2}{[10^{-2}]^3}$$

$$E_{\text{cell}} = 0.26\text{ V}$$

Commonly Made Error

- Sometimes students get confused to write correct formula for calculation of emf of the cell on the basis of oxidation and reduction in half cell.

Answering Tip

- Learn and understand Nernst equation for an electrochemical cell.

Q. 9. Explain redox potential.

Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidising power.

Ion	ClO_4^-	IO_4^-	BrO_4^-
Reduction potential E°/V	$E^\circ = 1.19\text{V}$	$E^\circ = 1.65\text{V}$	$E^\circ = 1.74\text{V}$

[A] [O.E.B.]

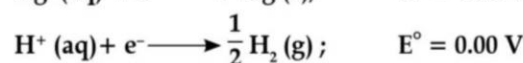
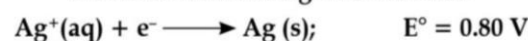
Ans. Redox potential (also known as reduction / oxidation potential) is a measure of the tendency of a chemical species to acquire electrons from or lose electrons to an electrode and thereby be reduced or oxidised respectively. Redox potential is measured in volts (V), or millivolts (mV). The more positive the reduction

potential of a species, the greater the species' affinity for electrons and tendency to be reduced.

The higher the reduction potential, the higher is its tendency to get reduced. Hence, the order of oxidising power is:



[AI] Q. 10. Following reactions can occur at cathode during the electrolysis of aqueous silver nitrate solution using Pt electrodes:

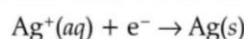


On the basis of their standard electrode potential values, which reaction is feasible at cathode and why? [A] [O.E.B.]

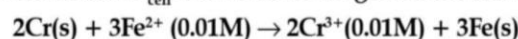
Ans. $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag(s)}$

Because it has higher reduction potential.

Detailed Answer: As reaction with higher value of standard electrode potential occurs at cathode, Ag gets reduced. So, the reaction occurring at cathode is



Q. 11. Calculate E°_{cell} for the following reaction at 298 K:



Given: $E_{\text{cell}} = 0.261\text{ V}$ [U] [O.E.B.]

Ans. Nernst Equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Prod.}]}{[\text{React.}]}$$

$$E^\circ_{\text{cell}} = E_{\text{cell}} + \frac{0.059}{n} \log \frac{[\text{Prod.}]}{[\text{React.}]}$$

$$= 0.261 + \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

$$= 0.261 + \frac{0.059}{6} \log \frac{(10^{-2})^2}{(10^{-2})^3}$$

$$= 0.261 + \frac{0.059}{6} \log 10^2$$

$$= 0.261 + \frac{0.059 \times 2}{6}$$

$$= 0.261 + 0.01966$$

$$= 0.28068\text{V} \approx 0.281\text{V}$$

OR

According to Nernst equation ✓

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Prod.}]}{[\text{React.}]}$$

$$E^\circ_{\text{cell}} = E_{\text{cell}} + \frac{0.059}{n} \log \frac{[\text{Prod.}]}{[\text{React.}]}$$

$$= 0.261 + \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$$

$$\begin{aligned}
 E_{Cu} &= E_0 - 0.261 + \frac{0.059}{6} \log \frac{10^{-4}}{10^{-6}} \\
 &= 0.261 + \frac{0.059}{6} \log 10^2 \\
 E_{Cu} &= 0.261 + \frac{0.059 \times 2}{6} \\
 &= 0.261 + 0.01966 \\
 E_{Cu} &= 0.28066 \text{ V} \\
 \boxed{E_{Cu} &= 0.28 \text{ V}}
 \end{aligned}$$

[Topper's Answer] [2]

Q. 12. Iron displaces copper from copper sulphate solution but Pt does not why? [A] [O.E.B.]

Ans. Electrode potential of Fe is more than electrode potential of Cu. So, Fe displaces Cu from copper sulphate while electrode potential of Pt is less than Cu. Due to this reason, Pt cannot displace Cu from copper sulphate.

[AI] Q. 13. 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.

[U] + [R] [CBSE Outside Dehi Set-1, 2017]

Ans. Mercury cell [1]
Anode: $\text{Zn(Hg)} + 2\text{OH}^- \rightarrow \text{ZnO(s)} + \text{H}_2\text{O} + 2\text{e}^-$ [½]
Cathode: $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg(l)} + 2\text{OH}^-$ [½]
[CBSE Marking Scheme, 2017]

Detailed Answer:

Mercury cell is generally used in hearing aids.

At anode: $\text{Zn(Hg)} + 2\text{OH}^- \rightarrow \text{ZnO(s)} + \text{H}_2\text{O} + 2\text{e}^-$

At cathode: $\text{HgO(s)} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg(l)} + 2\text{OH}^-$

Overall reaction: $\text{Zn(Hg)} + \text{HgO(s)} \rightarrow \text{ZnO(s)} + \text{Hg(l)}$

[AI] Q. 14. 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.

[U] + [R] [CBSE Outside Dehi Set-3, 2017]

Ans. Dry cell/Leclanche cell [1]
Anode: $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ [½]
Cathode: $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \rightarrow \text{MnO(OH)} + \text{NH}_3$ [½]
[CBSE Marking Scheme, 2017]

Detailed Answer:

The cell which is used in the transistors is Dry cell.

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

At cathode: $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \rightarrow \text{MnO(OH)} + \text{NH}_3$
Ammonia produced in the reaction forms a complex with Zn^{2+} ion.

$\text{Zn}^{2+} + 4\text{NH}_3 \rightarrow [\text{Zn(NH}_3)_4]^{2+}$

[AI] Q. 15. From the given cells:

Lead storage cell, Mercury cell, Fuel cell and Dry cell.

Answer the following:

- Which cell is used in hearing aids?
- Which cell was used in Apollo Space Programme?
- Which cell is used in automobiles and inverters?
- Which cell does not have long life?

[R] [CBSE Dehi Set-1, 2 & 3 2016]

Ans. (i) Mercury cell [½] (ii) Fuel cell [½ + ½]
(iii) Lead storage cell [½] (iv) Dry cell [½ + ½]
[CBSE Marking Scheme, 2016]

Q. 16. Write the electrode reactions for a $\text{H}_2\text{-O}_2$ fuel cell.

[R] [O.E.B.]

Ans. At anode,

$[\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O(l)} + 2\text{e}^-] \times 2$ [½]

At cathode,

$\text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$ [½]

Net cell reaction,

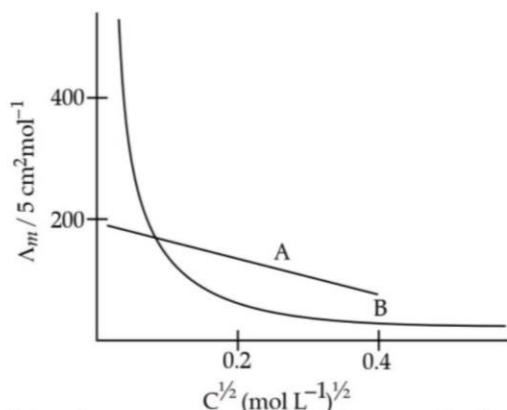
$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O(l)}$ [1]



Short Answer Type Questions-II

(3 Marks Each)

Q. 1. The following curve is obtained when molar conductivity (Λ_m) is plotted against the square root of concentration, $C^{1/2}$ for two electrolytes A and B:



- (i) How do you account for the increase in the molar conductivity of the electrolyte A on dilution?
(ii) As seen from the graph, the value of limiting molar conductivity (Λ_m°) for electrolyte B cannot be obtained graphically. How can this value be obtained?
(iii) Define limiting molar conductivity.

[U] + [R] [O.E.B.]

Ans. (i) As seen from the graph, electrolyte A is a strong electrolyte which is completely ionised in solution. With dilution, the ions are far apart from each other and hence the molar conductivity increases.

(ii) To determine the value of limiting molar conductivity for electrolyte B, indirect method based upon Kohlrausch's law of independent migration of ions is used.

(iii) When concentration approaches zero, the molar conductivity is known as limiting molar conductivity.

Q. 2. (i) Give Debye Huckel Onsager equation for strong electrolyte. [R]

(ii) Given are the conductivity and molar conductivity of NaCl solutions at 298K at different concentrations:

Concentration (M)	Conductivity (S cm ⁻¹)	Molar conductivity (S cm ² mol ⁻¹)
0.100	106.74×10^{-4}	106.7
0.05	55.53×10^{-4}	111.1
0.02	23.15×10^{-4}	115.8

Compare the variation of conductivity and molar conductivity of NaCl solutions on dilution. Give reason. [A] [O.E.B.]

Ans. (i) Debye Huckel Onsager equation for strong electrolyte is:

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

Where Λ_m = Molar conductivity

Λ_m° = Molar conductivity at infinite dilution

b = Constant

C = Concentration of solution

(ii) Conductivity of NaCl decreases on dilution as the number of ions per unit volume decreases.

Whereas molar conductivity of NaCl increases on dilution as on dilution the interionic interactions overcome and ions are free to move.

[AI] Q. 3. 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. [A] [CBSE Foreign Set-1, 2, 3 2017]

$$\begin{aligned} \text{Ans. } A &= \pi r^2 \\ &= 3.14 \times 0.5 \times 0.5 \text{ cm}^2 \\ &= 0.785 \text{ cm}^2 \quad [1/2] \\ l &= 45.5 \text{ cm} \\ G^* &= l/A = 45.5 \text{ cm}/0.785 \text{ cm}^2 \\ &= 57.96 \text{ cm}^{-1} \quad [1/2] \\ \kappa &= G^*/R \quad [1/2] \\ &= 57.96 \text{ cm}^{-1}/4.55 \times 10^3 \Omega \\ &= 1.27 \times 10^{-2} \text{ S cm}^{-1} \quad [1/2] \\ \Lambda_m &= \kappa \times 1000/C \quad [1/2] \\ &= [1.27 \times 10^{-2} \text{ S cm}^{-1}] \times 1000/0.05 \text{ mol/cm}^3 \\ &= 254.77 \text{ S cm}^2 \text{ mol}^{-1} \quad [1/2] \end{aligned}$$

[CBSE Marking Scheme 2017]

Commonly Made Error

- Students often convert centimeter into meter.

Answering Tip

- Check the compatibility of units.

Q. 4. (i) State the law which helps to determine the limiting molar conductivity of weak electrolyte.

(ii) Calculate limiting molar conductivity of CaSO_4 (limiting molar conductivity of calcium and sulphate ions are 119.0 and 160.0 S cm² mol⁻¹ respectively) [R + A] [O.E.B.]

Ans. Kohlrausch law of independent migration of ions:

(i) The limiting molar conductivity of an electrolyte can be represented as the sum of the individual contribution of the anions and cations of the electrolyte.

$$\begin{aligned} \text{(ii)} \quad \Lambda_m^\circ(\text{CaSO}_4) &= \Lambda^\circ_{\text{Ca}^{2+}} + \Lambda^\circ_{\text{SO}_4^{2-}} \\ &= 119.0 \text{ S cm}^2 \text{ mol}^{-1} + 160.0 \text{ S cm}^2 \text{ mol}^{-1} \\ &= 279.0 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

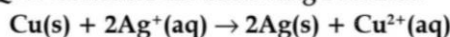
Commonly Made Error

- Students only write the mathematical expression.

Answering Tips

- Write the law as stated. Stick to the statement as the marks are allotted to that only.
- Do not forget to mention the units.

[AI] Q. 5. Consider the following reaction:



(i) Depict the galvanic cell in which the given reaction takes place.

- (ii) Give the direction of flow of current.
(iii) Write the half-cell reactions taking place at cathode and anode.

[CBSE Comptt. Delhi/OD 2018]

- Ans. (i) $\text{Cu(s)} | \text{Cu}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag(s)}$ [1]
(ii) Current will flow from silver to copper electrode in the external circuit. [1]
(iii) Cathode: $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Ag(s)}$
Anode: $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$ [1]
[CBSE Marking Scheme 2018]

- Q. 6. (a) The cell in which the following reaction occurs:
 $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{s})$
has $E^\circ_{\text{cell}} = 0.236 \text{ V}$ at 298 K. Calculate the standard Gibbs energy of the cell reaction. (Given: $1 \text{ F} = 96,500 \text{ C mol}^{-1}$)
(b) How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours? (Given: $1 \text{ F} = 96,500 \text{ C mol}^{-1}$) [A] [O.E.B.]

- Ans. (a) $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ [1/2]
 $n = 2$
 $\Delta G^\circ = -2 \times 96500 \text{ C/mol} \times 0.236 \text{ V}$ [1/2]
 $= -45548 \text{ J/mol}$
 $= -45.548 \text{ kJ/mol}$ [1/2]
(b) $Q = It = 0.5 \times 2 \times 60 \times 60$ [1/2]
 $= 3600 \text{ C}$
 $96500 \text{ C} = 6.023 \times 10^{23} \text{ electrons}$
 $3600 \text{ C} = 2.25 \times 10^{22} \text{ electrons}$ [1]
[CBSE Marking Scheme, 2017]

Detailed Answer:

- (a) $2\text{Fe}^{3+} + 2\text{e}^- \rightarrow 2\text{Fe}^{2+}$
 $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$
For the given cell reaction, $n = 2$.
 $\Delta G^\circ = -nFE^\circ_{\text{cell}}$
 $= -2 \times 96500 \times 0.236$
 $= -45548 \text{ J mol}^{-1}$
 $= -45.55 \text{ kJ mol}^{-1}$

- (b) $I = 0.5 \text{ A}$
 $t = 2 \text{ hours} = 2 \times 60 \times 60 \text{ s} = 7200 \text{ s}$
 $Q = It$
 $= 0.5 \times 7200$
 $= 3600 \text{ coulombs}$

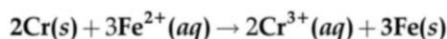
A flow of 96500 C is equal to flow of 1 mole of electrons is 6.023×10^{23} electrons.

$\therefore 3600 \text{ C}$ is equivalent to of electrons

$$= \frac{6.023 \times 10^{23}}{96500} \times 3600$$

$$= 2.246 \times 10^{22} \text{ electrons}$$

- Q. 7. Calculate $\Delta_r G^\circ$ and $\log K_c$ for the following reaction at 298 K.



$$[(E^\circ_{\text{cell}} = 0.30 \text{ V}), 1\text{F} = 96500 \text{ C mol}^{-1}]$$

[A] [CBSE Comptt. OD Set-2 2017]

Ans. $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}, n = 6$ [1/2]
 $= -6 \times 96500 \text{ C/mol} \times 0.30 \text{ V}$
 $= -173700 \text{ J/mol} = -173.7 \text{ kJ/mol}$ [1]
 $E^\circ_{\text{cell}} = 0.059 \text{ V}/n \times \log K_c$ [1/2]
 $\log K_c = 0.30 \text{ V} \times 6/0.059 \text{ V} = 30.5$ [1]
[CBSE Marking Scheme 2017]

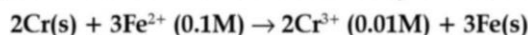
Commonly Made Error

- Students forget to mention the working formula and start the calculations or do not mention all the steps or specific units. Marks are allotted for formulas too.

Answering Tip

- Always write the working formula followed by the value substitution for each entity. Do not forget to mention units wherever required.

- Q. 8. Calculate e.m.f. of the following cell at 298 K:



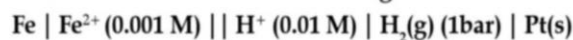
$$E^\circ(\text{Cr}^{3+}/\text{Cr}) = -0.74 \text{ V}$$

$$E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.44 \text{ V}$$

[U] [CBSE Delhi Set-1, 2 & 3, 2016]

Ans. $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ [1/2]
 $= (-0.44) - (-0.74) \text{ V}$
 $= 0.30 \text{ V}$
 $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$
 $= 0.30 - \frac{0.0591}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$ [1/2]
 $= 0.30 - \frac{0.0591}{6} \log \frac{[0.01]^2}{[0.1]^3}$ [1]
 $= 0.30 - \left(\frac{-0.0591}{6} \right)$
 $= 0.3098 \text{ V}$ [1]
[CBSE Marking Scheme 2016]

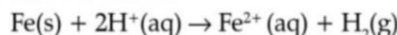
- Q. 9. Calculate the emf of the following cell at 25°C:



$$E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.44 \text{ V}, E^\circ(\text{H}^+/\text{H}_2) = 0.00 \text{ V}$$

[A] [CBSE Delhi 2015]

Ans. Cell reaction is



$$E^\circ_{\text{cell}} = 0.00 - (-0.44) = 0.44 \text{ V}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

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

$$= 0.44 \text{ V} - 0.02955 \text{ V}$$

$$E_{\text{cell}} = 0.41045 \text{ V}$$

Q. 10. A galvanic cell consists of a metallic zinc plate immersed in 0.1 M $\text{Zn}(\text{NO}_3)_2$ solution and metallic plate of lead in 0.02 M $\text{Pb}(\text{NO}_3)_2$ solution. Calculate the emf of the cell. Write the chemical equation for the electrode reactions and represent the cell.
(Given: $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$; $E^\circ_{\text{Pb}^{2+}/\text{Pb}} = -0.13 \text{ V}$)

[A] [O.E.B.]

Ans. Anode reaction: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2e^-$
Cathode reaction: $\text{Pb}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Pb(s)}$
Cell representation:
 $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq}) || \text{Pb}^{2+}(\text{aq}) | \text{Pb(s)}$
According to Nernst equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]}$$

$$E_{\text{cell}} = [-0.13 - (-0.76)] - \frac{0.0591}{2} \log \frac{0.1}{0.02}$$

$$= 0.63 - 0.02955 \times \log 5$$

$$= 0.63 - 0.02955 \times 0.6990$$

$$= 0.63 - 0.0206 = 0.6094 \text{ V}$$

Commonly Made Errors

- The cell representation is given incorrectly by many candidates.
- The calculation of emf of the cell by using Nernst equation is incorrect, in some cases.

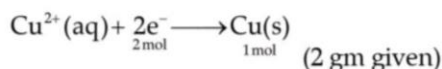
Answering Tip

- Do more practice of cell representation and numerical based on Nernst equation.

Q. 11. When a steady current of 2A was passed through two electrolytic cells A and B containing electrolytes ZnSO_4 and CuSO_4 connected in series, 2 g of Cu were deposited at the cathode of cell B. How long did the current flow? What mass of Zn was deposited at cathode of cell A?

[Atomic mass: $\text{Cu} = 63.5 \text{ g mol}^{-1}$, $\text{Zn} = 65 \text{ g mol}^{-1}$; $1 \text{ F} = 96500 \text{ C mol}^{-1}$] [A] [O.E.B.]

Ans. $\text{Zn}^{2+}(\text{aq}) + 2e^- \xrightarrow{2 \text{ mol}} \text{Zn(s)} \xrightarrow{1 \text{ mol}}$



The charge Q on a mole of electrons, $Q = nF$

Calculation of time for the flow of current:

$$n = 1 \text{ mol}$$

$$Q = 1 \times 96500 \text{ C mol}^{-1} = 96500 \text{ C}$$

$$\text{Molar mass of Cu} = 63.5 \text{ gm mol}^{-1}$$

$$\therefore 63.5 \text{ gm of Cu is deposited by electric charge} = 96500 \text{ C}$$

$$\therefore 2 \text{ gm of Cu is deposited by electric charge}$$

$$= \frac{96500}{63.5} \times 2 = 3039.37 \text{ C}$$

Let 2 A of current be passed for time t , quantity of electricity used = $2A \times t = 3039.37 \text{ C}$

$$\text{or, } t = \frac{3039.37 \text{ C}}{2} = 1519.68 \text{ s}$$

$$= 25 \text{ min } 33 \text{ s}$$

Calculation of mass of Zn deposited:

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{\text{Equivalent weight of Zn}}{\text{Equivalent weight of Cu}}$$

$$= \frac{\text{Molar mass of Zn} / \text{Charge on Cu}}{\text{Molar mass of Cu} / \text{Charge on Cu}}$$

Amount of Zn deposited:

$$= 2 \times \frac{65}{\frac{63.5}{2}} = 2.0472 \text{ g}$$

Q. 12. (a) 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} , $1 \text{ F} = 96500 \text{ C mol}^{-1}$)

(b) Define fuel cell. [R + A] [O.E.B.]

Ans. (a) $m = ZI$ [½]
 $= \frac{108 \times 2 \times 15 \times 60}{1 \times 96500}$ [1]
 $= 2.01 \text{ g}$ (or any other correct method) [½]

(b) Cells that convert the energy of combustion of fuels directly into electrical energy.

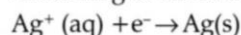
[CBSE Marking Scheme, 2017] [1]

Detailed Answer:

(a) $t = 900 \text{ s}$

$$\text{Charge} = \text{Current} \times \text{Time} = 2 \times 900 = 1800 \text{ C}$$

According to the reaction



We require 1 F to deposit 1 mol or 108 g of Ag

For 1800 C, the mass of Ag deposited will

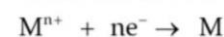
$$be = \frac{108 \times 1800}{1 \times 96500} = 2.0145 \text{ g}$$

(b) Fuel cell is the name given to the galvanic cells which are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy.

Q. 13. The electrolysis of a metal salt solution was carried out by passing a current of 4 A for 45 minutes. It resulted in deposition of 2.977 g of a metal. If atomic mass of the metal is 106.4 g mol^{-1} , calculate the charge on the metal cation. [A] [O.E.B.]

Ans. Let the charge on the metal ion = n^+

Reduction half-reaction,



$$(1 \text{ mol}) (n \text{ mol}) (106.4 \text{ g})$$

Quantity of electricity required for depositing 106.4 g of metal = $n \times 96500 \text{ C}$

Quantity of electricity required for depositing

$$2.977 \text{ g of metal} = \frac{n \times 96500 \times 2.977}{106.4} = n \times 2700$$

Quantity of electricity passed

$$= 4 \times 45 \times 60 \text{ C}$$

$$= 10800 \text{ C}$$

Applying law of conservation of charge,

$$10800 = n \times 2700$$

$$n = \frac{10800}{2700} = 4$$

Charge on metal ion = +4



Long Answer Type Questions

(5 Marks Each)

Q. 1. (a) The electrical resistance of a column of 0.05 M KOH solution of length 50 cm and area of cross-section 0.625 cm^2 is $5 \times 10^3 \text{ ohm}$. Calculate its resistivity, conductivity and molar conductivity.

(b) Predict the products of electrolysis of an aqueous solution of CuCl_2 with platinum electrodes.

(Given: $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$, $E^\circ_{(\frac{1}{2}\text{Cl}_2/\text{Cl}^-)} = +1.36 \text{ V}$;

$E^\circ_{\text{H}^+/\text{H}_2(\text{g}), \text{Pt}} = 0.00 \text{ V}$, $E^\circ_{(\frac{1}{2}\text{O}_2/\text{H}_2\text{O})} = +1.23 \text{ V}$)

[U] [CBSE, OD Set-1, 2020]

Ans. (a) Given: $A = 0.625 \text{ cm}^2$, $l = 50 \text{ cm}$

$$R = 5 \times 10^3 \text{ ohm}, \rho = ?$$

$$m = 0.05 \text{ m}, \kappa = ?$$

$$\Lambda_m = ?$$

$$\text{Cell constant} = \frac{l}{A} = \frac{50 \text{ cm}}{0.625 \text{ cm}^2} = 80 \text{ cm}^{-1}$$

$$\text{Resistivity} = \frac{R}{\text{cell constant}} \text{ or } \frac{R \times A}{l}$$

$$\Rightarrow \frac{5 \times 10^3 \text{ ohm}}{80 \text{ cm}^{-1}} \Rightarrow 62.5 \text{ ohm cm.}$$

$$\Rightarrow 62.5 \text{ ohm cm}$$

$$\text{Conductivity} = \frac{1}{\text{Resistance}} \times \frac{l}{A}$$

$$= \frac{1}{5 \times 10^3} \times 80 = 0.016 \text{ S cm}^{-1}$$

$$\text{Molar conductivity } (\Lambda_m) = \frac{10^3 \kappa}{M}$$

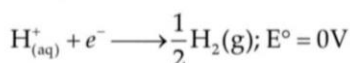
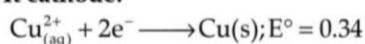
$$\Lambda_m = \frac{\kappa}{M} \times 1000 = \frac{10 \times 1000}{625 \times 0.05} = 320 \text{ S cm}^2 \text{ mol}^{-1}$$

(b) Given: $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$

$$E^\circ_{(\frac{1}{2}\text{Cl}_2/\text{Cl}^-)} = +1.36 \text{ V}$$

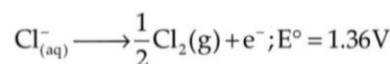
$$E^\circ_{\text{H}^+/\text{H}_2(\text{g}), \text{Pt}} = 0.00 \text{ V}, E^\circ_{(\frac{1}{2}\text{O}_2/\text{H}_2\text{O})} = +1.23 \text{ V}$$

At cathode:



The reaction with a higher value of E° takes place at the cathode, so deposition of copper will take place at the cathode.

At anode: The oxidation reactions are possible at the anode.



At the anode the reaction with a lower value of E° is preferred. But due to the over potential of oxygen, Cl^- gets oxidised at anode to produce Cl_2 gas.

Q. 2. The molar conductivities of acetic acid at 298 K at the concentrations of 0.1 M and 0.001 M are 5.20 and $49.2 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. Calculate the degree of dissociation of acetic acid at these concentration. Given $\lambda^\circ_{(\text{H}^+)}$ and $\lambda^\circ_{(\text{CH}_3\text{COO}^-)}$ are 349.8 and $40.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively.

[U] [O.E.B.]

Ans. Given

$$\lambda^\circ_{(\text{H}^+)} = 349.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\lambda^\circ_{(\text{CH}_3\text{COO}^-)} = 40.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\lambda^\circ_{\text{m}(\text{CH}_3\text{COOH})} = \lambda^\circ_{(\text{CH}_3\text{COO}^-)} + \lambda^\circ_{(\text{H}^+)}$$

$$= 40.9 + 349.8$$

$$= 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

At C = 0.1 M

Degree of dissociation

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

$$= \frac{5.20}{390.7} = 0.013 \text{ i.e. } 1.3\%$$

At C = 0.001 M

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

$$= \frac{49.2}{390.7} = 0.125 \text{ i.e. } 12.5\%$$

Commonly Made Error

- Sometimes students get confused to calculate degree of dissociation of acid.

Answering Tip

- Learn and understand the formula to calculate molar conductivity of solution at infinite dilution and degree of dissociation.

Q. 3. The resistance of 0.01 M acetic solution when measured in a conductivity cell of cell constant 0.366 cm^{-1} , is found to be 2220Ω . Calculate degree of dissociation of acetic acid at this concentration. Also find the dissociation constant of acetic acid. Given that value of $\lambda^\circ_{\text{H}^+}$ and $\lambda^\circ_{\text{CH}_3\text{COO}^-}$ as 349.1 and $40.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. [U] [O.E.B.]

Ans. Conductivity(κ) of 0.01 M acetic acid

$$\kappa = \frac{1}{R} \times (\text{cell constant})$$

$$= \frac{1}{2220 \Omega} \times 0.366 \text{ cm}^{-1}$$

$$= 1.648 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$$

Molar conductivity

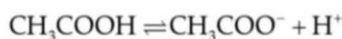
$$\begin{aligned}\Lambda_m &= \frac{\kappa \times 1000}{M} \\ &= \frac{1.648 \times 10^{-4} \times 1000}{0.01} \\ &= 16.48 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}\end{aligned}$$

Molar conductivity at infinite dilution

$$\begin{aligned}\Lambda_m^\infty(\text{CH}_3\text{COOH}) &= \lambda_{\text{H}^+}^\infty + \lambda_{\text{CH}_3\text{COO}^-}^\infty \\ &= 349.1 + 40.9 \\ &= 390 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}\end{aligned}$$

Degree of dissociation of acetic acid

$$\begin{aligned}\alpha &= \frac{\Lambda_m}{\Lambda_m^\infty} \\ &= \frac{16.48}{390} = 0.0422\end{aligned}$$



Initial conc. (mol/L)	C	0	0
Equilibrium conc. (mol/L)	C - Cα	Cα	Cα

Dissociation constant

$$\begin{aligned}K &= \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \\ &= \frac{C\alpha \times C\alpha}{C - C\alpha} \\ &= \frac{C\alpha^2}{(1 - \alpha)} \\ &= \frac{0.01 \times (0.0422)^2}{1 - 0.0422} \\ &= 1.86 \times 10^{-5}\end{aligned}$$

AI Q. 4. (a) Calculate e.m.f. of the following cell:



$$\text{Given: } E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76 \text{ V}, E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$$

$$[\text{Given: } \log 10 = 1]$$

(b) X and Y are two electrolytes. On dilution molar conductivity of 'X' increases 2.5 times while that Y increases 25 times. Which of the two is a weak electrolyte and why?

A&U [CBSE Outside Delhi Set-1, 2020]

Ans. (a) $\text{Zn(s)} / \text{Zn}^{2+} (0.1 \text{ M}) \parallel (0.01 \text{ M}) \text{Ag}^+ / \text{Ag(s)}$

$$E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76 \text{ V}$$

$$E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V} \quad \text{emf} = ?$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Anode}]}{[\text{Cathode}]}$$

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

$$= E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ$$

$$= 0.80 - (-0.76) = 1.56 \text{ V}$$

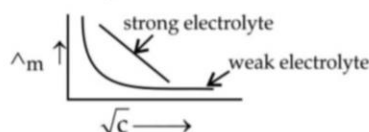
$$E_{\text{cell}} = 1.56 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 1.56 - \frac{0.0591}{2} \log \frac{[0.1]}{[0.01]^2}$$

$$= 1.56 - 0.0295 \log 1000$$

$$= 1.56 - 3(0.0295) = 1.56 - 0.09 = 1.4715$$

(b) Y is a weak electrolyte as on dilution complete dissociation of weak electrolyte takes place and thus a sharp increase in molar conductivity while in strong electrolyte it has already dissociated completely. So on dilution molar conductivity does not rise much.



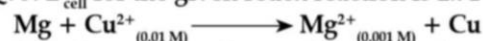
Commonly Made Error

- Some students get confused to find E_{cell}° correctly
- Confusion is found in relation of dilution with strong and weak electrolyses

Answering Tip

- Understand to identify the E_{cathode}° and E_{anode}° from given standard reduction potentials.
- Try to remember graph for electrolytes to identify comparison.

AI Q. 5. E_{cell}° for the given redox reaction is 2.71 V.



Calculate E_{cell}° for the reaction. Write the direction of flow of current when an external opposite potential applied is:

(i) Less than 2.71 V

(ii) Greater than 2.71 V **A** [CBSE Delhi Set-1, 2019]

$$\text{Ans. } E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log K_c \quad [1]$$

$$= E_{\text{cell}}^\circ - \frac{0.059}{2} \log \frac{10^{-3}}{10^{-2}} = 2.71 + 0.0295 \quad [1]$$

$$E_{\text{cell}} = 2.7395 \text{ V} \quad [1]$$

(i) Cu to Mg / Cathode to anode / Same direction [1]

(ii) Mg to Cu / Anode to cathode / Opposite direction [CBSE Marking Scheme, 2019] [1]

Detailed Answer:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

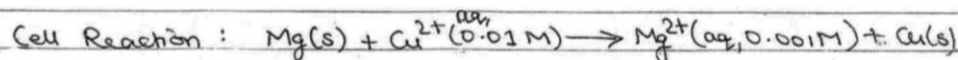
$$E_{\text{cell}} = 2.71 - \frac{0.059}{2} \log \frac{[0.001]}{[0.01]}$$

$$E_{\text{cell}} = 2.71 - (-0.0295) = 2.74 \text{ V}$$

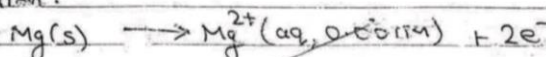
- (i) When external opposite applied voltage is less than 2.71, it is less than E_{cell}° , therefore, the electrons will flow from the anode to the cathode, and current will flow from cathode (copper electrode) to anode (magnesium electrode).

- (ii) When external opposite applied potential is greater than 2.71, which is greater than E_{cell}° , therefore, the reaction will be reversed, and the current will flow from anode to cathode.

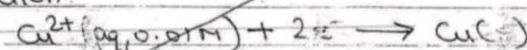
OR



Anode Reaction:



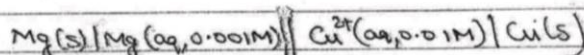
Cathode Reaction:



Total Electrons exchanged during redox reaction = $n = 2$ mol

Reaction quotient of the reaction, $Q = \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.001\text{M}}{0.01\text{M}} = \frac{1}{10} = 0.1$

Writing Cell Representation:



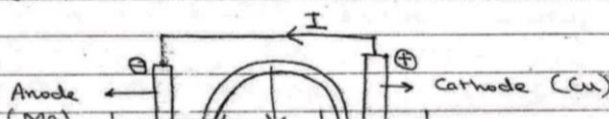
$E_{\text{cell}} = 2.71 + \frac{0.059}{2}$

$E_{\text{cell}} = 2.71 + 0.0295$

$E_{\text{cell}} = 2.7395\text{V}$

Hence, the E_{cell} for the reaction is 2.7395 V

Cell Construction:



- (i) However, if external applied voltage exceeds 2.71V, current will start flowing from Mg electrode to Cu electrode in standard conditions.

But in given conditions, the current will keep flowing from Cu electrode to Mg electrode as long as $2.71\text{V} < V_{\text{external}} < 2.7395\text{V}$.

- (i) But, when external applied voltage exceeds even 2.7395V, current will flow from Mg electrode to Cu electrode in given conditions as well.

[Topper's Answer 2016]

- Q. 6. (a) Represent the cell in which the following reaction takes place:



Calculate its emf if $E_{\text{cell}}^{\circ} = 1.41\text{V}$.

- (b) How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte? How can you obtain limiting molar conductivity (Λ_m°) for weak electrolyte?

[CBSE Outside Delhi Set-2, 2019]

Ans. (a) $\text{Al(s)} \mid \text{Al}^{3+}(0.01\text{M}) \parallel \text{Ni}^{2+}(0.1\text{M}) \mid \text{Ni(s)}$ [1]

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{6} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3} \quad [1/2]$$

$$E_{\text{cell}} = 1.41\text{V} - \frac{0.059}{6} \log \frac{[0.01]^2}{[0.1]^3} \quad [1]$$

$$E_{\text{cell}} = 1.4198\text{V} \text{ or } E_{\text{cell}} = 1.42\text{V} \quad [1/2]$$

(b) Λ_m decreases with increase in concentration for both strong & weak electrolyte. Λ_m° can be obtained for weak electrolyte by applying Kohlrausch law

$$\Lambda_m^{\circ} = V_+ \lambda_+^{\circ} + V_- \lambda_-^{\circ} \quad [1 + 1]$$

[CBSE Marking Scheme 2019]

Detailed Answer:



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{6} \log \frac{[0.01]^2}{[0.1]^3}$$

$$= 1.41 - \frac{0.0591}{6} \log 0.1$$

$$= 1.41 + \frac{0.0591}{6} \log 10$$

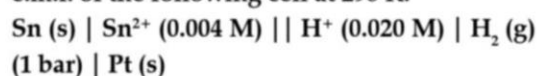
$$= 1.41 + \frac{0.0591}{6}$$

$$= 1.41 + 0.00985 = 1.42\text{V}$$

(b) When the concentration of weak electrolyte becomes very low, its degree of ionization rises. This increase leads to increase in the number of ions in the solution. Thus, the molar conductivity rises sharply of a weak electrolyte at low concentration. The molar conductivity of strong electrolyte decreases a bit with an increase in concentration. This is due to increase in interionic attraction due to higher number of ions per unit volume. On dilution, ions move apart, weakening interionic attractions and thus conductance increases.

Limiting molar conductivity for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions.

Q. 7. (a) Write the cell reaction and calculate the e.m.f. of the following cell at 298 K:



(Given: $E_{\text{Sn}^{2+}/\text{Sn}}^{\circ} = -0.14\text{V}$)

(b) Give reasons:

(i) 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 .

(ii) Conductivity of CH_3COOH decreases on dilution.

[A&U] [CBSE Delhi/Outside Delhi, 2018]

Ans. (a) $\text{Sn} + 2\text{H}^+ \rightarrow \text{Sn}^{2+} + \text{H}_2$ (Equation must be balanced) [1]

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2} \quad [1/2]$$

$$E_{\text{cell}} = [0 - (-0.14)] - 0.0295 \log \frac{(0.004)}{(0.02)^2} \quad [1/2]$$

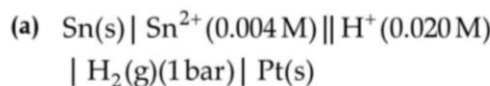
$$= 0.14 - 0.0295 \log 10 = 0.11\text{V} / 0.1105\text{V} \quad [1]$$

(b) (i) Due to over potential/ over voltage of O_2 [1]

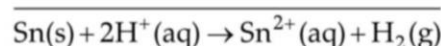
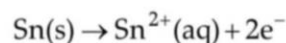
(ii) The number of ions per unit volume decreases. [1]

[CBSE Marking Scheme, 2018]

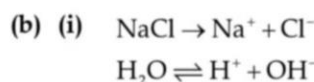
Detailed Answer:



$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{(\text{H}^+/\text{H}_2)}^{\circ} - E_{(\text{Sn}^{2+}/\text{Sn})}^{\circ} \\ &= 0.00 - (-0.14) \\ &= +0.14\text{V} \end{aligned}$$



$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2} \\ &= 0.14 - \frac{0.0591}{2} \log \frac{(4 \times 10^{-3})}{(2 \times 10^{-2})^2} \\ &= 0.14 - 0.0295 \log 10 \\ &= 0.14 - 0.0295 \\ &= 0.1105\text{V} \end{aligned}$$



The value of E° of O_2 is higher than Cl_2 but O_2 is evolved from H_2O only when the higher voltage is applied. So, because of this Cl_2 is evolved instead of O_2 .

(ii) Conductivity varies with the change in the concentration of the electrolyte. The number of ions per unit volume decreases on dilution. So, conductivity decreases with decrease in concentration. Therefore, conductivity of CH_3COOH decreases on dilution. [3+2]

Q. 8. (a) Calculate E°_{cell} for the following reaction at 298K:
 $2\text{Al(s)} + 3\text{Cu}^{2+} (0.01\text{M}) \rightarrow 2\text{Al}^{3+} (0.01\text{M}) + 3\text{Cu(s)}$
 Given: $E^\circ_{\text{cell}} = 1.98 \text{ V}$

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

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

[A] [CBSE Outside Delhi Set-1, 2 & 3, 2018]

Ans. (a) $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3}$ [1]

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

$$E^\circ_{\text{cell}} = 1.98 \text{ V} + \frac{0.0591}{6} \log \frac{(0.01)^2}{(0.01)^3}$$
 [1]

$$E^\circ_{\text{cell}} = 1.98 \text{ V} + \frac{0.0591}{6} \log 10^2$$

$$E^\circ_{\text{cell}} = 1.98 \text{ V} + \frac{0.0591}{6} \times 2 \times \log 10$$

$$[\because \log 10 = 1]$$

$$E^\circ_{\text{cell}} = 1.98 \text{ V} + \frac{0.0591 \text{ V}}{6} \times 2$$

$$E^\circ_{\text{cell}} = 1.98 \text{ V} + 0.0197 \text{ V}$$

$$E^\circ_{\text{cell}} = 1.9997 \text{ V}$$
 [1]

(b) A, because its E° value is more negative [1 + 1]

[CBSE Marking Scheme, 2016]

Commonly Made Error

- Students often make error identifying oxidation reaction and reduction reaction from a cell representation.

Answering Tip

- Practice numericals with oxidation and reduction reactions.

Q. 9. (a) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is $3.905 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation (α).

Given $\lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$

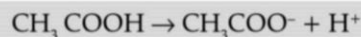
(b) Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell?

[A] [CBSE Outside Delhi Set-1, 2 & 3, 2016]

Ans. (a) $\Lambda_m = \kappa \times 1000/C$

$$= \frac{3.905 \times 10^{-5} \times 1000}{0.001}$$

$$= 39.05 \text{ S cm}^2/\text{mol}$$
 [1]



$$\Lambda^\circ_{\text{CH}_3\text{COOH}} = \lambda^\circ_{\text{CH}_3\text{COO}^-} + \lambda^\circ_{\text{H}^+}$$

$$= 40.9 + 349.6$$
 [1]

$$\Lambda^\circ_{\text{CH}_3\text{COOH}} = 390.5 \text{ S cm}^2/\text{mol}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{39.05}{390.5} = 0.1$$
 [1]

(b) Device used for the production of electricity from energy released during spontaneous chemical reaction and the use of electrical energy to bring about a chemical change. [1]
 The reaction gets reversed / It starts acting as an electrolytic cell & vice-versa. [1]

[CBSE Marking Scheme, 2016]

Commonly Made Error

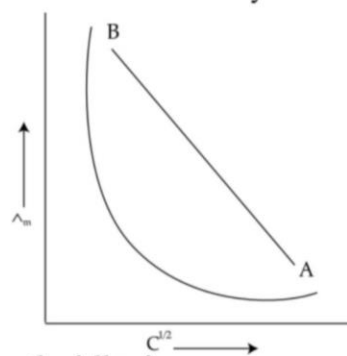
- Students often make mistakes in writing half-cell reactions. Also, in some cases calculation errors are seen while solving Nernst equation as the students miss out the power of concentration terms.

Answering Tip

- Practice numericals with Nernst equation, by writing every step clearly.

[A] Q. 10. (a) A steady current of 2 amperes 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 (Molar mass: $\text{Fe} = 56 \text{ g mol}^{-1}$, $\text{Zn} = 65.3 \text{ g mol}^{-1}$, $1 \text{ F} = 96500 \text{ C mol}^{-1}$)

(b) In the plot of molar conductivity Λ_m vs. square root of concentration ($C^{1/2}$), following curve obtained for two electrolytes A and B:



Answer the following:

(i) Predict the nature of electrolytes A and B:

(ii) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes A and B? [U] [CBSE Delhi Set 1, 2019]

Ans. (a) $m = Z I t$ [½]

$$2.8 = \frac{56 \times 2 \times t}{2 \times 96500}$$
 [½]

$$t = 4825 \text{ s} / 80.417 \text{ min}$$

$$\frac{m^1}{m^2} = \frac{E_1}{E_2}$$
 [½]

$$\frac{2.8}{m_{Zn}} = \frac{56}{2} \times \frac{2}{65.3} \quad [1/2]$$

$$m_{Zn} = 3.265 \quad [1]$$

(b) (i) A- Strong electrolyte, B-weak electrolyte [1]

(ii) \wedge_m° for weak electrolytes cannot be obtained by extrapolation while \wedge_m° for strong electrolytes can be obtained as intercept. [1]

[CBSE Marking Scheme, 2019]

Detailed Answer:

(a) Charge required to deposit 2.8 g of Fe

$$\text{moles of Fe} = \frac{\text{Given mass}}{\text{molar mass}} = \frac{2.8 \text{ g}}{56 \text{ gmol}^{-1}} = 0.05 \text{ mol}$$

2 F charge is required to discharge 1 mol of Fe^{2+} ions as Fe, therefore deposition of 0.05 mol Fe will need

$$0.05 \times 2 = 0.1 \text{ F} = 0.1 \text{ F} \times \frac{96500 \text{ C}}{\text{F}} = 9650 \text{ C}$$

The quantity of charge is related to current as

$$Q = It$$

Therefore, the time needed to deposit 2.8 g Fe is:

$$t = \frac{Q}{I} = \frac{9650 \text{ C}}{2 \text{ A}} = 4825 \text{ s}$$

So, the current flowed through the cells for 4825 seconds.

The amount of Zn deposited in cell Y can be calculated using Faraday's second law:

$$\frac{\text{mass of Zn}}{\text{mass of Fe}} = \frac{\text{Eq. wt of Zn}}{\text{Eq. wt of Fe}} = \frac{\text{molar mass of Zn} / \text{charge on zinc ion}}{\text{molar mass of Fe} / \text{charge on iron ion}}$$

$$\text{mass of Zn} = 2.8 \text{ g} \times \frac{65.3 \text{ g} / 2}{56 \text{ g} / 2} = 3.265 \text{ g} \approx 3.3 \text{ g}$$

Therefore, the mass of Zn deposited in cell Y in the same time is 3.3 g.

(b) (i) Molar conductivity of strong electrolytes increases linearly as the square root of the concentration decreases; therefore, electrolyte A is a strong electrolyte. Molar conductivity of weak electrolytes increases non-linearly as square root of concentration decreases; therefore, electrolyte B is a weak electrolyte.

(ii) As concentration of strong electrolyte approaches zero, the molar conductivity of the plot intercepts the molar conductivity axis, giving the limiting value of molar conductivity \wedge_m° . The plot of molar conductivity of weak electrolyte tends to infinity as its concentration approaches zero; it does not intersect the molar conductivity axis.

AI Q. 11. (a) The conductivity of 0.001 mol L^{-1} acetic acid is $4.95 \times 10^{-5} \text{ S cm}^{-1}$. Calculate the dissociation constant if \wedge_m° for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$.

(b) Write Nernst equation for the reaction at 25°C :



(c) What are secondary batteries? Give an example. **A&U**

$$\begin{aligned} \text{Ans. (a)} \quad \wedge_m &= \frac{\kappa}{C} = \frac{4.95 \times 10^{-5} \text{ S cm}^{-1}}{0.001 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \\ &= 49.5 \text{ S cm}^2 \text{ mol}^{-1} \\ \alpha &= \frac{\wedge_m}{\wedge_m^\circ} = \frac{49.5 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.126 \\ K &= \frac{C\alpha^2}{(1-\alpha)} = \frac{0.001 \text{ mol L}^{-1} \times (0.126)^2}{1-0.126} \\ &= 1.8 \times 10^{-5} \text{ mol L}^{-1} \quad [3] \end{aligned}$$

(If $K = C\alpha^2$, then $K = 1.6 \times 10^{-5} \text{ mol L}^{-1}$)

$$\text{(b)} \quad E_{(\text{cell})} = E^\circ_{(\text{cell})} - \frac{0.059}{6} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3} \quad [1]$$

(c) Batteries which are rechargeable
Example- Lead storage, Ni-Cd batteries (Or any other one example). $[\frac{1}{2} + \frac{1}{2}]$
[CBSE Marking Scheme 2019]

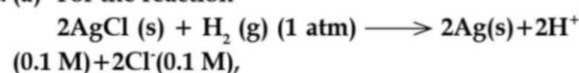
Commonly Made Error

- Some student do not write correct Nernst equation for the given cell reaction.

Answering Tip

- Do practice to write Nernst equation for the cell reaction.

Q. 12. (a) For the reaction



$$\Delta G^\circ = -43600 \text{ J at } 25^\circ\text{C}.$$

Calculate the e.m.f. of the cell.

$$[\log 10^{-n} = -n]$$

(b) Define fuel cell and write its two advantages. **A&U**

$$\begin{aligned} \text{Ans. (a)} \quad \Delta G^\circ &= -nFE^\circ \quad [1/2] \\ -43600 &= -2 \times 96500 \times E^\circ \\ E^\circ &= 0.226 \text{ V} \\ E &= E^\circ - 0.059/2 \log ([\text{H}^+]^2 [\text{Cl}^-]^2 / [\text{H}_2]) \quad [1/2] \\ &= 0.226 - 0.059/2 \log [(0.1)^2 \times (0.1)^2] / 1 \quad [1/2] \\ &= 0.226 - 0.059/2 \log 10^{-4} \quad [1/2] \\ &= 0.226 + 0.118 = 0.344 \text{ V (Deduct half mark if unit is wrong or not written)} \quad [1] \end{aligned}$$

(b) Cells that convert the energy of combustion of fuels (like hydrogen, methane, methanol etc.) directly into electrical energy are called fuel cells. [1]

Advantages: High efficiency, non polluting (or any other suitable advantage) $[\frac{1}{2} + \frac{1}{2}]$

[CBSE Marking Scheme, 2018]

Detailed Answer

$$\Delta G^\circ = -43600 \text{ J}$$

No. of electrons (n) = 2

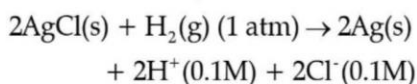
$$F = 96500 \text{ C}$$

$$\therefore \Delta G^\circ = -nFE^\circ$$

$$(a) -43600 = -2 \times 96500 \times E^\circ$$

$$\therefore E^\circ = \frac{-43600}{-2 \times 96500} = 0.226 \text{ V}$$

For the reaction,



From Nernst equation

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log \frac{[\text{H}^+]^2 [\text{Cl}^-]^2}{[\text{H}_2]}$$

(\therefore Concentration of solids are taken as unity)

$$= 0.226 - \frac{0.059}{2} \log \frac{(0.1)^2 (0.1)^2}{1}$$

$$= 0.226 - \frac{0.059}{2} \log 10^{-4}$$

$$= 0.226 + 0.0295 \log 10^4$$

$$= 0.226 + 0.118$$

$$= 0.344 \text{ V}$$

(b) **Fuel cell:** The cell which converts chemical energy of a fuel directly into electrical energy is called fuel cell.

Advantages of fuel cell:

- Pollution free working
- High efficiency