CHAPTER

3

ELECTROCHEMISTRY

Syllabus

- *Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibb's energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, fuel cells, corrosion.*

Trend Analysis

List of Concept names	2018	2019		2020	
	D/OD	D	OD	D	OD
Electrolytic & molar conductivity and Numericals	1 Q (2 marks)	1 Q (2 marks)	1 Q (2 marks) 1 Q (3 marks)	2 Q (1 mark)	1 Q (2 marks) 1 Q (3 marks)
Electrochemical cell, Nernst equation and Numericals	2 Q (3 marks) 1 Q (5 marks)	1 Q (5 marks)	1 Q (1 mark) 1 Q (3 marks)	-	1 Q (1 mark) 1 Q (3 marks)
Electrolysis and Numericals	-	1 Q (3 marks)	-	1 Q (1 mark) 1 Q (3 marks)	1 Q (2 marks)
Primary and Secondary cells, Fuel cell	1 Q (2 marks)	-	1 Q (1 mark)	1 Q (1 mark)	1 Q (1 mark)
Corrosion and its protection	-	-	-	1 Q (1 mark)	-

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TOPIC-1

Electrolytic Conductivity, Electrolytes and Kohlrausch's Law

Revision Notes

- 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).

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

  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/ length
  A = Area of cross section

  Its SI unit is S m^{-1}. Also expressed as S 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
- Wheatstone bridge helps us to measure R_4.
- **Cell constant (G) :** It is the ratio of distance between electrodes to the cross-sectional area between electrodes.

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

  It depends on the :

  (i) Distance between the electrodes

  (ii) Area of cross section.

- **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 m^2 mol^{-1}.

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

$$\Lambda = \Lambda^\circ - A\sqrt{C},$$

where Λ° = Limiting molar conductivity, Λ = 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

$$\Lambda_m^\infty = v^+ \lambda_+^\infty + v^- \lambda_-^\infty \text{ or } \Lambda^0 = v^+ \lambda_+^0 + v^- \lambda_-^0,$$

where, v^+ and v^- are the number of cations and anions per formula of electrolyte.

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 :

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

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

$$K_a = \frac{c\alpha^2}{(1-\alpha)} = \frac{c\Lambda_m{}^2}{\Lambda_m{}^0(\Lambda_m{}^0 - \Lambda_m{}^2)}$$

(iv) Determination of solubility of sparingly soluble salts :

$$\text{Solubility} = \frac{K \times 1000}{\overset{\circ}{\Lambda}_m}$$

Know the Formulae

- $\text{Current (I)} = \dfrac{\text{Potential difference (V)}}{\text{Resistance (R)}}$
- $\text{Resistance (R)} = \rho\dfrac{l}{A}$
- $\text{Conductance (C)} = K\dfrac{A}{l}$

$\text{Specific conductivity } (k) = C \times \dfrac{l}{A} = \dfrac{\text{Cell constant}}{R}$

- $\text{Cell constant (G)} = \dfrac{l}{A}$
- $\text{For strong electrolyte, } \Lambda_m = \Lambda_m^\circ - A\sqrt{C}$

$\Lambda^\circ = \nu_+\Lambda_+^\circ + \nu_-\Lambda_-^\circ$

- $\text{Degree of dissociation } (\alpha) = \dfrac{\Lambda_m^c}{\overset{\circ}{\Lambda}_m}$
- $K = \dfrac{c\alpha^2}{(1-\alpha)} = \dfrac{c(\overset{\circ}{\Lambda}_m)}{\overset{\circ}{\Lambda}_m(\overset{\circ}{\Lambda}_m - \Lambda_m)}$
- $\text{Solubility} = \dfrac{K \times 1000}{\overset{\circ}{\Lambda}_m}$

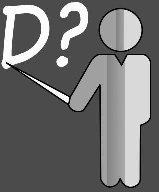
Mnemonics

- **Concept:** Electrolyte
- **Mnemonic: SEDC**
- **Interpretation:** **S**trong **E**lectrolytes **D**issociate **C**ompletely.
- **Mnemonic: WED Prime**
- **Interpretation:** **W**eak **E**lectrolytes **D**issociate **P**artially.

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.

How is it done on the GREENBOARD?



Q. Calculate the molar conductivity and degree of dissociation. Conductivity of 2.5 × 10^{-4} M methanoic acid is 5.25 × 10^{-5} S cm^{-1}.

(Given : $\Lambda^o_{(H^+)}$ = 349.5 S cm^2 mol^{-1} and $\Lambda^o_{(HCOO^-)}$ = 50.5 S cm^2 mol^{-1}.)

Solution:

STEP-1: $\Lambda_m = \dfrac{1000\times\kappa}{C}$ S cm^2 mol^{-1} **[1]**

STEP-2: Λ_m

$= \dfrac{1000\times5.25\times10^{-5}}{2.5\times10^{-4}}$ S cm^2mol^{-1}

= 210 S cm^2mol^{-1} **[1]**

STEP-3: Λ^0_m HCOOH

$= \Lambda^o_{HCOO-} + \Lambda^o_{H+}$

= (50.5 + 349.5)S cm^2mol^{-1}

= 400 S cm^2mol^{-1}

a = $\Lambda_m / \Lambda^\circ_m$

a = 210 / 400 = 0.525 **[1]**

Objective Type Questions

(1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

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

$\wedge = \wedge_o - A\sqrt{C}$

Which of the following equality holds?

(a) $\wedge = \wedge_o$ as $C \longrightarrow \sqrt{A}$

(b) $\wedge = \wedge_o$ as $C \longrightarrow \infty$

(c) $\wedge = \wedge_o$ as $C \longrightarrow 0$

(d) $\wedge = \wedge_o$ as $C \longrightarrow 1$

$\boxed{A}$ **[CBSE, Delhi Set-2, 2020]**

Ans. Correct option : (b)

Explanation : When $c \rightarrow \infty$

Then $\wedge = \wedge_o$

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 Scm^2mol^{-1}? Limiting molar conductivity for individual ions are given in the following table.

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

(a) 350 Scm^2mol^{-1} **(b) 375.3 Scm^2mol^{-1}**

(c) 390.5 Scm^2mol^{-1} **(d) 340.4 Scm^2mol^{-1}**

U **[CBSE, SQP 2020-21]**

Ans. Correct option : (c)

Explanation : The limiting molar conductivity ($\wedge_m^o$) 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."

$\wedge CH_3COONa = \wedge CH_3COO^- + \wedge Na^+$

$91\ Scm^2mol^{-1} = \wedge CH_3COO^- + 50.1\ Scm^2mol^{-1}$

$\Rightarrow \wedge CH_3COO^- = 40.9\ Scm^2mol^{-1}$

For acetic acid,

$\wedge CH_3COOH = \wedge CH_3COO^- + \wedge H^+$

$= 40.9\ Scm^2mol^{-1} + 349.6\ Scm^2mol^{-1}$

$= 390.5\ Scm^2mol^{-1}$

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. Correct option : (c)

Explanation : Conductivity depends upon 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 $CoCl_3(NH_3)_5$ 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. Correct option : (b)

Explanation : When 0.1 mole of $CoCl_3(NH_3)_5$ was reacted with excess of $AgNO_3$, we get 0.2 moles of AgCl. So, there are two chloride ions that are free and not part of the complex. The formula for complex has to be $[Co(NH_3)_5Cl]Cl_2$.

$[Co(NH_3)Cl]Cl_2 \rightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$

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

[B] ASSERTION AND REASON TYPE QUESTIONS :

In the following questions a statement of assertion followed by a statement of reason is given. 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 : Conductivity of an electrolyte increases with decrease in concentration.

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

Ans. Correct option : (d)

Explanation : Conductivity of an electrolyte decreases with decrease in concentration because of ions per unit volume decreases on dilution.

Q. 2. Assertion : Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

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

Ans. Correct option : (a)

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

Q. 3. Assertion : Electrolytic conduction increases with increase in temperature.

Reason : Increase in temperature cause the electronic movement more rapid

Ans. Correct Option : (c)

Explanation : As the temperature of electrolytic solution is increased, the kinetic energy of the ion increases. This results in the increase of electrical conductance of electrolytic solutions.

[C] VERY SHORT ANSWER TYPE QUESTIONS :

Q. 1. What is electrolyte? R

Ans. Substance that dissociates into electrically conducting ions in molten state or aqueous solution.

AI **Q. 2. State Kohlrausch's law.** R

Ans. The molar conductivity of an electrolyte at infinite dilution is equal to sum of the conductivities of the individual ions.

$$\wedge_m^\infty = \nu + \lambda_+^\infty + \nu - \lambda_-^\infty$$

Q. 3. What is meant by the term of infinite dilution? A

Ans. The term 'infinite dilution' means a solution that is so dilute that it has a maximum or limiting molar conductivity which does not increase on further dilution.

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 S cm^2 mol^{-1}. Given $\Lambda^\circ(H^+)$ = 349.6 S cm^2 mol^{-1} and $\Lambda^0(CH_3COO^-)$ = 40.9 S cm^2 mol^{-1}.

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

Ans. $\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COO^-} + \Lambda^\circ_{H^+}$ [½]

= 40.9 + 349.6 = 390.5 S cm^2/mol [½]

Now, $\alpha = \Lambda_m/\Lambda^0_m$ [½]

= 39.05/390.5 = 0.1 [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 alongwith the answer.

AI Q. 2. The conductivity of a 0.01 M solution of acetic acid at 298 K is 1.65 × 10^{-4} 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]

$$\Lambda_m = \frac{1.65\times10^{-4}\text{S cm}^{-1}\times1000\text{ cm}^3L^{-1}}{0.01\text{ mol}L^{-1}}$$ [½]

= 16.5 S cm^2 mol^{-1} [1]

[CBSE Marking Scheme 2018]

Q. 3. The conductivity of 10^{-3} mol/L acetic acid at 25°C is 4.1 × 10^{-5} S cm^{-1}. Calculate its degree of dissociation if Λ^0_m for acetic acid at 25°C is 390.5 S cm^2 mol^{-1}. **A**

Ans.

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

$$\Lambda_m = \frac{1000\text{ cm}^3L^{-1}\times4.1\times10^{-5}S\text{cm}^{-1}}{10^{-3}\text{mol }L^{-1}}$$ [½]

$$= 41\text{ S cm}^2\text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^0_m}$$ [½]

$$\alpha = \frac{41}{390.5} = 0.105$$ [½]

Q. 4. Why on dilution the Λ_m of CH_3COOH increases drastically, while that of CH_3COONa increases gradually? **U**

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. **[1]**

$$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$$

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. **[1]**

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**

Ans. 'B' is a strong electrolyte. **[1]**

A 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. **[1]**

Q. 6. The resistivity of a 0.8M solution of electrolyte is 5 × 10^{-3} Ωcm. Calculate its molar conductivity. **A**

Ans. Resistivity (ρ) = 5×10^{-3} Ωcm

Conductivity of solution(k)

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

$$= \frac{1}{5\times10^{-3}\Omega\text{cm}}$$

$$= 0.2\times10^{-3}\ \Omega^{-1}\text{cm}^{-1}$$

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

[1]

Molar conductivity

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

$$= \frac{1000\times200}{0.8} = 2.5\times10^5\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$ **[1]**

Commonly Made Error

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

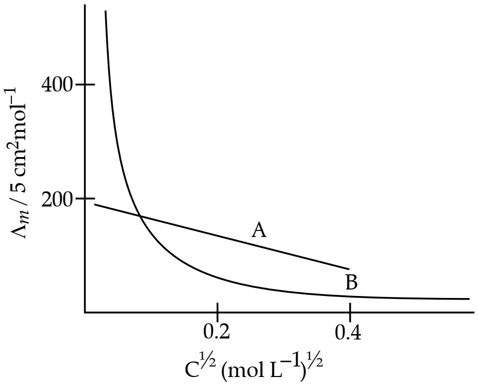
Answering Tip

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

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, c½ 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

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. **[1]**

(ii) To determine the value of limiting molar conductivity for electrolyte B, indirect method based upon Kohlrausch law of independent migration of ions is used. **[1]**

(iii) When concentration approaches zero, the molar conductivity is known as limiting molar conductivity. **[1]**

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	**Conductivity**	**Molar conductivity**
(M)	**(S cm^{-1})**	**(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

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

$$\wedge_m = \wedge_m^\infty - b\sqrt{c}$$

Where $\wedge_m$ = Molar conductivity

$\wedge_m^\infty$ = molar conductivity at infinite dilution

b = constant

c = Concentration of solution **[1]**

(ii) Conductivity of NaCl decreases on dilution as the number of ions per unit volume decreases. **[1]**

Whereas molar conductivity of NaCl increases on dilution as on dilution the interionic interactions overcome and ions are free to move. **[1]**

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]**

Ans. $A = \pi r^2$

$= 3.14 \times 0.5 \times 0.5$ cm^2

$= 0.785$ cm^2 [½]

$l = 45.5$ cm

$G^* = l/A = 45.5$ cm/0.785 cm^2

$= 57.96$ cm^{-1} [½]

$\kappa = G^*/R$ [½]

$= 57.96$ cm^{-1}/$4.55 \times 10^3\ \Omega$

$= 1.27 \times 10^{-2}$ S cm^{-1} [½]

$\Lambda_m = \kappa \times 1000/C$ [½]

$= [1.27 \times 10^{-2}$ S cm$^{-1}] \times 1000/0.05$ mol/cm^3

$= 254.77$ S cm^2 mol^{-1} [½]

[CBSE Marking Scheme 2017]

Commonly Made Error

- Students often convert centimeter into meter.

Answering Tip

- Check the compatibility of units.

Q. 5. (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 cm^2 mol^{-1} respectively) R + A

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. **[1]**

(ii) $\Lambda_m^o\ (CaSO_4) = \Lambda^o Ca^{2+} + \Lambda^o\ SO_4^{2-}$ **[1]**

$= 119.0$ S cm^2 mol^{-1} + 160.0 S cm^2 mol^{-1}

$= 279.0$ S cm^2 mol^{-1} **[1]**

Commonly Made Error

- Students only write the mathematical expression.

Answering Tips

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

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 × 10^3 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 : $E^o_{Cu^{2+}/Cu} = +0.34$ V, $E^o_{(½ Cl_2/Cl^-)} = +1.36$V ;

$E^o_{H^+/H_2(g), Pt} = 0.00$ V, $E^o_{(½ O_2/H_2O)} = +1.23$V)

[CBSE, OD Set-1, 2020]

Ans. (a) Given : A = 0.625 cm^2, l = 50 cm

$R = 5 \times 10^3$ ohm, ρ = ?

$m = 0.05$ m, K = ?

$\wedge_m$ = ?

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

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

$$\Rightarrow \frac{5 \times 10^3 \times 0.625}{50}$$

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

$\Rightarrow$ 62.5 ohm cm.

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

$$\frac{1}{5 \times 10^3} \times \frac{50}{0.625} = \frac{50}{5 \times 10^3 \times 625 \times 10^{-3}}$$

$$= \frac{10}{625} = 0.016 \text{scm}^{-1}$$

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

$$\Lambda_m = \frac{K}{M} \times 1000 = \frac{10 \times 1000}{625 \times 0.05} = 320 \text{ sm}^2 \text{mol}$$ **[3]**

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

$E^\circ_{(½Cl_2/Cl^-)} = +1.36$V

$E^\circ_{H^+/H_2(g)}, Pt = 0.00 V, E^\circ_{(½O_2/H_2O)} = +1.23$V

At cathode :

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu(s); E° = 0.34$$

$H^+_{(aq)} + e^-$ ¾ ¾® $\frac{1}{2}H_2(g); E° = 0V$

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.

$$Cl^-_{(aq)} \longrightarrow \frac{1}{2}Cl_2(g) + e^-; E° = 1.36V$$

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-; E° = +1.23V$$

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. **[2]**

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 S cm^{2}mol^{-1} respectively. Calculate the degree of dissociation of acetic acid at these concentration. Given $\lambda^\infty_{(CH^{+1})}$ and $\lambda^\infty_{(CH_3COO^-)}$ are 349.8 and 40.9 ohm^{-1}cm^{2}mol^{-1} respectively. U

Ans. Given

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

$$\lambda^\infty_{(CH_3COO^-)} = 40.9 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$$

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

$$= 40.9 + 349.8$$

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

At C = 0.1 M

Degree of dissociation

$$\alpha = \frac{\wedge_m}{\wedge^\infty_m}$$

$$= \frac{5.20}{390.7} = 0.013 \text{ i.e. } 1.3\%$$ **[1½]**

At C = 0.001 M

$$\alpha = \frac{\wedge_m}{\wedge^\infty_m}$$

$$= \frac{49.2}{390.7} = 0.125 \text{ i.e. } 12.5\%$$ **[1½]**

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 2220 Ω. Calculate degree of dissociation of acetic acid at this concentration. Also find the dissociation constant of acetic acid. Given that value of $\lambda^{\infty}_{H^+}$ and $\lambda^{\infty}_{CH_3COO^-}$ as 349.1 and 40.9 $\Omega^{-1}cm^2mol^{-1}$ respectively.**

Ans. Conductivity(k) of 0.01 M acetic acid

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

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

$$= 1.648 \times 10^{-4}\ \Omega^{-1}cm^{-1}$$ **[1]**

Molar conductivity

$$\wedge_m = \frac{k \times 1000}{M}$$

$$= \frac{1.648 \times 10^{-4} \times 1000}{0.01}$$

$$= 16.48\ \Omega^{-1}cm^2mol^{-1}$$ **[1]**

Molar conductivity at infinite dilution

$$\wedge^{\infty}_{m(CH_3COOH)} = \lambda^{\infty}_{H^+} + \lambda^{\infty}_{CH_3COO^-}$$

$$= 349.1 + 40.9$$

$$= 390\,\Omega^{-1}cm^2mol^{-1}$$ **[1]**

Degree of dissociation of acetic acid

$$\alpha = \frac{\wedge_m}{\wedge^{\infty}_m}$$

$$= \frac{16.48}{390} = 0.0422$$ **[1]**

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Initial conc (mol/L)	C	0	0
Equilibrium conc (mol/L)	C – Cα	Cα	Cα

Dissociation constant

$$K = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$= \frac{C \propto \times C \propto}{C - C \propto}$$

$$= \frac{C \propto^2}{(1 - \propto)}$$

$$= \frac{0.01 \times (0.0422)^2}{1 - 0.0422}$$

$$= 1.86 \times 10^{-5}$$ **[1]**

TOPIC-2

Redox Reactions and Electrochemical Cells, Electrode Potential and Nernst Equation

Revision Notes

- **Redox reaction :** A chemical reaction in which oxidation and reduction both processes take place 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.
- **Concept : Electrochemical cell**
  Interpretation : Electrochemical **c**ell converts **c**hemical **e**nergy into **e**lectrical **e**nergy or vice-versa.
- **Concept : Redox reaction**
  Mnemonic : eRROR
  Interpretation : Redox **r**eaction involves both **o**xidation and **r**eduction
- **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 & Cu) in contact with the solution of its own ion i.e., $ZnSo_4$ & $CuSo_4$ respectively.

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

Cell is represented as,

$$\mathbf{Zn}(s)\ |\mathbf{Zn}^{2+}(aq)\ (\mathbf{C_1})\ ||\ \mathbf{Cu}^{2+}(aq)\ (\mathbf{C_2})|\ \mathbf{Cu}(s)$$

- **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 $H^+ = 1$ 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.

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

  In terms of standard oxidation electrode potential :

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

  where $E^\circ_{cathode}$ = 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 versus M, then we use Nernst equation. For a general electrode,

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

  the Nernst equation can be written as

  $$E_{\left(M^{n+}/M\right)} = E^0_{\left(M^{n+}/M\right)} - \frac{RT}{nF} ln \frac{[M]}{\left[M^{n+}_{(aq)}\right]}$$

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

  At equilibrium,

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

  $$K_c = \text{Equilibrium constant}$$

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

  For the cell with the net reaction,

  $$aA + bB \xrightarrow{ne^-} mM + nN$$

  the Nernst equation at 298 K can be written as

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

  where $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
- **Gibbs energy :**

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

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

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

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

  and $\Delta_r G = -nF\, E_{cell}$

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

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

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

Mnemonics

- **Concept:** Nernst equation
- Interpretation: **OPIIEc**
- **Interpretation:** Oxidising Power Increases With Increase In E° Value.

Know the Formulae

- $E_{cell} = E_{cathode} - E_{anode}$
- $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
- **Nernst equation :**

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

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ at 298 K}$$

- $\Delta_r G^\circ = -nFE^\circ_{cell}$
- $\Delta_r G^\circ = -2.303\ RT \log K_C$.

Objective Type Questions

(1 mark each)

[A] MULTIPLE CHOICE QUESTIONS :

Q. 1. An electrochemical cell behaves like an electrolytic cell when

(a) $E_{cell} = E_{external}$

(b) $E_{cell} = 0$

(c) $E_{external} > E_{cell}$

(d) $E_{external} < E_{cell}$

R **[CBSE Outside Delhi Set-2, 2020]**

Ans. Correct option : (c)

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 1.1V. At this stage, no current flow 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.

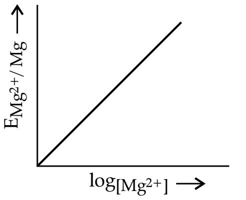
$E_{external} > E_{cell}$

Q. 2. Electrode potential for Mg electrode varies according to the equation :

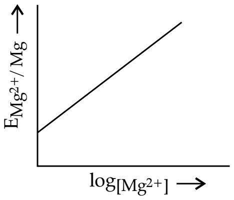
$$E_{Mg^{2+}/Mg} = E^\circ_{Mg^{2+}/Mg} - \frac{0.059}{2}\log\frac{1}{[Mg^{2+}]}.$$

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

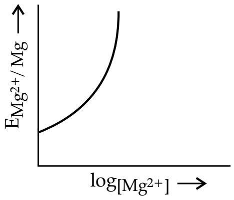
(a)



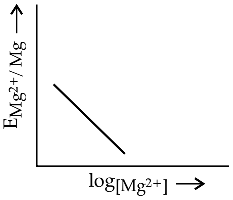
(b)



(c)



(d)



U

Ans. Correct option : (b)

Explanation :

$$E_{Mg^{2+}/Mg} = E^0_{Mg^{2+}/Mg} + \frac{0.059}{2}\log\left[Mg^{2+}\right]$$

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

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

Q. 3. 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. Correct option : (c)

Explanation : In an electrochemical cell, a salt bridge is used to complete the circuit so that current can flow.

Q. 4. Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution :

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

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

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

(a) $Ag^+(aq) + e^- \rightarrow Ag(s)$ E° = +0.80 V

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

(c) Both reactions are feasible

(d) None of the above $\boxed{U}$

Ans. Correct option : (a)

Explanation : $Ag^+(aq) + e^- \rightarrow Ag(s)$; E° = + 0.80 V.

$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$; E° = 0.00 V.

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

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

Q. 5. Consider the following reaction :

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

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

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

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

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

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

Ans. Correct option : (b)

Explanation :

Oxidation half reaction

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

Reduction half reaction

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

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

Anode salt Cathode

(Oxidation) bridge (Reduction)

Q. 6. 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. $\boxed{A}$

Ans. Correct option : (a)

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 form compounds in which oxidation state of hydrogen is +1.

Q. 7. Calculate the emf of the following cell at 298 K :

$Mg(s)|Mg^{2+}(0.1\ M)||Cu^{2+}(1.0 \times 10^{-3}\ M)|Cu(s)$

[Given = E°_{Cell} = 2.71 V]

(a) 1.426 V **(b) 2.503 V**

(c) 2.651 V **(d) 1.8 V** $\boxed{U}$

Ans. Correct option : (c)

Explanation :

$$E_{Cell} = E^0_{Cell} - \frac{0.059}{n}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$= 2.71V - \frac{0.059}{2}\log\frac{0.1}{0.001}$$

$$= 2.71V - \frac{0.059}{2}\log 10^2$$

E_{Cell} = 2.651 V

Q. 8. 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 $E^\ominus$/V	**$E^\ominus$=1.19V**	**$E^\ominus$=1.65V**	**$E^\ominus$=1.74V**

(a) $ClO_4^- > IO_4^- > BrO_4^-$ **(b) $IO_4^- > BrO_4^- > ClO_4^-$**

(c) $BrO_4^- > IO_4^- > ClO_4^-$ **(d) $BrO_4^- > ClO_4^- > IO_4^-$** $\boxed{A}$

Ans. Correct option : (a)

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

$BrO_4^- > IO_4^- > ClO_4^-$

Q. 9. Using the data given below find strongest reduction agent.

$$\mathbf{E^-_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\,V, E^-_{Cl_2/Cl^-} = 1.36\ V}$$

$$\mathbf{E^-_{MnO_4^-/Mn^{2+}} = 1.51\,V, E^-_{Cr^{3+}/Cr} = -0.74\ V}$$

(a) Cl^- **(b) Cr**

(c) Cr^{3+} **(d) Mn^{2+}** $\boxed{A}$

Ans. Correct option : (b)

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

[B] ASSERTIONS AND REASONS:

In the following questions, a statement of assertion followed by a statement of reason is given. 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 : E_{cell} should have a positive value for the cell to function.

Reason : $E_{cathode} < E_{anode}$.

Ans. Correct option : (c)

Explanation : $E_{cell} = E_{cathode} - E_{anode}$.

To have positive value of E_{cell}, $E_{cathode}$ should be greater than E_{anode}.

Q. 2. 0Assertion : Cu is less reactive than hydrogen.

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

Ans. **Correct option :** (c)

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

Q. 3. **Assertion : Copper sulphate can be stored in zinc vessel.**

Reason : Zinc is more reactive than copper.

Ans. **Correct option :** (d)

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

Q. 4. **Assertion :** $E_{Ag^+/Ag}$ increases with increase in concentration of Ag^+ ions.

Reason : $E_{Ag^+/Ag}$ has a positive value.

Ans. **Correct option :** (b)

Explanation :

$$Ag + e^- \rightarrow Ag,$$

$$E_{Ag^+/Ag} = E^{\ominus}_{Ag^+/Ag} - \frac{RT}{nF}\log\frac{1}{\left[Ag^+\right]}$$

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

[C] VERY SHORT ANSWER TYPE QUESTIONS :

Q. 1. **Can we store copper sulphate in a iron vessel?** A

Ans. No, we can not store copper sulphate in an iron vessel because copper having higher reduction potential will accept the electron and will change into solid copper. So, iron will react with copper sulphate.

Q. 2. **Define electrochemical series.** R

Ans. The arrangement of various elements in the order of increasing values of standard reduction potentials is called electrochemical series.

Q. 3. **What is the charge of free energy for a galvanic cell?** R

Ans. Free energy decreases in Galvanic cell, so its value is negative, i.e. $\Delta G < 0$.

Short Answer Type Questions-I

(2 marks each)

AI Q. 1. **In a galvanic cell, the following cell reaction occurs:**

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

$E^o_{cell} = +1.56$ 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.2. **Calculate the emf of the following cell at 298 K**

$Cr(s)/Cr^{3+}$ (0.1M)//Fe^{2+} (0.01M)/Fe(s)

[Given : $E^{\circ}_{cell} = +0.30$ V]

Ans. $2Cr(s) + 3Fe^{2+}(aq.) \rightarrow 3Fe(s) + 2Cr^{3+}(aq.)$ **[½]**

$n = 6$

$$E_{Cell} = E^o_{Cell} - \frac{2.303RT}{nF}\log\frac{\left[Cr^{3+}\right]^2}{\left[Fe^{2+}\right]^3}$$ **[½]**

$$E_{Cell} = 0.30\,V - \frac{0.059}{6}V\log\frac{\left[10^{-1}\right]^2}{\left[10^{-2}\right]^3}$$

$E_{Cell} = 0.26$ V **[½]**

Commonly Made Error

- Sometimes students get confused to write correct formula for calculation of emf of the cell.

Answering Tip

- Learn and understand Nernst equation for an electrochemical cell.

Q.3. **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 $E^{\ominus}$/V	$E^{\ominus}$=1.19V	$E^{\ominus}$=1.65V	$E^{\ominus}$=1.74V

A

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. **[1]**

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

$BrO_4^- > IO_4^- > ClO_4^-$ **[1]**

AI Q. 4. **Following reactions can occur at cathode during the electrolysis of aqueous silver nitrate solution using Pt electrodes :**

$Ag^+(aq) + e^- \longrightarrow Ag(s)$; $E^0 = 0.80$ V

$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$; $E^0 = 0.00$ V

On the basis of their standard electrode potential values, which reaction is feasible at cathode and why ? A

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

Because it has higher reduction potential. **[1]**

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

$Ag^+(aq) + e^- \rightarrow Ag(s)$ **[2]**

Q. 5. Calculate E°_{cell} for the following reaction at 298 K :

$2Cr(s) + 3Fe^{2+}(0.01M) \rightarrow 2Cr^{3+}(0.01M) + 3Fe(s)$

Given : $E_{cell} = 0.261$ V U

Ans. Nernst Equation :

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

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

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

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

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

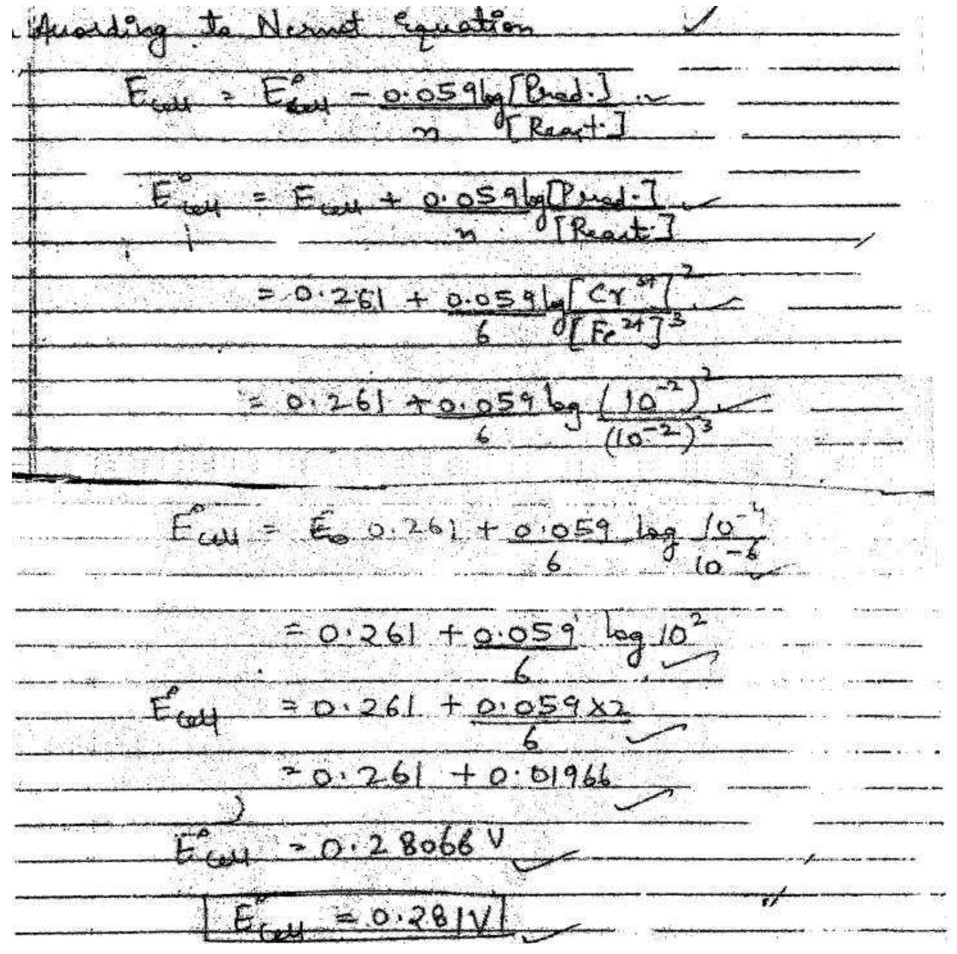
$$= 0.261 + \frac{0.059 \times 2}{6}$$

$$= 0.261 + 0.01966$$

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

[2]

OR



According to Nernst Equation

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

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

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

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

$$E_{cell} = E_o\ 0.261 + \frac{0.059}{6}\log\frac{10^{-4}}{10^{-6}}$$

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

$$E^{o}_{cell} = 0.261 + \frac{0.059 \times 2}{6}$$

$$= 0.261 + 0.01966$$

$$E^{o}_{cell} = 0.28066\text{ V}$$

$$\boxed{E^{o}_{cell} = 0.281\text{V}}$$

[Topper's Answer] [2]

Q.6. Iron displaces copper from copper sulphate solution but Pt does not why?

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. **[2]**

Short Answer Type Questions-II

(3 marks each)

AI Q. 1. Consider the following reaction :

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

(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.**

U [CBSE Comptt. Delhi/OD 2018]

Ans. **(i)** Cu(s) | Cu^{2+}(aq) | | Ag^{+} (aq) | Ag(s) **[1]**

(ii) Current will flow from silver to copper electrode in the external circuit. **[1]**

(iii) Cathode: $2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$

Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ **[1]**

[CBSE Marking Scheme 2018]

AI Q. 2. (a) The cell in which the following reaction occurs :

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

has E°_{cell} = 0.236 V at 298 K. Calculate the standard Gibb's energy of the cell reaction. (Given : 1 F = 96,500 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 F = 96,500 C mol^{-1}) 3

Ans. (a)

$$\Delta G^0 = -\,nFE^0_{cell} \quad [½]$$
$$n = 2$$
$$\Delta G^0 = -\,2 \times 96500\ C/mol \times 0.236\ V \quad [½]$$
$$= -\,45548\ J/mol$$
$$= -\,45.548\ kJ/mol \quad [½]$$

(b)

$$Q = I\,t = 0.5 \times 2 \times 60 \times 60 \quad [½]$$
$$= 3600\ C$$
$$96500\ C = 6.023 \times 10^{23}\ electrons$$
$$3600\ C = 2.25 \times 10^{22}\ electrons \quad [1]$$

[CBSE Marking Scheme, 2017]

Detailed Answer :

(a) $2\,Fe^{3+} + 2e^{-} \rightarrow 2\,Fe^{2+}$

$2I^{-} \rightarrow I_2 + 2e^{-}$

For the given cell reaction, n = 2.

$$\Delta G^{\circ} = -\,n\,FE^{\circ}_{cell}$$
$$= -\,2 \times 96500 \times 0.236$$
$$= -\,45548\ J\ mol^{-1}$$
$$= -\,45.55\ kJ\ mol^{-1}$$

(b) I = 0.5A

t = 2 hours = 2 × 60 × 60 s = 7200s **[1½]**

$$Q = It$$
$$= 0.5 \times 7200$$
$$= 3600\ coulombs$$

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

∴ 3600 c is equivalent to of electrons

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

$= 2.246 \times 10^{22}$ electrons **[1½]**

Q. 3. Calculate Δ_rG^0 and log K_c for the following reaction at 298 K.

$2Cr(s) + 3Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Fe(s)$

[(E°_{cell} = 0.30 V), 1F = 96500 C mol^{-1}]

A [CBSE Comptt. OD Set-2 2017]

Ans.

$$\Delta_rG^0 = -nFE^{\circ}_{cell},\ n = 6 \quad [½]$$
$$= -6 \times 96500\ C/mol \times 0.30\ V$$
$$= -173700\ J/mol = -173.7\ kJ/mol \quad [1]$$
$$E^{\circ}_{cell} = 0.059V/n \times \log K_c \quad [½]$$
$$\log K_c = 0.30\ V \times 6/0.059V = 30.5 \quad [1]$$

[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.

AI Q. 4. Calculate e.m.f. of the following cell at 298 K :

$2Cr(s) + 3Fe^{2+}(0.1M) \rightarrow 2Cr^{3+}(0.01M) + 3Fe(s)$

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

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

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

Ans.

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$
$$= (-\,0.44) - (-\,0.74)\ V \quad [½]$$
$$= 0.30\ V$$
$$E = E^{\circ} - \frac{0.0591}{n}\log\frac{[Products]}{[Reactants]}$$
$$= 0.30 - \frac{0.0591}{6}\log\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3} \quad [½]$$
$$= 0.30 - \frac{0.0591}{6}\log\frac{[0.01]^2}{[0.1]^3} \quad [1]$$
$$= 0.30 - \left(\frac{-\,0.0591}{6}\right) = 0.3098\ V \quad [1]$$

[CBSE Marking Scheme 2016]

Q. 5. Calculate the emf of the following cell at 25° C :

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

$E^{\circ}(Fe^{2+}/Fe) = -\,0.44$ V $E^{\circ}(H^{+}/H_2) = 0.00$ V

A [CBSE Delhi 2015]

Ans. Cell reaction is

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

$$E^{\circ}_{cell} = 0.00 - (-\,0.44) = 0.44\ V$$
$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]}{[H^{+}]^2}$$
$$= 0.44\ V - \frac{0.0591}{2}V\log\frac{0.001}{(0.01)^2}$$
$$= 0.44\ V - 0.02955\ V$$
$$E_{cell} = 0.41045\ V \quad [3]$$

Q. 6. **A galvanic cell consists of a metallic zinc plate immersed in 0.1 M $Zn(NO_3)_2$ solution and metallic plate of lead in 0.02 M $Pb(NO_3)_2$ solution. Calculate the emf of the cell. Write the chemical equation for the electrode reactions and represent the cell.**
(Given : $E^\circ_{Zn^{2+}/Zn} = -0.76$ V; $E^\circ_{Pb^{2+}/Pb} = -0.13$V) A

Ans. **Anode reaction :** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ [½]
Cathode reaction : $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ [½]
Cell representation :
$Zn(s)|Zn^{2+}(aq)||Pb^{2+}(aq)|Pb(s)$ [½]
According to Nernst equation :

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Pb^{2+}]} \quad [½]$$

$$E_{cell} = [-0.13 - (-0.76)] - \frac{0.0591}{2}\log\frac{0.1}{0.02} \quad [½]$$

$$= 0.63 - 0.02955 \times \log 5$$
$$= 0.63 - 0.02955 \times 0.6990$$
$$= 0.63 - 0.0206 = 0.6094 \text{ V} \quad [½]$$

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.

Long Answer Type Questions

(5 marks each)

AI **Q. 1. (a) Calculate e.m.f. of the following cell :**
$Zn(s)/Zn^{2+}$ (0.1 M) || (0.01 M) $Ag^+/Ag(s)$
Given : $E^\circ_{Zn^{2+}/Zn} = -0.76$ V, $E^\circ_{Ag^+/Ag} = +0.80$ V
[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?

[CBSE Outside Delhi Set-1, 2020]

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

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

$$E^\circ_{Ag^+/Ag} = +0.80\text{V} \qquad \text{emf} = ?$$

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

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

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

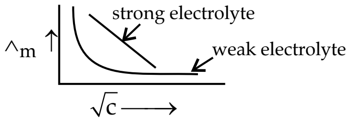
$$= 0.80 - (-0.76) = 1.56 \text{ V}$$

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

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

$$= 1.56 - 0.0295 \log 1000$$
$$= 1.56 - 3\,(0.0295) = 1.56 - 0.09 = 1.4715 \quad [3]$$

(b) *Y* is a weak electrolyte as n 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 rises much.



[2]

Commonly Made Error

- Some students get confused to find E°_{cell} correctly

Answering Tip

- Understand to identify the $E^\circ_{cathode}$ and E°_{anode} from given standard reduction potentials.

AI **Q. 2. E°_{cell} for the given redox reaction is 2.71 V.**
$Mg + Cu^{2+}_{(0.01\,M)} \longrightarrow Mg^{2+}_{(0.001\,M)} + Cu$
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 [CBSE Delhi Set-1, 2019]

Ans. $E_{cell} = E^\circ_{cellS}\frac{0.059}{n}\log Kc$ **[1]**

$= E^\circ_{cellS}\frac{0.059}{2}\log\frac{10^{-3}}{10^{-2}} = 2.71 + 0.0295$ **[1]**

$E_{cell} = 2.7395$ V

(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 :

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

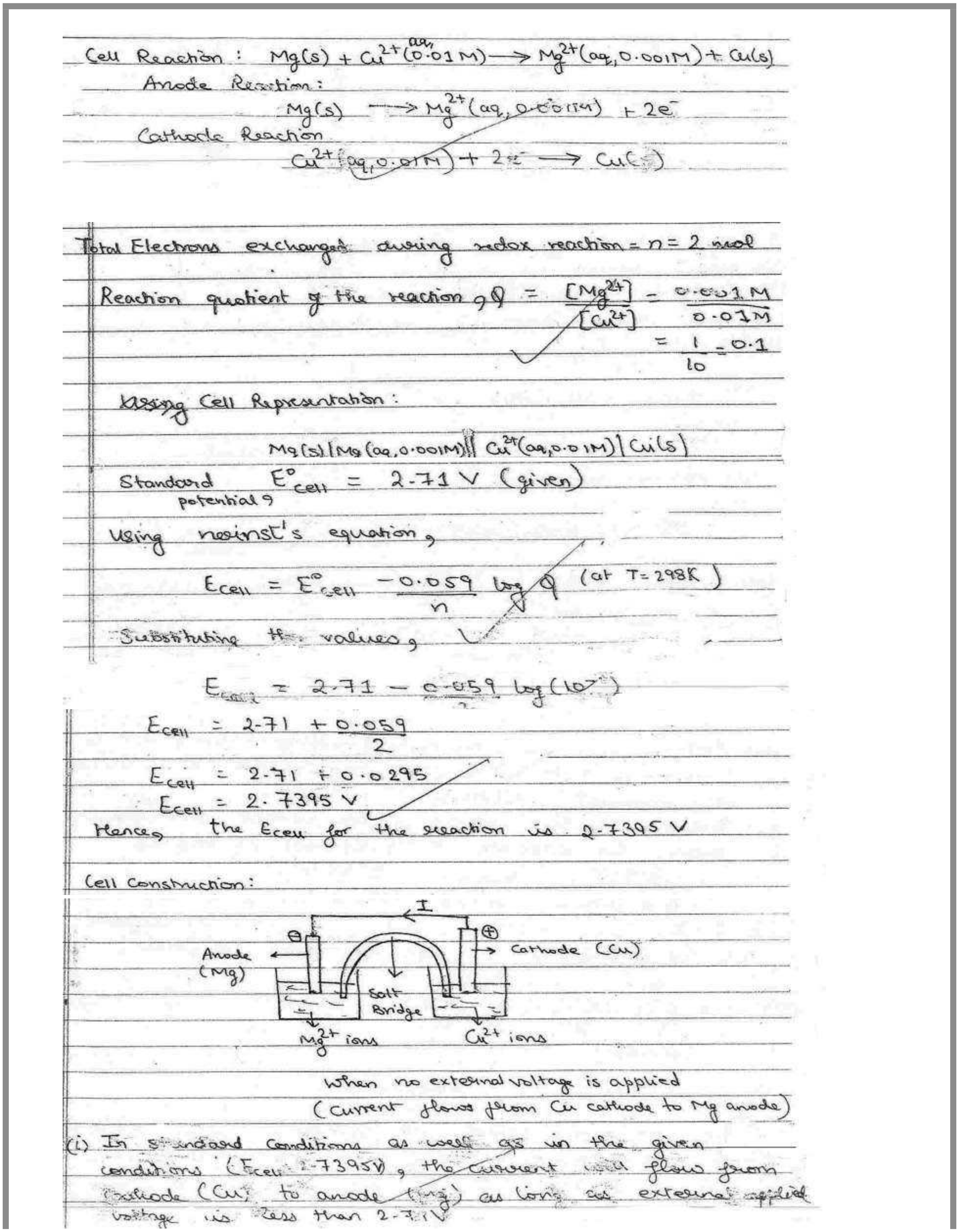
$$E_{cell} = 2.71 - \frac{0.059}{2}\log\frac{[0.001]}{[0.01]}$$

$$E_{cell} = 2.71 - (-0.0295) = 2.74\text{V} \quad [3]$$

(i) When external opposite applied voltage is less than 2.71, it is less than E^o_{cell}, therefore, the electrons will flow from the anode to the cathode, and current will flow from cathode (copper electrode) to anode (magnesium electrode). **[1]**

(ii) When external opposite applied potential is greater than 2.71, it is greater than E^o_{cell}, therefore, the reaction will be reversed, and the current will flow from anode to cathode. **[1]**

OR



Cell Reaction : $Mg(s) + Cu^{2+}(\overset{aq,}{0.01\,M}) \longrightarrow Mg^{2+}(aq, 0.001M) + Cu(s)$

Anode Reaction:

$Mg(s) \longrightarrow Mg^{2+}(aq, 0.001M) + 2e^-$

Cathode Reaction

$Cu^{2+}(aq, 0.01M) + 2e^- \longrightarrow Cu(s)$

Total Electrons exchanged during redox reaction = n = 2 mol

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

$= \frac{1}{10} = 0.1$

~~Using~~ Cell Representation:

$Mg(s) | Mg(aq, 0.001M) || Cu^{2+}(aq, 0.01M) | Cu(s)$

Standard potential, $E^o_{cell} = 2.71\,V$ (given)

Using nernst's equation,

$E_{cell} = E^o_{cell} - \frac{0.059}{n} \log Q$ (at T = 298K)

Substituting the values,

$E_{cell} = 2.71 - \frac{0.059}{2} \log(10^{-1})$

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

$E_{cell} = 2.71 + 0.0295$

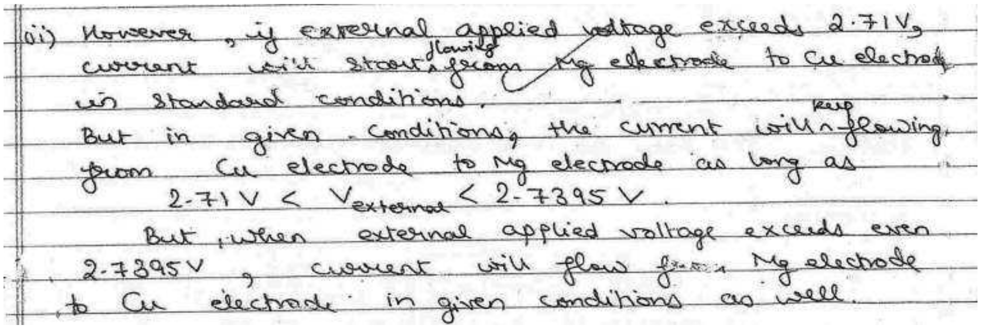
$E_{cell} = 2.7395\,V$

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

Cell Construction:

When no external voltage is applied
(current flows from Cu cathode to Mg anode)

(i) In standard conditions as well as in the given conditions (E_{cell} = 2.7395V), the current will flow from cathode (Cu) to anode (Mg) as long as external applied voltage is less than 2.71V



(ii) 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

$2{\cdot}71\,V < V_{external} < 2{\cdot}7395\,V$.

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]

AI Q. 3. (a) Represent the cell in which the following reaction takes place :

$$2Al(s) + 3Ni^{2+}(0.1M) \longrightarrow 2Al^{3+}(0.01M) + 3Ni(s)$$

Calculate its emf if E^o_{cell} = 1.41V.

(b) How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte? How can you obtain limiting molar conductivity $(\wedge\ \ )$ for weak electrolyte? [CBSE Outside Delhi Set-2, 2019]

Ans. (a) Al(s) | Al^{3+}(0.01M) | | Ni^{2+} (0.1 M) | Ni(s) **[1]**

$$E_{cell} = E^o_{cell} - \frac{0.059}{6}\log\frac{[Al^{3+}]^2}{[Cu^{2+}]^3} \quad [½]$$

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

$$E_{cell} = 1.4198\,V \text{ or } E_{cell} = 1.42\,V \quad [½]$$

(b) Λ_m decreases with increase in concentration for both strong & weak electrolyte. Λ^0_m can be obtained for weak electrolyte by applying Kohlrausch law

$\Lambda^0_m = V+\lambda^0_+ + V_-\lambda^0_-$ **[1 + 1]**

[CBSE Marking Scheme 2019]

Detailed Answer :

(a) $2Al(s) + 3Ni^{2+}(0.1M) \longrightarrow 2Al^{3+}(0.01M) + 3Ni(s)$

$Al(s) | Al^{3+} | | Ni^{2+} | Ni(s) \longrightarrow$ Cell reaction

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

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

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

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

$= 1.41 + 0.00985 = 1.42$ V **[3]**

(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. **[2]**

AI Q.4. (a) Write the cell reaction and calculate the e.m.f. of the following cell at 298 K :

Sn (s) | Sn^{2+} (0.004 M) | | H^+ (0.020 M) | H_2 (g) (1 bar) | Pt (s)

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

(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.

[CBSE Delhi/Outside Delhi, 2018]

Ans. (a) $Sn + 2H^+ \rightarrow Sn^{2+} + H_2$ (Equation must be balanced) **[1]**

$$E = E^o - \frac{0.059}{2}\log\frac{\left[Sn^{2+}\right]}{\left[H^+\right]^2} \quad [½]$$

$$0 = [0 - (-0.14)] - 0.0295\log\frac{(0.004)}{(0.02)^2} \quad [½]$$

$= 0.14 - 0.0295 \log 10 = 0.11$ V / 0.1105 V **[1]**

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

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

[CBSE Marking Scheme, 2018]

Detailed Answer :

(a) $\text{Sn(s)} \mid \text{Sn}^{2+}(0.004\,\text{M}) \parallel \text{H}^+(0.020\,\text{M}) \mid \text{H}_2(\text{g})(1\,\text{bar}) \mid \text{Pt(s)}$

$$E^\circ_{cell} = E^\circ_{(H^+/H_2)} - E^\circ_{(Sn^{2+}/Sn)}$$
$$= 0.00 - (-\,0.14)$$
$$= +0.14\text{V}$$

$$\text{Sn(s)} \rightarrow \text{Sn}^{2+}(\text{aq}) + 2\text{e}^-$$
$$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$$
$$\overline{\text{Sn(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + \text{H}_2(\text{g})}$$

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

(b) **(i)** $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$

$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

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. 5. (a) Calculate E°$_{cell}$ for the following reaction at 298K:

$2Al(s) + 3Cu^{2+}\ (0.01M) \rightarrow 2Al^{3+}\ (0.01M) + 3Cu(s)$

Given : E°$_{cell}$ = 1.98 V

(b) Using the E° values of A and B, predict which is better for coating the surface of iron [E°$_{(Fe2+/Fe)}$ = – 0.44V] to prevent corrosion and why ?

Given : E°$_{(A^{2+}/A)}$ = – 2.37V : E°$_{(B2+/B)}$ = – 0.14V

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

Ans. (a)
$$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[Al^{3+}]^2}{[Cu^{2+}]^3} \quad \textbf{[1]}$$
$$E^0_{cell} = E_{cell} + \frac{0.0591}{n}\log\frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$
$$E^0_{cell} = 1.98\text{ V} + \frac{0.0591}{6}\log\frac{(0.01)^2}{(0.01)^3} \quad \textbf{[1]}$$
$$E^0_{cell} = 1.98\text{ V} + \frac{0.0591}{6}\log 10^2$$
$$E^0_{cell} = 1.98\text{ V} + \frac{0.0591}{6} \times 2 \times \log 10$$
$$[\because \log 10 = 1]$$
$$E^0_{cell} = 1.98\text{ V} + \frac{0.0591\text{ V}}{6} \times 2$$
$$E^0_{cell} = 1.98\text{ V} + 0.0197\text{ V}$$
$$E^0_{cell} = 1.9997\text{ V} \quad \textbf{[1]}$$

(b) A, because its E^0 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. 6. (a) The conductivity of 0.001 mol L^{-1} solution of CH$_3$COOH is 3.905 × 10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α). Given λ^0 (H$^+$) = 349.6 S cm^2 mol^{-1} and λ^0 (CH$_3$COO$^-$) = 40.9 S cm^2 mol^{-1}

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

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

Ans. (a)
$$\Lambda m = \kappa \times 1000/C$$
$$= \frac{3.905 \times 10^{-5} \times 1000}{0.001}$$
$$= 39.05\text{ S cm}^2/\text{mol} \quad \textbf{[1]}$$
$$\text{CH}_3\text{ COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+$$
$$\Lambda^0_{CH3COOH} = \lambda^0_{CH3COO-} + \lambda^0_{H+}$$
$$= 40.9 + 349.6 \quad \textbf{[1]}$$
$$\Lambda^0_{CH3COOH} = 390.5\text{ S cm}^2/\text{mol}$$
$$\alpha = \frac{\Lambda_m}{\Lambda^0_m} = \frac{39.05}{390.5} = 0.1 \quad \textbf{[1]}$$

(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.

TOPIC-3

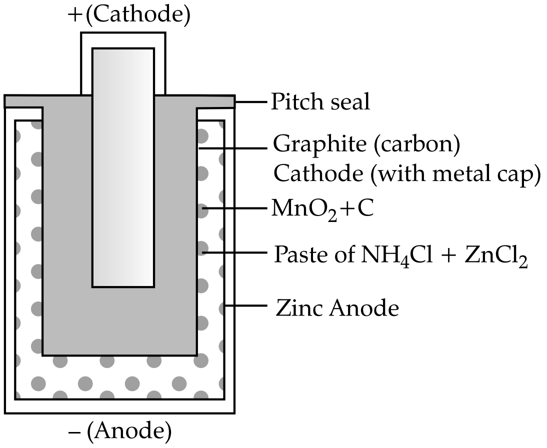
Electrolysis, Law of Electrolysis, Batteries, Fuel Cells and Corrosion

Revision Notes

- 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.

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

- **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 nonchargeable batteries such as Lechlanche cell and Dry cell.
  (ii) Secondary batteries are chargeable cells involving reversible reaction. Example, Lead storage battery and Nickel-cadmium cells.
- **Dry cell (Lechlanche 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 $ZnCl_2$.



Scan to know more about this topic

Faraday's law of electrolysis

Fig 1 : Dry Cell

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

At cathode: $MnO_2(s) + NH_4^+(aq) + 2e^- \rightarrow MnO(OH) + NH_3$

The net reaction: $Zn + NH_4^+(aq) + MnO_2 \rightarrow Zn^{2+} + MnO(OH) + NH_3$

- **Lead storage battery :**

  Anode - Spongy lead

  Cathode - Lead packed with lead dioxide

  Electrolyte -Aqueous solution of H_2SO_4

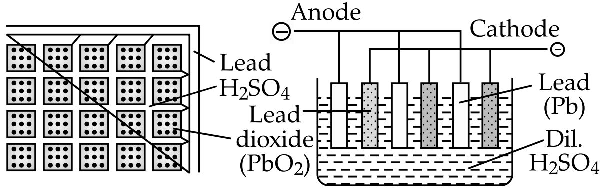


Fig 2 : Lead storage battery

Discharge reaction of cell :

At anode: Following reaction takes place at anode:

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

Reaction at cathode: PbO_2 filled in lead grid gets reduced to Pb^{2+} ions which combines with SO_4^{2-} ions to form $PbSO_4(s)$.

Complete cathode reaction is as follows :

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

Complete cell reaction: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

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

At cathode, $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$

At anode, $PbSO_4$ gets oxidised to PbO_2.

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

Complete cell reaction would be as follows:

$PbSO_4(s) + 2H_2O(l) \xrightarrow{\text{charge}} Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$

- **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:

    $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ We use inert electrode

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

- **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:

Anode: $[H_2(g) + 2OH^-(aq) \rightarrow 2H_2O\ (l) + 2e^-] \times 2$

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

Net reaction: $2H_2(g) + O_2 \rightarrow 2H_2O$ (l).

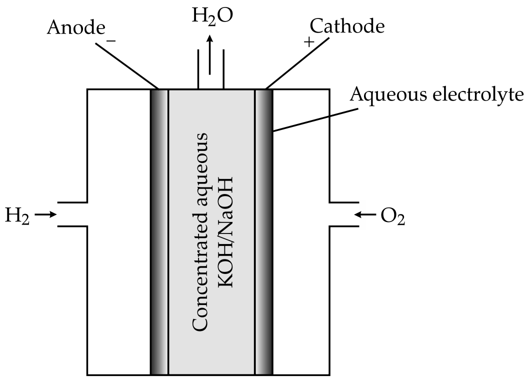


Fig 3 : Fuel cell using H_2 and O_2 produces electricity

- **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 :

$$Fe(s) + 2H^+(aq) + \frac{1}{2}O_2(aq) \rightarrow Fe^{2+}(aq) + H_2O(l)$$

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

$$Fe_2O_3 + xH_2O \rightarrow \underset{\text{(Rust)}}{Fe_2O_3xH_2O}$$

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.

Mnemonics

- **Concept:** Fuel Cell
- **Interpretation:** **FCCEE**
- **Interpretation: Fuel Cell Converts Chemical Energy of a Fuel Into Electrical Energy**

Know the Formulae

- $Q = It$
- $m = ZIt$

Objective Type Questions

(1 mark each)

[A] MULTIPLE CHOICE QUESTIONS:

Q. 1. The amount of electricity required to produce one mole of Zn from $ZnSO_4$ solution will be

(a) 3F **(b) 2F**

(c) 1F **(d) 4F**

[CBSE Delhi Set-3, 2020]

Ans. Correct option : (b)

Explanation :

$$\underset{1\text{mol}}{ZnSO_4} \rightleftharpoons \underset{1\text{mol}}{Zn^{2+}} + SO_4^{2-}$$

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

∵ Number of electrons gain = 2

∴ The amount of electricity required to produce one mole of Zn from $ZnSO_4$ Solution = 2F

Q. 2. Zinc is coated over iron to prevent rusting of iron because

(a) $E^o_{Zn^{2+}/Zn} = E^o_{Fe^{2+}/Fe}$ **(b)** $E^o_{Zn^{2+}/Zn} < E^o_{Fe^{2+}/Fe}$

(c) $E^o_{Zn^{2+}/Zn} > E^o_{Fe^{2+}/Fe}$ **(d) None of these**

[CBSE Delhi Set-3, 2020]

Ans. Correct option : (b)

Explanation : Zinc is coated over iron to prevent rusting of iron because standard reduction potential of Zn is lesser than Fe.

$$E^o_{Zn^{2+}/Zn} < E^o_{Fe^{2+}/Fe}$$

Q. 3. In a lead storage battery :

(a) PbO_2 is reduced to $PbSO_4$ at the cathode.
(b) Pb is oxidised to $PbSO_4$ at the anode.
(c) Both electrodes are immersed in the same aqueous solution of H_2SO_4.
(d) All the above are true.

[CBSE Outside Delhi Set 1, 2020]

Ans. Correct option : (b)

Explanation : In a lead storage battery,

- At Cathode,

$$PbO_2 + 2H_2O + 2e^- \rightarrow Pb^{2+} + 4OH^-$$
$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$$

- At Anode,

$$Pb \rightarrow Pb^{2+} + 2e^-$$
$$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$$

- Both electrodes are immersed in the same aqueous solution of H_2SO_4.

Q. 4. Which of the following is correct for spontaneity of a cell ?

(a) ΔG = –ve, E^O = +ve **(b)** ΔG = +ve, E^O = 0

(c) ΔG = –ve, E^O = 0 **(d)** ΔG = +ve, E^O = –ve

Ans. Correct option : (a)

Explanation : For spontaneity of cell,

$\Delta G = -\text{ve}$

$E^o = 0$

[B] ASSERTIONS & REASONS:

In the following questions, a statement of assertion followed by a statement of reason is given. 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 : Mercury cell does not give steady potential.

Reason : In the cell reaction, ions are not involved in solution.

Ans. Correct option : (d)

Explanation : Mercury cell gives a steady potential because in the cell reaction, ions are not involved in the solution.

Q.2. Assertion : Electrolysis of NaCl solution gives chlorine at anode instead of O_2.

Reason : Formation of oxygen at anode requires over voltage.

Ans. **Correct option:** (a)

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

Q. 3. **Assertion : Zinc protects the iron better than tin even after the cracks.**

Reason : Oxidation potential of Zn > Fe but oxidation potential of Sn < Fe.

Ans. **Correct option :** (a)

Exaplanation : Oxidation potential of Zn > Fe and Sn < Fe

∴ Zinc protects the iron better than tin even after the cracks.

[C] VERY SHORT ANSWER TYPE QUESTIONS:

Q. 1. **The products of electrolysis of aqueous NaCl at the respective electrodes are :**

Cathode : H_2

Anode : Cl_2 and not O_2. Explain. A

Ans. At anode, water should get oxidised in preference to Cl^-, but due to over voltage/ over potential Cl^- is oxidised in preference to water.

Q.2. **Which electrolyte is used in fuel cell? What is the relation which expresses thermodynamic efficiency of cell?** R

Ans. Aqueous sodium hydroxide is used in fuel cell. **[½]**

$$\eta = \frac{\Delta G}{\Delta H} = \frac{-nFE}{\Delta H}$$ **[½]**

Q.3. **Give an example of fuel cell.** R

Ans. H_2–O_2 fuel cell

Q.4. **Name the cell used in hearing aids and watches** **[CBSE, Delhi Set-1, 2020]**

Ans. Primary cell.

Short Answer Type Questions-I (2 marks each)

AI **Q. 1. 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 : $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$ [½]

Cathode : $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$ [½]

[CBSE Marking Scheme, 2017]

Detailed Answer :

Mercury cell is generally used in hearing aids. **[1]**

At anode : $Zn (Hg) + 2\,OH^- \rightarrow ZnO(s) + H_2O + 2e^-$

At cathode : $HgO(s) + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

Overall reaction : $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$ **[1]**

AI **Q. 2. 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 : $Zn(s) \rightarrow Zn^{2+} + 2e^-$ [½]

Cathode : $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$ [½]

[CBSE Marking Scheme, 2017]

Detailed Answer :

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

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

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

Ammonia produced in the reaction forms a complex with Zn^{2+} ion.

$Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+}$ **[2]**

AI **Q. 3. From the given cells :**

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

Answer the following :

(i) Which cell is used in hearing aids?

(ii) Which cell was used in Apollo Space Programme?

(iii) Which cell is used in automobiles and inverters?

(iv) Which cell does not have long life?

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

Ans. **(i)**	Mercury cell	**(ii)**	Fuel cell	[½ + ½]
(iii)	Lead storage cell	**(iv)**	Dry cell	[½ + ½]

[CBSE Marking Scheme, 2016]

Q.4. **Write the electrode reactions for a H_2–O_2 fuel cell.** R

Ans. At anode,

$$\left[H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-\right] \times 2$$ **[½]**

At cathode,

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$ **[½]**

Net reaction,

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$ **[1]**

Short Answer Type Questions-II (3 marks each)

Q. 1. **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 : Cu = 63.5 g mol^{-1}, Zn = 65 g mol^{-1}; 1F = 96500 C mol^{-1}]

Ans. $\mathrm{Zn^{2+}(aq)} + \underset{2\,\text{mol}}{2e^-} \longrightarrow \underset{1\,\text{mol}}{\mathrm{Zn(s)}}$

$\mathrm{Cu^{2+}} + \underset{2\,\text{mol}}{2e^-} \longrightarrow \underset{1\,\text{mol}}{\mathrm{Cu(s)}}$ (2 gm given)

The charge Q on a mole of electrons, $Q = n\text{F}$

Calculation of time for the flow of current :

$n = 1$ mol

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

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

∵ 63.5 gm of Cu is deposited by electric charge = 96500C

∴ 2 gm of Cu is deposited by electric charge

$$= \frac{96500}{63.5} \times 2 = 3039.37 \text{ C}$$ **[1]**

Let 2 A of current be passed for time t, quantity of electricity used = 2A × t = 3039.37 C

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

= 25 min. 33 s **[1]**

Calculation of mass of Zn deposited :

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

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

Amount of Zn deposited :

$$= 2 \times \frac{\frac{65}{2}}{\frac{635}{2}} = 2.0472 \text{ g}$$ **[1]**

Q.2. (a) Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of $\mathbf{AgNO_3}$ for 15 minutes.

(Given : Molar mass of Ag = 108 g $\mathbf{mol^{-1}}$, 1 F = 96500 C $\mathbf{mol^{-1}}$)

(b) Define fuel cell.

Ans. (a) $m = Zit$ [½]

$$= \frac{108 ´ 2 ´ 15 ´ 60}{1 ´ 96500}$$ **[1]**

= 2.01 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) $t = 900\ s$

Charge = Current × Time = 2 × 900 = 1800 C

According to the reaction

$\mathrm{Ag^+ (aq)} + e^- \rightarrow \mathrm{Ag(s)}$

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

For 1800 C, the mass of Ag deposited will be $= \dfrac{108 ´ 1800}{1 ´ 96500} = 2.0145$ g **[1½]**

(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. **[1½]**

Q.3. 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 in 106.4 g $\mathbf{mol^{-1}}$, calculate the charge on the metal cation.

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

Reduction half-reaction,

$$\mathrm{M^{n+}} + ne^- \rightarrow \mathrm{M}$$
$$(1\text{mol})\ (n\,\text{mol})\ (106.4\,\text{g})$$

Quantity of electricity required for depositing 106.4 g of metal = $n \times 96500$ C **[1]**

Quantity of electricity required for depositing 2.977 g of metal $= \dfrac{n \times 96500 \times 2.977}{106.4} = n \times 2700$ **[1]**

Quantity of electricity passed

$= 4 \times 45 \times 60$ C

= 10800 C

$10800 = n \times 2700$

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

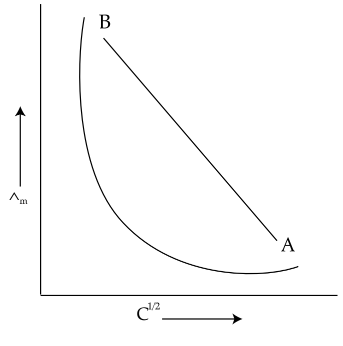
Charge on metal ion = +4 **[1]**

Long Answer Type Questions (5 marks each)

AI Q.1. (a) A steady current of 2 amperes was passed through two electrolytic cells X and Y connected in series containing electrolytes $\mathbf{FeSO_4}$ and $\mathbf{ZnSO_4}$ until 2.8 g of Fe deposited at the cathode of cell X. How long did the current flow? Calculate the mass

(Molar mass: Fe = 56 g $\mathbf{mol^{-1}}$, Zn = 65.3 g $\mathbf{mol^{-1}}$, 1 F = 96500 C $\mathbf{mol^{-1}}$)

(b) In the plot of molar conductivity L_m vs. square root of concentration ($\mathbf{C^{1/2}}$), 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 L_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]

$$\frac{2.8}{mZn} = \frac{56}{2} \times \frac{2}{65.3}$$ [½]

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

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

(ii) $\wedge^{\circ}\text{m}$ for weak electrolytes cannot be obtained by extrapolation while $\wedge^{\circ}\text{m}$ for strong electrolytes can be obtained as intercept. [1]

[CBSE Marking Scheme, 2019]

Detailed Answer :

(a) Charge required to deposite 2.8 g Fe:

$$\text{mol Fe} = \frac{\text{mass}}{\text{molar mass}} = \frac{2.8\,\text{g}}{56\,\text{g.mol}^{-1}} = 0.05\,\text{mol}$$

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 :

$$\frac{\text{mass of Zn}}{\text{mass of Fe}} = \frac{\text{Eq.wt of Zn}}{\text{Eq wt of Fe}}$$

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

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

Therefore, the mass of Zn deposited in cell Y in the same time is 3.3 g. [3]

(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. [1]

(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 E^0_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. [1]

Q.2. (a) The conductivity of 0.001 mol L^{-1} acetic acid is 4.95 × 10^{-5} S cm^{-1}. Calculate the dissociation constant if $\wedge^{o}_{m}$ for acetic acid is 390.5 S cm^2 mol^{-1}.

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

$$2Al(S) + 3Cu^2 + (aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s)$$

(c) What are secondary batteries? Give an example. [5]

Ans. (a) $$\Lambda_m = \frac{k}{c} = \frac{4.95 \times 10^{-5}\,\text{S cm}^{-1}}{0.001\ \text{mol L}^{-1}} \times \frac{1000\,\text{cm}^3}{\text{L}}$$

$$= 49.5\,\text{S cm}^2\text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m} = \frac{49.5\ \text{S cm}^2\text{mol}^{-1}}{390.5\ \text{S cm}^2\text{mol}^{-1}} = 0.126$$

$$K = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001\text{mol L}^{-1} \times (0.126)^2}{1 - 0.126}$$

$$= 1.8 \times 10^{-5}\,\text{mol L}^{-1}$$

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

(b) $$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{0.059}{6} \log \frac{[Al^{3+}]^2}{[cu^{2+}]^3}$$ [1]

(c) Batteries which are rechargeable

Example- Lead storage, Ni-Cd batteries (Or any other one example) [½ + ½]

[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.3. (a) For the reaction

$2AgCl(s) + H_2(g)$ (1 atm) $\longrightarrow 2Ag(s) + 2H^+$ (0.1 M)$+ 2Cl^-$(0.1 M),

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

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

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

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

Ans. (a) $\Delta G^o = -nFE^o$ [½]

$-43600 = -2 \times 96500 \times E^o$

$E^o = 0.226$ V

$E = E^o - 0.059/2 \log ([H^+]^2 [Cl^-]^2 / [H_2])$ [½]

$= 0.226 - 0.059/2 \log[(0.1)^2 \times (0.1)^2] / 1$ [½]

$= 0.226 - 0.059/2 \log 10^{-4}$ [½]

= 0.226 + 0.118 = 0.344 V (Deduct half mark if unit is wrong or not written) **[1]**

(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) **[½+½]**

[CBSE Marking Scheme, 2018]

Detailed Answer

(a)

$\Delta G^{o} = -43600\,J$

No. of electrons (n) = 2

F = 96500 C

$\because \Delta G^{o} = -nFE^{o}$

$-43600 = -2 \times 96500 \times E^{o}$

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

For the reaction,

$2AgCl(s) + H_2(g)$ (1 atm)

$\rightarrow 2Ag(s) + 2H^{+}(0.1M) + 2Cl^{-}(0.1M)$

From Nernst equation

$$E = E^{o} - \frac{0.059}{2}\log\frac{[H^{+}]^{2}[Cl^{-}]^{2}}{[H_2]}$$

($\because$Concentration of solids are taken as unity)

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

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

$$= 0.226 + 0.118 = 0.344\,V$$

[3]

(b) **Fuel Cell :** The cell which converts chemical energy of a fuel directly into electrical energy is called fuel cell. **[1]**

Adavntages of fuel cell :

- Pollution free working
- High efficiency **[1]**

Visual Case Based Questions **(4 marks each)**

Q. 1. 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 Ohm. If the resistance of the same cell when filled with 0.02 M KCl solution is 420 Ohm.

(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:

(i) 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}

(ii) 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

(iii) 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.

(iv) SI unit for conductivity of a solution is

(a) S m^{-1}

(b) S m^{2} mol^{-1}

(c) mol cm^{-3}

(d) S cm^{2} mol^{-1}

OR

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. (i) Correct option : (c)

Explanation : Conductivity of 0.02 mol L^{-1} KCl Solution= Cell constant resistance

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

$$= 0.614\,Sm^{-1}$$

(ii) Correct option : (d)

Explanation : The conductivity decreases with dilution.

(iii) Correct option : (d)

Explanation : The cell constant of a conductivity cell remains constant for a cell.

(iv) Correct option: (a)

Explanation: SI unit for conductivity of a solution is S m^{-1}.

OR

Correct option: (d)

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.

Q.2. Read the passage given below and answer the following questions : (1 × 4 = 4)

A galvanic cell consists of a metallic zinc plate immersed in 0.1 M $Zn(NO_3)_2$ solution and metallic plate of lead in 0.02 M $Pb(NO_3)_2$ solution.

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

(i) How will the cell be represented ?

(a) $Zn(s) | Zn^{2+}(aq) || Pb^{2+}(aq) | Pb(s)$

(b) $Zn^{2+}(s) | Zn(aq) || Pb^{2+}(aq) | Pb(s)$

(c) $Pb^{2+}(aq) | Pb(s) || Zn^{2+}(s) | Zn(aq)$

(d) $Pb(s) | Pb^{2+}(aq) || Zn^{2+}(s) | Zn(aq)$

(ii) Calculate the emf of the cell.

(a) 6.01 V **(b)** 0.412 V

(c) 0.609 V **(d)** 4.12 V

(iii) What product is obtained at cathode ?

(a) Zn **(b)** Pb

(c) $\mathbf{Zn^{2+}}$ **(d)** Pb^{2+}

(iv) 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. (i) Correct option : (a)

Cell representation :

$Zn(s) | Zn^{2+}(aq) || Pb^{2+}(aq) | Pb(s)$ **[1]**

(ii) Correct option : (c)

According to Nernst equation :

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Pb^{2+}]} \quad [½]$$

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

$= 0.63 - 0.02955 \times \log 5$

$= 0.63 - 0.02955 \times 0.6990$

$= 0.63 - 0.0206 = 0.6094$ V **[½]**

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.

(iii) Correct option : (b)

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

Cathode reaction : $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ **[1]**

(iv) Correct option : (a)

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. **[1]**

Q.3. Read the passage given below and answer the following questions : (1 x 4 = 4)

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the cell electromotive force (emf) of the cell when no current is drawn through the cell. It is now an accepted convention that we keep the anode on the left and the cathode on the right while representing the galvanic cell. A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge.

In a galvanic cell, the following cell reaction occurs :

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

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

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

(i) What is the direction of the flow of electrons ?

(a) First from silver to zinc, then the direction reverses

(b) Silver to zinc

(c) First from zinc to silver, then the direction reverses

(d) Zinc to silver

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

(a) Concentration of both Zn^{2+} and Ag^+ ions increase

(b) Concentration of Zn^{2+} increases and Ag^+ ions decreases

(c) Concentration of Zn^{2+} decreases and Ag^+ ions increases

(d) Concentration of both Zn^{2+} and Ag^+ ions decreases

(iii) Name the cell which is generally used in inverters ?

(a) Mercury cell

(b) Leclanche cell

(c) Lead storage battery

(d) Lithium ion battery

OR

Which cell uses a 38% solution of sulphuric acid as an electrolyte ?

(a) Lead storage cell

(b) Leclanche cell

(c) Lithium ion battery

(d) Fuel cell

(iv) The standard electrode potential for Daniell cell is 1.1V. Calculate the standard Gibbs energy for the reaction : Zn(s) + Cu^{2+}(aq) → Zn^{2+}(aq) + Cu(s).

(a) 215.36 kJ mol^{-1}

(b) –212. 27 kJ mol^{-1}

(c) 212.27 kJ mol^{-1}

(d) –218 kJ mol^{-1}

Ans. (i) Correct option : (d)

Zinc to silver is the flow of electrons. **[1]**

(ii) Correct option : (b)

Concentration of Zn^{2+} increases and Ag^{+} ions decreases **[1]**

(iii) Correct option : (c)

Lead storage battery is used in inverters. **[1]**

OR

Correct option : (a)

Explanation : Lead storage battery is the most common secondary cell. It consists of a lead anode and a grid of lead packed with lead oxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as electrolyte. **[1]**

(iv) Correct option : (b)

$\Delta_r G^o = -nFE^o_{cell}$

n in the above equation is 2,

F = 96487 C mol^{-1} and $E^o_{cell} = 1.1$ V

Therefore, $\Delta_r G^o = -2 \times 1.1V \times 96487$ C mol^{-1}

r = – 21227 J mol^{-1}

= – 212.27 kJ mol^{-1}

Q.4. 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.

(i) Assertion : The mass of copper and silver, deposited on the cathode be same.

Reason : Copper and silver have different equivalent masses.

(ii) Assertion : At equilibrium condition E_{cell} = 0 or $\Delta_r G = 0$.

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

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

Reason :

(iv) Assertion : In a galvanic cell, chemical energy is converted into electrical energy.

Reason : Redox reactions provide the chemical energy to the cell.

OR

Assertion : Copper sulphate cannot be stored in zinc vessel.

Reason : Zinc is less reactive than copper.

Ans. (i) Correct option : (d)

Explanation : W = itE/96500

= 1 × 10 × 60 × 31.8/96500 for copper.

It will be different for silver since the equivalent weight of silver is different. **[1]**

(ii) Correct option : (b)

At equilibrium, condition of E_{cell} = 0, $\Delta' G = 0$ **[1]**

(iii) Correct option : (a)

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. **[1]**

(iv) Correct option : (a)

Explanation: The redox reactions provide the chemical energy to the galvanic cell which is converted into electrical energy. **[1]**

OR

Correct option: (c)

Explanation: Copper sulphate cannot be stored in zinc vessel as zinc is more reactive than copper. **[1]**

●●

Self Assessment Test-3

Time : 1 Hour **Max. Marks : 25**

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

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. The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials.

The following questions are Multiple Choice Questions. Choose the most appropriate answer:

(i) On the basis of the standard electrode potential values stated for acid solutions, predict whether Ti^{4+} species may be used to oxidise Fe(II) to Fe(III)

$Ti^{4+} + e^- \rightarrow Ti^{3+} \quad E^\circ = +0.01V$

$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E^\circ = +0.77V$

(a) Ti^{4+} can oxidise Fe(II) to Fe(III)
(b) Ti^{4+} cannot oxidise Fe(II) to Fe(III)
(c) Ti^{4+} can oxidise Fe(III) to Fe(II)
(d) Ti^{4+} can reduce Fe(II) to Fe(III)

(ii) Based on the data, arrange Fe^{2+}, Mn^{2+} and Cr^{2+} in the increasing order of stability of +2 oxidation state. (Give a brief reason)

$E^\circ_{Cr^{3+}/Cr^{2+}} = -0.4V$

$E^\circ_{Mn^{3+}/Mn^{2+}} = +1.5V$

$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.8V$

(a) $Fe^{2+} < Mn^{2+} < Cr^{2+}$
(b) $Mn^{2+} < Cr^{2+} < Fe^{2+}$
(c) $Cr^{2+} < Fe^{2+} < Mn^{2+}$
(d) $Mn^{2+} < Cr^{2+} < Fe^{2+}$

(iii) Name the cell which is generally used in hearing aids.

(a) Daniell cell
(b) Mercury cell
(c) Lead storage battery
(d) Lithium cell

(iv) Which of the following statement is not true.

(a) Graphite is used as an inert electrode.
(b) An active electrode may affect the outcome of the electrode reaction in the cell.
(c) Products of electrolysis is independent of the electrode potential of the species participating.
(d) The electrolysis products are dependent on electrolytic solution and electrodes.

OR

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

The following questions (No. 2 to 5) are Multiple Choice Questions carrying 1 mark each.

2. **Galvanised iron is formed by coating of zinc on iron, while its reverse is not possible. Its reason is:**

(a) negative electrode potential of zinc is more than iron.
(b) Zinc is lighter than iron.
(c) the melting point of zinc is lesser than iron.
(d) negative electrode potential of zinc is lesser than iron. $\boxed{A}$

3. **A device which converts chemical energy of fuel like hydrogen and methane into electric energy directly is called directly is called:**

(a) electrolytic cell **(b)** dynamo
(c) Ni-Cd cell **(d)** Fuel cell $\boxed{R}$

4. **Standard reduction potentials of half-cell reaction are given below:**

$F_2(g) + 2e^- \rightarrow 2F^-(aq); E^o = +2.85V$

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq); E^o = +1.36V$

$Br_2(g) + 2e^- \rightarrow 2Br^-(aq); E^o = +1.06V$

$I_2(g) + 2e^- \rightarrow 2I^-(aq); E^o = +0.53V$

Statement oxidant and reductant are respectively

(a) F, I **(b)** Cl, F
(c) Br, I **(d)** F, Br $\boxed{U}$

5. **The conductivity of aqueous solution of an electrolyte depends on**

(a) charge present on ions
(b) movement of ions
(c) number of ions
(d) all of the above $\boxed{R}$

In the following questions (No. 6 & 7), a statement of assertion is followed by a statement of Reason is given. 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 the correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

6. **Assertion :** Zinc displaces copper from copper sulphate solution.
Reason : Zinc is more reactive than copper.

7. **Assertion :** Following reaction is possible
$2Ag + H_2SO_4 \rightarrow Ag_2SO_4 + H_2$
Reason : The tendency to oxidize Ag in less than Hz.

The following questions (No. 8 & 9), are Short Answer Type-I and carry 2 marks each.

8. Why on dilution the Λ_m of CH_3COOH increases drastically, while that of CH_3COONa increases gradually? A&E

9. **(i)** Calculate $\Delta_rG°$ for the reaction

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

Given : $E^0_{cell} = +2.71$ V, 1 F = 96500 C mol^{-1}

(ii) Name the type of cell which was used in Apollo space programme for providing electric power.

A + R

Q.No. 10 & 11 are Short Answer Type-II carrying 3 marks each.

10. What is corrosion? Explain the electrochemical theory of rusting of iron and write the reactions involved in rusting of iron.

11. **(i)** The cell in which following reaction occurs :

$$2\,Fe^{3+}(aq) + 2I(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$$

has $E^0_{cell} = 0.236$ V at 298 K. Calculate the standard gibbs energy of the cell reaction. (Given 1F = 96,500 C mol^{-1})

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

Q.No 12 is a Long Answer Type Question carrying 5 marks each.

Q.12. (i) Define the following terms :

(a) Molar conductivity (Λ_m)

(b) Secondary batteries

(c) fuel cell

(ii) State the following laws :

(a) Faraday first law of electrolysis

(b) Kohlrausch's law of independent migration of ions R

OR

(i) Define the term degree of dissociation. Write an expression that relates the molar conductivity of a weak electrolyte to its degree of dissociation.

(ii) For the cell reaction

Ni(s) | Ni^{2+}(aq) || Ag^+(aq) | Ag(s)

Calculate the equilibrium constant at 25°C.

How much mnimum work would be obtained by operation of the cell?

$E^o_{Ni^{2+}/Ni} = 0.25\,V$ and $E^o_{Ag^+/Ag} = 0.80\,V$ R + U