

## CHAPTER

# 2

# ELECTROCHEMISTRY

## Syllabus

- Redox reactions, 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, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, fuel cells, corrosion.

## Chapter Analysis

List of Topics	2016		2017		2018
	D	OD	D	OD	D/OD
Cell	1 Q. (2 marks)	1 Q. (5 marks)#	1 Q. (3 marks) ^	1 Q. (2 marks)	1 Q. (5 marks)''
Electrode Potential		1 Q. (5 marks)*			
Numerical on emf, Electrode Potential, Molar Conductivity, Degree of Dissociation, Standard Gibbs Energy and Electrolysis	1 Q. (3 marks)	1 Q. (3 marks)*#	1 Q. (2 marks) 1 Q. (3 marks) ^	1 Q. (3 marks)	1 Q. (5 marks)@''

- \* One question of 5 marks with two choices was asked.
- \*First choice has one numerical of 3 marks and one question of 2 marks on Electrode Potential.
- #Second choice has one numerical of 3 marks Molar Conductivity and Degree of Dissociation and one question of 2 marks on Electrochemical Cell.
- ^ One question of 3 marks with one numerical of 2 marks on Electrolysis and one question of 1 mark on Secondary Cell was asked.
- One question of 5 marks with two choices was asked.
- @First choice has a numerical of 3 marks on Cell Representation and Calculation of E.M.F of a cell and Give Reasons question of 2 marks.
- ''Second choice has a numerical of 3 marks on Calculation of E.M.F of a cell and a 2 marks question on Fuel cells.

On the basis of above analysis, it can be said that from exam point of view, Cells and numerical on E.M.F, Electrode Potential, Molar Conductivity, Degree of Dissociation, Standard Gibbs Energy and Electrolysis are the most important topics of the chapter.



## TOPIC-1

### Conductance in Electrolytic Solutions, Specific and Molar Conductivity, Variations of Conductivity with Concentration, Gibbs Energy, 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.

### TOPIC - 1

Conductance in Electrolytic Solutions, Specific and Molar Conductivity, Variations of Conductivity with Concentration, Gibbs Energy, Kohlrausch's Law .... P. 30

### TOPIC - 2

Redox Reaction, Electrochemical Cell, Galvanic Cell, EMF of a Cell, Standard Electrode Potential, Nernst Equation .... P. 36

### TOPIC - 3

Electrolysis, Laws of Electrolysis, Batteries, Fuel Cells and Corrosion .... P. 44

- **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 –  $\text{H}_2\text{CO}_3$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{HCN}$ ,  $\text{MgCl}_2$ .  
Strong electrolyte –  $\text{NaCl}$ ,  $\text{HCl}$ ,  $\text{NaOH}$ .
- **Degree of ionisation** : It is the ratio of number of ions produced to the total number of molecules of electrolyte.
- Resistance is defined as the property of given substance to obstruct the flow of charge. It is directly proportional to the length ( $l$ ) and inversely proportional to its area of cross-section ( $A$ ).

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

$\rho$  : Resistivity or specific resistance.

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

$$R = \rho \frac{l}{A}, \quad \text{where } \rho \text{ is specific resistivity.}$$

The unit of specific resistivity is Ohm cm or Ohm m.

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

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

The unit of conductance is Siemens,  $S$  or  $\text{ohm}^{-1}$ .

(*i.e.*,  $1 \text{ s} = 1 \text{ ohm}^{-1} = 1 \Omega^{-1}$ )

- **Specific conductivity (electrolytic conductivity)** : It is reciprocal of the specific resistivity of an electrolytic solution. It is denoted by  $\kappa$  (Kappa).

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

where  $C$  is conductance of solution,  $l$  is the distance and  $A$  is the area of cross section.

Its unit is  $\text{ohm}^{-1} \text{ cm}^{-1}$  or in S. I. unit  $\text{S m}^{-1}$ .

It depends upon the :

- (i) Nature of the material
- (ii) Temperature
- (iii) Pressure

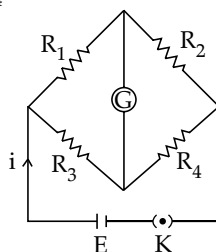
- Metallic conductance is the electrical conductance through metal that occurs due to the movement of electrons. It depends upon the :

- (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  $R_4$ .



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

- **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  $\Lambda_m$ .

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

where  $\kappa$  = Conductivity and  $C$  = Concentration of solution.

Conductivity decreases with dilution while molar conductivity increases with dilution.

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

$$\Lambda = \Lambda^\circ - AC^{1/2},$$

where  $\Lambda^\circ$  = Limiting molar conductivity,  $\Lambda$  = 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  $\lambda_+^\infty$  and that of the anions by  $\lambda_-^\infty$  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.

**Application of Kohlrausch's Law :**

- (i) Calculation of molar conductivities of weak electrolyte at infinite dilution.  
(ii) Calculation of degree of dissociation ( $\alpha$ ) of weak electrolytes.

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

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

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

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

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

## Know the Formulae

- $$\text{Current (I)} = \frac{\text{Potential difference (V)}}{\text{Resistance (R)}}$$
- $$\text{Resistance (R)} = \rho \frac{l}{A}$$
- $$\text{Conductance (C)} = K \frac{A}{l}$$
- $$\text{Specific conductivity (k)} = C \times \frac{l}{A} = \frac{\text{Cell constant}}{R}$$
- $$\text{Cell constant (G)} = \frac{l}{A}$$
- For strong electrolyte,  $\Lambda_m = \Lambda_m^\circ - A \sqrt{C}$   

$$\Lambda^\circ = v_+ \Lambda_+^\circ + v_- \Lambda_-^\circ$$
- $$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^\circ}$$

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

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

## Know the Terms

- **Superconductors** : Material with a zero resistance.
- **Limiting molar conductivity** : Molar conductivity when concentration approaches zero.
- **Electrolyte** : Substance which splits into ions in dissolved or molten state by passing electricity.
- **Over voltage** : It is the difference between the potential required for the evolution of a gas and its standard reduction potential.



## Very Short Answer-Objective Type Questions (1 mark each)

### A. Multiple Choice Questions:

Q. 1. Which of the statements about solutions of electrolytes is not correct?

- Conductivity of solution depends upon size of ions.
- Conductivity depends upon viscosity of solution.
- Conductivity does not depend upon solvation of ions present in solution.
- Conductivity of solution increases with temperature. [A] [NCERT Exemp. Q. 7, Page 34]

Ans. Correct option : (c)

*Explanation* : Conductivity depends upon solvation of ions present in the solution. So, as the solvation of ions increases, the conductivity will decrease.

Q. 2. Which of the following statement is not correct about an inert electrode in a cell?

- It does not participate in the cell reaction.
- It provides surface either for oxidation or for reduction reaction.
- It provides surface for conduction of electrons.
- It provides surface for redox reaction. [U] [NCERT Exemp. Q. 5, Page 34]

Ans. Correct option : (d)

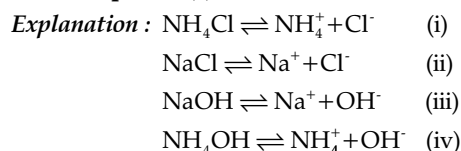
*Explanation* : Inert electrode does not participate in redox reaction and acts only as source or sink for electrons. It provides surface either for oxidation or for reduction reaction.

Q. 3.  $\Lambda_m^\circ(\text{NH}_4\text{OH})$  is equal to .....

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

[A] [NCERT Exemp. Q. 16, Page 36]

Ans. Correct option : (c)



To get equation (iv)

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

### B. Match the following :

Q. 1. Match the species given in Column I with those mentioned in Column II.

	Column I		Column II
(i)	$\Lambda_m$	(a)	$\text{Scm}^{-1}$
(ii)	$E_{\text{Cell}}$	(b)	$\text{m}^{-1}$
(iii)	$\kappa$	(c)	$\text{S cm}^2\text{mol}^{-1}$
(iv)	$G^*$	(d)	V

[NCERT Exemp. Q. 50, Page 40]

Ans. Correct option :

- (c)
- (d)
- (a)
- (b)

*Explanation* : The SI unit of conductivity is  $\text{S cm}^{-1}$ . The unit of  $E_{\text{cell}}$  is Volt. The SI unit of molar conductivity is  $\text{S m}^2\text{mol}^{-1}$ . The unit  $G^*$  is  $\text{m}^{-1}$ .

### C. Answer the following:

Q. 1. In an aqueous solution how does specific conductivity of electrolytes change with addition of water? [U] [NCERT Exemp. Q. 43, Page 40]

Ans. Conductivity decreases because number of ions per unit volume decreases. 1



## Short Answer Type Questions

(2 marks each)

Q. 1. Define the following terms :

(i) Fuel cell

(ii) Limiting molar conductivity ( $\Lambda_m^\circ$ )

[R] [CBSE OD 2014]

Ans. (i) Galvanic cells that are designed to convert the energy of combustion of fuels (methane, methanol etc.) directly into electrical energy are called fuel cells. 1

(ii) When the concentration approaches zero, the molar conductivity is known as limiting molar conductivity. It is represented by  $\Lambda_m^\circ$ . 1

[CBSE Marking Scheme 2014]

[AI] Q. 2. Define the following terms :

(i) Molar conductivity ( $\Lambda_m$ ),

(ii) Secondary batteries.

[R] [CBSE OD 2014]

Ans. (i) **Molar conductivity ( $\Lambda_m$ )** : Molar conductivity is defined as the conductivity due to all the ions produced by dissolving one mole of an electrolyte in solution. 1

(ii) In secondary batteries, the reactions can be reversed the cell reactions imposing a higher voltage than the E.M.F. of cell (external voltage). These batteries can be recharged by passing electric current and used again and again. 1

[CBSE Marking Scheme 2014]

Q. 3. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution ?

[R + A&E] [CBSE OD 2014]

Ans. **Kohlrausch law of independent migration of ions** : The law states that limiting molar conductivity of an electrolyte can be represented by the sum of the individual contributions of the anion and cation of the electrolyte. 1

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

On dilution, the conductivity ( $\kappa$ ) of the electrolyte decreases as the number of ions per unit volume of solution decreases.

[CBSE Marking Scheme 2014] 1

### Commonly Made Error

- Students often reframe the definition or write only the mathematical expression. Write the law as stated.

Q. 4. Calculate the degree of dissociation ( $\alpha$ ) of acetic acid if its molar conductivity ( $\Lambda_m$ ) is  $39.05 \text{ S cm}^2 \text{ mol}^{-1}$ . Given  $\Lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$  and  $\Lambda^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$ .

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

Ans.  $\Lambda^\circ_{\text{CH}_3\text{COOH}} = \Lambda^\circ_{\text{CH}_3\text{COO}^-} + \Lambda^\circ_{\text{H}^+}$  1/2

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

$$\text{Now, } \alpha = \Lambda_m / \Lambda_m^\circ \quad 1/2$$

$$= 39.05 / 390.5 = 0.1 \quad 1/2$$

[CBSE Marking Scheme 2017]

### Answering Tip

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

[AI] Q. 5. The conductivity of  $0.20 \text{ M}$  solution of  $\text{KCl}$  at  $298 \text{ K}$  is  $0.025 \text{ S cm}^{-1}$ . Calculate its molar conductivity.

[A] [CBSE Delhi 2013]

Ans. Concentration of solution =  $0.20 \text{ M}$

$$\text{Conductivity} = 0.025 \text{ S cm}^{-1}$$

$$\text{Molar conductivity } \Lambda_m$$

$$= \frac{\text{Conductivity (K)} \times 1000}{\text{Concentration of solution}} \quad 1$$

$$= \frac{0.025 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.20 \text{ mol L}^{-1}}$$

$$= 125 \text{ S cm}^2 \text{ mol}^{-1} \quad 1$$

Q. 6. The conductivity of a  $0.01 \text{ M}$  solution of acetic acid at  $298 \text{ K}$  is  $1.65 \times 10^{-4} \text{ S cm}^{-1}$ .

Calculate molar conductivity ( $\Lambda_m$ ) of the solution.

[A] [CBSE Comptt. D/OD 2018]

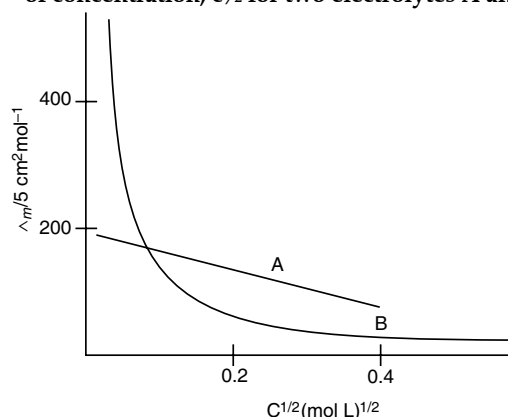
$$\text{Ans. } \Lambda_m = \frac{1000\kappa}{C} \quad 1/2$$

$$\Lambda_m = \frac{1.65 \times 10^{-4} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.01 \text{ mol L}^{-1}} \quad 1/2$$

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

[CBSE Marking Scheme 2018]

Q. 7. The following curve is obtained when molar conductivity ( $\Lambda_m$ ) is plotted against the square root of concentration,  $c^{1/2}$  for two electrolytes A and B :



(i) How do you account for the increase in the molar conductivity of the electrolyte A on dilution ?

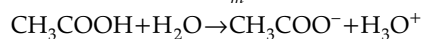
(ii) As seen from the graph, the value of limiting molar conductivity ( $\Lambda_m^\circ$ ) for electrolyte B cannot be obtained graphically. How can this value be obtained ? [A&E] [CBSE SQP 2016]

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

Q. 8. Why on dilution the  $\Lambda_m$  of  $\text{CH}_3\text{COOH}$  increases drastically, while that of  $\text{CH}_3\text{COONa}$  increases gradually? [A&E] [NCERT Exemp. Q. 49, Page 40]

Ans. In case of  $\text{CH}_3\text{COOH}$  which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation resulting in drastic increase in  $\Lambda_m$ . 1



In the case of  $\text{CH}_3\text{COONa}$  which is a strong electrolyte, the number of ions remains the same but the inter-ionic attraction decreases resulting in gradual increase in  $\Lambda_m$ . 1



## Long Answer Type Questions-I

(3 marks each)

Q. 1. (i) State the law which helps to determine the limiting molar conductivity of weak electrolyte.

(ii) Calculate limiting molar conductivity of  $\text{CaSO}_4$  (limiting molar conductivity of calcium and sulphate ions are 119.0 and 160.0  $\text{S cm}^2 \text{mol}^{-1}$  respectively)

[R + A] [CBSE SQP 2016]

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)  $\Lambda_m^0 (\text{CaSO}_4) = \Lambda^0 \text{Ca}^{2+} + \Lambda^0 \text{SO}_4^{2-}$  1  
 $= 119.0 \text{ S cm}^2 \text{mol}^{-1} + 160.0 \text{ S cm}^2 \text{mol}^{-1}$   
 $= 279.0 \text{ S cm}^2 \text{mol}^{-1}$  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 allotted to that only.
- Do not forget to mention the units.

Q. 2. The electrical resistance of a column of 0.05 M KOH solution of diameter 1 cm and length 45.5 cm is  $4.55 \times 10^3 \text{ ohm}$ . Calculate its molar conductivity.

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

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

[CBSE Marking Scheme 2017]

### Commonly Made Error

- Students often convert centimeter into meter.

### Answering Tip

- Check the compatibility of units.

Detailed Answer :

$$A = \pi r^2$$

$$= 3.14 \cdot 0.5 \cdot 0.5 \text{ cm}^2$$

$$= 0.785 \text{ cm}^2$$
 1/2
$$l = 45.5 \text{ cm}$$

$$\rho = R \cdot A/l$$

$$\rho = 4.55 \cdot 10^3 \Omega \cdot 0.785 \text{ cm}^2/45.5 \text{ cm}$$

$$\rho = 78.5 \Omega \text{ cm}$$
 1/2
$$\text{Conductivity, } \kappa = 1/\rho$$
 1/2
$$= 1/78.5 \text{ S cm}^{-1} = 0.0127 \text{ S cm}^{-1}$$
 1/2
$$\text{Molar conductivity, } \Lambda_m = \kappa \cdot 1000/C$$
 1/2
$$= 0.0127 \text{ S cm}^{-1} \cdot 1000/0.05 \text{ mol/cm}^3$$

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

Q. 3. Calculate the molar conductivity and degree of dissociation.

Conductivity of  $2.5 \times 10^{-4} \text{ M}$  methanoic acid is  $5.25 \times 10^{-5} \text{ S cm}^{-1}$ .

Given :  $\Lambda^0(\text{H}^+) = 349.5 \text{ S cm}^2 \text{mol}^{-1}$  and  $\Lambda^0(\text{HCOO}^-) = 50.5 \text{ S cm}^2 \text{mol}^{-1}$ . [A] [CBSE OD 2015]

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

$$\Lambda_m = \frac{1000 \times 5.25 \times 10^{-5} \text{ S cm}^{-1}}{2.5 \times 10^{-4}} \text{ S cm}^2 \text{mol}^{-1}$$

$$= 210 \text{ S cm}^2 \text{mol}^{-1}$$
 1
$$\Lambda_m^0 \text{ HCOOH} = \Lambda^0 \text{ HCOO}^- + \Lambda^0 \text{ H}^+$$

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

$$= 400 \text{ S cm}^2 \text{mol}^{-1}$$

$$\alpha = \Lambda_m / \Lambda_m^0$$

$$\alpha = 210 / 400 = 0.525$$
 1

### Answering Tip

- Always mention the working formula followed by substitution of values in it.

**Q. 4.** When a certain conductance cell was filled with 0.1 M KCl, it has a resistance of 85 ohm at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.

[Specific conductance of 0.1 M KCl =  $1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ ] **[A] [CBSE Comptt. OD 2012]**

**Ans.** Calculation of cell constant

Conductivity of 0.1 M KCl =  $1.29 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$

Resistance = 85 ohm

Conductivity,

$$K = \frac{1}{R} \times \text{Cell constant (G)}$$

$$\begin{aligned} G &= R \times K \\ &= 85 \times 1.29 \times 10^{-2} \text{ cm}^{-1} \\ &= 109.6 \times 10^{-2} \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} &= 1.09 \text{ cm}^{-1} \quad \mathbf{1} \\ \text{Conductivity of unknown electrolyte K,} \\ &= \frac{1}{R} \times G \\ &= \frac{1}{96} \times 1.09 \Omega \\ &= 1.13 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1} \quad \mathbf{1} \\ \therefore \text{Molar conductance } \Lambda_m &= \frac{1000 K}{M} \\ &= \frac{1.13 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.052 \text{ mol L}^{-1}} \\ &= 217.307 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \quad \mathbf{1} \end{aligned}$$

#### Answering Tip

- Separate marks are allotted for formula, so remember to write it. Also check compatibility of units.

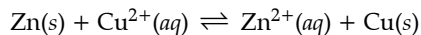


## TOPIC-2

### Redox Reaction, Electrochemical Cell, Galvanic Cell, EMF of a Cell, Standard Electrode Potential, Nernst Equation

#### Revision Notes

- **Redox reaction** : A chemical reaction in which oxidation and reduction both processes takes 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.
- **Electrochemical cell** : A device in which the redox reaction is carried indirectly and chemical energy is converted to electrical energy. It is also called galvanic cell or voltaic cell.
- **Redox couple** : It is defined as having together the oxidised and reduced form of a substance taking part in an oxidation or reduction half reaction.
- **Galvanic cell or Voltaic cell** : It consists of two metallic electrodes dipped in electrolytic solutions. Electrical energy is produced as a result of chemical reaction which takes place in this cell.
- **Daniell cell** : It is the improved form of galvanic cell. It consists of zinc rod dipped in  $\text{ZnSO}_4$  solution which acts as the oxidation half-cell. In the reduction half-cell, the copper vessel itself acts as cathode while the saturated solution of  $\text{CuSO}_4$  acts as the electrolyte. Both solutions are kept apart by taking zinc sulphate in porous pot and putting it in a copper sulphate solution.



Cell is represented as,



- **Salt Bridge and its function** : It is an inverted U-shaped glass tube which contains a suitable salt in the form of a thick paste made in agar-agar. It performs following functions—
  - It completes inner cell circuit.
  - It prevents transference of electrolyte from one half-cell to the other.
  - It maintains the electrical neutrality of the electrolytes in the two half-cells.
- **Electrode Potential** : It is the potential difference set up between the metal and solution of its own ions. It shows the tendency of an electrode to either lose or gain electrons. When the concentration of all the species involved in a half-cell is unity, then the electrode potential is called standard electrode potential.
- **Standard Electrode Potential** : Electrode potential at 25°C, 1 bar pressure and 1 M solution is known as standard electrode potential ( $E^\circ$ ). The standard electrode potential of any electrode can be measured by connecting it to standard hydrogen electrode (SHE).

SHE has a standard potential at all temperatures. It consists of a platinum foil coated with platinum black dipped into an aqueous solution in which the  $\text{H}^+ = 1 \text{ M}$  at 25°C and 1 bar pressure.

The potential difference between the two electrodes of a galvanic cell is called the cell potential (measured in volts). It is also called the emf of the cell when no current is flowing through the circuit.

- **EMF of the cell :** Electromotive force is also called emf (denoted and measured in volts). It is the voltage developed by any source of electrical energy such as battery or dynamo. It is generally defined as the potential for a source in a circuit.

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

In terms of standard oxidation electrode potential :

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

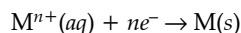
where

$$E^{\circ}_{\text{cathode}} = \text{standard electrode potential of cathode}$$

and

$$E^{\circ}_{\text{anode}} = \text{standard electrode potential of anode}$$

- **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.
- The higher value of  $E^{\circ}$  for a half-cell indicates that reductant in the half-cell is stronger reducing agent than hydrogen gas.
- The series in which all the standard electrode potentials have been arranged in order of increasing value is known as electrochemical series. The characteristics of the electrochemical series are :
- The reducing agent with lowest  $E^{\circ}$  value, considered as the strongest reducing agent, is placed well above (top) of the electrochemical series. The oxidising agent with highest  $E^{\circ}$  value, considered as the strongest oxidising agent, is placed below (bottom) of the electrochemical series.
  - Oxidising power increases with increase in  $E^{\circ}$  value.
  - Any metal of lower  $E^{\circ}$  value can reduce other metal of higher  $E^{\circ}$  value.  
Similarly, any metal of higher  $E^{\circ}$  value can oxidise other metal of lower  $E^{\circ}$  value.
- **Applications of electrochemical series :** Important applications are as follows—
- In comparing relative reducing or oxidising power of the elements.
  - In predicting the feasibility of spontaneity of a redox reaction.
  - In predicting whether a metal can evolve hydrogen from an acid or not.
  - Comparison of reactivities of metals and non-metals.
  - Determination of standard Gibbs energy change.
  - Determination of equilibrium constant.
- **Nernst equation :** If the concentration of species in the electrode reaction is not equal to 1 M, then we use Nernst equation. For a general electrode,



the Nernst equation can be written as

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

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

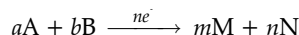
At equilibrium,

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

$K_c$  = Equilibrium constant

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

For the cell with the net reaction,



the Nernst equation at 298 K can be written as

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

where

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

- **Gibbs energy :**

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

for cell reaction to be spontaneous,  $\Delta G$  must be negative,

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

$$\Delta_r G^{\circ} = -nF E^{\circ}_{\text{cell}}$$

and

$$\Delta_r G = -nF E_{\text{cell}}$$

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



For cell reaction to be spontaneous,  $\Delta G$  must be negative.

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

## Know the Formulae



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



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

➤ Nernst equation :

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

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

$$E_{\text{cell}} = \frac{2.303 RT}{nF} \log \frac{C_2}{C_1} \text{ where } C_2 > C_1$$



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



$$\Delta_r G^\circ = -2.303 RT \log K_c.$$

## Know the Terms

- **Concentration cell** : A cell in which both electrodes and electrolytic solutions are of same substance but the solution of electrolyte in which they dip have different concentrations.
- **Gibbs energy** : Energy associated with a chemical reaction that can be used to do work.



## Very Short Answer-Objective Type Questions (1 mark each)

A. Multiple Choice Questions:

Q. 1. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called \_\_\_\_\_.

- (a) Cell potential (b) Cell emf  
(c) Potential difference (d) Cell voltage

[R] [NCERT Exemp. Q. 4, Page 34]

Ans. Correct option : (b)

Q. 2. Which cell will measure standard electrode potential of copper electrode?

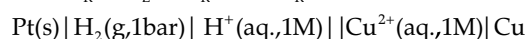
- (a)  $\text{Pt(s)} | \text{H}_2(\text{g}, 0.1 \text{ bar}) | \text{H}^+(\text{aq}, 1 \text{ M}) || \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) | \text{Cu}$   
(b)  $\text{Pt(s)} | \text{H}_2(\text{g}, 1 \text{ bar}) | \text{H}^+(\text{aq}, 1 \text{ M}) || \text{Cu}^{2+}(\text{aq}, 2 \text{ M}) | \text{Cu}$   
(c)  $\text{Pt(s)} | \text{H}_2(\text{g}, 1 \text{ bar}) | \text{H}^+(\text{aq}, 1 \text{ M}) || \text{Cu}^{2+}(\text{aq}, 2 \text{ M}) | \text{Cu}$   
(d)  $\text{Pt(s)} | \text{H}_2(\text{g}, 1 \text{ bar}) | \text{H}^+(\text{aq}, 0.1 \text{ M}) || \text{Cu}^{2+}(\text{aq}, 1 \text{ M}) | \text{Cu}$

[U] [NCERT Exemp. Q. 1, Page 33]

Ans. Correct option : (c)

**Explanation** : When copper electrode is connected to standard hydrogen electrode, it acts as cathode and its standard electrode potential can be measured by the following way :

$$E^\circ = E^\circ_{\text{R}} - E^\circ_{\text{L}} = E^\circ_{\text{R}} - 0 = E^\circ_{\text{R}}$$



will measure standard electrode potential of copper electrode.

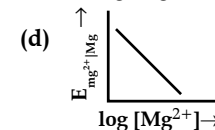
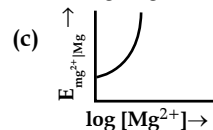
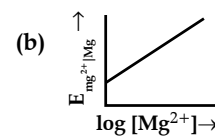
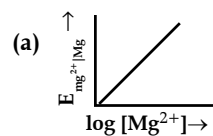
So, to calculate the standard electrode potential of the given cell it is coupled with the standard

hydrogen electrode in which pressure of hydrogen gas is one bar and  $\text{H}^+$  ion in the solution is one molar and also the concentrations of the oxidized and the reduced forms of the species in the right hand half-cell is unity.

Q. 3. Electrode potential for Mg electrode varies according to the equation :

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

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



[A] [NCERT Exemp. Q. 2, Page 33]

Ans. Correct option : (b)

$$\text{Explanation : } E_{\text{Mg}^{2+}/\text{Mg}} = E^\circ_{\text{Mg}^{2+}/\text{Mg}} - \frac{0.059}{2} \log [\text{Mg}^{2+}]$$

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

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

Q. 4. Using the data given below find strongest reduction agent.

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

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

- (a)  $\text{Cl}^-$  (b)  $\text{Cr}$   
(c)  $\text{Cr}^{3+}$  (d)  $\text{Mn}^{2+}$

[NCERT Exemp. Q. 8, Page 34]

Ans. Correct option : (b)

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

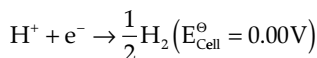
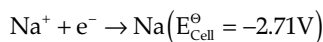
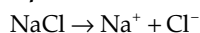
Q. 5. In the electrolysis of aqueous sodium chloride solution which of the half cell reaction will occur at anode?

- (a)  $\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s}); E_{\text{cell}}^\ominus = 2.71 \text{ V}$   
(b)  $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-; E_{\text{cell}}^\ominus = 1.23 \text{ V}$   
(c)  $\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2(\text{g}); E_{\text{cell}}^\ominus = 0.00 \text{ V}$   
(d)  $\text{Cl}^-(\text{aq}) \rightarrow \frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^-; E_{\text{cell}}^\ominus = 1.36 \text{ V}$

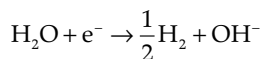
[NCERT Exemp. Q. 17, Page 36]

Ans. Correct option : (b)

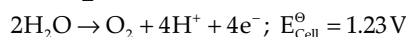
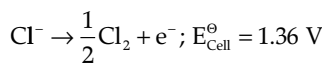
**Explanation :** During electrolysis



At cathode,



At anode, two reactions are possible.



C. Answer the following:

Q. 1. Under what condition is  $E_{\text{cell}} = 0$  or  $\Delta_r G = 0$ ?

[NCERT Exemp. 30, Page 38]

Ans. At equilibrium, that is, when the cell is completely discharged. 1

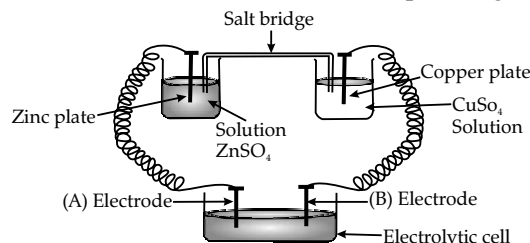
Q. 2. Depict the galvanic cell in which the cell reaction is  $\text{Cu} + 2\text{Ag}^+ \rightarrow 2\text{Ag} + \text{Cu}^{2+}$ .

[NCERT Exemp. 33, Page 39]

Ans.  $\text{Cu}|\text{Cu}^{2+}||\text{Ag}^+|\text{Ag}$  1

Q. 3. Consider the following diagram in which an electrochemical cell is coupled to an electrolytic cell. What will be the polarity of electrodes 'A' and 'B' in the electrolytic cell?

[NCERT Exemp. 36, Page 39]

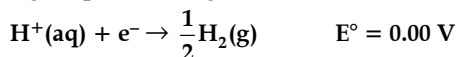
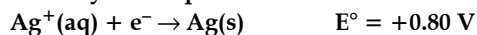


Ans. 'A' will have negative polarity; 'B' will have positive polarity. 1

## ? Short Answer Type Questions

(2 marks each)

Q. 1. (i) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution :

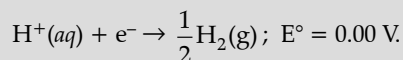


On the basis of their standard reduction electrode potential ( $E^\ominus$ ) values, which reaction is feasible at the cathode and why ?

(ii) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration ?

[CBSE Delhi 2015]

Ans. (i)  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}); E^\ominus = +0.80 \text{ V}$ .



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

Thus  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$  reaction will be more feasible at cathode. 1

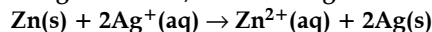
(ii) **Limiting molar conductivity :** When the concentration approaches zero, the molar conductivity is known as limiting molar conductivity.

It is represented by  $\Lambda_m^\ominus$ .

The conductivity decreases with decrease in concentration due to decrease in the no. of ions that carry the current in a solution. 1

[CBSE Marking Scheme 2015]

Q. 2. In a galvanic cell, the following cell reactions occurs:



$$E_{\text{cell}}^\ominus = +1.56 \text{ V}$$

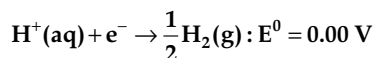
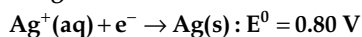
(i) Is the direction of flow of electrons from zinc to silver or silver to zinc?

(ii) How will concentration of  $\text{Zn}^{2+}$  ions and  $\text{Ag}^+$  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  $\text{Zn}^{2+}$  ions will increase and  $\text{Ag}^+$  ions will decrease. 1  
 [CBSE Marking Scheme 2017]

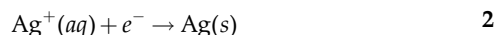
**Q. 3.** Following reactions can occur at cathode during the electrolysis of aqueous silver nitrate solution using Pt electrodes:



On the basis of their standard electrode potential values, which reaction is feasible at cathode and why? [A&E] [CBSE Comptt. OD Set-1, 2 2017]

**Ans.**  $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$  1  
 Because it has higher reduction potential. 1  
 [CBSE Marking Scheme 2017]

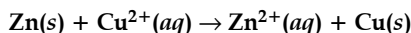
**Detailed Answer:** As reaction with higher value of standard electrode potential occurs at cathode, Ag gets reduced. So, the reaction occurring at cathode is



**Q. 4. (i)** On the basis of the standard electrode potential values stated for acid solutions, predict whether  $\text{Ti}^{4+}$  species may be used to oxidise Fe(II) to Fe(III)  
 $\text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+} \quad E^\circ = +0.01 \text{ V}$   
 $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \quad E^\circ = +0.77 \text{ V}$   
**(ii)** Based on the data arrange  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Cr}^{2+}$  in the increasing order of stability of +2 oxidation state. (Give a brief reason)  
 $E^\circ \text{Cr}^{3+}/\text{Cr}^{2+} = -0.4 \text{ V}$   
 $E^\circ \text{Mn}^{3+}/\text{Mn}^{2+} = +1.5 \text{ V}$   
 $E^\circ \text{Fe}^{3+}/\text{Fe}^{2+} = +0.8 \text{ V}$  [A&E] [CBSE SQP 2018-2019]

**Ans. (i)** Since  $\text{Ti}^{4+}/\text{Ti}^{3+}$  has lower reduction potential than  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , it cannot be reduced in comparison with  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ions. ½  
 Hence  $\text{Ti}^{4+}$  cannot oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . ½  
 As the value of reduction potential increases the stability of +2 oxidation increases. ½  
 Therefore correct order of stability is  
 $\text{Cr}^{3+}/\text{Cr}^{2+} < \text{Fe}^{3+}/\text{Fe}^{2+} < \text{Mn}^{3+}/\text{Mn}^{2+}$  ½  
 [CBSE Marking Scheme 2018]

**Q. 5.** The standard electrode potential ( $E^\circ$ ) for Daniell is +1.1 V. Calculate the  $\Delta G^\circ$  for the reaction.



(1 F = 96500 C mol<sup>-1</sup>) [A] [CBSE OD 2013; NCERT]

**Ans.**  $\Delta G^\circ = -n F E^\circ_{\text{cell}}$   
 $= -2 \times 96500 \text{ C mol}^{-1} \times 1.1 \text{ V}$   
 $= -212300 \text{ J mol}^{-1}$   
 or  $= -212.3 \text{ kJ mol}^{-1}$  2  
 [CBSE Marking Scheme 2013]

**[AI] Q. 6.** Calculate the emf of the following cell at 298 K  
 $\text{Cr}(\text{s})/\text{Cr}^{3+} (0.1 \text{ M})/\text{Fe}^{2+} (0.01 \text{ M})/\text{Fe}(\text{s})$   
 [Given:  $E^\circ_{\text{cell}} = +0.30 \text{ V}$ ]

OR

The conductivity of  $10^{-3} \text{ mol/L}$  acetic acid at 25°C is  $4.1 \times 10^{-5} \text{ S cm}^{-1}$ . Calculate its degree of dissociation if  $\Lambda_m^0$  for acetic acid at 25°C is  $390.5 \text{ S cm}^2 \text{ mol}^{-1}$ . [A] [CBSE SQP 2017]

**Ans.**  $2\text{Cr}(\text{s}) + 3\text{Fe}^{2+}(\text{aq.}) \rightarrow 3\text{Fe}(\text{s}) + 2\text{Cr}^{3+}(\text{aq.})$  ½  
 $n = 6$

$$E_{\text{Cell}} = E^\circ_{\text{Cell}} - \frac{2.303RT}{nF} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3} \quad ½$$

$$E_{\text{Cell}} = 0.30 \text{ V} - \frac{0.059}{6} \text{ V} \log \frac{[10^{-1}]^2}{[10^{-2}]^3} \quad ½$$

$$E_{\text{Cell}} = 0.26 \text{ V} \quad ½$$

OR

$$\Lambda_m = \frac{1000\kappa}{C} \quad ½$$

$$\Lambda_m = \frac{1000 \text{ cm}^3 \text{ L}^{-1} \times 4.1 \times 10^{-5} \text{ S cm}^{-1}}{10^{-3} \text{ mol L}^{-1}} \quad ½$$

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

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} \quad ½$$

$$\alpha = \frac{41}{390.5} = 0.105 \quad ½$$

[CBSE Marking Scheme 2017]

**Q.7.** Suggest a list of metals that are extracted electrolytically. [C] [NCERT]

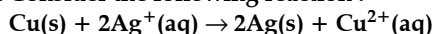
**Ans.** Metals that are on the top of the reactivity series such as sodium, potassium, calcium, lithium, magnesium, aluminium are extracted electrolytically. 2



## Long Answer Type Questions-I

(3 marks each)

**Q. 1.** Consider the following reaction :



- (i) Depict the galvanic cell in which the given reaction takes place.  
 (ii) Give the direction of flow of current.  
 (iii) Write the half-cell reactions taking place at cathode and anode. [U] [CBSE Comptt. Delhi/OD 2018]

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

Q. 2. (i) 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.

(ii) The products of electrolysis of aqueous NaCl at the respective electrodes are:

Cathode: H<sub>2</sub>

Anode: Cl<sub>2</sub> and not O<sub>2</sub>. Explain.

[A&E] [CBSE SQP 2017]

Ans. (i) 'B' is a strong electrolyte. 1

A strong electrolyte is already dissociated into ions, but on dilution interionic forces are overcome, ions are free to move. So there is slight increase in molar conductivity on dilution. 1

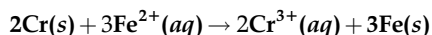
(ii) On anode water should get oxidised in preference to Cl<sup>-</sup>, but due to overvoltage/overpotential Cl<sup>-</sup> is oxidised in preference to water. 1

[CBSE Marking Scheme 2017]

### Commonly Made Error

- (i) Students often get confused between the weak electrolyte and strong electrolyte. They sometimes make mistake in identifying the correct answer.

Q. 3. Calculate  $\Delta_r G^0$  and  $\log K_c$  for the following reaction at 298 K.



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

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

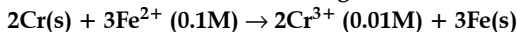
Ans.  $\Delta_r G^0 = -nFE^\circ_{\text{cell}}$ ,  $n = 6$  1/2  
 $= -6 \cdot 96500 \text{ C/mol} \cdot 0.30 \text{ V}$   
 $= -173700 \text{ J/mol} = -173.7 \text{ kJ/mol}$  1  
 $E^\circ_{\text{cell}} = 0.059 \text{ V/n} \cdot \log K_c$  1/2  
 $\log K_c = 0.30 \text{ V} \cdot 6/0.059 \text{ V} = 30.5$  1

[CBSE Marking Scheme 2017]

### Answering Tip

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

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



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

$E^\circ(\text{Fe}^{2+} | \text{Fe}) = -0.44 \text{ V}$ . [A] [CBSE Delhi 2016]

Ans.  $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$  1/2  
 $= (-0.44) - (-0.74) \text{ V}$   
 $= 0.30 \text{ V}$   
 $E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$   
 $= 0.30 - \frac{0.0591}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$  1/2

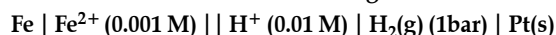
$$= 0.30 - \frac{0.0591}{6} \log \frac{[0.01]^2}{[0.1]^3} \quad 1$$

$$= 0.30 - \left( \frac{-0.059}{6} \right)$$

$$= 0.3098 \text{ V} \quad 1$$

[CBSE Marking Scheme 2016]

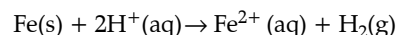
Q. 5. Calculate the emf of the following cell at 25° C :



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

[A] [CBSE Delhi 2015]

Ans. Cell reaction is



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

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

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

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

$$= 0.41045 \text{ V} \quad 3$$

Q. 6. A galvanic cell consists of a metallic zinc plate immersed in 0.1 M Zn(NO<sub>3</sub>)<sub>2</sub> solution and metallic plate of lead in 0.02 M Pb(NO<sub>3</sub>)<sub>2</sub> solution. Calculate the emf of the cell. Write the chemical equation for the electrode reactions and represent the cell.

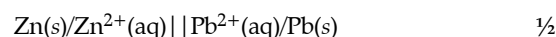
(Given :  $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ ;  $E^\circ_{\text{Pb}^{2+}/\text{Pb}} = -0.13 \text{ V}$ )

[A] [CBSE SQP 2016]

Ans. Anode reaction :  $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-$  1/2

Cathode reaction :  $\text{Pb}^{2+}(aq) + 2e^- \rightarrow \text{Pb}(s)$  1/2

Cell representation :



According to Nernst equation :

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]} \quad 1/2$$

$$E_{\text{cell}} = [-0.13 - (-0.76)] - \frac{0.0591}{2} \log \frac{0.1}{0.02} \quad 1/2$$

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

$$= 0.63 - 0.02955 \times 0.6990$$

$$= 0.63 - 0.0206 = 0.6094 \text{ V} \quad 1/2$$

### Commonly Made Errors

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

### Answering Tip

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

Q. 7. A strip of nickel metal is placed in a 1 molar solution of  $\text{Ni}(\text{NO}_3)_2$  and a strip of silver metal is placed in a one molar solution of  $\text{AgNO}_3$ . An electrochemical cell is created when the two solution are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

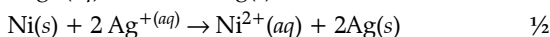
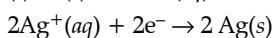
(i) Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.

(ii) Calculate the cell potential,  $E$  at  $25^\circ\text{C}$  for the cell, if the initial concentration of  $\text{Ni}(\text{NO}_3)_2$  is 0.100 molar and the initial concentration of  $\text{AgNO}_3$  is 1.00 molar.

$$[E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25\text{ V}, E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80\text{ V}]$$

$$\log 10^{-1} = -1 \quad \text{[A] [CBSE Foreign 2012]}$$

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



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ = 0.80 - (-0.25) = 1.05\text{ V} \quad 1$$

$$\begin{aligned} \text{(ii)} \quad E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} \quad \frac{1}{2} \\ &= E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{0.1}{(1)^2} \\ &= 1.05 - \frac{0.0591}{2} \times (\log 10^{-1}) \\ &= 1.05 - 0.295 \times (-1) \\ &= 1.05 + 0.295 = 1.0795\text{ V} \quad 1 \end{aligned}$$

#### Commonly Made Errors

- The cell reaction is given incorrectly by many students.
- In the calculation of emf of the cell by using Nernst equation, students ignore the power of concentration terms.

#### Answering Tip

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



## Long Answer Type Questions-II

(5 marks each)

**[AI]** Q. 1. (i) What is limiting molar conductivity? Why there is steep rise in the molar conductivity of weak electrolyte on dilution?

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



$$[\text{Given} = E^\circ_{\text{cell}} = 2.71\text{ V}] \quad \text{[R + A] [CBSE OD 2016]}$$

Ans. (i) When concentration approaches zero, the molar conductivity is known as **limiting molar conductivity**. 1

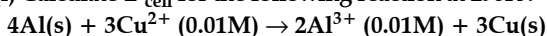
The change in  $\Lambda_m$  with dilution is due to the increase in the degree of dissociation and consequently the number of ions in the total volume of the solution that contains 1 mol of electrolyte, hence  $\Lambda_m$  increases steeply. 1

$$\begin{aligned} \text{(ii)} \quad E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} \quad 1 \\ &= 2.71\text{ V} - \frac{0.059}{2} \log \frac{0.1}{0.001} \\ &= 2.71\text{ V} - \frac{0.059}{2} \log 10^2 \quad 1 \\ &= 2.651\text{ V} \quad 1 \end{aligned}$$

#### Commonly Made Error

- Students often write incorrect formula or concentrations in the working formula. Practice numericals with different cell reactions.

Q. 2. (i) Calculate  $E^\circ_{\text{cell}}$  for the following reaction at 298K :



$$\text{Given} : E_{\text{cell}} = 1.98\text{ V}$$

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

$$\text{Given} : E^\circ(\text{A}^{2+}/\text{A}) = -2.37\text{ V} : E^\circ(\text{B}^{2+}/\text{B}) = -0.14\text{ V} \quad \text{[A]} \\ \text{OR}$$

(i) The conductivity of 0.001 mol  $\text{L}^{-1}$  solution of  $\text{CH}_3\text{COOH}$  is  $3.905 \times 10^{-5}\text{ S cm}^{-1}$ . Calculate its molar conductivity and degree of dissociation ( $\alpha$ ). Given  $\Lambda^\circ(\text{H}^+) = 349.6\text{ S cm}^2\text{ mol}^{-1}$  and  $\Lambda^\circ(\text{CH}_3\text{COO}^-) = 40.9\text{ S cm}^2\text{ mol}^{-1}$

(ii) Define electrochemical cell. What happens if external potential applied becomes greater than  $E^\circ_{\text{cell}}$  of electrochemical cell ?

$$\text{[A + R] [CBSE OD 2016]}$$

Ans. (i)  $\text{Al(s)} | \text{Al}^{3+}(\text{aq}) (0.01\text{ M}) || \text{Cu}^{2+}(\text{aq}) (0.01\text{ M}) | \text{Cu(s)}$   
LHE  $[\text{Al(s)} \rightarrow \text{Al}^{3+}(\text{aq}) + 3e^-] \times 2$  (Oxidation at anode)  
RHE  $[\text{Cu}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Cu(s)}] \times 3$  (Reduction at cathode)  
 $\therefore n = 6$

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

$$\begin{aligned} E^\circ_{\text{cell}} &= E_{\text{cell}} + \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3} \\ &= 1.98 + \frac{0.0591}{6} \log \frac{(0.01)^2}{(0.01)^3} \quad 1 \end{aligned}$$

$$\begin{aligned} &= 1.98 + \frac{0.0591}{6} \log 10^2 \\ &= 1.98 + \frac{0.0591}{6} \times 2 \log 10 \end{aligned}$$

$$= 1.98 + \frac{0.0591}{6} \times 2 \quad [\because \log 10 = 1]$$

$$= 1.98 + 0.0197$$

$$= 1.9997 \text{ V} \quad 1$$

(ii) A is better than B because its  $E^\circ$  value is more negative. 1 + 1

#### Commonly Made Error

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

OR

(i)  $C = 0.001 \text{ mol L}^{-1}$ ,  $k = 3.905 \times 10^{-5} \text{ S cm}^{-1}$

Molar conductivity

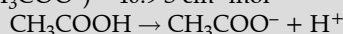
$$\lambda_m = \frac{k \times 1000}{C}$$

$$= \frac{3.95 \times 10^{-5} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.001 \text{ mol L}^{-1}}$$

$$= 39.05 \text{ S cm}^2 \text{ mol}^{-1} \text{ or } \Omega^{-1} \text{ cm}^3 \text{ mol}^{-1} \quad 1$$

$$\lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1},$$

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



$$\Lambda^\circ(\text{CH}_3\text{COOH}) = \Lambda^\circ \text{CH}_3\text{COO}^- + \Lambda^\circ \text{H}^+$$

$$= (40.9 + 349.6) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 390.5 \text{ S cm}^2 \text{ mol}^{-1} \quad 1$$

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

$$= \frac{39.05}{390.5}$$

$$= 0.1 \quad 1$$

(ii) Electrochemical cell is a device used for the production of electricity from energy released during spontaneous chemical reaction and use electrical energy to bring about the chemical change. 1

If the external potential applied becomes greater than  $E_{\text{cell}}^\circ$  of electrochemical cell, the reaction gets reversed. It starts acting as an electrolytic cell and vice-versa. 1

[CBSE Marking Scheme 2016]

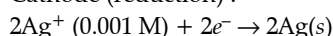
**Q. 3.** A voltaic cell is set up at  $25^\circ\text{C}$  with the half cells  $\text{Ag}^+$  (0.001 M) Ag and  $\text{Cu}^{2+}$  (0.10 M) Cu. What should be its cell potential? [ $E^\circ = 0.46 \text{ V}$ ,  $\log 10^5 = 5$ ]

[CBSE Foreign 2012]

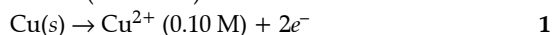
**Ans.**  $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$  1

Half cell reactions :

Cathode (reduction) :



Anode (oxidation) :



$\therefore$

$$n = 2$$

$$E_{\text{cell}}^\circ = 0.46 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} \quad 1$$

$$= 0.46 - \frac{0.059}{2} \log \frac{(0.1)}{(0.001)^2} \quad 1$$

$$= 0.46 \text{ V} - \frac{0.059}{2} \text{ V} \log 10^5$$

$$= 0.46 \text{ V} - \frac{0.059}{2} \text{ V} \times 5$$

$$= 0.46 \text{ V} - 0.1475 \text{ V}$$

$$= 0.3125 \text{ V} \quad 1$$

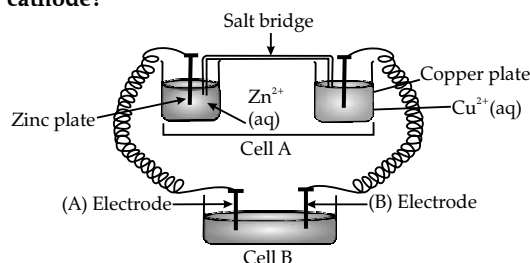
#### Commonly Made Error

- Students often make mistake 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.

**Q. 4.** Consider the given below figure (inside) and answer the following questions :

(a) Cell 'A' has  $E_{\text{cell}} = 2 \text{ V}$  and Cell 'B' has  $E_{\text{cell}} = 1.1 \text{ V}$  which of the two cells 'A' or 'B' will act as electrolytic cell. Which electrode reactions will occur in this cell?

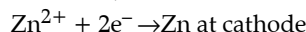
(b) If cell 'A' has  $E_{\text{cell}} = 0.5 \text{ V}$  and Cell 'B' has  $E_{\text{cell}} = 1.1 \text{ V}$  then what will be the reactions at anode and cathode?



[NCERT Exemp. Q. 66, Page 43]

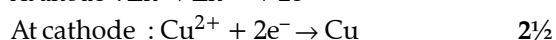
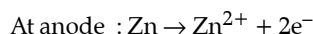
**Ans. (a)** Cell 'B' will act as electrolytic cell as it has lower EMF

Therefore, the electrode reactions will be :



(b) Now cell 'B' acts as galvanic cell as it has higher EMF and will push electrons into cell 'A'.

The electrode reaction will be :





## TOPIC-3

### Electrolysis, Laws 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 by a current is proportional to the quantity of electricity passed through the electrolyte.

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

- **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.

$$\frac{w}{E_1} = \frac{w}{E_2}$$

- **Products of electrolysis depend on**

- Physical state of material.
- 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 :

- Primary battery are non-chargeable batteries such as Leclanche cell and Dry cell.
  - Secondary battery are chargeable cells involving reversible reaction. Example, Lead storage battery and Nickel-cadmium cells.
- **Dry cell (Leclanche cell)** : The anode consists of a zinc container and the cathode is a graphite electrode surrounded by powdered  $\text{MnO}_2$  and C. The space is filled with paste of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$ .

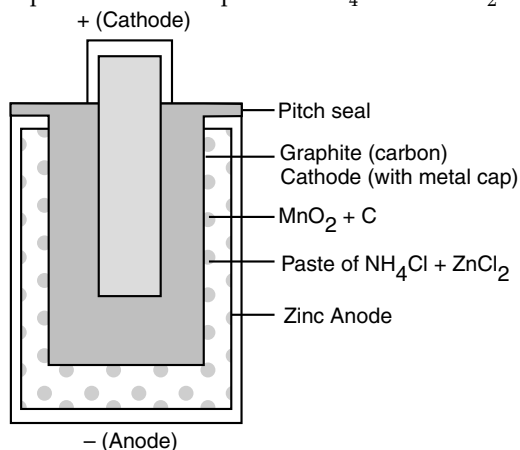


Fig. 1 : A dry cell

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

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

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

- **Lead storage battery :**

**Anode** – Spongy lead

**Cathode** – Lead packed with lead dioxide

**Electrolyte** – Aqueous solution of  $\text{H}_2\text{SO}_4$

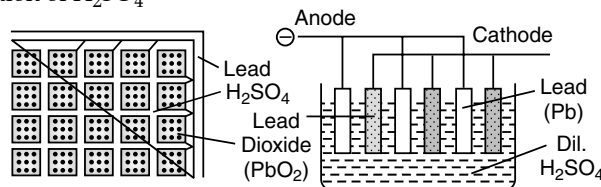
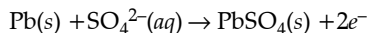


Fig. 2 : Storage battery

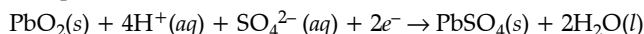
**Discharge reaction of cell :**

**At anode :** Following reaction takes place at anode :



**Reaction at cathode :**  $\text{PbO}_2$  filled in lead grid gets reduced to  $\text{Pb}^{2+}$  ions which combines with  $\text{SO}_4^{2-}$  ions to form  $\text{PbSO}_4(\text{s})$ .

Complete cathode reaction is as follows :

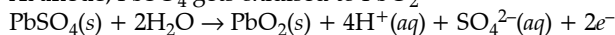


**Complete cell reaction :**  $\text{Pb(s)} + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$

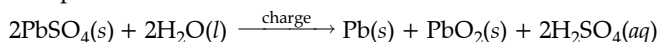
**Recharge reaction of cell :** It changes the direction of electrode reaction  $\text{PbSO}_4$  accumulated at cathode gets reduced to Pb.

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

**At anode,**  $\text{PbSO}_4$  gets oxidised to  $\text{PbO}_2$

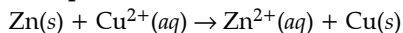


Complete cell reaction would be as follows :

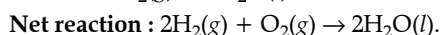
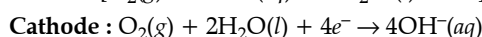
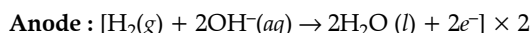


➤ **Conventions for representing the galvanic cell :**

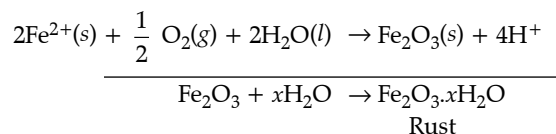
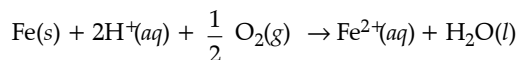
- (i) Double vertical line is used for salt bridge. Left hand side of the double line is anode and the cathode is on the right hand side.
- (ii) A single vertical line is used to separate metal and the electrolytic solution.
- (iii) If there is no metallic surface involved, we write Pt.

**Example :**

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

**In the cell :**

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

**Rusting of iron :****Prevention of corrosion :**

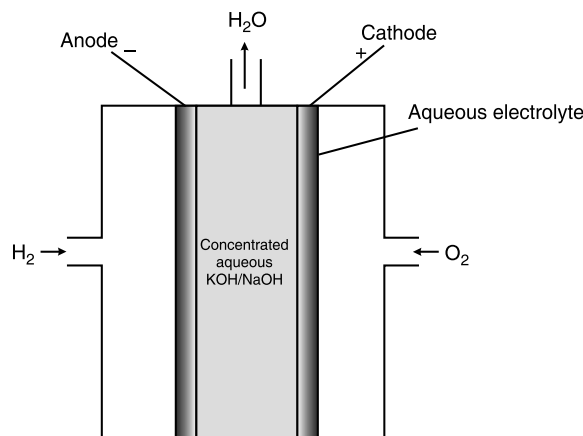
- (i) **Barrier protection :** By covering the surface with paint or a thin film of grease or by electroplating.
- (ii) **Sacrificial protection :** By galvanization.
- (iii) **Alloying.**

**Know the Formulae**

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

**Know the Terms**

- **Electrolytic cell :** A cell in which the electrical energy is used to carry out a non-spontaneous reaction.



**Fig. 3 : Fuel cell using  $\text{H}_2$  and  $\text{O}_2$  produces electricity**



- **Faraday constant** : It is the quantity of electricity.  
1 F = 96500 C
- **Electrosynthesis** : It is a method of producing substance through non-spontaneous reaction carried by electrolysis.
- **Tinning** : Coating of iron with tin.



## Very Short Answer-Objective Type Questions (1 mark each)

### A. Multiple choice Questions:

Q. 1. While charging the lead storage battery \_\_\_\_\_.

- (a)  $\text{PbSO}_4$  anode is reduced to Pb.
- (b)  $\text{PbSO}_4$  cathode is reduced to Pb.
- (c)  $\text{PbSO}_4$  cathode is oxidised to  $\text{PbO}_2$ .
- (d)  $\text{PbSO}_4$  anode is oxidised to  $\text{PbO}_2$ .

[NCERT Exemp. Q. 15, Page 35]

Ans. Correct option : (a)

**Explanation :** While charging the lead storage battery the reaction occurring on cell is reversed and lead sulphate ( $\text{PbSO}_4$ ) on anode and cathode is converted into (lead) Pb and lead dioxide ( $\text{PbO}_2$ ), respectively. The electrode reactions are as follows :

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

**At anode :**  $\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2(\text{s}) + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$  (Oxidation)

**Overall reaction :**  $2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O} \rightarrow \text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq.}) + 2\text{SO}_4^{2-}(\text{aq.})$

### B. Match of the following :

Q. 1. Match the items of Column I and Column II.

Column I		Column II	
(i)	Lead storage battery	(a)	maximum efficiency
(ii)	Mercury cell	(b)	prevented by galvanisation
(iii)	Fuel cell	(c)	gives steady potential
(iv)	Rusting	(d)	Pb is anode, $\text{PbO}_2$ is cathode

[NCERT Exemp. Q. 52, Page 40]

Ans. (i)  $\rightarrow$  (d)

(ii)  $\rightarrow$  (c)

(iii)  $\rightarrow$  (a)

(iv)  $\rightarrow$  (b)

**Explanation :**

(i) **Lead storage battery** : The cell reactions when the battery is in use are given below :

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

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

Overall cell reaction :

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

(ii) **Mercury cell** : The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

(iii) **Fuel cell** runs continuously as long as the reactants are supplied. It produces electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%.

(iv) **Rusting of iron** is an example of corrosion. Corrosion results in huge material loss resulting in damage to buildings, ships, bridges, machinery, etc. Galvanization is a process of coating of zinc over iron, so as to protect it from rusting.

### C. Answer the following:

Q. 1. What are secondary cell? [NCERT Exemplar]

Ans. Those cell which are rechargeable, i.e., in which products can convert back into reactants. 1

Q. 2. Suggest two materials other than hydrogen that can be used as fuels in fuel cells. [NCERT Exemplar]

Ans. Methane and methanol can be used as fuels in fuel cells. 1



## Short Answer Type Questions

(2 marks each)

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.

[CBSE OD Set-1 2017]

Ans. Mercury cell.

**Anode:**  $\text{Zn}(\text{Hg}) + 2\text{OH}^- \rightarrow \text{ZnO}(\text{s}) + \text{H}_2\text{O} + 2\text{e}^-$   
1/2

**Cathode:**  $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg}(\text{l}) + 2\text{OH}^-$  1/2  
[CBSE Marking Scheme 2017]

### Commonly Made Error

- The cell reaction is given incorrectly by many students. They often fail to balance the reaction.

### Answering Tip

- Do more practice of cell reaction.

Q. 2. Write the name of the cell which is generally used in inverters. Write the reactions taking place at the anode and the cathode of this cell.

[U] [CBSE OD Set-2 2017]

Ans. Lead storage battery 1  
 Anode:  $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$   $\frac{1}{2}$   
 Cathode:  $\text{PbO}_2 + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$   $\frac{1}{2}$   
 [CBSE Marking Scheme 2017]

### Commonly Made Error

- Students generally mix up the reactions at cathode and anode.

### Answering Tip

- Learn the reactions taking place at cathode and anode carefully.

OR

2  
[Topper's Answer 2017]

Q. 3. 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] [CBSE OD Set-3 2017]

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

### Commonly Made Error

- The cell reaction is given incorrectly by many students. They often fail to balance the reaction.

### Answering Tip

- Do more practice of cell reaction.

[AI] Q. 4. From the given cells :

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

Answer the following :

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

[R] [CBSE Delhi 2016]

Ans. (i) Mercury cell,  
 (ii) Fuel cell,  
 (iii) Lead storage cell,  
 (iv) Dry cell.  $\frac{1}{2} \times 4$   
 [CBSE Marking Scheme 2016]

Q. 5. A current of 1.50 A was passed through an electrolytic cell containing  $\text{AgNO}_3$  solution with inert electrodes. The weight of silver deposited was 1.50 g. How long did the current flow ? (Molar mass of  $\text{Ag} = 108 \text{ g mol}^{-1}$ ,  $1\text{F} = 96500 \text{ C mol}^{-1}$ ).

[A] [CBSE Comptt. D/OD 2018]

Ans. Quantity of charge required to deposit 108 g of silver = 96500 C  $\frac{1}{2}$   
 Quantity of charge required to deposit 1.50 g of silver =  $\frac{96500}{108} \times 1.50 = 1340.28 \text{ C}$   $\frac{1}{2}$   
 Time taken =  $\frac{Q}{I} = \frac{1340.28}{1.50} = 893.5 \text{ s}$  1  
 (or by any other suitable method)  
 [CBSE Marking Scheme 2018]

Q. 6. (i) Calculate  $\Delta_r G^\circ$  for the reaction  $\text{Mg(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu(s)}$

Given :  $E^\circ_{\text{cell}} = +2.7 \text{ V}$ ,  $1\text{F} = 96500 \text{ C mol}^{-1}$

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

[A + R] [CBSE OD 2014]

Ans. (i) Given,  $E^\circ_{\text{Cell}} = +2.71\text{V}$  and  $F = 96500 \text{ C mol}^{-1}$ ,  $n = 2$  (from the given reaction)  
 $\Delta_r G^\circ = -n \times F \times E^\circ_{\text{cell}}$   
 $\Delta_r G^\circ = -2 \times 96500 \text{ C mol}^{-1} \times 2.71\text{V}$   
 $= -523030 \text{ J/mol}$   
 or  $-523.03 \text{ KJ/mol}$  1  
 (ii) Hydrogen – oxygen fuel Cell / fuel cell.  
 [CBSE Marking Scheme 2014] 1



## Long Answer Type Questions-I

(3 marks each)

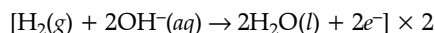
Q. 1. (i) What are fuel cells ? Explain the electrode reactions involved in the working of  $\text{H}_2 - \text{O}_2$  fuel cell.

(ii) Represent the galvanic cell in which the reaction  $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$  takes place.

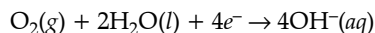
[R + U] [CBSE Comptt. Delhi/OD 2013]

**Ans. (i)** The cells which convert chemical energy of a fuel directly into electrical energy is known as **fuel cells**. 1  
The electrode reactions are :

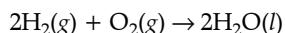
**Anode :**



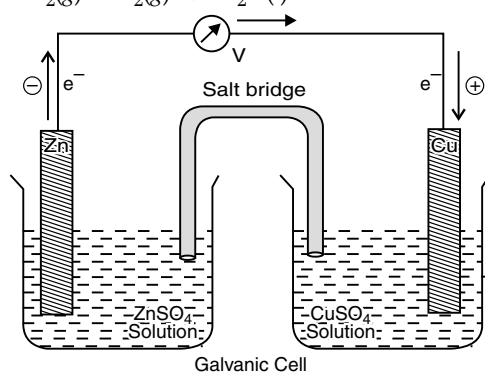
**Cathode :**



**Net reaction :**



(ii)



Galvanic Cell

May be represented as  $\text{Zn}(\text{s}) | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}(\text{s})$  1

#### Commonly Made Error

- Students often make errors in writing the half-cell reactions and cell representations.

#### Answering Tip

- Understand the concept clearly and practice to write cell reactions and representations.

**Q. 2.** Write the reactions taking place at cathode and anode in lead storage battery when the battery is in use. What happens on charging the battery?

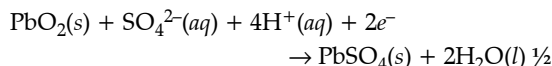
[CBSE Comptt. OD 2012]

**Ans.** The cell reactions when the battery is in use are given below :

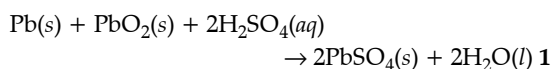
**Anode :**



**Cathode :**



i.e., Overall cell reaction consisting of cathode and anode reactions is :



On charging the battery, the electrode reactions are reverse of those that occur during discharge. 1

#### Commonly Made Error

- Students often get confused between reaction taking place on cathode and anode.

**Q. 3. (i)** Calculate the mass of Ag deposited at cathode when a current of 2 amperes was passed through a solution of  $\text{AgNO}_3$  for 15 minutes.

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

(ii) Define fuel cell.

[CBSE Delhi Set-1, 2 2017]

$$\begin{aligned} \text{Ans. (i)} \quad m &= Zit \quad \frac{1}{2} \\ &= \frac{108 \times 2 \times 15 \times 60}{1 \times 96500} \quad 1 \\ &= 2.01 \text{ g} \quad (\text{or any other correct method}) \quad \frac{1}{2} \end{aligned}$$

(ii) Cells that convert the energy of combustion of fuels directly into electrical energy. 1

[CBSE Marking Scheme 2017]

**Q. 4.** Silver is uniformly electro-deposited on a metallic vessel of surface area of  $900 \text{ cm}^2$  by passing a current of 0.5 ampere for 2 hours. Calculate the thickness of silver deposited.

[Given : the density of silver is  $10.5 \text{ g cm}^{-3}$  and atomic mass of Ag = 108 amu.]

[CBSE Comptt. OD 2013]

**Ans.** Calculation of mass of Ag deposited :

The electrode reaction is  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$

The quantity of electricity passed

= Current  $\times$  Time

$$= 0.5 \text{ (amp.)} \times 2 \times 60 \times 60 \text{ (sec)}$$

$$= 3600 \text{ C.} \quad 1$$

From the electrode reaction, it is clear that 96500 C of electricity deposit Ag = 108 g

$$3600 \text{ C of electricity will deposit Ag} = \frac{108}{96500} \times 3600$$

$$= 4.03 \text{ g} \quad 1$$

**Calculation of thickness:**

Let the thickness of silver deposited be  $x \text{ cm}$ .

Mass = Volume  $\times$  Density

$$= \text{Area} \times \text{Thickness} \times \text{Density}$$

(Volume = Area  $\times$  thickness)

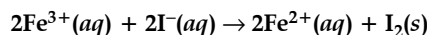
$$4.03 \text{ g} = 900 \text{ (cm}^2) \times x \text{ (cm)} \times 10.5 \text{ (g cm}^{-3})$$

$$x = \frac{4.03 \text{ cm}}{900 \times 10.5} = 4.26 \times 10^{-4} \text{ cm.} \quad 1$$

#### Answering Tip

- Always write working formula followed by the step substituting the value of each entity. Do not forget to mention the units.

**Q. 5. (i)** The cell in which the following reaction occurs :



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

[CBSE Comptt. OD 2012; NCERT]

(ii) How many electrons flow through a metallic wire if a current of 0.5 A is passed for 2 hours? (Given:  $1\text{F} = 96,500 \text{ C mol}^{-1}$ ) [CBSE OD Set-1, 2, 3 2017]

$$\text{Ans. (i)} \quad \Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$n = 2 \quad \frac{1}{2}$$

$$\Delta G^\circ = -2 \times 96500 \text{ C/mol} \times 0.236 \text{ V} \quad \frac{1}{2}$$

$$= -45548 \text{ J/mol}$$

$$= -45.548 \text{ kJ/mol} \quad \frac{1}{2}$$

$$\text{(ii)} \quad Q = It = 0.5 \times 2 \times 60 \times 60 \quad \frac{1}{2}$$

$$= 3600 \text{ C}$$

$$96500 \text{ C} = 6.023 \times 10^{23} \text{ electrons}$$

$$3600 \text{ C} = 2.25 \times 10^{22} \text{ electrons}$$

1

[CBSE Marking Scheme 2017]

**Answering Tip**

- Always write working formula followed by the step substituting the value of each entity. Do not forget to mention the units.

OR

(12) (a) Given reaction is:-  

$$2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \longrightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{s})$$

$\therefore$  n-factor,  $n=2$   
 $E^{\circ}_{\text{cell}} = 0.236 \text{ V}$  (given)

$\Delta G^{\circ} = ?$   
 We know,  
 $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$   
 $= -(2)(96500)(0.236) = -45548 \text{ J mol}^{-1}$   
 $\Delta G^{\circ} = -45.548 \text{ kJ mol}^{-1}$

(b) Given:- Current,  $i = 0.5 \text{ A}$  & time,  $t = 2 \text{ hrs}$   
 Let 'n' electrons pass through it.  
 We know  
 charge,  $Q = It = ne$   
 'e' is charge on one electron ( $e = 1.6 \times 10^{-19} \text{ C}$ )  
 Substituting, we get,  
 $0.5 \times 2 \times 3600 = n \times 1.6 \times 10^{-19}$   
 $\therefore n = \frac{0.5 \times 2 \times 3600}{1.6 \times 10^{-19}}$   
 $n = 2.25 \times 10^{22} \text{ electrons}$

[Topper's Answer 2017] 3

Q. 6. (i) How many coulombs are required to reduce 1 mole  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$ ?

(ii) The conductivity of 0.001 M acetic acid is  $4 \times 10^{-5} \text{ S/cm}$ . Calculate the dissociation constant of acetic acid if  $\Lambda^{\circ}_m$  for acetic acid is  $390 \text{ S cm}^2 \text{ mol}^{-1}$ .

[A] [CBSE Comptt. OD 2012]

Ans. (i)  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^{+} + 6\text{e}^{-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

One mole  $\text{Cr}_2\text{O}_7^{2-}$  requires 6 moles of electrons for reduction.

Thus, quantity of electricity required

$$\begin{aligned} &= 6 \times 96,500 \\ &= 579000 \text{ Coulomb} \quad 1 \\ &= 5.79 \times 10^5 \text{ Coulomb} \end{aligned}$$

(ii)

$$C = 0.001 \text{ M}$$

$$k = 4 \times 10^{-5} \text{ S cm}^{-1}$$

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

$$\Lambda_m = \frac{1000 \text{ cm}^3 \text{ L}^{-1} \times 4 \times 10^{-5} \text{ S cm L}^{-1}}{0.001 \text{ mol L}^{-1}}$$

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

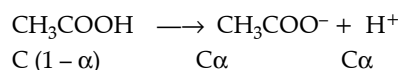
$$\Lambda^{\circ} = 390 \text{ S cm}^2 \text{ mol}^{-1} \quad \frac{1}{2}$$

$\alpha$  = degree of dissociation of  $\text{CH}_3\text{COOH}$

$$\alpha = \frac{\Lambda_m}{\Lambda^{\circ}} = \frac{40}{390} = 0.1025$$

$$\alpha = 0.1025 \approx 0.103 \quad \frac{1}{2}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^{-}][\text{H}^{+}]}{[\text{CH}_3\text{COOH}]}$$



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

$$= \frac{0.001 \times (0.103)^2}{1 - 0.103}$$

$$= 1.18 \times 10^{-5} \quad 1$$

**Answering Tips**

- Always write working formula followed by the step substituting the value of each entity.
- Do not forget to mention the units.
- Remember to put the power of concentration terms as mentioned in stoichiometry of the balance chemical equation

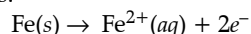
**Q. 7. What is corrosion ? Explain the electro-chemical theory of rusting of iron and write the reactions involved in the rusting of iron.**

[R + U] [CBSE Comptt. Delhi 2012]

**Ans.** The process of slowly eating away of the metal due to attack of the moisture and atmospheric gases on the surface of the metal resulting into the formation of compound such as oxides, sulphides, carbonates, sulphates etc., is called corrosion. **1**

**The electrochemical phenomenon of rusting of iron can be described as :**

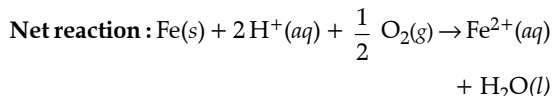
**At anode :** Fe(s) undergoes oxidation to releases electrons.



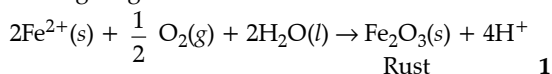
**At cathode :**  $\text{O}_2(\text{g}) + 4\text{H}^{+} + 4\text{e}^{-} \rightarrow 2\text{H}_2\text{O}(\text{l})$

Electrons released at anode move to another metal and reduce oxygen in presence of  $\text{H}^{+}$ . It is available from  $\text{H}_2\text{CO}_3$  formed from the dissolution of  $\text{CO}_2$  from air into water.  $\text{H}^{+}$  in water may be available also through dissolution of other acidic oxides from the atmosphere. **1**

This site behaves as cathode



$\text{Fe}^{2+}$  again gets oxidised to form rust.



## Long Answer Type Questions-II

(5 marks each)

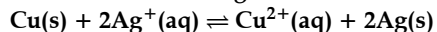
**Q. 1. (i) What are the two classifications of batteries ? What is the difference between them ?**

**(ii) The resistance of 0.01 M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell is unity. Calculate the molar conductivity of the solution.**

OR

**(i) What are fuel cells ? Give an example of a fuel cell.**

**(ii) Calculate the equilibrium constant ( $\log K_c$ ) and  $\Delta^\circ G$  for the following reaction at 298 K.**



Given  $E^\circ_{\text{cell}} = 0.46 \text{ V}$  and  $IF = 96500 \text{ C mol}^{-1}$

[R + U + A] [CBSE Comptt. OD 2016]

**Ans. (i) Classification of batteries : (a) Primary batteries**

**(b) Secondary batteries **1****

Primary batteries are non-chargeable batteries whereas secondary batteries are rechargeable. **1**

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

$$k = \frac{1}{R} \left( \frac{l}{A} \right)$$

$$= \frac{1}{200} \times 1 \text{ S cm}^{-1} \quad \mathbf{1}$$

$$= \frac{1}{200} \text{ S cm}^{-1}$$

$$\Lambda_m = \frac{1 \times 1000}{200 \times 0.01} \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 500 \text{ S cm}^2 \text{ mol}^{-1} \quad \mathbf{1}$$

OR

**(i) Fuel cells are the cells which converts energy of combustion of fuel directly into electricity. Example  $\text{H}_2 - \text{O}_2$  fuel cell. **1****

**(ii)  $\log K_c = \frac{nE^\circ_{\text{cell}}}{0.059} \quad \frac{1}{2}$**

$$= \frac{2 \times 0.46 \text{ V}}{0.059} = \frac{0.92}{0.059}$$

$$\log K_c = 15.59 \quad \mathbf{1}$$

$$\Delta_r G^\circ = -n F E^\circ_{\text{cell}} \quad \mathbf{1}$$

$$= -2 \times 96500 \text{ C mol}^{-1} \times 0.46 \text{ V} \quad \frac{1}{2}$$

$$= -88,780 \text{ J mol}^{-1}$$

$$= -88.78 \text{ kJ mol}^{-1} \quad \mathbf{1}$$

[CBSE Marking Scheme 2016]

### Answering Tip

- While solving the numerical, write the working formula followed by the data in it. Write proper unit.

**Q. 2. (i) Define the following terms :**

**(a) Molar conductivity ( $\Lambda_m$ )**

**(b) Secondary batteries**

**(c) Fuel cell**

**(ii) State the following laws :**

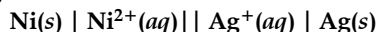
**(a) Faraday first law of electrolysis**

**(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**



Calculate the equilibrium constant at 25 °C. How much maximum work would be obtained by operation of this cell ?

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

[R + U + A] [CBSE Comptt. Delhi 2015]

**Ans. (i) (a) Molar conductivity of a solution at a given concentration is the conducting power of all the ions produced by 1 mol of an electrolyte. **1****

**(b) Secondary battery can be recharged by passing current through it in opposite direction so that it can be used again. **1****

**(c) Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells. **1****

(ii) (a) Faraday's first law of electrolysis states that the amount of chemical reaction which occurs at any electrode during electrolysis by current is proportional to the quantity of electricity passed through the electrolyte (solution or melt). 1

(b) According to Kohlrausch law of independent migration of ions limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. 1

[CBSE Marking Scheme 2015]

#### Commonly Made Error

- Students re-frame the statement or only give the statement.

#### Answering Tip

- Write the laws as stated.

OR

(i) Degree of dissociation is the ratio of molar conductivity at a specific concentration to the molar conductivity at infinite solution. 1

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^0} \quad 1$$

(ii)  $E^\circ_{\text{cell}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Ni}^{2+}/\text{Ni}}$  1/2  
 $= 0.80\text{V} - 0.25\text{V}$  1/2  
 $= 0.55\text{V}$  1/2

$$\log K_c = \left( \frac{nE^\circ_{\text{cell}}}{0.059} \right) = \frac{2 \times 0.55}{0.059} \quad \frac{1}{2}$$

$$\log K_c = 18.644 \quad \frac{1}{2}$$

$$K_c = \text{Antilog } 18.644 \quad K_c = 4 \times 10^{18}$$

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

$$= -2 \times 96500 \text{ C mol}^{-1} \times 0.55\text{V}$$

$$= -106,150 \text{ J mol}^{-1}$$

$$\text{Max. work} = +106150 \text{ J mol}^{-1}$$

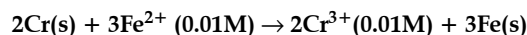
$$\text{or } 106.150 \text{ kJ mol}^{-1} \quad 1$$

[CBSE Marking Scheme 2015]

#### Answering Tip

- While solving the numerical, write the working formula followed by the data in it. Write proper unit.

Q. 3. (i) Calculate  $E^\circ_{\text{cell}}$  for the following reaction at 298 K:



Given :  $E_{\text{cell}} = 0.261 \text{ V}$

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

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

[A] [CBSE OD Set-2 2016]

Ans.

b.a) According to Nernst Equation ✓

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

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

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

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

$$E_{\text{cell}} = E^\circ_{\text{cell}} = 0.261 + \frac{0.059 \log 10^{-4}}{6 \cdot 10^{-6}}$$

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

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

$$= 0.261 + 0.01966$$

$$= 0.261 + 0.01966$$

$$E_{\text{cell}} = 0.28066 \text{ V}$$

$$E_{\text{cell}} = 0.281 \text{ V}$$

(b) From the reduction potential values, we can conclude that the more negative the reduction potential is, the better is the species a reducing agent i.e. it has higher tendency to get oxidised.

Rusting of iron is due to its oxidation from  $\text{Fe} \rightarrow \text{Fe}^{2+}$ . If we coat the surface with a substance of iron that has more tendency to get oxidised than iron, then iron will not oxidise and corrosion will be prevented.

Thus we have to choose a metal whose reduction potential is more negative than that of iron. From the data we can see that metal A has a more negative reduction potential. Thus metal A is better for coating iron. The metal A will work as a sacrificial metal and will get oxidised instead of iron.

3 + 2

[Topper's Answer 2016]

**Detailed Answer :**

(i) Nernst Equation :

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

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

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

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

$$0.0261 = \frac{0.059}{6} \log 10^2$$

$$0.0261 = \frac{0.059 \times 2}{6}$$

$$0.0261 + 0.01966$$

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

3

(ii) As corrosion is a phenomenon of oxidation of iron considering the oxidation potential of all the elements is essential. Element with higher oxidation potential than Fe will oxidise faster than iron preventing corrosion in iron.

Oxidation potential of Fe = 0.44 V

Oxidation potential of A = 2.37 V

Oxidation potential of B = 0.14 V

As A has higher oxidation potential than iron, it can be used for coating the surface of iron.

2

**Commonly Made Error**

- Students often write incorrect formula of concentrations in the working formula. Practice numericals with different cell reactions.

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

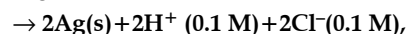
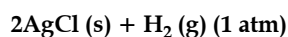
$\text{Sn (s)} \mid \text{Sn}^{2+} (0.004 \text{ M}) \parallel \text{H}^{+} (0.020 \text{ M}) \mid \text{H}_2 (\text{g}) (1 \text{ bar}) \mid \text{Pt (s)}$  (Given :  $E^{\circ} \text{Sn}^{2+}/\text{Sn} = -0.14 \text{ V}$ )

(b) Give reasons :

- On the basis of  $E^{\circ}$  values,  $\text{O}_2$  gas should be liberated at anode but it is  $\text{Cl}_2$  gas which is liberated in the electrolysis of aqueous NaCl.
- Conductivity of  $\text{CH}_3\text{COOH}$  decreases on dilution.

OR

(a) For the reaction



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

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

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

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

[R + U + A] [CBSE Delhi/OD 2018]

Ans. (a)  $\text{Sn} + 2\text{H}^+ \rightarrow \text{Sn}^{2+} + \text{H}_2$

(Equation must be balanced) 1

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

$$= [0 - (-0.14)] - 0.295 \log \frac{(0.004)}{(0.02)^2} \quad \frac{1}{2}$$

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

(b) (i) Due to overpotential/ Overvoltage of  $\text{O}_2$  1

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

OR

(a)  $\Delta G^\circ = -nFE^\circ$   $\frac{1}{2}$

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

$$E^\circ = 0.226 \text{ V} \quad \frac{1}{2}$$

$$E = E^\circ - 0.059/2 \log ([\text{H}^+]^2 [\text{Cl}^-]^2 / [\text{H}_2]) \quad \frac{1}{2}$$

$$= 0.226 - 0.059/2 \log [(0.1)^2 \times (0.1)^2] / 1 \quad \frac{1}{2}$$

$$= 0.226 - 0.059/2 \log 10^{-4} \quad 1$$

$$= 0.226 + 0.118 = 0.344 \text{ V}$$

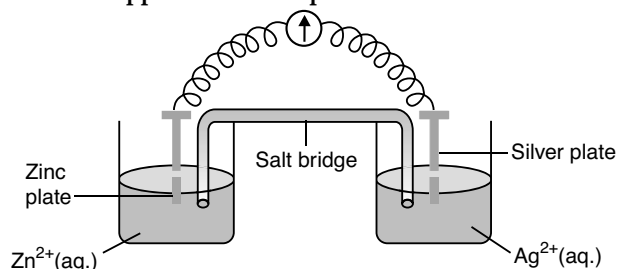
(Deduct half mark if unit is wrong or not written) 1

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

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

[CBSE Marking Scheme 2018]

Q. 5. (i) When a bright silver object is placed in the solution of gold chloride, it acquires a golden tinge but nothing happens when it is placed in a solution of copper chloride. Explain the behaviour of silver.



(ii) Consider the figure given above and answer the following questions :

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

(b) Which is anode and which is cathode?

(c) What will happen if the salt bridge is removed?

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

(e) How will concentration of these ions be affected when the cell becomes dead?

[A&E] [CBSE Comptt. Delhi Set-1, 2, 3 2017]

Ans. (i)  $E^\circ$  value of silver is lower than that of gold, hence silver displaces gold which gets deposited on the silver object. 1

$E^\circ$  value of copper is lower than that of silver, hence silver cannot displace copper from its solution. 1

(ii) (a) Electrons flow from Zn to Ag plate.  $\frac{1}{2}$

(b) Zn as anode and Ag acts as cathode  $\frac{1}{2}$

(c) Cell will stop functioning  $\frac{1}{2}$

(d) Concentration of  $\text{Zn}^{2+}$  ions will increase and that of  $\text{Ag}^+$  ions will decrease.  $\frac{1}{2}, \frac{1}{2}$

(e) No change  $\frac{1}{2}$

[CBSE Marking Scheme 2017]

Q. 6. (a) A cell is prepared by dipping a zinc rod in 1M zinc sulphate solution and a silver electrode in 1M silver nitrate solution. The standard electrode potential given:

$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}, E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$$

What is the effect of increase in concentration of  $\text{Zn}^{2+}$  on the  $E_{\text{cell}}$ ?

(b) Write the products of electrolysis of aqueous solution of NaCl with platinum electrodes.

(c) Calculate e.m.f. of the following cell at 298 K:

$$\text{Ni(s)} / \text{Ni}^{2+} (0.01 \text{ M}) // \text{Cu}^{2+} (0.1 \text{ M}) / \text{Cu (s)}$$

$$[\text{Given } E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}, E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}]$$

Write the overall cell reaction. [A+U]

OR

(a) Apply Kohlrausch law of independent migration of ions, write the expression to determine the limiting molar conductivity of calcium chloride.

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

Concentration	Conductivity	Molar conductivity
M	$\text{Scm}^{-1}$	$\text{S cm}^2 \text{mol}^{-1}$
0.100	$106.74 \times 10^{-4}$	106.7
0.05	$55.53 \times 10^{-4}$	111.1
0.02	$23.15 \times 10^{-4}$	115.8

Compare the variation of conductivity and molar conductivity of NaCl solutions on dilution. Give reason.

(c) 0.1 M KCl solution offered a resistance of 100 ohms in a conductivity cell at 298 K. If the cell constant of the cell is  $1.29 \text{ cm}^{-1}$ , calculate the molar conductivity of KCl solution.

[C + A & E + A] [CBSE SQP 2018-2019]

Ans. (a)  $E_{\text{cell}}$  decreases. 1

(b) Anode:  $\text{Cl}_2 \uparrow$   $\frac{1}{2}$

Cathode :  $\text{H}_2 \uparrow$   $\frac{1}{2}$

(c)  $\text{Cu}^{2+}(\text{aq.}) + \text{Ni(s)} \rightarrow \text{Ni}^{2+}(\text{aq.}) + \text{Cu(s)}$   $\frac{1}{2}$

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

$$E^\circ_{\text{cell}} = 0.34 - (-0.25)$$

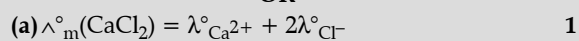
$$E^\circ_{\text{cell}} = 0.59 \text{ V} \quad \frac{1}{2}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[\text{Ni}^{2+}]}{[\text{Cu}^{2+}]} \quad \frac{1}{2}$$

$$E_{\text{cell}} = 0.59 - \frac{0.059}{2} \log \frac{[0.01]}{[0.1]} \quad \frac{1}{2}$$

$$E_{\text{cell}} = 0.6195 \text{ V} \quad \frac{1}{2} + \frac{1}{2}$$



**OR**

(b) 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 are overcome and ions are free to move. 1

(c)  $G^* = \kappa R$   $\frac{1}{2}$

$\kappa = \frac{1.29}{100} = 0.0129 \text{ S cm}^{-1}$   $\frac{1}{2}$

$$\Lambda_m = \frac{1000 \kappa}{C} \quad \frac{1}{2}$$

$$\Lambda_m = \frac{1000 \text{ cm}^3 \text{ L}^{-1} \times 0.0129 \text{ S cm}^{-1}}{0.1 \text{ mol L}^{-1}}$$

$$\Lambda_m = 129 \text{ S cm}^2 \text{ mol}^{-1} \quad \frac{1}{2}$$

**[CBSE Marking Scheme 2018]**