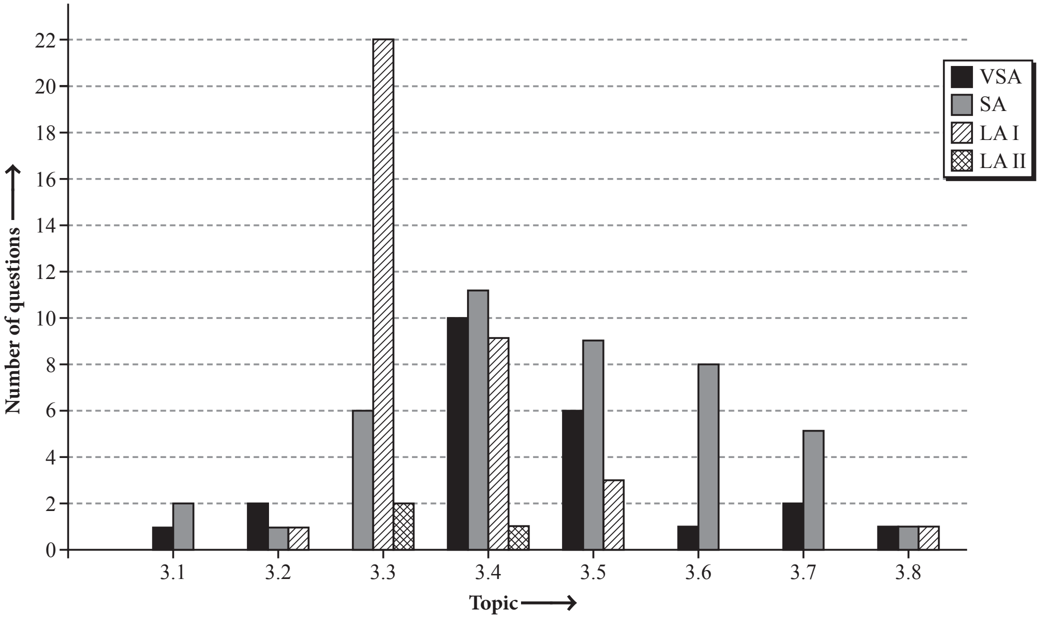
CHAPTER
3

Electrochemistry

3.1 Electrochemical Cells
3.2 Galvanic Cells
3.3 Nernst Equation
3.4 Conductance of Electrolytic Solutions
3.5 Electrolytic Cells and Electrolysis
3.6 Batteries
3.7 Fuel Cells
3.8 Corrosion

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2020-2011)



- Maximum total weightage is of *Nernst Equation.*
- Maximum VSA and SA type questions were asked from *Conductance of Electrolytic Solutions*.
- Maximum LA I type questions were asked from *Nernst Equation*.

QUICK RECAP

- **Electrochemistry :** It is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Differences between electrochemical cell and electrolytic cell

Electrochemical cell (Galvanic or Voltaic cell)	Electrolytic cell
1. It is a device which converts chemical energy into electrical energy.	1. It is a device which converts electrical energy into chemical energy.
2. It is based upon the redox reaction which is spontaneous. *i.e.*, $\Delta G = -\text{ve}$	2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied. *i.e.*, $\Delta G = +\text{ve}$
3. Two electrodes are usually set up in two separate beakers.	3. Both the electrodes are suspended in the solution or melt of the electrolyte in the same beaker.
4. The electrolytes taken in the two beakers are different.	4. Only one electrolyte is taken.
5. The electrodes taken are of different materials.	5. The electrodes taken may be of the same or different materials.
6. The electrode on which oxidation takes place is called the *anode* (or –ve pole) and the electrode on which reduction takes place is called the *cathode* (or +ve pole)	6. The electrode which is connected to the –ve terminal of the battery is called the *cathode*; the cations migrate to it which gain electrons and hence, a reduction takes place, the other electrode is called the *anode*.
7. To set up this cell, a salt bridge/porous pot is used.	7. No salt bridge is used in this case.

Nernst equation : For a reduction reaction, $M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$;

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}_{(aq)}]}$$

At 298 K,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}_{(aq)}]}$$

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

$$E_{\text{cell}} = \frac{0.0591}{n}\log\frac{C_2}{C_1}$$

where $C_2 > C_1$

Applications of Nernst equation :

- **To calculate electrode potential of a cell :**

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

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[X]^x[Y]^y}{[A]^a[B]^b}\text{(At 298 K)}$$

- **To calculate equilibrium constant :**

At equilibrium, $E_{\text{cell}} = 0$

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{n}\log K_c \quad \text{at 298 K}$$

Relation between cell potential and Gibbs energy change :

$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$; $\Delta G^{\circ} = -2.303\,RT\log K_c$

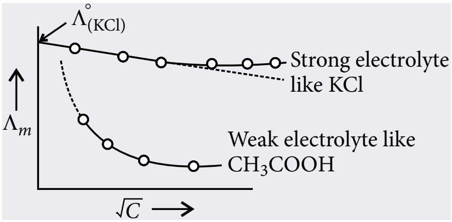
Conductance in electrolytic solutions :

Property	Formula	Units	Effect of dilution
Conductance (G)	$\frac{1}{R} = \frac{a}{\rho l} = \frac{\kappa a}{l}$	Ohm^{-1} (Ω^{-1})/Siemens (S)	Increases as larger number of ions are produced.
Specific conductance (κ) or conductivity	$\frac{1}{\rho}$ or $G\frac{l}{a}$	Ohm^{-1} cm^{-1}/S m^{-1}	Decreases as number of ions per cm^3 decreases.
Equivalent conductivity (Λ_{eq})	$\kappa \times V$ or $\kappa \times \frac{1000}{N}$	Ω^{-1} cm^2 eq^{-1}/S m^2 eq^{-1}	Increases with dilution due to large increase in V.
Molar conductivity (Λ_m)	$\kappa \times V$ or $\kappa \times \frac{1000}{M}$	Ω^{-1} cm^2 mol^{-1}/S m^2 mol^{-1}	Increases with dilution due to large increase in V.

- **Limiting molar conductivity :** When concentration approaches zero *i.e.*; at infinite dilution, the molar conductivity is known as *limiting molar conductivity* (Λ_m°).

- **Variation of molar conductivity with concentration :** For a strong electrolyte it is shown by *Debye-Huckel Onsager equation* as follows :

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



Here, Λ_m°= Molar conductivity at infinite dilution (Limiting molar conductivity)

Λ_m = Molar conductivity at *V*-dilution

A = Constant which depends upon nature of solvent and temperature

C = Concentration

Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to Λ_m° and slope equal to '$-A$'.

Thus, Λ_m decreases linearly with $\sqrt{C}$, when $C = 0$, $\Lambda_m = \Lambda_m^\circ$ and Λ_m° can be determined experimentally.

  - **For weak electrolytes :** There is a very large increase in conductance with dilution especially near infinite dilution as no. of ions increases. Λ_m increases as *C* decreases but does not reach a constant value even at infinite dilution. Hence, their Λ_m° cannot be determined experimentally.
  - **For a strong electrolyte :** There is only a small increase in conductance with dilution. This is because a strong electrolyte is completely dissociated in solution and so, the number of ions remain constant and on dilution, interionic attractions decreases as ions move far apart.

- **Kohlrausch's law of independent migration of ions :** It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

$\Lambda_m^\circ = \upsilon_+\lambda_+^\circ + \upsilon_-\lambda_-^\circ$; where λ_+° and λ_-° are the limiting molar conductivities of the cation and anion respectively and υ_+ and υ_- are stoichiometric number of cations and anions respectively in one formula unit of the electrolyte.

- **Applications of Kohlrausch's law :**
  - **Calculation of molar conductivity of weak electrolytes :**

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

$$= \left(\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}\right) + \left(\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}\right) - \left(\lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}\right)$$

$$= \Lambda^\circ_{m\,(HCl)} + \Lambda^\circ_{m\,(CH_3COONa)} - \Lambda^\circ_{m\,(NaCl)}$$

  - **Calculation of degree of dissociation :**

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

$$= \frac{\text{Molar conductivity at concentration } c}{\text{Molar conductivity at infinite dilution}}$$

  - **Calculation of dissociation constant (K_c) of weak electrolyte :**

	$AB \rightleftharpoons$	$A^+ +$	B^-
Initial conc.	c	0	0
Conc. at equil.	$(c - c\alpha)$	$c\alpha$	$c\alpha$

$$K_c = \frac{c\alpha \times c\alpha}{(c - c\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

- **Electrolysis :** It is the process of decomposition of an electrolyte by passing electricity through its aqueous solution or molten state.
  - **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 (solution or melt).

    $w \propto Q$ or $w = ZQ = Z \times I \times t$; where, *Z* is electrochemical equivalent of the substance deposited and $Z = \dfrac{\text{Eq. wt. of substance}}{96500}$.
  - **Faraday's second law of electrolysis :** The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.

    $\dfrac{w_1}{w_2} = \dfrac{E_1}{E_2}$ where *E* is the equivalent weight.

Products of electrolysis :

Electrolyte	Products		Reactions involved	
	At cathode	At anode	At cathode	At anode
Molten NaCl	Na metal	Cl_2 gas	$Na^+_{(l)} + e^- \longrightarrow Na_{(l)}$	$Cl^-_{(l)} \longrightarrow \frac{1}{2} Cl_{2(g)} + e^-$
Aqueous NaCl	H_2 gas	Cl_2 gas	$H_2O_{(l)} + e^- \longrightarrow \frac{1}{2} H_{2(g)} + OH^-_{(aq)}$	$Cl^-_{(aq)} \longrightarrow \frac{1}{2} Cl_{2(g)} + e^-$
Dil. H_2SO_4	H_2 gas	O_2 gas	$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2} H_{2(g)}$	$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$
Conc. H_2SO_4	H_2 gas	$S_2O_8^{2-}$	$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2} H_{2(g)}$	$2SO^{2-}_{4(aq)} \longrightarrow S_2O^{2-}_{8(aq)} + 2e^-$

Some commercial cells :

- **Primary cells :** Cells once exhausted cannot be used again *e.g.*, dry cell and mercury cell.
- **Secondary cells :** Rechargeable cell which can be used again and again *e.g.*, nickel-cadmium cell and lead storage battery.
- **Fuel cells :** Cells which can convert the energy of combustion of fuels such as H_2, CO, CH_4, etc. into electrical energy, *e.g.*, $H_2 - O_2$ fuel cell.

Dry cell, lead accumulator and fuel cell :

	Dry cell	Lead storage battery	Fuel cell
Anode	Zinc	Lead	Porous carbon containing catalysts (H_2 passed)
Cathode	Graphite	Lead dioxide	Porous carbon containing catalysts (O_2 passed)
Electrolyte	MnO_2 + C (touching cathode) $NH_4Cl + ZnCl_2$ (touching anode)	H_2SO_4 (38%)	Conc. aqueous KOH
Anode reaction	$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$	$Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$	$H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O_{(l)} + 2e^-$
Cathode reaction	$MnO_{2(s)} + NH^+_{4(aq)} + e^- \longrightarrow MnO(OH)_{(s)} + NH_{3(g)}$	$PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+ + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$	$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Corrosion : The slow eating away of metals when exposed to the atmosphere is called *corrosion.*

Corrosion of iron (Rusting) : It is an electrochemical phenomenon which occurs in the presence of moisture and oxygen.

At anode : $2Fe_{(s)} \longrightarrow 2Fe^{2+}{}_{(aq)} + 4e^-$

At cathode : $O_{2(g)} + 4H^+{}_{(aq)} + 4e^- \longrightarrow 2H_2O_{(l)}$

Overall reaction : $2Fe_{(s)} + O_{2(g)} + 4H^+{}_{(aq)} \longrightarrow 2Fe^{2+}{}_{(aq)} + 2H_2O_{(l)}$.

Methods used for prevention of corrosion : Barrier protection, sacrificial protection, anti-rust solutions.

Previous Years' CBSE Board Questions

3.1 Electrochemical Cells

VSA **(1 mark)**

1. An electrochemical cell behave like an electrolytic cell when

(a) $E_{\text{cell}} = E_{\text{external}}$ (b) $E_{\text{cell}} = 0$

(c) $E_{\text{external}} > E_{\text{cell}}$ (d) $E_{\text{external}} < E_{\text{cell}}$

(2020)

SA **(2 marks)**

2. Give two points of differences between electrochemical and electrolytic cells. *(2/5, 2020)*

3. Define electrochemical cell. What happens if external potential applied becomes greater than $E°_{\text{cell}}$ of electrochemical cell?

(AI 2019, 2/5, AI 2016)

3.2 Galvanic Cells

VSA **(1 mark)**

4. Represent the galvanic cell in which the reaction

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ takes place.

(1/3, Delhi 2013C)

5. What is the necessity to use a salt bridge in a Galvanic cell? *(Delhi 2011C)*

SA **(2 marks)**

6. Two half-reactions of an electrochemical cell are given below :

$MnO^{-}_{4(aq)} + 8H^{+}_{(aq)} + 5e^{-} \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$, $E° = + 1.51V$

$Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^{-}$, $E° = + 0.15$ V

Construct the redox equation from the standard potential of the cell and predict if the reaction is reactant favoured or product favoured. *(Delhi 2011)*

LA I **(3 marks)**

7. A cell is prepared by dipping copper rod in 1 M copper sulphate solution and zinc rod in 1 M zinc sulphate solution. The standard reduction potential of copper and zinc are 0.34 V and –0.76 V respectively.

(i) What will be the cell reaction?

(ii) What will be the standard electromotive force of the cell?

(iii) Which electrode will be positive?

(Delhi 2011C)

3.3 Nernst Equation

SA **(2 marks)**

8. Calculate $\Delta_r G°$ for the reaction :

$Mg_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

Given $E^{\circ}_{\text{cell}} = +2.71$ V, 1 F = 96500 C mol^{-1}

(2/3,AI 2014)

9. Equilibrium constant (K_c) for the given cell reaction is 10. Calculate $E°_{\text{cell}}$.

$A_{(s)} + B^{2+}_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + B_{(s)}$

(2/3,Foreign 2014)

10. The standard electrode potential ($E°$) for Daniell cell is +1.1 V. Calculate the $\Delta G°$ for the reaction.

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

(1 F = 96500 C mol^{-1}) *(AI 2013)*

11. The standard electrode potential for Daniell cell is 1.1 V. Calculate the standard Gibbs energy for the cell reaction.

(F = 96,500 C mol^{-1}) *(Delhi 2013C)*

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

$[E°_{Zn^{2+}/Zn} = -0.76 \text{ V}]$ *(Delhi 2012C)*

13. Determine the value of equilibrium constant (K_c) and $\Delta G°$ for the following reaction :

$Ni_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$, $E° = 1.05$ V

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

(Delhi, Foreign 2011)

LA I (3 marks)

14. Calculate $\Delta G°$ for the reaction,

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

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

$E°$ for $Cu^{2+}/Cu = +0.34$ V

$R = 8.314\ J\ K^{-1}\ mol^{-1}$, $F = 96500\ C\ mol^{-1}$.

(3/5, 2020)

15. Calculate the maximum work and log K_c for the given reaction at 298 K :

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

Given :

$E°_{Ni^{2+}/Ni} = -0.25$ V, $E°_{Ag^{+}/Ag} = +0.80$ V

$1F = 96500\ C\ mol^{-1}$ *(2020)*

16. (a) Calculate e.m.f of the following cell :

$Zn_{(s)}/Zn^{2+}$ (0.1 M) || (0.01 M) $Ag^{+}/Ag_{(s)}$

Given : $E°_{Zn^{2+}/Zn} = -0.76$ V, $E°_{Ag^{+}/Ag} = +0.80$ V

[Given : log 10 = 1] *(3/5, 2020)*

17. Calculate $\Delta_r G°$ and log K_c for the following reaction.

$Cd^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + Cd_{(s)}$

Given : $E°_{Cd^{2+}/Cd} = -0.403$ V ; $E°_{Zn^{2+}/Zn} = -0.763$ V

(AI 2019)

18. Write the cell reaction and calculate the e.m.f. of the following cell at 298 K.

$Sn_{(s)}$ | Sn^{2+} (0.004 M) || H^{+} (0.020 M) | $H_{2(g)}$ (1 bar) | $Pt_{(s)}$

(Given : $E°_{Sn^{2+}/Sn} = -0.14$ V) *(3/5, 2018)*

19. For the reaction,

$2AgCl_{(s)} + H_{2(g)}\,(1\ atm) \rightarrow 2Ag_{(s)} + 2H^{+}(0.1\ M) + 2Cl^{-}(0.1\ M)$

$\Delta G° = -43600$ J at 25 °C.

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

($\log 10^{-n} = -n$) *(3/5, 2018)*

20. Calculate e.m.f. of the following cell at 298 K.

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

Given : $E°_{(Cr^{3+}|Cr)} = -0.74$ V, $E°_{(Fe^{2+}|Fe)} = -0.44$ V

(Delhi 2016)

21. Calculate $E°_{cell}$ for the following reaction at 298 K.

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

Given : $E_{cell} = 1.98$ V *(3/5,AI 2016)*

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

$Fe|Fe^{2+}(0.001\ M)||H^{+}(0.01\ M)|H_{2(g)}(1\ bar)|Pt_{(s)}$

$E°(Fe^{2+}|Fe) = -0.44$ V, $E°(H^{+}|H_2) = 0.00$ V

(Delhi 2015)

23. Calculate the emf of the following cell at 25°C.

$Zn|Zn^{2+}(0.001\ M)||H^{+}(0.01M)|H_{2(g)}(1\ bar)|Pt_{(s)}$

$\left(E^{\circ}_{Zn^{2+}/Zn} = -0.76\ V,\ E^{\circ}_{(H^{+}/H_2)} = 0.00\ V\right)$

(Foreign 2015)

24. For the cell reaction,

$Ni_{(s)}\,|Ni^{2+}_{(aq)}||Ag^{+}_{(aq)}|Ag_{(s)}$

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

$E^{\circ}_{(Ni^{2+}/Ni)} = -0.25$ V and $E^{\circ}_{Ag^{+}/Ag} = 0.80$V

(3/5, Delhi 2015C)

25. Calculate the standard cell potential of the galvanic cell in which the following reaction takes place :

$Fe^{2+}_{(aq)} + Ag^{+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Ag_{(s)}$

Calculate the $\Delta_r G°$ and equilibrium constant of the reaction.

$\left(E^{\circ}_{Ag^{+}/Ag} = 0.80\ V\ ;\ E^{\circ}_{Fe^{3+}/Fe^{2+}} = 0.77\ V\right)$

(3/5, Delhi 2015C)

26. Calculate the emf of following cell at 298 K :

$Mg_{(s)}$ | Mg^{2+}(0.1 M) || Cu^{2+}(0.01 M)|$Cu_{(s)}$

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

(3/5, Delhi 2014)

27. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The Gibbs energy change for the decomposition reaction,

$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$ is 960 kJ.

($F = 96500\ C\ mol^{-1}$) *(3/5,Delhi 2014C)*

28. Calculate the emf of the following cell at 298 K :

$Fe_{(s)}|Fe^{2+}(0.001\ M)||H^{+}(1\ M)|H_{2(g)}$ (1 bar), $Pt_{(s)}$

(Given $E°_{cell} = +0.44$ V) *(Delhi 2013)*

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

$Ag_{(s)}|Ag^{+}(10^{-3}\ M)||Cu^{2+}\ (10^{-1}\ M)|Cu_{(s)}$

Given : $E°_{cell} = +0.46$ V and $\log 10^{n} = n$.

(AI 2013)

30. In the button cell, widely used in watches, the following reaction takes place.

$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$

Determine $E°$ and $\Delta G°$ for the reaction.

Given : $E°_{Ag^+/Ag} = +0.80$ V, $E°_{Zn^{2+}/Zn} = -0.76$ V)

(3/5, Delhi 2012)

31. A voltaic cell is set up at 25°C with the following half cells :

Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M)

Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

$E°_{Ni^{2+}/Ni} = -0.25$ V and $E°_{Al^{3+}/Al} = -1.66$ V.

($\log 8 \times 10^{-6} = -5.09$)

(3/5, AI 2012, 2011, 3/5, Foreign 2011)

32. The cell in which the following reaction occurs :

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

has $E°_{cell} = 0.236$ V at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

(Antilog of 6.5 = 3.162×10^6 ; of 8.0 = 10×10^8 ; of 8.5 = 3.162×10^8)

(Delhi 2012C)

33. Calculate the potential for half-cell containing 0.10 M $K_2Cr_2O_{7(aq)}$, 0.20 M $Cr^{3+}_{(aq)}$ and 1.0×10^{-4} M $H^+_{(aq)}$. The half cell reaction is :

$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

and the standard electrode potential is given as $E° = 1.33$ V. *(3/5, AI 2011)*

34. For the cell,

$Zn_{(s)} \mid Zn^{2+}$ (2 M) $\parallel Cu^{2+}$ (0.5 M) $\mid Cu_{(s)}$

(a) Write equation for each half-reaction.

(b) Calculate the cell potential at 25°C

Given :

$$E^{\circ}_{Zn^{2+}/Zn} = -0.76\text{ V} ;\ E^{\circ}_{Cu^{2+}/Cu} = +0.34\text{V}$$

(Delhi 2011C)

35. Calculate the equilibrium constant, K for the reaction at 298 K,

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

Given : $\Delta G° = -212.300$ kJ mol^{-1}

$$E^{\circ}_{Zn^{2+}/Zn} = -0.76\text{ V} ;\ E^{\circ}_{Cu^{2+}/Cu} = +\ 0.34\text{ V}$$

(AI 2011C)

LA II (5 marks)

36. $E°_{cell}$ for the given redox reaction is 2.71 V.

$$Mg_{(s)} + Cu^{2+}(0.01M) \rightarrow Mg^{2+}(0.001M) + Cu_{(s)}$$

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

(i) less than 2.71 V and

(ii) greater than 2.71 V *(Delhi 2019)*

37. Calculate e.m.f and ΔG for the following cell

$Mg_{(s)} \mid Mg^{2+}$ (0.001 M) $\parallel Cu^{2+}$ (0.0001 M) $\mid Cu_{(s)}$

$$E^{\circ}_{(Mg^{2+}/Mg)} = -2\cdot37\text{ V}, E^{\circ}_{(Cu^{2+}/Cu)} = +0.34\text{ V}$$

(AI 2015)

3.4 Conductance of Electrolytic Solutions

VSA (1 mark)

38. **Assertion (A) :** Conductivity of an electrolyte decreases with decrease in concentration.

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

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

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

(c) Assertion (A) is correct, but Reason (R) is incorrect statement.

(d) Assertion (A) is incorrect, but Reason (R) is correct statement. *(2020)*

39. Give reason :

Conductivity of CH_3COOH decreases on dilution. *(1/5, 2018)*

40. Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration? *(1/2, Delhi 2015)*

41. State Kohlrausch's law of independent migration of ions. Write its one application. *(1/2, Foreign 2015)*

42. Define the following term :

Molar conductivity (Λ_m) *(1/5, Delhi 2015C)*

43. Define the following term :
Kohlrausch's law of independent migration of ions. *(1/5, Delhi 2015C)*

44. Define the following term :
Limiting molar conductivity *(1/5, Delhi 2014)*

45. State and explain Kohlrausch's law. *(1/3, Delhi 2013C)*

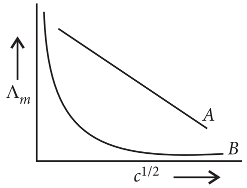
46. Express the relation between conductivity and molar conductivity of a solution held in a cell? *(Delhi 2011)*

47. Express the relation among the conductivity of solution in the cell, the cell constant and the resistance of solution in the cell. *(Delhi 2011)*

SA (2 marks)

48. Predict the products of electrolysis of an aqueous solution of $CuCl_2$ with platinum electrodes.
(Given : $E^\circ_{Cu^{2+}/Cu} = +0.34$ V,
$E^\circ_{(1/2Cl_2/Cl^-)} = +1.36$ V
$E^\circ_{H^+/H_2(g),\,Pt} = 0.00$ V, $E^\circ_{(1/2\,O_2/H_2O)} = +1.23$ V) *(2/5, 2020)*

49. In the plot of molar conductivity (Λ_m) *vs* square root of concentration ($c^{1/2}$),following curves are obtained for two electrolytes *A* and *B*



Answer the following :
(i) Predict the nature of electrolytes *A* and *B*.
(ii) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes *A* and *B*? *(2/5, Delhi 2019)*

50. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}.
(Given : $\lambda^\circ(H^+) = 349.68$ S cm^{2}mol^{-1} and
$\lambda^\circ(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}) *(Delhi 2017)*

51. Define the term degree of dissociation. Write an expression that relates the molar conductivity of a weak electrolyte to its degree of dissociation. *(2/5, Delhi 2015C)*

52. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration. *(2/5, AI 2015C)*

53. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? *(AI 2014)*

54. Define the terms conductivity and molar conductivity for the solution of an electrolyte. Comment on their variation with temperature. *(Delhi, AI 2014C)*

55. The resistance of 0.01 M NaCl solution at 25°C is 200 Ω. The cell constant of the conductivity cell used is unity. Calculate the molar conductivity of the solution. *(2/3, AI 2014C)*

56. The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity. *(Delhi 2013)*

57. The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/mol. *(2/3, Delhi 2013C, 2012C)*

58. Express the relation among cell constant, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solution related to its conductivity? *(AI 2012)*

LA I (3 marks)

59. Out of the following pairs, predict with reason which pair will allow greater conduction of electricity.
(i) Silver wire at 30°C or silver wire at 60°C.
(ii) 0.1 M CH_3COOH solution or 1 M CH_3COOH solution.
(iii) KCl solution at 20°C or KCl solution at 50°C. *(3/5, 2020)*

60. The electrical resistance of a column of 0.05 M KOH solution of length 50 cm and area of cross-section 0.625 cm^2 is 5×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity. *(3/5, 2020)*

61. The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).
[Given : $\lambda°$ (H^+) = 349.6 S cm^2 mol^{-1} and $\lambda°(CH_3COO^-)$ = 40.9 S cm^2 mol^{-1}]
(3/5, AI 2016)

62. The conductivity of 0·20 mol L^{-1} solution of KCl is 2.48×10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).
Given : λ° (K^+) = 73.5 S cm^2 mol^{-1} and λ° (Cl^-) = 76.5 S cm^2 mol^{-1}. *(AI 2015)*

63. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29×10^{-2} Ω^{-1} cm^{-1}. *(3/5, AI 2014)*

64. The value of $\Lambda°_m$ of $Al_2(SO_4)_3$ is 858 S cm^2 mol^{-1}, while λ° SO_4^{2-} is 160 S cm^2 mol^{-1}, calculate the limiting ionic conductivity of Al^{3+}.
(AI 2013C)

65. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity. *(AI 2012)*

66. When a certain conductance cell was filled with 0.1 M KCl, it has a resistance of 85 ohms at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.
[Specific conductance of 0.1 M KCl
= 1.29×10^{-2} ohm^{-1} cm^{-1}]
(AI 2012C)

67. Calculate the degree of dissociation of acetic acid at 298 K, given that :
Λ_m (CH_3COOH) = 11.7 S cm^2 mol^{-1}
$\Lambda°_m(CH_3COO^-)$ = 49.9 S cm^2 mol^{-1}
$\Lambda°_m(H^+)$ = 349.1 S cm^2 mol^{-1} *(Delhi 2011C)*

LA II (5 marks)

68. (a) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.
(b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}? *(AI 2012)*

3.5 Electrolytic Cells and Electrolysis

VSA (1 mark)

69. How many coulombs are required for the oxidation of 1 mol of H_2O to O_2?
(One word, 2020)

70. Give reason :
On the basis of $E°$ values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.
(1/5, 2018)

71. Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution: $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$, $E° = +0.80$ V

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}, \; E° = 0.00 \text{ V}$$

On the basis of their standard reduction electrode potential ($E°$) values, which reaction is feasible at the cathode and why?
(AI 2017C, 1/2, Delhi 2015)

72. How much charge is required for the reduction of 1 mol of Zn^{2+} to Zn?
(Delhi 2015)

73. Following reactions occur at cathode during the electrolysis of aqueous copper (II) chloride solution :

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

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

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

(1/2, Foreign 2015)

74. State the Faraday's first law of electrolysis. *(Delhi 2015C)*

SA (2 marks)

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

(2/5, 2020)

76. Calculate the mass of Ag deposited at cathode when a current of 2 ampere was passed through a solution of $AgNO_3$ for 15 minutes.
(Given : Molar mass of Ag = 108 g mol^{-1}, 1 F = 96500 C mol^{-1}) *(2/3, Delhi 2017)*

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

(2/5, Delhi 2014)

78. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 ampere for 20 minutes. What mass of nickel will be deposited at the cathode?
(Given : At. mass of Ni = 58.7 g mol^{-1},
1F = 96500 C mol^{-1}) *(Foreign 2014)*

79. Predict the products of electrolysis in each of the following :

(i) An aqueous solution of $AgNO_3$ with platinum electrodes.

(ii) An aqueous solution of H_2SO_4 with platinum electrodes. *(2/5, Delhi 2014C)*

80. How much electricity in terms of Faradays is required to produce 20 g of calcium from molten $CaCl_2$? *(2/3, Delhi 2013C)*

81. Silver is uniformly electrodeposited on a metallic vessel of surface area of 900 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 g cm^{-3} and atomic mass of Ag = 108 amu.

(2/3, AI 2013C)

82. How many coulombs are required to reduce 1 mole $Cr_2O_7^{2-}$ to Cr^{3+}?

(2/3, Delhi 2012C)

83. How many moles of mercury will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours?

(2/5, AI 2011)

LA I (3 marks)

84. A steady current of 2 amperes was passed through two electrolytic cells X and Y connected in series containing electrolytes $FeSO_4$ and $ZnSO_4$ until 2.8 g of Fe deposited at the cathode of cell X. How long did the current flow? Calculate the mass of Zn deposited at the cathode of cell Y. (Molar mass : Fe = 56 g mol^{-1}, Zn = 65.3 g mol^{-1}, 1 F = 96500 C mol^{-1}) *(3/5, Delhi 2019)*

85. Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation :

$CrO_{3(aq)} + 6H^+ + 6e^- \longrightarrow Cr_{(s)} + 3H_2O$

Calculate how many grams of chromium will be electroplated by 24,000 coulombs. How long will it take to electroplate 1.5 g chromium using 12.5 A current?
[Atomic mass of Cr = 52 g mol^{-1},
1 F = 96500 C mol^{-1}]

(AI 2019)

86. (a) The cell in which the following reaction occurs :

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

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

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

(AI 2017)

3.6 Batteries

VSA **(1 mark)**

87. Define : Secondary batteries *(1/5, Delhi 2015C)*

SA **(2 marks)**

88. 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. *(AI 2017)*

89. 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. *(AI 2017)*

90. 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. *(AI 2017)*

91. From the given cells :
Lead storage cell, Mercury cell, Fuel cell and Dry cell
Answer the following :
(i) Which cell is used in hearing aids?
(ii) Which cell was used in Apollo Space Programme?
(iii) Which cell is used in automobiles and inverters?
(iv) Which cell does not have long life? *(Delhi 2016)*

92. What type of battery is mercury cell? Why is it more advantageous than dry cell? *(2/5, AI 2015)*

93. What type of a battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it. *(2/5, Delhi 2012, AI 2011)*

94. 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? *(AI 2012C)*

95. Mention the reactions occurring at (i) anode, (ii) cathode, during working of a mercury cell. Why does the voltage of a mercury cell remain constant during its operation? *(Delhi 2011C)*

3.7 Fuel Cells

VSA **(1 mark)**

96. Name the type of cell which was used in Apollo space programme. *(2020, 1/3, AI 2014)*

97. Define : Fuel cell *(Delhi 2017, 1/5, Delhi 2015C, 2014)*

SA **(2 marks)**

98. Give two advantages of fuel cells. *(2/5, 2020)*

99. Define fuel cell and write its two advantages. *(2/5, 2018)*

100. Write two advantages of $H_2—O_2$ fuel cell over ordinary cell. *(2/3, Foreign 2014)*

101. What are fuel cells? Explain the electrode reactions involved in the working of $H_2—O_2$ fuel cell. *(2/3, Delhi 2013C)*

102. Give an example of a fuel cell and write the cathode and anode reactions for it. *(AI 2011C)*

3.8 Corrosion

VSA **(1 mark)**

103. Using the $E°$ values of A and B predict which is better for coating the surface of iron

$$\left[E^{\circ}_{(\mathrm{Fe}^{2+}/\mathrm{Fe})} = -0.44\ \mathrm{V}\right]$$

to prevent corrosion and why?

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

(AI 2016)

SA **(2 marks)**

104. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere. *(Delhi 2011)*

LA I **(3 marks)**

105. What is corrosion? Explain the electrochemical theory of rusting of iron and write the reactions involved in the rusting of iron. *(Delhi 2012C)*

Detailed Solutions

1. **(c) :** The device which converts the chemical energy liberated during the chemical reaction to electrical energy is called electrochemical cell.
If external potential applied becomes greater than $E°_{cell}$ of electrochemical cell then the cell behaves as an electrolytic cell and the direction of flow of current is reversed.

2.

S.No.	Electrochemical cell	Electrolytic cell
1.	It is a device to convert chemical energy into electrical energy, *i.e.*, electrical energy is produced as a result of the redox reaction.	It is a device to convert electrical energy into chemical energy, *i.e.*, electrical energy is supplied to the electrolytic solution to bring about the redox reaction.
2.	It is based upon the redox reaction which is spontaneous *i.e.*, $\Delta G = -$ve	The redox reaction is non-spontaneous and takes place only when electrical energy is supplied *i.e.*, $\Delta G = +$ve.

3. *Refer to answer 1.*

4. Representation of the galvanic cell for the given reaction is :

$$\underset{\text{Anode}}{\text{Zn} \mid \text{Zn}^{2+}_{(aq)}} \underset{\text{Salt bridge}}{\parallel} \underset{\text{Cathode}}{\text{Cu}^{2+}_{(aq)} \mid \text{Cu}}$$

5. The salt bridge allows the movement of ions from one solution to the other without mixing of the two solutions. Moreover, it helps to maintain the electrical neutrality of the solutions in the two half cells.

6. At anode : $Sn^{2+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2e^-] \times 5$

At cathode : $MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \longrightarrow$

$Mn^{2+}_{(aq)} + 4H_2O_{(l)}] \times 2$

Net cell reaction :

$2MnO^-_{4(aq)} + 5Sn^{2+}_{(aq)} + 16H^+_{(aq)} \longrightarrow$

$2Mn^{2+}_{(aq)} + 5Sn^{4+}_{(aq)} + 8H_2O_{(l)}$

$E°_{cell} = E°_{cathode} - E°_{anode} = 1.51\text{ V} - 0.15\text{ V} = 1.36\text{ V}$

Since, cell potential is positive therefore the reaction is product favoured.

7. (i) The cell reactions are :

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

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

Net reaction :

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

(ii) $E°_{cell} = E°_{right} - E°_{left} = 0.34\text{ V} - (-0.76\text{ V})$
$= 1.10\text{ V}$

(iii) Copper electrode will be positive on which reduction takes place.

8. Given : $E°_{cell} = 2.71$ V

For the reaction,

$Mg_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$

$n = 2, \Delta_r G° = ?$

Using formula, $\Delta_r G° = -nFE°_{cell}$

$\Delta_r G° = -2 \times 96500\text{ C mol}^{-1} \times 2.71\text{ V}$

or $\Delta_r G° = 523.03\text{ kJ mol}^{-1}$

9. $A_{(s)} + B^{2+}_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + B_{(s)}$

Here, $n = 2$

Using formula,

$$E°_{cell} = \frac{0.059}{n}\log K_c$$

$$E°_{cell} = \frac{0.059}{2}\log 10$$

$E°_{cell} = 0.0295$ V

10. Here $n = 2$, $E°_{cell} = 1.1$ V, $F = 96500\text{ C mol}^{-1}$

$\Delta_r G° = -nFE°_{cell}$

$\Delta_r G° = -2 \times 1.1 \times 96500 = -212300\text{ J mol}^{-1}$
$= -212.3\text{ kJ mol}^{-1}$

11. *Refer to answer 10.*

12. The electrode reaction is

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

Applying Nernst equation, we get,

$$\left[E_{Zn^{2+}/Zn} = E°_{Zn^{2+}/Zn} - \frac{0.0591}{2}\log\frac{1}{Zn^{2+}}\right]$$

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

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

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

$= -0.76 - 0.02955\ (\log 1000 - \log 95)$

$= -0.76 - 0.0295\ (3 - 1.9777) = -0.79015$ V

13. $Ni_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$, $E° = 1.05$ V

Here, $n = 2$

Using formula, $\log K_c = \frac{nE°_{cell}}{0.059}$

or $\log K_c = \frac{2 \times 1.05}{0.059} = 35.5932$

K_c = antilog 35.5932 or $K_c = 3.92 \times 10^{35}$

Again, $\Delta G° = -nFE°_{cell}$

$\Delta G° = -2 \times 96500 \times 1.05 = -202650\ J\ mol^{-1}$

$\Delta G° = -202.65\ kJ\ mol^{-1}$

14. $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Here, $n = 2$

$E°_{cell} = E°_{cathode} - E°_{anode}$

$= 0.34 - (-0.76) = 1.1$ V

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

$\Delta_r G° = -nFE°_{cell} = -2 \times 1.1 \times 96500 = -212300\ J\ mol^{-1}$

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

15. At anode : $Ni \longrightarrow Ni^{2+} + 2e^-$

At cathode : $[Ag^+ + e^- \longrightarrow Ag] \times 2$

Cell reaction : $Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$

$E°_{cell} = E°_{cathode} - E°_{anode}$

$= E°_{Ag^+/Ag} - E°_{Ni^{2+}/Ni} = 0.80\ V - (-0.25)$

$E°_{cell} = 1.05$ V

$E°_{cell} = \frac{0.0591}{n}\log K_c$

$\log K_c = \frac{E°_{cell} \times n}{0.0591} = \frac{1.05 \times 2}{0.0591}$

$\log K_c = 35.53$

K_c = antilog 35.53 = 3.38×10^{35}

$\Delta G° = -nFE° = -2 \times 96500 \times 1.05$

$= -202650\ J\ mol^{-1} = -202.65\ kJ\ mol^{-1}$

The maximum work that can be obtained from the cell is 202.65 kJ

16. At anode : $Zn \rightarrow Zn^{2+} + 2e^-$

At cathode : $2Ag^+ + 2e^- \rightarrow 2Ag$

$E°_{cell} = E°_{cathode} - E°_{anode} = E°_{Ag^+/Ag} - E°_{Zn^{2+}/Zn}$

$= 0.80 - (-0.76) = 1.56$ V

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

$= 1.56 - \frac{0.059}{2}\log\frac{0.1}{(0.01)^2} = 1.4715$ V

17. $E°_{cell} = E°_{right} - E°_{left} = -0.403 - (-0.763) = 0.36$ V

$\Delta_r G° = -nFE°_{cell} = -2 \times 96500 \times 0.36$

$= -69480\ J\ mol^{-1} = -69.48\ kJ\ mol^{-1}$

Using formula, $\log K_c = \frac{nE°_{cell}}{0.059}$

$= \frac{2 \times 0.36}{0.059} = 12.20$

K_c = antilog 12.20 = 1.58×10^{12}

18. The electrode reactions are

At anode : $Sn_{(s)} \rightarrow Sn^{2+}\ (0.004\ M) + 2e^-$

At cathode : $2H^+\ (0.02\ M) + 2e^- \rightarrow H_2\ (1\ bar)$

Net reaction :

$Sn_{(s)} + 2H^+\ (0.02\ M) \rightarrow Sn^{2+}\ (0.004\ M) + H_2\ (1\ bar)$

The Nernst equation of this cell at 25 °C

$$E_{cell} = E°_{cell} - \frac{0.0591}{2}\log\frac{[Sn^{2+}](p_{H_2})}{[H^+]^2}$$

$E°_{cell} = E°_{H^+|H_2} - E°_{Sn^{2+}|Sn}$

$= 0.000\ V - (-0.14\ V) = +0.14$ V

or, $E_{cell} = E°_{cell} - 0.0296\log\frac{0.004 \times 1}{(0.02)^2}$

$= E°_{cell} - 0.0296\log\left(\frac{0.004}{0.0004}\right)$

$= E°_{cell} - 0.0296\ (\log 10)$

$= E°_{cell} - 0.0296 \times 1 = E°_{cell} - 0.0296$

$E_{cell} = 0.14 - 0.0296 = 0.1104$ V

19. $\Delta G° = -nFE°_{cell}$

$E°_{cell} = \frac{\Delta G°}{-nF} = \frac{-43600}{-2 \times 96500} = 0.226$ V

$2AgCl_{(s)} + H_{2(g)}\ (1\ atm) \longrightarrow 2Ag_{(s)} + 2H^+(0.1\ M) + 2Cl^-(0.1\ M)$

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

$= 0.226 - \frac{0.0591}{2}\log\frac{(0.1)^2}{(1)}$

$= 0.226 - \frac{0.0591}{2}\log(10^{-2})$

$= 0.226 - \frac{0.0591}{2}\ (-2)$

$= 0.226 + 0.0591 = 0.2851$ V

20. $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left} = -0.44 - (-0.74) = 0.30\ V$

$$E_{cell} = 0.30 - \frac{0.0591}{6}\log\frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - 0.0394 = 0.26\ V$$

21. Given cell,

$2Al_{(s)} + 3Cu^{2+}(0.01\,M) \longrightarrow 2Al^{3+}(0.01\,M) + 3Cu_{(s)}$

$E_{cell} = 1.98\ V$, $E^\circ_{cell} = ?$

Using Nernst equation at 298 K

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{6}\log\frac{[Al^{3+}]^2}{[Cu^{2+}]^3}$$

$$1.98\ V = E^\circ_{cell} - \frac{0.0591}{6}\log\frac{[10^{-2}]^2}{[10^{-2}]^3}$$

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

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

$$\therefore \quad E^\circ_{cell} = 1.98 + \frac{0.0591}{6} = 1.99\ V$$

22. The cell reaction is

$Fe_{(s)} + 2H^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_{2(g)}$

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

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

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

$$= 0.44 - 0.02955 = 0.41045\ V$$

23. The cell reaction is

$Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$

$E^\circ_{cell} = 0.00 - (-0.76) = 0.76\ V$

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

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

$$= 0.76 - 0.02955 = 0.730\ V$$

24. At anode : $Ni \longrightarrow Ni^{2+} + 2e^-$

At cathode : $[Ag^+ + e^- \longrightarrow Ag] \times 2$

Cell reaction : $Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$

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

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

$E^\circ_{cell} = 1.05\ V$

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_c$$

$$\log K_c = \frac{E^\circ_{cell}\times n}{0.0591} = \frac{1.05\times 2}{0.0591}$$

$\log K_c = 35.53$

$K_c = \text{antilog } 35.53 = 3.38 \times 10^{35}$

$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.05$

$= -202650\ J\ mol^{-1}$

$= -202.65\ kJ\ mol^{-1}$

The maximum work that can be obtained = 202.65 kJ.

25. $E^\circ_{cell} = +0.80\ V - 0.77\ V = +0.03\ V$

$\Delta_r G^\circ = -nFE^\circ_{cell} = -1 \times 96500 \times 0.03$

$= -2895\ J\ mol^{-1} = -2.895\ kJ\ mol^{-1}$

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

$-2895 = -2.303 \times 8.314 \times 298 \times \log K_c$

or $\quad \log K_c = 0.5074$

$K_c = \text{Antilog } (0.5074) = 3.22$

26. The cell reaction can be represented as :

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

Given: $E^\circ_{cell} = +2.71\ V$, $T = 298\ K$

According to the Nernst equation :

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

$$= 2.71 - \frac{0.0591}{2}\log\frac{0.1}{0.01} = 2.6805\ V$$

27. $Al_2O_3\ (2Al^{3+} + 3O^{2-}) \longrightarrow 2Al + \frac{3}{2}O_2,\ n = 6e^-$

$\therefore\ \frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2,\ n = \frac{2}{3}\times 6e^- = 4e^-$

$\Delta G = 960 \times 1000 = 960000\ J$

Now, $\Delta G = -nFE^\circ_{cell}$

$$E^\circ_{cell} = -\frac{\Delta G}{nF} = \frac{-960000}{4\times 96500} = -2.487\ V$$

Minimum potential difference needed to reduce Al_2O_3 is -2.487 V.

28. $Fe_{(s)}|Fe^{2+}(0.001M)||H^+(1M)|H_{2(g)}(1bar)|Pt_{(s)}$

Reactions :

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

Cathode : $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

Cell reaction : $Fe_{(s)} + 2H^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_{2(g)}$

$n = 2.$

Using Nernst equation at 298 K

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}]\times p_{H_2}}{[H^+]^2}$$

For the given cell,

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{H^+/H_2} - E^\circ_{Fe^{2+}/Fe}$

$= 0 - (-0.44) = +0.44\text{ V}$

Given : $[Fe^{2+}] = 0.001\text{ M}; [H^+] = 1\text{ M}; P_{H_2} = 1\text{ bar}$

Putting in Nernst equation

$$E_{\text{cell}} = 0.44 - 0.0295 \log \frac{0.001\times 1}{1^2}$$

$= 0.44 - 0.0295 \log 10^{-3}$

$= 0.44 - [(0.0295) \times (-3)]$

$= 0.44 + 0.0885 = 0.53\text{ V}$

29. The cell may be represented as

$Ag_{(s)}\,|Ag^+\,(10^{-3}\text{ M})||Cu^{2+}\,(10^{-1}\text{ M})|\,Cu_{(s)}$

Using formula $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{2}\log\dfrac{[Ag^+]^2}{[Cu^{2+}]}$

$$E_{\text{cell}} = 0.46\text{ V} - 0.0295 \log \frac{(10^{-3})^2}{10^{-1}}$$

$= 0.46 - 0.0295 \log 10^{-5} = 0.46 - 0.0295\,(-5)$

$= 0.46 + 0.0295 \times 5 = 0.6075\text{ V}$

30. The cell reaction in button cell :

$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$

(i) Calculation of E°_{cell}

Reactions :

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

Cathode :

$Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow 2Ag_{(s)} + 2OH^-_{(aq)} + 2e^-$

$n = 2$

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{Ag_2O/Ag} - E^\circ_{Zn^{2+}/Zn}$

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

(ii) Calculation of $\Delta_r G^\circ$

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

$= -2 \times 96500\text{ C mol}^{-1} \times 1.56\text{ V}$

$= -301080\text{ C V mol}^{-1}$

$= -301080\text{ J mol}^{-1} = -301\text{ kJ mol}^{-1}$

31. At anode : $Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-] \times 2$

At cathode : $Ni^{2+} + 2e^- \rightarrow Ni_{(s)}] \times 3$

Cell reaction : $2Al_{(s)} + 3Ni^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Ni_{(s)}$

Applying Nernst equation to the above cell reaction,

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

Now, $E^\circ_{\text{cell}} = E^\circ_{Ni^{2+}/Ni} - E^\circ_{Al^{3+}/Al}$

$= -0.25\text{ V} - (-1.66) = 1.41\text{ V}$

$$\therefore\quad E_{\text{cell}} = 1.41\text{ V} - \frac{0.0591}{6}\log\frac{(10^{-3})^2}{(0.5)^3}$$

$$= 1.41\text{ V} - \frac{0.0591}{6}\log(8\times 10^{-6})$$

$$= 1.41\text{ V} - \frac{0.0591}{6}(-5.09)$$

$= 1.41\text{V} + 0.050\text{ V} = 1.46\text{ V}$

32. $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ and $2I^- \longrightarrow I_2 + 2e^-$

Hence, for the given cell reaction, $n = 2$

$\Delta_r G^\circ = -nFE^\circ_{\text{cell}} = -2 \times 96500 \times 0.236$

$= -45.55\text{ kJ mol}^{-1}$

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

or $\quad \log K_c = -\dfrac{\Delta_r G^\circ}{2.303RT}$

$$= -\frac{-45.55\text{ kJ mol}^{-1}}{2.303\times 8.314\times 10^{-3}\text{kJ K}^{-1}\text{mol}^{-1}\times 298\text{K}} = 7.983$$

$\therefore\quad K_c = \text{Antilog }(7.983) = 9.616 \times 10^7$

33. For half cell reaction,

$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

Given, $E^\circ_{\text{cell}} = 1.33\text{ V}, n = 6, [Cr^{3+}] = 0.2\text{ M}$

$[Cr_2O_7^{2-}] = 0.1\text{ M}, [H^+] = 1 \times 10^{-4}\text{ M}$

$$\Rightarrow\quad E_{\text{cell}} = 1.33\text{V} - \frac{0.0591}{6}\log\frac{(0.20)^2}{(0.1)\,(10^{-4})^{14}}$$

$$= 1.33\text{V} - \frac{0.0591}{6}\log(4\times 10^{55})$$

$$= 1.33\text{ V} - \frac{0.0591}{6}[\log 4 + \log 10^{55}]$$

$$= 1.33\text{ V} - \frac{0.0591}{6}[\log 4 + 55\log 10]$$

$$= 1.33\text{ V} - \frac{0.0591}{6}[0.602 + 55]$$

$= 1.33\text{ V} - 0.548\text{ V} = 0.782\text{ V}$

34. (a) Oxidation half reaction :

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

Reduction half reaction :

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

(b) $\quad E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.10\text{ V}$

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

$$\Rightarrow \quad E_{\text{cell}} = 1.10 - \frac{0.0591}{2}\log\frac{2}{0.5}$$

$$= 1.10 - \frac{0.0591}{2}\log\frac{2}{0.5}$$

$$= 1.10 - \frac{0.059}{2} \times 0.6021$$

$$= 1.10 - 0.0177 = 1.0823 \text{ V}$$

35. $\Delta G^\circ = -RT \ln K_c = -2.303\,RT \log K_c$

$\Rightarrow -212300 = -2.303 \times 8.314 \times 298 \times \log K_c$

$$\text{or} \quad \log K_c = \frac{212300}{2.303 \times 8.314 \times 298} = 37.2074$$

$K_c = \text{Antilog } 37.2074 = 1.6 \times 10^{37}$.

36. $$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 2.71 - \frac{0.0591}{2}\log\frac{0.001}{0.01} = 2.73955 \text{ V}$$

(i) If external opposing potential is less than 2.71 V then current will flow from Cu to Mg.

(ii) If external opposing potential is greater than 2.71 V then current will flow in opposite direction *i.e.* from Mg to Cu.

37. $\text{Mg}_{(s)} \,|\, \text{Mg}^{2+}(0.001\text{ M}) \,||\, \text{Cu}^{2+}(0.0001\text{ M}) \,|\, \text{Cu}_{(s)}$

Reactions :

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

Cathode : $\text{Cu}^{2+}_{(aq)} + 2e^- \longrightarrow \text{Cu}_{(s)}$

Net cell reaction : $\text{Mg}_{(s)} + \text{Cu}^{2+}_{(aq)} \longrightarrow \text{Mg}^{2+}_{(aq)} + \text{Cu}_{(s)}$

$\therefore \quad n = 2$

Using Nernst equation :

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

For the given cell

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Mg}^{2+}/\text{Mg}}$

$= 0.34 \text{ V} - (-2.37 \text{ V}) = 2.71 \text{ V}$

Given $[\text{Mg}^{2+}] = 0.001$ M, $[\text{Cu}^{2+}] = 0.0001$ M

Putting in Nernst equation at 298 K

$$E_{\text{cell}} = 2.71 \text{ V} - \frac{0.059}{2}\log\frac{0.001}{0.0001}$$

$$E_{\text{cell}} = 2.71 - 0.0295 \log 10 = 2.68 \text{ V}$$

$\Delta_r G = -nFE_{\text{cell}} = -2 \times 96500 \text{ C mol}^{-1} \times 2.68$

$= -517.240 \text{ J mol}^{-1} = -517.24 \text{ kJ mol}^{-1}$

38. **(c) :** Conductivity decreases with decrease in concentration for both weak and strong electrolytes, because the number of ions per unit volume that carry the current in a solution decreases on dilution.

39. Conductivity of CH_3COOH (weak electrolyte) decreases with dilution because the number of current carrying particles *i.e.,* ions present per cm^3 of the solution becomes less and less on dilution.

40. The limiting molar conductivity of an electrolyte is defined as its molar conductivity when the concentration of the electrolyte in the solution approaches zero.

Conductivity of an electrolyte decreases with dilution because the number of current carrying particles *i.e.,* ions present per cm^3 of the solution becomes less and less on dilution.

41. **Kohlrausch's law of independent migration of ions :** It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

If $\lambda^\circ_{\text{Na}^+}$ and $\lambda^\circ_{\text{Cl}^-}$ are limiting molar conductivities of the sodium and chloride ions respectively then the limiting molar conductivity for sodium chloride is given by

$$\Lambda^\circ_{m\,(\text{NaCl})} = \lambda^\circ_{\text{Na}^+} \lambda^\circ_{\text{Cl}^-}$$

Kohlrausch's law helps in the calculation of degree of dissociation of weak electrolyte like acetic acid. The degree of dissociation α is given by

$$\alpha = \frac{\Lambda_m}{\overset{\circ}{\Lambda}_m}$$

where, Λ_m is the molar conductivity and Λ°_m is the limiting molar conductivity.

42. **Molar Conductivity :** Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from one mole of the electrolyte dissolved in V cm^3 of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole solution is contained between them.

$$\Lambda_m = \kappa V$$

It units is $S\text{ cm}^2\text{mol}^{-1}$

43. *Refer to answer 41.*

44. *Refer to answer 40.*

45. *Refer to answer 41.*

46. $$\Lambda_m = \frac{\kappa \times 1000}{M} \text{ in CGS units}$$

$$\Lambda_m = \frac{\kappa \times 10^{-3}}{M} \text{ in SI units}$$

where, κ is the conductivity, M is the molar concentration and Λ_m is molar conductivity.

47. $$\kappa = \frac{1}{R} \times \frac{l}{a}$$

where, κ is the conductivity R is resistance and l/a is the cell constant.

48. In aqueous solution, CuCl2 ionises into
$CuCl_2 \longrightarrow Cu^{2+} + 2Cl^-$
At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$
At anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$
At the cathode, the copper ion will be deposited because it has a higher reduction potential than the water molecule.
At the anode, the lower electrode potential value will be preferred but due to over potential of oxygen, chloride ion gets oxidized at the anode.

49. (i) Electrolyte A is a strong electrolyte while electrolyte B is a weak electrolyte.
(ii) For electrolyte A, the plot becomes linear near high dilution and thus can be extrapolated to zero concentration to get the molar conductivity at infinite dilution.
For weak electrolyte B, Λ_m increases steeply on dilution and extrapolation to zero concentration is not possible. Hence, molar conductivity at infinite dilution cannot be determined.

50. Degree of dissociation $(\alpha) = \dfrac{\Lambda_m}{\Lambda_m^\circ}$

$$\alpha = \frac{39.05 \text{ S cm}^2\text{mol}^{-1}}{(349.68 + 40.9) \text{ S cm}^2\text{ mol}^{-1}} = 0.1$$

51. The fraction of the total number of molecules present in solution as ions is known as degree of dissociation.
Molar conductivity $(\lambda_m) = \alpha\lambda^\circ_m$
where λ°_m is the molar conductivity at infinite dilution.

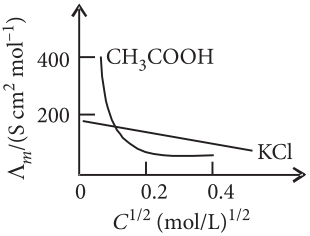
52. The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by κ (kappa).

$$\kappa = \frac{1}{\rho} \quad \text{or} \quad \kappa = G \times \frac{l}{a}$$

Hence, conductivity of a solution is defined as the conductance of a conductor of 1 cm length and having 1 sq. cm as the area of cross section. Alternatively, it may be defined as conductance of one centimetre cube of the solution of the electrolyte. Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from 1 mole of the electrolyte dissolved in V cm^3 of the solution. It is represented by Λ_m.

$$\Lambda_m = \kappa V$$

Variation of conductivity and molar conductivity with concentration : Conductivity always decreases with decrease in concentration, for both weak and strong electrolytes. Because the number of ions per unit volume that carry the current in a solution decreases on dilution.



Molar conductivity *vs* $C^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions

Molar conductivity increases with decrease in concentration. Because the total volume, V of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume.

53. *Refer to answers 41 and 40.*

54. *Refer to answer 52.*

Variation of conductivity and molar conductivity with temperature : Both increase with increase in temperature as degree of ionisation increases.

55. Conductivity $(\kappa) = \dfrac{1}{R} \times G = \dfrac{1}{200} \times 1$
$= 5 \times 10^{-3}\ \Omega^{-1}\text{ cm}^{-1}$

Molar conductivity (Λ_m)

$$= \frac{\kappa\times1000}{M} = \frac{5\times10^{-3}\times1000}{0.01}$$

$$= 500\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

56. Here, $\kappa = 0.025\ \text{S cm}^{-1}$, Molarity = 0.20 M

Molar conductivity $\Lambda_m^c = \frac{\kappa\times1000}{\text{Molarity}}$

$$= \frac{0.025\times1000}{0.20} = 125\ \text{S cm}^2\ \text{mol}^{-1}$$

57. $C = 0.001$ M, $\kappa = 4\times10^{-5}\ \text{S cm}^{-1}$,

$\Lambda_m^{\infty} = 390\ \text{S cm}^2/\text{mol}$

$$\Lambda_m^c = \frac{\kappa\times1000}{C}$$

Substituting the values,

$$\Lambda_m^c = \frac{4\times10^{-5}\times1000}{0.001} = 40\ \text{S cm}^2/\text{mol}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^{\infty}} = \frac{40}{390} = 0.10256 \simeq 0.103$$

$$\begin{array}{cccc} \text{CH}_3\text{COOH} & \rightleftharpoons & \text{CH}_3\text{COO}^- & + \ \text{H}^+ \\ c & & 0 & 0 \\ c(1-\alpha) & & c\alpha & c\alpha \end{array}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{c\alpha\cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$K_a = \frac{0.001(0.103)^2}{(1-0.103)} = \frac{1.061\times10^{-5}}{0.897} = 1.18\times10^{-5}$$

58. *Refer to answers 47 and 46.*

59. (i) Silver wire at 30°C allows greater conduction of electricity than 60°C because with increase in temperature metallic conduction decreases due to vibration of kernels.

(ii) 0.1 M acetic acid solution allows greater conduction of electricity because with dilution degree of dissociation increases and hence, number of ions increases.

(iii) KCl solution at 50°C will have greater conductance. This is because ionic mobilities increases with increase in temperature.

60. Given : $a = 0.625\ \text{cm}^2$, $l = 50$ cm

$R = 5\times10^3$ ohm, M = 0.05 M

Resistivity, $\rho = R\times\frac{a}{l} = 5\times10^3\times\frac{0.625}{50}$ ohm cm

$= 62.5$ ohm cm

Conductivity, $\kappa = \frac{1}{\rho} = \frac{1}{62.5} = 0.016\ \text{ohm}^{-1}\ \text{cm}^{-1}$

Molar conductivity, $\Lambda_m = \frac{\kappa\times1000}{M}$

$$= \frac{0.016\times1000}{0.05} = 320\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

61. Using formula, $\Lambda_m^c = \frac{\kappa\times1000}{C}$

Given $\kappa = 3.905\times10^{-5}\ \text{S cm}^{-1}$

$C = 0.001\ \text{mol L}^{-1}$

$$\therefore\ \Lambda_m^c = \frac{3.905\times10^{-5}\times1000}{0.001} = 39.05\ \text{S cm}^2\ \text{mol}^{-1}$$

The degree of dissociation,

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{39.05}{390.5} = 0.1$$

$[\because \Lambda_m^\circ = 349.6 + 40.9 = 390.5\ \text{S cm}^2\ \text{mol}^{-1}]$

62. Given : Conductivity, $\kappa = 0.0248\ \text{S cm}^{-1}$

Molarity, $C = 0.20\ \text{M} = 0.20\ \text{mol L}^{-1}$

Using formula, $\Lambda_m^c = \frac{1000\times\kappa}{C}$

$$\Lambda_m^c = \frac{1000\times0.0248}{0.20}$$

$$= 124\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{124}{73.5+76.5} = 0.82$$

63. Resistance of 0.1 M KCl solution $R = 100\ \Omega$

Conductivity $\kappa = 1.29\ \text{S m}^{-1}$

Cell constant $G^* = \kappa\times R = 1.29\times100 = 129\ \text{m}^{-1}$

Resistance of 0.02 M KCl solution, $R = 520\ \Omega$

$$\text{Conductivity, } \kappa = \frac{\text{cell constant}}{R} = \frac{129\ \text{m}^{-1}}{520\ \Omega}$$

$$= 0.248\ \text{S m}^{-1}$$

Concentration, $C = 0.02\ \text{mol L}^{-1}$

$= 1000\times0.02\ \text{mol m}^{-3} = 20\ \text{mol m}^{-3}$

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa}{C} = \frac{0.248\ \text{S m}^{-1}}{20\ \text{mol m}^{-3}}$$

$$= 0.0124\ \text{S m}^2\ \text{mol}^{-1}$$

64. $\Lambda^\circ_m\ \text{Al}_2(\text{SO}_4)_3 = 2\lambda^\circ_m\text{Al}^{3+} + 3\lambda^\circ_m\text{SO}_4^{2-}$

$\Rightarrow\ 858 = 2\lambda^\circ_m\text{Al}^{3+} + 3\times160$

$$\Rightarrow\ \lambda^\circ_m\text{Al}^{3+} = \frac{858-480}{2} = 189\ \text{S cm}^2\ \text{mol}^{-1}$$

65. Given : Diameter = 1 cm, length = 50 cm

$R = 5.5\times10^3$ ohm, $M = 0.05$ M

$\rho = ?\ \ \kappa = ?\ \ \Lambda_m = ?$

Area of the column,

$$a = \pi r^2 = 3.14 \times \left(\frac{1}{2}\ \text{cm}\right)^2 = \frac{3.14}{4}\ \text{cm}^2$$

Resistivity,

$$\rho = R \cdot \frac{a}{l} = 5.5 \times 10^3\ \text{ohm} \times \frac{3.14\ \text{cm}^2}{4 \times 50\ \text{cm}}$$

$$= 86.35\ \text{ohm cm}$$

Again, conductivity, $\kappa = \frac{1}{\rho}$

$$= \frac{1}{86.35} = 1.158 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

and molar conductivity, $\Lambda_m = \kappa \cdot \frac{10^3}{M}$

$$= 1.158 \times 10^{-2} \times \frac{10^3}{5 \times 10^{-2}}$$

$= 231.6\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

66. $\kappa = 1.29 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1}$

$\kappa = \frac{1}{R} \times$ Cell constant

$\Rightarrow$ Cell constant $= \kappa \times R$

$= 1.29\ \Omega^{-1}\ \text{m}^{-1} \times 85\ \Omega = 109.65\ \text{m}^{-1}$

For second solution,

$\kappa = \frac{1}{R} \times$ Cell constant $= \frac{1}{96\ \Omega} \times 109.65\ \text{m}^{-1}$

$= 1.142\ \Omega^{-1}\text{m}^{-1}$

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.142\ \Omega^{-1}\text{m}^{-1} \times 1000\ \text{cm}^3}{0.052\ \text{mol}}$$

$$\Lambda_m = \frac{1.142\ \Omega^{-1}\text{cm}^{-1} \times 10^{-2} \times 1000\ \text{cm}^3}{0.052\ \text{mol}}$$

$= 219.61\ \text{S cm}^2\ \text{mol}^{-1}$

67. According to Kohlrausch's law,

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

Degree of dissociation, $\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$

$$= \frac{11.7\ \text{S cm}^2\text{mol}^{-1}}{(49.9 + 349.1)\ \text{S cm}^2\text{mol}^{-1}} = \frac{11.7}{399} = 3 \times 10^{-2}$$

68. (a) *Refer to answers 52.*

(b) Here, conductivity (κ) $= 0.146 \times 10^{-3}\ \text{S cm}^{-1}$, resistance ($R$) $= 1500\ \Omega$

Cell constant $= \frac{\text{Conductivity}}{\text{Conductance}}$

= Conductivity × Resistance

$= \kappa \times R \qquad \left[\because \text{conductance} = \frac{1}{\text{resistance}}\right]$

$= 0.146 \times 10^{-3} \times 1500 = 0.219\ \text{cm}^{-1}$

69. 193000 Coulomb

70. The reaction at anode with lower value of E° is preferred *i.e.*, O_2 gas should be liberated but on account of overpotential of oxygen reaction at anode, preferred reaction is

$$Cl^-_{(aq)} \rightarrow \frac{1}{2} Cl_{2(g)} + e^-$$

i.e., Cl_2 gas is liberated at anode in the electrolysis of aq. NaCl.

71. The species that get reduced at cathode is the one having higher value of standard reduction potential. Hence, the reaction that will occur at cathode is $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$.

72. $\underset{1\ \text{mol}}{Zn^{2+}_{(aq)}} + \underset{2\ \text{mol}}{2e^-} \longrightarrow Zn_{(s)}$

One mole of Zn^{2+} requires 2 moles of electrons for reduction *i.e.*

$Q = 2 \times F = 2 \times 96500 = 193000\ \text{C}$

73. The species that get reduced at cathode is the one which have higher value of standard reduction potential. Hence, the reaction that will occur at cathode is

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

74. Faraday's first law of electrolysis : During electrolysis the amount of any substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte *i.e.*,

$w \propto Q$ or $w \propto I \times t \qquad [\because Q = I \times t]$

$w = Z \times I \times t$

where, Z is a constant of proportionality known as electrochemical equivalent of the substance deposited.

75. Y is a weak electrolyte. As the concentration of the weak electrolyte is reduced, more of it ionises. Hence a weak electrolyte shows a very large increase in concentration with dilution. A strong electrolyte shows only small increases in conductance with dilution, because a strong electrolyte is completely dissociated in solution so the number of ions remain constant.

76. Given : $I = 2$ A, $t = 15$ min $= 15 \times 60$ s $= 900$ s

$w = ?$

$Q = I \times t = 2 \times 900 = 1800$ C

Reaction for deposition of Ag is as follows :

$$\begin{array}{ccccc} Ag^+ & + & 1e^- & \longrightarrow & Ag \\ & & 1\ F & & 1\ mol \\ & & 1 \times 96500\ C & & 108\ g \end{array}$$

Thus, 1 × 96500 C of electricity is required to deposit 108 g of Ag.

∴ 1800 C of electricity would deposit

$$= \frac{108 \times 1800}{1 \times 96500} = 2.014 \text{ g of Ag}$$

77. *Refer to answers 74.*

The electrode reaction is $Cu^{2+} + 2e^- \rightarrow Cu$

∴ Quantity of charge required for reduction of 1 mol of Cu^{2+} = 2F

$= 2 \times 96500 = 193000$ C

78. Given : Current $I = 5$ A; $t = 20 \times 60$ s, $w = ?$

$Q = I \times t = 5 \times 20 \times 60 = 6000$ C

Reaction for deposition of Ni,

$$\begin{array}{ccccc} Ni^{2+} & + & 2e^- & \longrightarrow & Ni \\ & & 2\ mol & & 1\ mol \\ & & 2 \times 96500\ C & & 58.7\ g \end{array}$$

Thus, 2 × 96500 C of electricity produces 58.7 g Ni

∴ 6000 C of electricity would produce

$$= \frac{58.7 \times 6000}{2 \times 96500} = 1.825 \text{ g}$$

79. (i) At the cathode the following reduction reactions compete to take place at the cathode.

$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$; $E° = 0.80$ V

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

The reaction with a higher value of $E°$ takes place at the cathode. Therefore, the deposition of silver will take place at the cathode.

Since, Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or NO_3^- ions can be oxidized at the anode. But OH^- ions having a lower discharge potential get preference and decompose to liberate O_2.

$OH^- \longrightarrow OH + e^-$

$4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

(ii) At the cathode, the following reduction reaction occurs to produce H_2 gas.

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2} H_{2(g)}$

At the anode, the following processes are possible :

$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$; $E° = +1.23$ V ...(1)

$2SO^{2-}_{4(aq)} \longrightarrow S_2O^{2-}_{8(aq)} + 2e^-$; $E° = +1.96$ V ...(2)

For dilute sulphuric acid, reaction (1) is preferred to produce O_2 gas but for concentrated sulphuric acid, (2) occurs.

80. Reaction for production of Ca from molten $CaCl_2$:

$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$

$$\begin{array}{ccc} Ca^{2+} + 2e^- & \longrightarrow & Ca \\ 2F & & 40\ g \end{array}$$

Electricity required to produce 40 g = 2 F

∴ Electricity required to produce 20 g

$= 0.5 \times 2$ F $= 1$ F

81. Calculation of mass of Ag deposited

The electrode reaction is $Ag^+ + e^- \longrightarrow Ag$

The quantity of electricity passed

= Current × Time

= 0.5 (amp) × 2 × 60 × 60 (sec) = 3600 C

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

3600 C of electricity will deposit Ag

$$= \frac{108}{96500} \times 3600 = 4.03 \text{ g}$$

Calculation of thickness :

Let the thickness of deposit be x cm

Mass=volume×density=Area×thickness×density

[∵ volume = area × thickness]

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

∴ $x = \dfrac{4.03}{900 \times 10.5}$ cm $= 4.26 \times 10^{-4}$ cm

82. The given reaction is

$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

one mole $Cr_2O_7^{2-}$ requires 6 mol of electrons for reduction. Hence, quantity of electricity required $= 6 \text{ mol} \times 96500 \text{ C mol}^{-1} = 5.79 \times 10^5$ coulomb

83. Quantity of electricity passed

$Q = I \times t = 2.0$ A $\times 3 \times 60 \times 60$ s $= 21600$ C

$$\begin{array}{ccc} Hg^{2+} + 2e^- & \longrightarrow & Hg \\ 2\ F & & 1\ mol \end{array}$$

2 × 96500 C electricity produces 1 mole Hg

∴ 21600 C will produce $= \dfrac{21600}{2 \times 96500}$

$= 0.112$ mole of Hg

84. According to Faraday's first law of electrolysis,

mass of substance deposited ∝ quantity of electricity passed

$$\Rightarrow \quad W = ZQ = \frac{E}{F} \times Q \Rightarrow \quad 2.8 = \frac{28}{96500} \times Q$$

$$\Rightarrow \quad Q = \frac{2.8 \times 96500}{28} = 9650\ C$$

$$\text{Now } Q = It \quad \Rightarrow \quad t = \frac{Q}{I} = \frac{9650}{2} = 4825\ \text{s}$$

According to Faraday's second law of electrolysis,

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

$$\Rightarrow \quad \frac{2.8}{\text{Mass of Zn deposited}} = \frac{28}{32.65}$$

$$\Rightarrow \quad \text{Mass of Zn deposited} = \frac{2.8}{28} \times 32.65$$

$$= 3.265\ \text{g}$$

85. Charge = 24,000 coulombs

According to reaction,

$Cr^{6+} + 6e^- \rightarrow Cr_{(s)}$

We require 6F or 6 × 96500 C to deposit 1 mole or 52 g of Cr

For 24,000 C, the mass of Cr deposited

$$= \frac{52 \times 24{,}000}{6 \times 96500} = 2.15\ \text{g}$$

According to Faraday's second law of electrolysis,

$$\frac{w_1}{w_2} = \frac{Q_1}{Q_2} \quad \text{or} \quad \frac{2.15}{1.5} = \frac{24{,}000}{12.5 \times t}$$

$$t = \frac{24{,}000 \times 1.5}{12.5 \times 2.15} = 1340\ \text{s}$$

86. *Refer to answer 32.*

(b) Given, $I = 0.5$ A, $t = 2$ hrs.

Number of electrons = ?

Total charge $(Q) = I \times t$

$= 0.5 \times 2 \times 60 \times 60 = 3600$ C

$$\therefore \quad \text{Number of electrons} = \frac{\text{Total charge}}{\text{Charge of one electron}}$$

$$= \frac{3600}{1.6 \times 10^{-19}}$$

$= 2.25 \times 10^{22}$ electrons.

87. **Secondary batteries :** The batteries which can be recharged again and again are called as secondary batteries. *e.g.*, lead storage battery.

88. The mercury cell is generally used in hearing aids.

Reaction at cathode :

$$HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^-$$

Reaction at anode :

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

89. The cell which is generally used in inverters is secondary cell *i.e.*, lead storage battery.

At cathode : $PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

At anode : $Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$

90. Mercury cell is generally used in transistors.

At cathode : $HgO + H_2O + 2e^- \longrightarrow Hg + 2OH^-$

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

91. (i) Mercury cell is used for low current devices like watches and hearing aids.

(ii) The hydrogen oxygen fuel cell was used in Apollo space programme.

(iii) Lead storage battery is used in automobiles and inverters.

(iv) Dry cell

92. Mercury cell is a primary battery. Hence, it can be used only once and cannot be recharged.

Advantage : The cell potential remains constant during its life time. Hence, it is useful for devices requiring constant current *e.g.*, hearing aids and watches.

93. Lead storage battery is a secondary cell.

Cell reactions during operation

At anode : $Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

At cathode :

$$PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$

Overall reaction :

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

94. The lead storage battery is most important secondary cell. The cell reactions when the battery is in use.

At anode:

$$Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$$

At cathode :

$$PbO_{2(s)} + SO^{2-}_{4(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$

The overall cell reaction is

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

Following reaction takes place during recharging

At cathode : $PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO^{2-}_{4(aq)}$

At anode : $PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow PbO_{2(s)} + SO^{2-}_{4\,(aq)} + 4H^+_{(aq)} + 2e^-$

Net reaction : $2PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$

95. **Mercury cell :** It is a miniature cell which finds a frequent use these days to supply energy for watches, video cameras, hearing aids and other compact devices. In mercury cell the anode is zinc-mercury amalgam, and the cathode is a paste of mercury (II) oxide and carbon, electrolyte is a moist paste of KOH - ZnO.

The cell reactions are as follows :

Anode :

$Zn(Hg) + 2OH^- \longrightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$

(Amalgam)

Cathode : $HgO_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow Hg_{(l)} + 2OH^-$

Net reaction :

$Zn(Hg) + HgO_{(s)} \longrightarrow ZnO_{(s)} + Hg_{(l)}$

The cell potential remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its use.

96. *Refer to answer 91(ii).*

97. Those galvanic cells which give us direct electrical energy by the combustion of fuels like hydrogen, methane, methanol etc. are called fuel cells.

98. The two advantages of fuel cells are :

(i) They produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%.

(ii) They are pollution free.

99. *Refer to answer 97 and 98.*

100. (i) It is pollution free.

(ii) It has high efficiency of 70 - 75% and its rate can be controlled.

101. Fuel cells : *Refer to answer 97.*

The reactions taking place in hydrogen - oxygen fuel cell :

At cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

At anode : $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$

Net reaction : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

102. *Refer to answer 101.*

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

104. According to electrochemical theory of rusting the impure iron surface behaves like small electrochemical cell. In this any point of iron acts as anode and other iron surface acts as cathode. Moisture having dissolved CO_2 or O_2 acts as an electrolyte. The reactions are given below.

At anode :

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

At cathode :

$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O;\ E^\circ_{H^+/O_2/H_2O} = 1.23\text{ V}$$

Overall reaction :

$$Fe + 2H^+ + \frac{1}{2}O_2 \rightarrow Fe^{2+} + H_2O;\ E^\circ_{cell} = 1.67\text{ V}$$

The Fe^{2+} ions are further oxidised by atmospheric oxygen to Fe^{3+} ions, which form hydrated ferric oxide (rust).

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+$$

$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 \cdot xH_2O$ (Rust)

105. Corrosion is the process of slowly eating away of the metal due to attack of the atmospheric gases on the surface of the metal resulting into the formation of compounds such as oxides, sulphides, carbonates, etc. The corrosion of iron is called rusting.

Electrochemical theory of rusting of iron : *Refer to answer 104.*