03

Electrochemistry

3.1 Electrochemical Cells
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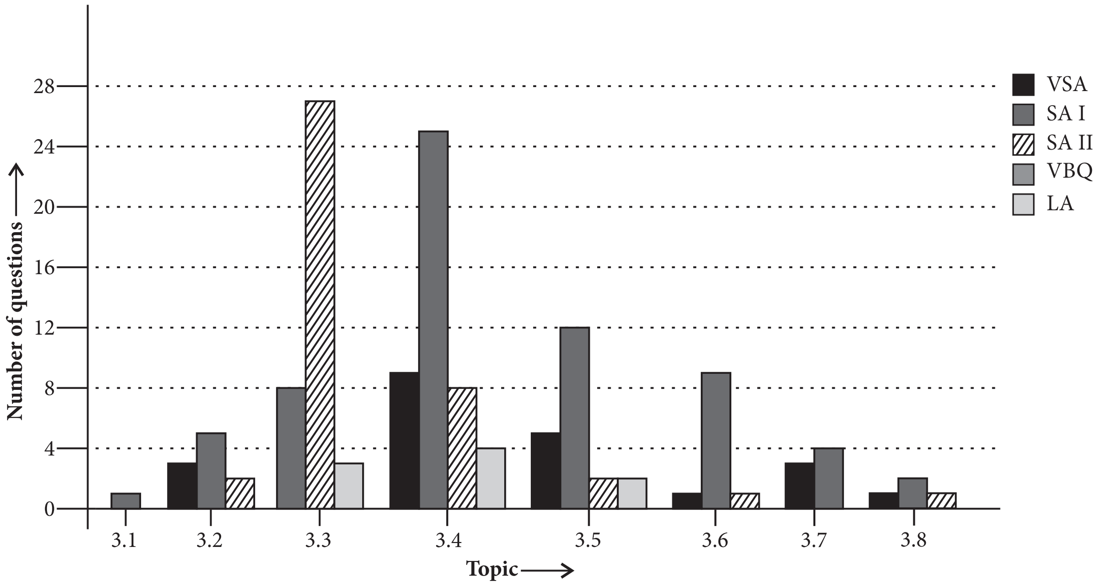
Topicwise Analysis of Last 10 Years' CBSE Board Questions



- Maximum total weightage is of *Nernst Equation.*
- Maximum VSA and SA I type questions were asked from *Conductance of Electrolytic Solutions*.
- Maximum SA II 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.*, $\Delta G = -ve$	2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied. *i.e.*, $\Delta G = +ve$
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,
$M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$;

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

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

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

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

Applications of Nernst equation :

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

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

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

- **To calculate equilibrium constant :**
  At equilibrium, $E_{\text{cell}} = 0$

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

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 :

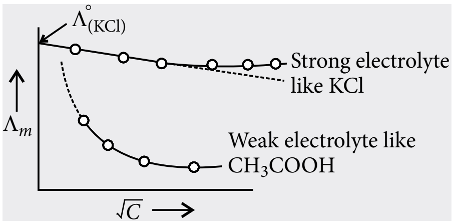
Property	Formula	Units	Effect of dilution
Conductance (G)	$\frac{1}{R} = \frac{a}{\rho l} = \frac{\kappa a}{l}$	Ohm^{-1} (Ω^{-1})/Siemens (S)	Increases as larger number of ions are produced.
Specific conductance (κ) or conductivity	$\frac{1}{\rho}$ or $G\frac{l}{a}$	Ohm^{-1} cm^{-1}/S m^{-1}	Decreases 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^c decreases linearly with $\sqrt{C}$, when $C = 0$, $\Lambda_m^c = \Lambda_m^\circ$ 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^c_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, inter-ionic 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 no. of cations and anions respectively in one formula unit of the electrolyte.

Applications of Kohlrausch's law :

- **Calculation of molar conductivity of weak electrolytes :**

$$\Lambda_m^\circ(CH_3COOH) = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$

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

$$= \Lambda_m^\circ(HCl) + \Lambda_m^\circ(CH_3COONa) - \Lambda_m^\circ(NaCl)$$

- **Calculation of degree of dissociation :**

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

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

- **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

SA I (2 marks)

1. Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell? *(2/5, AI 2016)*

3.2 Galvanic Cells

VSA (1 mark)

2. 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)

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

SA I (2 marks)

4. On the basis of standard electrode potential values stated for acid solutions, predict whether Ti^{4+} species may be used to oxidise Fe^{II} to Fe^{III}.
Reactions :
$Ti^{4+} + e^- \rightarrow Ti^{3+}$; + 0.01
$Fe^{3+} + e^- \rightarrow Fe^{2+}$; + 0.77 *(AI 2007)*

5. Two half-reactions of an electrochemical cell are given below :
$MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}, E^\circ = +1.51V$
$Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^-,\ E^\circ = +0.15$ 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, AI 2010, 2009)

6. Given that the standard electrode potential (E°) of metals are :
$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V,
$Cu^{2+}/Cu = 0.34$ V,
$Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$ V,
$Fe^{2+}/Fe = -0.44$ V.
Arrange these metals in an increasing order of their reducing power *(AI 2010)*

7. Formulate the galvanic cell in which the following reaction takes place :
$Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$
State :
(i) Which one of its electrodes is negatively charged.
(ii) The reaction taking place at each of its electrode.
(iii) The carriers of current within this cell.
(Delhi 2008)

SA II (3 marks)

8. 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)

9. Depict the galvanic cell in which the reaction $Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$ takes place. Further show :
(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
(iii) Individual reaction at each electrode.
(Delhi 2010C)

3.3 Nernst Equation

SA I (2 marks)

10. Calculate $\Delta_r G^\circ$ for the reaction :
$Mg_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$
Given $E^\circ_{cell} = +2.71$ V, 1 F = 96500 C mol^{-1}
(2/3,AI 2014)

11. Equilibrium constant (K_c) for the given cell reaction is 10. Calculate E°_{cell}.
$A_{(s)} + B^{2+}_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + B_{(s)}$
(2/3,Foreign 2014)

12. The standard electrode potential (E°) for Daniell cell is +1.1 V. Calculate the ΔG° for the reaction.
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
(1 F = 96500 C mol^{-1}) *(AI 2013)*

13. 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)*

14. 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.
[$E^\circ_{Zn^{2+}/Zn} = -\ 0.76$ V] *(Delhi 2012C)*

15. Determine the value of equilibrium constant (K_c) and ΔG° for the following reactions :
$Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$, $E^\circ = 1.05$ V
(1 F = 96500 C mol^{-1})
(Delhi 2011, Foreign 2011)

16. Calculate the emf for the given cell at 25° C :
$Cr|Cr^{3+}$ (0.1 M) || Fe^{2+} (0.01 M)| Fe
Given :

$$E^\circ_{Cr^{3+}/Cr} = -0.74\ \text{V},\ E^\circ_{Fe^{2+}/Fe} = -0.44\text{V}$$

(2/5, Delhi 2009C)

SA II (3 marks)

17. 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 : $E^\circ_{(Cr^{3+}|Cr)} = -0.74$ V, $E^\circ_{(Fe^{2+}|Fe)} = -0.44$ V
(Delhi 2016)

18. 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)*

19. Calculate emf of the following cell at 25°C:
$Fe|Fe^{2+}(0.001\ M)||H^+(0.01\ M)|H_{2(g)}(1\ \text{bar})|Pt_{(s)}$
$E^\circ(Fe^{2+}|Fe) = -0.44$ V, $E^\circ(H^+|H_2) = 0.00$ V
(Delhi 2015)

20. Calculate the emf of the following cell at 25°C
$Zn|Zn^{2+}$ (0.001 M) || H^+(0.01M)| $H_{2(g)}$ (1 bar) | $Pt_{(s)}$

$$E^\circ_{(Zn^{2+}/Zn)} = -\ 0.76\ \text{V},\ E^\circ_{(H^+/H_2)} = 0.00\ \text{V}$$

(Foreign 2015)

21. 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?

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

(3/5, Delhi 2015C)

22. 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 $\Delta_r G^\circ$ and equilibrium constant of the reaction also,

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

(3/5, Delhi 2015C)

23. Calculate the emf of following cell at 298 K :
$Mg_{(s)}\ |\ Mg^{2+}(0.1\ M)\ ||\ Cu^{2+}(0.01\ M)|Cu_{(s)}$
[Given : $E^\circ_{cell} = +\ 2.71$ V, 1 F = 96500 C mol^{-1}]
(3/5, Delhi 2014)

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

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

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

25. 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 $E^\circ_{cell} = +\ 0.44$ V) *(Delhi 2013)*

26. Calculate the emf of the following cell at 25°C :
$Ag_{(s)}|Ag^+(10^{-3}\ M)||Cu^{2+}\ (10^{-1}\ M)|Cu_{(s)}$
Given : $E^\circ_{cell} = +\ 0.46$ V and $\log 10^n = n$.
(AI 2013)

27. 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 ΔG° for the reaction.
(Given : $E^\circ_{Ag^+/Ag} = +\ 0.80$ V, $E^\circ_{Zn^{2+}/Zn} = -\ 0.76$ V)
(3/5, Delhi 2012)

28. 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.
$E^\circ_{Ni^{2+}/Ni} = -\ 0.25$ V and $E^\circ_{Al^{3+}/Al} = -\ 1.66$ V.
($\log 8 \times 10^{-6} = -\ 5.09$) *(3/5, AI 2012, 2011, 3/5, Foreign 2011, 3/5, Delhi 2009)*

29. 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)

30. 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)*

31. For the cell
$Zn_{(s)} \mid Zn^{2+}$ (2 M) || Cu^{2+} (0.5 M) | $Cu_{(s)}$
(a) Write equation for each half-reaction.
(b) Calculate the cell potential at 25°C
Given :

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

(Delhi 2011C)

32. Calculate the equilibrium constant, *K* for the reaction at 298 K,
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightleftharpoons Zn^{2+}_{(aq)} + Cu_{(s)}$
Given : $\Delta G^\circ = -\ 212.300\ kJ\ mol^{-1}$

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

(AI 2011C)

33. A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.
Given :

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

(3/5, Delhi 2010, AI 2009)

34. A voltaic cell is set up at 25° with the following half cells :
Ag^+(0.001 M) | Ag and Cu^{2+} (0.10 M) | Cu
What would be the voltage of this cell?
(E°_{cell} = 0.46 V) *(AI 2009)*

35. 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)
Calculate the cell voltage

$$[E^\circ_{Ni^{2+}|Ni} = -0.25\ V,\ E^\circ_{Al^{3+}|Al} = -\ 1.66\ V]$$

(3/5, Delhi 2009)

36. Calculate the equilibrium constant for the reaction
$Fe_{(s)} + Cd^{2+}_{(aq)} \rightleftharpoons Fe^{2+}_{(aq)} + Cd_{(s)}$
Given :

$$[E^\circ_{Cd^{2+}|Cd} = -\ 0.40\ V,\ E^\circ_{Fe^{2+}|Fe} = -\ 0.44\ V]$$

(3/5, Delhi 2009, 2009C, 3/5, AI 2009)

37. One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. Its other half-cell consists of a zinc electrode dipping in 1.0 M solution of $Zn(NO_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver nitrate solution used.

$$[E^\circ_{Zn^{2+}|Zn} = -\ 0.76\ V,\ E^\circ_{Ag^+|Ag} = +\ 0.80\ V]$$

(3/5, Delhi 2009)

38. Calculate the standard cell potential of a galvanic cell in which the following reaction takes place :
$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Cd_{(s)}$
Calculate $\Delta_r G^\circ$ and equilibrium constant, *K* of the above reaction at 25°C.
Given :

$$E^\circ_{Cr^{3+}/Cr} = -\ 0.74\ V,\ E^\circ_{Fe^{2+}/Fe} = -\ 0.44\ V$$

(F = 96,500 C mol^{-1}) *(Delhi 2008C)*

39. (i) Formulate the electrochemical cell representing the reaction ;
$2Cr_{(s)} + 3Fe^{2+}_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 3Fe_{(s)}$
(ii) Calculate E°_{cell}.
(iii) Calculate E_{cell} at 25°C if
$[Cr^{3+}]$ = 0.1 M and $[Fe^{2+}]$ = 0.01 M
Given :

$$E^\circ_{Cr^{3+}/Cr} = -\ 0.74\ V,\ E^\circ_{Fe^{2+}/Fe} = -\ 0.44\ V$$

(3/5, AI 2008C)

LA (5 marks)

40. Calculate e.m.f and ΔG for the following cell
$Mg_{(s)} \mid Mg^{2+}$ (0.001 M) || Cu^{2+} (0.0001 M) | $Cu_{(s)}$

$$E^\circ_{(Mg^{2+}/Mg)} = -2 \cdot 37\ V,\ E^\circ_{(Cu^{2+}/Cu)} = +0.34\ V$$

(AI 2015)

41. Calculate the standard electrode potential of Ni^{2+}/Ni electrode if emf of the cell

$Ni_{(s)}|Ni^{2+}(0.01\,M)||Cu^{2+}(0.1M)|Cu_{(s)}$ is 0.059 V.

[Given : $E^\circ_{Cu^{2+}/Cu} = +0.34$ V] *(Delhi 2009C)*

42. Calculate the cell emf and $\Delta_r G^\circ$ for the cell reaction at 25°C

$Zn_{(s)} \mid Zn^{2+}$ (0.1 M) || Cd^{2+} (0.01 M)| $Cd_{(s)}$

Given :

$E^\circ_{Zn^{2+}/Zn} = -0.763$ V, $E^\circ_{Cd^{2+}/Cd} = -0.403$ V

1 F = 96,500 C mol^{-1}, $R = 8.314$ J K^{-1} mol^{-1}

(AI 2009C)

3.4 Conductance of Electrolytic Solutions

VSA (1 mark)

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

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

45. Define the following term :

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

46. Define the following term :

Kohlrausch's law of independent migration of ions. *(1/5, Delhi 2015C)*

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

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

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

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

51. Express the relation between the conductivity and the molar conductivity of a solution. *(AI 2008)*

SA I (2 marks)

52. 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)*

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

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

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

56. 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)*

57. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with change in temperature. *(AI 2014C)*

58. The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity. *(Delhi 2013, 2008, AI 2007)*

59. 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)*

60. 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, 2010, 2/5,Delhi 2009)*

61. The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution. *(AI 2012, 2010C)*

62. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}? *(Delhi 2010C, 2009C, 2008, 2007)*

63. Define molar conductivity of a substance and describe how for weak and strong electrolytes, molar conductivity changes with concentration of solute. How is such change explained?

(2/5, Delhi 2009)

64. Define the term molar conductivity. How is it related to conductivity of the related solution?

(2/5, Delhi 2009)

65. State Kohlrausch's law of independent migration of ions. How can the degree of dissociation of acetic acid in a solution be calculated from its molar conductivity data? *(2/5, AI 2008C)*

66. Explain with examples the terms weak and strong electrolytes. *(Delhi 2007)*

SA II (3 marks)

67. 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)

68. 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)*

69. 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)*

70. 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)

71. 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)

72. 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)

73. 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)*

74. The resistance of a conductivity cell when filled with 0.05 M solution of an electrolyte *X* is 100 ohms at 40°C. The same conductivity cell filled with 0.01 M solution of electrolyte *Y* has a resistance of 50 ohms. The conductivity of 0.05 M solution of electrolyte *X* is 1.0×10^{-4} S cm^{-1}. Calculate
(i) Cell constant
(ii) Conductivity of 0.01 M *Y* solution
(iii) Molar conductivity of 0.01 M *Y* solution

(3/5, AI 2008C)

LA (5 marks)

75. (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)*

76. (a) State Kohlrausch's law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch's law.
(b) Calculate $\Lambda°_m$ for acetic acid.
Given that
$\Lambda°_m(HCl)$ = 426 S cm^2 mol^{-1}
$\Lambda°_m(NaCl)$ = 126 S cm^2 mol^{-1}
$\Lambda°_m(CH_3COONa)$ = 91 S cm^2 mol^{-1}

(Delhi 2010)

77. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity if Λ°_m for acetic acid is 390.5 S cm^2 mol^{-1}. What is its dissociation constant? *(Delhi, AI 2008)*

3.5 Electrolytic Cells and Electrolysis

VSA (1 mark)

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

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

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

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

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

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

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

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

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

82. How much charge is required for the reduction of 1 mole of Cu^{2+} to Cu? *(Delhi 2007)*

SA I (2 marks)

83. 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)*

84. 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)*

85. 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)*

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

87. 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)*

88. How many coulombs are required to reduce 1 mole $Cr_2O_7^{2-}$ to Cr^{3+}? *(2/3, Delhi 2012C)*

89. 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)*

90. A solution of $CuSO_4$ is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode? *(AI 2009)*

91. Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write overall reaction.
Given :

$$E^\circ_{Na^+/Na} = -2.71\text{ V}, E^\circ_{H_2O/H_2} = -0.83\text{ V},$$

$$E^\circ_{Cl_2/Cl^-} = +1.36\text{ V}, E^\circ_{H^+/H_2/H_2O} = +1.23\text{ V}$$

(2/5, Delhi 2009C)

92. Consider the reaction :
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 8H_2O$
What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$? *(AI 2008)*

93. Explain why electrolysis of an aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode.

$$E^\circ_{Na^+/Na} = -2.71\text{ V}, E^\circ_{H_2O/H_2} = -0.83\text{ V}$$

$$E^\circ_{Cl_2/2Cl^-} = +1.36\text{ V},$$

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

(2/5, Delhi 2008C)

94. Predict the products of electrolysis obtained at the electrodes in each if the electrodes used are of platinum?

(i) An aqueous solution of $AgNO_3$.

(ii) An aqueous solution of H_2SO_4. *(AI 2007)*

SA II **(3 marks)**

95. Calculate the strength of the current required to deposit 1.2 g of magnesium from molten $MgCl_2$ in 1 hour.
[1 F = 96,500 C mol^{-1} ;
Atomic mass : Mg = 24.0] *(3/5, Delhi 2009C)*

96. A solution of $CuSO_4$ is electrolysed for 16 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode? *(AI 2007)*

LA **(5 marks)**

97. Three electrolytic cells *A*, *B* and *C* containing solutions of zinc sulphate, silver nitrate and copper sulphate, respectively are connected in series. A steady current of 1.5 ampere is passed through them until 1.45 g of silver is deposited at the cathode of cell *B*. How long did the current flow? What mass of copper and what mass of zinc were deposited on the concerned electrodes? (Atomic masses of Ag = 108, Zn = 65.4, Cu = 63.5) *(Delhi, AI 2008)*

3.6 Batteries

VSA **(1 mark)**

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

SA I **(2 marks)**

99. 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 invertors?

(iv) Which cell does not have long life? *(Delhi 2016)*

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

101. 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)*

102. 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)*

103. What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery. *(2/5, AI 2011, 2009, 2/5, Delhi 2009)*

104. 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)*

105. Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery. *(2/5, Delhi 2010)*

SA II **(3 marks)**

106. What is a nickel-cadmium cell? State its one merit and one demerit over lead storage cell. Write the overall reaction that occurs during discharging of this cell. *(AI 2010C)*

3.7 Fuel Cells

VSA **(1 mark)**

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

108. Name the type of cell which was used in Apollo space programme for providing electrical power. *(1/3, AI 2014)*

SA I **(2 marks)**

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

110. What are fuel cells? Explain the electrode reactions involved in the working of $H_2 — O_2$ fuel cell. *(2/3, Delhi 2013C, 2009)*

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

3.8 Corrosion

VSA (1 mark)

112. Using the $E°$ values of A and B predict which is better for coating the surface of iron $\left[E^{\circ}_{(\mathrm{Fe}^{2+}/\mathrm{Fe})} = -0.44\right]$ 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 II (2 marks)

113. 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)*

114. Corrosion is essentially an electrochemical phenomenon. Explain the reactions occurring during corrosion of iron kept in an open atmosphere. *(2/5, AI 2009)*

SA II (3 marks)

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

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

3. 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.

4. Because standard electrode potential of Ti^{4+}/Ti^{3+} is less than that of Fe^{3+}/Fe^{2+} so, it cannot oxidise Fe^{II} to Fe^{III}.

5. 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 :

$$2MnO^-_{4(aq)} + 5Sn^{2+}_{(aq)} + 16H^+_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5Sn^{4+}_{(aq)} + 8H_2O_{(l)}$$

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

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

6. The reducing power increases with decreasing value of electrode potential. Hence, the order is Ag < Cu < Fe < Cr < Mg < K.

7. The cell reaction is

$$Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$$

The cell is represented as

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \| Ag^+_{(aq)} \mid Ag_{(s)}$$

(i) Anode *i.e.,* zinc electrode will be negatively charged.

(ii) At anode :

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

At cathode :

$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$ (Reduction)

(iii) Ions are the carriers of current within the cell.

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

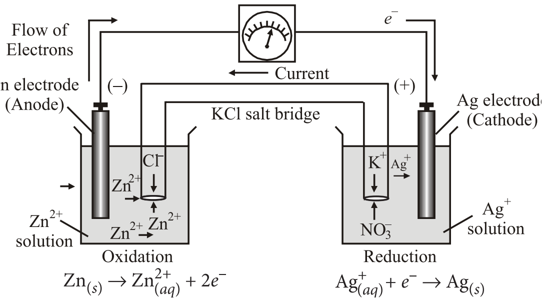
(iii) Copper electrode will be positive on which reduction takes place.

9. The reaction is

$$Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$$

Cell can be represented as

$$Zn \mid Zn^{2+}_{(aq)} \| Ag^+_{(aq)} \mid Ag$$



(i) The zinc electrode is negatively charged (anode) as it pushes the electrons into the external circuit.

(ii) Ions are the current carriers within the cell.

(iii) The reactions occurring at two electrodes are :

At zinc electrode (anode) : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

At silver electrode (cathode) : $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$

10. **(a)** 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, $\Delta_r G° = -nFE°_{cell}$

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

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

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

Here, $n = 2$

using formula,

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

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

$E°_{cell} = 0.0295\ V$

12. Here $n = 2$, $E^\circ_{cell} = 1.1$ V

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

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

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

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

13. *Refer to answer 12.*

14. The electrode reaction written as reduction reaction is

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

Applying Nernst equation, we get,

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

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

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

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

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

$= -0.76 - 0.0295 (3 - 1.9777) = -0.79021$ V

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

Here, $n = 2$

Using formula, $\log K_c = \dfrac{nE^\circ_{cell}}{0.059}$

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

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

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

$\Delta G^\circ = -2 \times 96500 \times 1.05 = -202650$ J

$\Delta G^\circ = -202.65$ kJ

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

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

$= 0.30 - 0.0394 = 0.26$ V

17. *Refer to answer 16.*

18. Given cell,

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

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

Using Nernst equation at 298 K

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

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

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

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

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

19. 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

20. 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

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

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

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

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

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

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

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

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

$\log k_c = 35.53$

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

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

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

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

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

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

or $\quad \log K_c = 0.5074$

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

23. 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 :

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

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

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

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

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

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

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

$E^\circ_{cell} = -2.487\ V$

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

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

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

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

For the given cell,

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

$= 0 - (-0.44) = +\ 0.44\ V$

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

Putting in Nernst equation

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

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

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

$= 0.44 + 0.0885 = 0.53\ V$

26. The cell may be represented as

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

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

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

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

$= 0.46 + 0.0295 \times 5 = 0.6075\ V$

27. 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 :

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

$n = 2$

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

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

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

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

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

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

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

28. 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,

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

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

$= -\ 0.25\ V - (-1.66) = 1.41\ V$

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

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

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

$= 1.41V + 0.050\ V = 1.46\ V$

29. $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ and $2I^- \longrightarrow I_2 + 2e^-$

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

$\Delta_r G^\circ = -nFE^\circ_{cell} = -2 \times 96500 \times 0.236 = -45.55\ kJ\ mol^{-1}$

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

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

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

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

30. For half cell reaction,

$Cr_2O_{7(aq)}^{2-} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

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

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

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

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

$$= 1.33\,V - \frac{0.0591}{6}\log\,(4\times10^{55})$$

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

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

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

$= 1.33$ V $- 0.548$ V$= 0.782$ V

31. (a) Oxidation half reaction :

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

Reduction half reaction :

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

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

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

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

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

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

$= 1.10 - 0.0177 = 1.0823$ V

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

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

$$\text{or} \quad \log K_c = \frac{212300}{2.303\times8.314\times298} = 37.2074$$

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

33. The given cell may be represented as

$Cu_{(s)}\,|Cu^{2+}\,(0.10\text{ M})||\,Ag^+\,(C)|\,Ag_{(s)}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.80\text{ V} - 0.34\text{ V} = 0.46\text{ V}$

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

$$\text{or,}\quad 0.422\text{ V} = 0.46\text{ V} - \frac{0.0591}{2}\log\frac{0.1}{[Ag^+]^2}$$

$$-\,0.038\text{ V} = -\,0.0295\log\frac{0.1}{[Ag^+]^2}$$

$$\text{or, }\log\frac{0.1}{[Ag^+]^2} = \frac{-0.038}{-0.0295} = 1.288$$

$$\text{or,}\quad \frac{0.1}{[Ag^+]^2} = \text{antilog } 1.288 = 19.41$$

$$\therefore \quad [Ag^+]^2 = \frac{0.1}{19.41} = 5.1519\times10^{-3}$$

$[Ag^+] = 7.1 \times 10^{-2}$ M

34. *Refer to answer 26.*

35. *Refer to answer 28.*

36. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.40\text{V} - (-0.44\text{V}) = 0.04\text{V}$

Using formula, $\log K_c = \dfrac{nE^\circ}{0.0591}$ at 298 K

$$\text{or,}\quad K_c = \text{antilog}\,\frac{2\times0.04\text{ V}}{0.0591\text{ V}}$$

or, $K_c = \text{antilog } 1.356 = 22.38$

37. The cell may be represented as

$Zn_{(s)}\,|Zn^{2+}_{(aq)}(1\text{ M})\,||Ag^+_{(aq)}|Ag_{(s)}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.80\text{ V} - (-\,0.76\text{ V}) = 1.56\text{ V}$

Using formula,

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

$$\text{or,}\quad 1.48 = 1.56 - \frac{0.0591}{2}\log\frac{1}{[Ag^+]^2}$$

or, $\log[Ag^+] = -\,1.354$

or, $[Ag^+] = \text{antilog}\,(-\,1.354)$

or, $[Ag^+] = 4.426 \times 10^{-2}$ M

38. $T = 273 + 25°C = 298$ K and $n = 6$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.40 - (-\,0.74) = 0.34$ V

$\Delta_r G^\circ = -\,nFE^\circ_{cell} = -\,6\times96500\times0.34 = -196860\text{ J mol}^{-1}$

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

$\Rightarrow \quad -\,196860 = -\,2.303 \times 8.314 \times 298 \times \log K$

$\Rightarrow \quad \log K = 34.5014$

$\Rightarrow \quad K = \text{antilog } 34.5014 = 3.172 \times 10^{34}$

39. (i) The cell can be represented as

$Cr_{(s)} \,|\, Cr^{3+}_{(aq)} \,||\, Fe^{2+}_{(aq)} \,|\, Fe_{(s)}$

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

$= -0.44 - (-0.74) = -0.44 + 0.74 = 0.30\text{ V}$

(iii) *Refer to answer 16.*

40. $Mg_{(s)} \,|\, Mg^{2+}(0.001\text{ M}) \,||\, Cu^{2+}(0.0001\text{ M}) \,|\, Cu_{(s)}$

Reactions :

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

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

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

∴ $n = 2$

Using Nernst equation :

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

For the given cell

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

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

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

Putting in Nernst equation at 298 K

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

$E_{cell} = 2.71 - 0.0295 \log 10 = 2.71 - 0.03 = 2.68\text{ V}$

$\Delta_r G = -nFE_{cell}$

$= -2 \times 96500\text{ C mol}^{-1} \times 2.68$

$= -517{,}240\text{ J mol}^{-1} = -517.24\text{ kJ mol}^{-1}$

41. We have

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{\left[Ni^{2+}_{(aq)}\right]}{\left[Cu^{2+}_{(aq)}\right]}$$

$$0.059 = E^\circ_{cell} - \frac{0.059}{2}\log\left(\frac{0.01}{0.1}\right) \qquad [\text{Here } n = 2]$$

$$0.059 = E^\circ_{cell} - \frac{0.059}{2}\log\left(\frac{1}{10}\right)$$

$$0.059 = E^\circ_{cell} - \frac{0.059}{2}(-\log 10)$$

$$0.059 = E^\circ_{cell} + \frac{0.059}{2}$$

$$\Rightarrow E^\circ_{cell} = 0.059 - \frac{0.059}{2}$$

$$\therefore \quad E^\circ_{cell} = \frac{0.059}{2} = 0.0295 \approx 0.03$$

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

$0.03 = 0.34 - E^\circ_{anode}$

$E^\circ_{anode} = 0.34 - 0.03 = 0.31\text{ V}$

Hence, $E^\circ_{Ni^{2+}/Ni} = +0.31\text{ V}$

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

$= -0.403 - (-0.763) = -0.403 + 0.763 = 0.360\text{ V}$

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\frac{\left[Zn^{2+}_{(aq)}\right]}{\left[Cd^{2+}_{(aq)}\right]}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{\left[Zn^{2+}_{(aq)}\right]}{\left[Cd^{2+}_{(aq)}\right]}$$

$$\left[\because \frac{2.303RT}{F} = 0.059\right]$$

$$= 0.36 - \frac{0.059}{2}\log\left(\frac{0.1}{0.01}\right) = 0.36 - \frac{0.059}{2}\log 10$$

$= 0.36 - 0.0295 = 0.3305 = 0.33\text{ V}$

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

$= -2 \times 96500 \times 0.36 = -69480\text{ J mol}^{-1}$

$= -69.48\text{ kJ mol}^{-1}$

43. 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.

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

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

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.

45. 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 cm^{2}mol^{-1}

46. *Refer to answer 44.*

47. *Refer to answer 43.*

48. *Refer to answer 44.*

49. $\Lambda_m = \dfrac{\kappa \times 1000}{M}$ in CGS units

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

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

50. $\kappa = \dfrac{1}{R} \times \dfrac{l}{A}$

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

51. *Refer to answer 49.*

52. The fraction of the total number of molecules present in solution as ions is known as degree of dissociation.

Molar conductivity $(\lambda_m) = \alpha\lambda°_m$

where $\lambda°_m$ is the molar conductivity at infinite dilution.

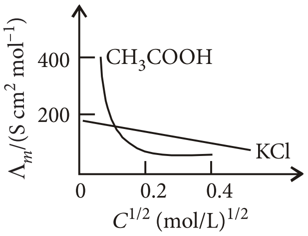
53. The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by κ (kappa).

$\kappa = \dfrac{1}{\rho}$ or $\kappa = G \times \dfrac{l}{a}$

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 that 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.

54. *Refer to answers 43 and 44.*

55. *Refer to answer 53.*

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

56. 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)

$= \dfrac{\kappa \times 1000}{M} = \dfrac{5 \times 10^{-3} \times 1000}{0.01} = 500\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

57. *Refer to answer 55.*

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

Molar conductivity $\Lambda_m^c = \dfrac{\kappa \times 1000}{\text{Molarity}}$

$= \dfrac{0.025 \times 1000}{0.20} = 125$ S cm^2 mol^{-1}

59. $C = 0.001$ M, $\kappa = 4 \times 10^{-5}$ S cm^{-1},

$\Lambda_m^c = 390$ S cm^2/mol

$\Lambda_m^c = \dfrac{\kappa \times 1000}{C}$

Substituting the values,

$\Lambda_m^c = \dfrac{4 \times 10^{-5} \times 1000}{0.001} = 40$ S cm^2/mol

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

$$\begin{array}{ccccc} CH_3COOH & \rightleftharpoons & CH_3COO^- & + & H^+ \\ c & & 0 & & 0 \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$K_a = \frac{0.001(0.103)^2}{(1-0.103)} = \frac{1.061\times10^{-5}}{0.897} = 1.18 \times 10^{-5}$$

60. *Refer to answers 49 and 50.*

61. $\Lambda_m^c = \dfrac{\kappa \times 1000}{M}$

$$\Rightarrow \kappa = \frac{\Lambda_m^c \times M}{1000} = \frac{138.9\times1.5}{1000} = 0.20835 \text{ S cm}^{-1}$$

62. Here, conductivity (κ) = 0.146×10^{-3} S cm^{-1}, resistance (R) = 1500 Ω

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

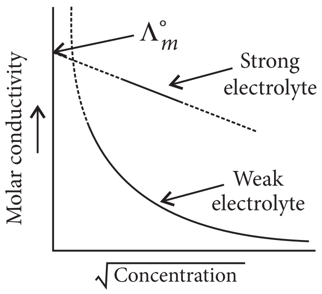
= Conductivity × Resistance

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

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

63. Strong electrolyte : The molar conductivity of strong electrolyte decreases slightly with the increase in concentration. This increase is due to increase in attraction as a result of greater number of ions per unit volume. With dilution the ions are far apart, interionic attractions become weaker and conductance increases.

Weak electrolyte : When the concentration of weak electrolyte becomes very low, its degree of ionisation rises sharply. There is sharp increase in the number of ions in the solution. Hence the molar conductivity of a weak electrolyte rises steeply at low concentration.



64. *Refer to answers 45 and 49.*

65. *Refer to answer 44.*

66. Weak electrolytes : The electrolytes which are not completely dissociated into ions in solution are called weak electrolytes *e.g.*, CH_3COOH, NH_4OH, HCN, etc.

Strong electrolytes : The electrolytes which are completely dissociated into ions in solution are called strong electrolytes. *e.g.*, HCl, KCl, NaOH, NaCl, etc.

67. Using formula, $\Lambda_m^c = \dfrac{\kappa \times 1000}{C}$

Given $\kappa = 3.905 \times 10^{-5}$ S cm^{-1}

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

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

The degree of dissociation,

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

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

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

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

Using formula, $\Lambda_m = \dfrac{1000\times\kappa}{C}$

$$\Lambda_m^c = \frac{(1000\,\text{cm}^3\,\text{L}^{-1})\times(0.0248\text{ S cm}^{-1})}{(0.20\text{ mol L}^{-1})}$$

= 124 S cm^2 mol^{-1}

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

69. Resistance of 0.1 M KCl solution R = 100 Ω

Conductivity κ = 1.29 S m^{-1}

Cell constant $G^* = \kappa \times R = 1.29 \times 100 = 129$ m^{-1}

Resistance of 0.02 M KCl solution, R = 520 Ω

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

= 0.248 S m^{-1}

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

= 1000 × 0.02 mol m^{-3} = 20 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 S m^2 mol^{-1}

70. $\Lambda^\circ_m\ Al_2(SO_4)_3 = 2\lambda^\circ_m Al^{3+} + 3\lambda^\circ_m SO_4^{2-}$

$\Rightarrow\ 858 = 2\lambda^\circ_m Al^{3+} + 3 \times 160$

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

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

$R = 5.5 \times 10^3$ 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, $\kappa = \dfrac{1}{\rho}$

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

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

$$= 1.158 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1} \times \frac{10^3}{5 \times 10^{-2}}$$

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

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

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

$\Rightarrow$ Cell constant $= \kappa \times R = 1.29\ \text{S m}^{-1} \times 85 = 109.65\ \text{m}^{-1}$

For second solution,

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

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

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

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

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

73. According to Kohlrauch's law,

$\Lambda^\circ CH_3COOH = \lambda^\circ CH_3COO^- + \lambda^\circ H^+$

Degree of dissociation, $\alpha = \dfrac{\Lambda_m}{\overset{\circ}{\Lambda}_m}$

$$= \frac{11.7\ \text{S cm}^2\text{mol}^{-1}}{(49.9 + 349.1)\ \text{S cm}^2\text{mol}^{-1}} = \frac{11.7}{390} = 3 \times 10^{-2}$$

74. For electrolyte X :

Molarity = 0.05 M

resistance = 100 ohms

conductivity = $1.0 \times 10^{-4}\ \text{S cm}^{-1}$

For electrolyte Y :

Molarity = 0.01 M

resistance = 50 ohms

conductivity = ?

(i) Cell constant, G^*

= conductivity (κ) × resistance (R)

$= 100 \times 1 \times 10^{-4} = 10^{-2}\ \text{cm}^{-1}$

$\therefore$ Conductivity of solution Y is

$$\kappa = \frac{G^*}{R} = \frac{10^{-2}}{50} = 0.02 \times 10^{-2} = 2 \times 10^{-4}\ \text{S cm}^{-1}$$

Molar conductance, $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

$$= \frac{2 \times 10^{-4} \times 1000}{0.01} = 20\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

75. (a) *Refer to answers 45 and 63.*

(b) *Refer to answer 62.*

76. (a) *Refer to answer 44.*

$\overset{\circ}{\Lambda}_m(CH_3COOH) = \overset{\circ}{\lambda}_{H^+} + \overset{\circ}{\lambda}_{CH_3COO^-}$

(b) $\overset{\circ}{\Lambda}_m\ (HCl) = \overset{\circ}{\lambda}_{H^+} + \overset{\circ}{\lambda}_{Cl^-}$

$\overset{\circ}{\Lambda}_m\ (NaCl) = \overset{\circ}{\lambda}_{Na^+} + \overset{\circ}{\lambda}_{Cl^-}$

$\overset{\circ}{\Lambda}_m\ (CH_3COONa) = \overset{\circ}{\lambda}_{CH_3COO^-} + \overset{\circ}{\lambda}_{Na^+}$

$\Lambda^\circ_m(CH_3COOH) = \overset{\circ}{\lambda}_{CH_3COO^-} + \overset{\circ}{\lambda}_{H^+}$

$= \overset{\circ}{\lambda}_{H^+} + \overset{\circ}{\lambda}_{Cl^-} + \overset{\circ}{\lambda}_{CH_3COO^-} + \overset{\circ}{\lambda}_{Na^+} - \overset{\circ}{\lambda}_{Cl^-} - \overset{\circ}{\lambda}_{Na^+}$

$= \overset{\circ}{\Lambda}_m(HCl) + \overset{\circ}{\Lambda}_m(CH_3COONa) - \overset{\circ}{\Lambda}_m\ NaCl$

$= 426 + 91 - 126 = 391\ \text{S cm}^2\ \text{mol}^{-1}$

77. Conductivity of acetic acid,

$\kappa = 7.896 \times 10^{-5}\ \text{S cm}^{-1}$,

Λ°_m for acetic acid $= 390.5\ \text{S cm}^2\ \text{mol}^{-1}$.

Molar conductivity, $\Lambda^c_m = \dfrac{\kappa \times 1000}{\text{Molarity}}$

$$= \frac{7.896 \times 10^{-5} \times 1000}{0.00241} = 32.76\ \text{S cm}^2\ \text{mol}^{-1}$$

Degree of dissociation,

$$\alpha = \frac{\Lambda^c_m}{\overset{\circ}{\Lambda}_m} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

Dissociation constant of acetic acid,

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{(0.00241) \times (8.4 \times 10^{-2})^2}{1 - 0.084} = 1.86 \times 10^{-5}$$

78. 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 $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$.

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

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

$Q = 2 \times F = 2 \times 96500 = 193000$ C

80. 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

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

81. 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.*,

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

$w = Z \times I \times t$

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

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

$\therefore$ Quantity of charge required for reduction of 1 mole of $Cu^{2+} = 2F = 2 \times 96500 = 193000$ C

83. *Refer to answers 81 and 82.*

84. 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,

$$Ni^{2+} + \underset{\substack{2\text{ mol}\\ 2 \times 96500\text{ C}}}{2e^-} \longrightarrow \underset{\substack{1\text{ mol}\\ 58.7\text{ g}}}{Ni}$$

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

$\therefore$ 6000 C of electricity would produce

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

85. (i) **At 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 ...(i)

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

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

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

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

$$Ca^{2+} + \underset{2F}{2e^-} \longrightarrow \underset{40\text{ g}}{Ca}$$

Electricity required to produce 40 g = 2 F

$\therefore$ Electricity required to produce 20 g = 0.5×2 F = 1 F

87. 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

[$\because$ volume = area × thickness]

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

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

88. 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 mol × 96500 C mol^{-1} = 5.79×10^5 coulomb

89. Quantity of electricity passed

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

$$Hg^{2+} + \underset{2\text{ F}}{2e^-} \longrightarrow \underset{1\text{ mol}}{Hg}$$

2×96500 C electricity produces 1 mole Hg

$\therefore$ 21600 C will produce $= \frac{21600}{2 \times 96500}$

= 0.112 mole of Hg

90. Current (I) = 1.5 A

Time (t) = 10 min = 10 × 60 = 600 s

Quantity of electricity passed = $I \times t$

= (1.5 A) × (600 s) = 900 C

Copper is deposited as :

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

2 × 96500 C of current deposit copper = 63.56 g

∴ 900 C of current will deposit copper

$$= \frac{63.56}{2\times 96500}\times 900 = 0.296 \text{ g}$$

91. Aqueous NaCl ionises as

$NaCl \longrightarrow Na^+ + Cl^-$

(i) Following reactions are possible at cathode,

$2Na^+_{(aq)} + 2e^- \longrightarrow 2Na_{(s)};\ E° = -2.71$ V

$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)};\ E° = -0.83$ V

The reaction with higher $E°$ value will take place, hence H_2 is produced at cathode.

(ii) Following reactions may take place at anode

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

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

The reaction with lower $E°$ value will take place, but due to over voltage. Cl_2 is liberated at anode.

92. *Refer to answer 88.*

93. *Refer to answer 91.*

94. *Refer to answer 85.*

95. Reaction for deposition of Mg from molten $MgCl_2$:

$MgCl_2 \longrightarrow Mg^{2+} + 2Cl^-$

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

24 g of Mg is deposited by 2 × 96500 C of electricity

∴ 1.2 g of Mg will be deposited by

$$\frac{2\times 96500}{24}\times 1.2 = 9650 \text{ C of electricity}$$

Now, $Q = It$

$$\therefore\quad I = \frac{Q}{t} = \frac{9650}{60\times 60} = 2.68 \text{ A}$$

96. According to the reaction :

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

Charge = Current × time = 1.5 amp × 16 × 60 s = 1440 C

2 × 96500 C electricity deposits = 63.5 g Cu

$$\therefore \text{ 1440 electricity deposits } = \frac{63.5\times 1440}{2\times 96500} = 0.47 \text{ g}$$

97. Reaction for deposition of silver :

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

108 g of silver is deposited by 96500 C of electricity

∴ 1.45 g of silver would be deposited by

$$\frac{96500\times 1.45}{108} = 1295.6 \text{ C}$$

Q = 1295.6 C

Given, current strength I = 1.5 A

$$\therefore\quad t = \frac{Q}{I} = \frac{1295.6}{1.5} = 863.7 \text{ s} = 14.4 \text{ min}$$

Reaction for deposition of zinc :

$$\begin{array}{cccc} Zn^{2+} + & 2e^- & \longrightarrow & Zn \\ & 2 \text{ mol} & & 1 \text{ mol} \\ & 2\times 96500 \text{ C} & & 65.3 \text{ g} \end{array}$$

Thus, 2 × 96500 C electricity deposits 65.3 g Zn

∴ 1295.6 C electricity would deposit

$$= \frac{65.3\times 1295.6}{2\times 96500} = 0.438 \text{ g Zn}$$

Reaction for deposition of copper :

$$\begin{array}{cccc} Cu^{2+} + & 2e^- & \longrightarrow & Cu \\ & 2 \text{ mol} & & 1 \text{ mol} \\ & 2\times 96500 \text{ C} & & 63.5 \text{ g} \end{array}$$

Thus, 2 × 96500 C electricity deposits 63.5 g Cu

∴ 1295.6 C electricity would deposit

$$= \frac{63.5\times 1295.6}{2\times 96500} = 0.426 \text{ g Cu}$$

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

99. (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 invertors.

(iv) Dry cell

100. 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.

101. 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 :

$Pb_{(s)} + PbO_{2(s)} + 2H_2SO^{2-}_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

102. 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 : $2PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$

103. *Refer to answer 101.*

104. 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 :

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

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.

105. *Refer to answer 101.*

106. Nickel cadmium cell is a secondary battery which consists of a cadmium anode, nickel hydroxide as cathode and sodium or potassium hydroxide acts as electrolyte.

Merit : It has longer life than lead storage battery.

Demerit : It is more expensive than lead storage battery.

The following reaction takes place during discharging :

$Cd_{(s)} + 2Ni(OH)_{3(s)} \rightarrow CdO_{(s)} + 2Ni(OH)_{2(s)} + H_2O_{(l)}$

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

108. H_2 — O_2 fuel cell was used in Appollo space programme.

109. (i) It is pollution free.

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

110. Fuel cells : *Refer to answer 107.*

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

111. *Refer to answer 111.*

112. 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.

113. 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 :

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

At cathode :

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

Overall reaction :

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

$E^\circ_{cell} = 1.67$ 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)

114. *Refer to answer 113.*

115. 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 113.*