Electrochemistry

1. Calculate the potential of Iron electrode in which the concentration of Fe^{2+} ion is 0·01 M. (2024)

($E^o_{Fe^{2+}/Fe}$ = 0·45 V at 298 K)

[Given : log 10 = 1]

Ans.

$$E_{Fe^{2+}/Fe} = E^o_{Fe^{2+}/Fe} - \frac{0\cdot059}{2}\log\frac{1}{[Fe^{2+}]}$$

$$= -0\cdot45\ V - \frac{0\cdot059}{2}\log\frac{1}{0\cdot01}$$

$$= -0\cdot45\ V - 0\cdot059\ V$$

$$= -0\cdot509\ V$$

2. When a certain conductivity cell was filled with 0·05 M KCl solution, it has a resistance of 100 ohm at 25ºC. When the same cell was filled with 0·02 M $AgNO_3$ solution, the resistance was 90 ohm. Calculate the conductivity and molar conductivity of $AgNO_3$ solution. (2024)

(Given : Conductivity of 0·05 M KCl solution = 1·35 10^{-2} $ohm^{-1}cm^{-1}$)

Ans. Cell constant(G*) = Conductivity x Resistance

= 1.35 x 10^{-2} x 100

= 1.35 cm^{-1}

Cell constant (G*) = Conductivity x Resistance

1.35cm^{-1}k x 90

1.35/90 = k

k = 0.015 Scm-1

Molar conductivity(Λ_m)= k x 1000/C

$$= \frac{0.015\ \text{x}1000}{0.02}$$

$$= 750\ Scm^2/mol$$

3. The following questions are case-based questions. Read the case carefully and answer the questions that follow. (2024)

Batteries and fuel cells are very useful forms of galvanic cell. Any battery or cell that we use as a source of electrical energy is basically a galvanic cell. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries — primary batteries and secondary batteries.

In the primary batteries, the reaction occurs only once and after use over a period of time the battery becomes dead and cannot be reused again, whereas the secondary batteries are rechargeable.

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. To solve this problem, galvanic cells are designed in such a way that energy of combustion of fuels is directly converted into electrical energy, and these are known as fuel cells. One such fuel cell was used in the Apollo space programme.

Answer the following questions :

(a) How do primary batteries differ from secondary batteries ?

Ans. Primary batteries are not rechargeable while secondary batteries are rechargeable.

(b) The cell potential of Mercury cell is 1·35 V, and remains constant during its life. Give reason.

Ans. Overall reaction does not involve any ion in solution whose concentration can change during its lifetime.

(c) Write the reactions involved in the recharging of the lead storage battery.

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

Anode: $PbSO_4\ (s) + 2H_2O\ (1) \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

4. Write two advantages of fuel cells over other galvanic cells. (2024)

Ans. (i) More efficiency, (ii) Pollution free

Previous Years' CBSE Board Questions

2.1 Electrochemical Cells

MCQ

1. An electrochemical cell behaves like an electrolytic cell when
   (a) $E_{cell} = E_{external}$ (b) $E_{cell} = 0$
   (c) $E_{external} > E_{cell}$ (d) $E_{external} < E_{cell}$
   (2020) R

SA I (2 marks)

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

3. Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell? *(AI 2019, 2/5, AI 2016)* U

2.2 Galvanic Cells

MCQ

4. The correct cell to represent the following reaction is

$$Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$$

   (a) $2Ag \mid Ag^+ \parallel Zn \mid Zn^{2+}$ (b) $Ag^+ \mid Ag \parallel Zn^{2+} \mid Zn$
   (c) $Ag \mid Ag^+ \parallel Zn \mid Zn^{2+}$ (d) $Zn \mid Zn^{2+} \parallel Ag^+ \mid Ag$
   (2023)

5. If the standard electrode potential of an electrode is greater than zero, then we can infer that its
   (a) reduced form is more stable compared to hydrogen gas
   (b) oxidised form is more stable compared to hydrogen gas
   (c) reduced and oxidised forms are equally stable.
   (d) reduced form is less stable than the hydrogen gas. *(2020)* U

2.3 Nernst Equation

MCQ

6. ΔG and E°_{cell} for a spontaneous reaction will be
   (a) positive, negative (b) negative, negative
   (c) negative, positive (d) positive, positive.
   (2023)

7. $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$; $E^\circ = +0.80\ V$
   $Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$; $E^\circ = -0.44\ V$
   Find the E°_{cell} for :
   $Fe_{(s)} + 2Ag^+_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + 2Ag_{(s)}$
   (a) 1.6 V (b) −1.16 V (c) 2.04 V (d) 1.24 V
   (2023)

8. Consider the following standard electrode potential values
   $Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ $E^\circ = -0.14\ V$
   $Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$ $E^\circ = +0.77\ V$
   What is the cell reaction and potential for the spontaneous reaction that occurs?
   (a) $2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow 2Fe^{3+}_{(aq)} + Sn_{(s)}$; $E^\circ = -0.91\ V$
   (b) $2Fe^{3+}_{(aq)} + Sn_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$; $E^\circ = +0.91\ V$
   (c) $2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)} \rightarrow 2Fe^{3+}_{(aq)} + Sn_{(s)}$; $E^\circ = +0.91\ V$
   (d) $2Fe^{3+}_{(aq)} + Sn_{(s)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$; $E^\circ = +1.68\ V$
   (2023)

SA I (2 marks)

9. Calculate the emf of the following cell at 298 K:
   $Fe_{(s)} \mid Fe^{2+}(0.01\ M) \parallel H^+_{(1M)} \mid H_{2(g)}\ (1\ bar), Pt_{(s)}$
   Given $E^\circ_{cell} = 0.44\ V$. *(2023)*

10. Calculate $\Delta_r G^\circ$ for the cell reaction at 25°C:
    $Zn \mid Zn^{2+} \parallel Cd^{2+} \mid Cd$
    Given that : $E^\circ_{Zn^{2+}/Zn} = -0.76\ V$,
    $E^\circ_{Cd^{2+}/Cd} = 0/.40\ V$, $1\ F = 96500\ C\ mol^{-1}$ *(2023)*

11. Write the Nernst equation for the following cell reaction:
    $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
    How will the E_{cell} be affected when concentration of
    (i) Cu^{2+} ions is increased and
    (ii) Zn^{2+} ions is increased? *(Term II, 2021-22)*

12. For an electrochemical cell
    $Mg_{(s)} + Ag^+_{(aq)} \longrightarrow Ag_{(s)} + Mg^{2+}_{(aq)}$,
    give the cell representation. Also write the Nernst equation for the above cell at 25°C. *(2020)*

13. Calculate the emf of the following cell at 25°C :
    $Al_{(s)} \mid Al^{3+}\ (0{\cdot}001\ M) \parallel Ni^{2+}\ (0.1\ M) \mid Ni_{(s)}$
    Given : $E^\circ_{(Ni^{2+}/Ni)} = -0{\cdot}25\ V$
    $E^\circ_{(Al^{3+}/Al)} = -1{\cdot}66\ V$
    [$\log 2 = 0{\cdot}3010$, $\log 3 = 0{\cdot}4771$] *(2019)* Ev

14. 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) Ap

15. 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)*

SA II (3 marks)

16. Write the Nernst equation and calculate the emf of the following cell at 298 K :

$\mathrm{Zn}\,|\,\mathrm{Zn}^{2+}(0.001\ \mathrm{M})\,||\,\mathrm{H}^+(0.01\ \mathrm{M})\,|\,\mathrm{H}_{2(g)}(1\ \mathrm{bar})\,|\,\mathrm{Pt}_{(s)}$
Given : $E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.76\ \mathrm{V}, E^\circ_{\mathrm{H}^+/\mathrm{H}_2} = 0.00\ \mathrm{V}$, [log 10 = 1]
(Term II, 2021-22, Foreign 2015) Cr

17. Calculate $\Delta_r G^\circ$ and $\log K_c$ for the following cell :
$\mathrm{Ni}_{(s)} + 2\mathrm{Ag}^+_{(aq)} \rightarrow \mathrm{Ni}^{2+}_{(aq)} + 2\mathrm{Ag}_{(s)}$
Given that $E^\circ_{\mathrm{cell}} = 1.05\ \mathrm{V}$, $1\mathrm{F} = 96{,}500\ \mathrm{C\ mol^{-1}}$
(Term II, 2021-22)

OR

Calculate the maximum work and $\log K_c$ for the given reaction at 298 K :
$\mathrm{Ni}_{(s)} + 2\mathrm{Ag}^+_{(aq)} \rightleftharpoons \mathrm{Ni}^{2+}_{(aq)} + 2\mathrm{Ag}_{(s)}$
Given : $E^\circ_{\mathrm{Ni}^{2+}/\mathrm{Ni}} = -0.25\ \mathrm{V}, E^\circ_{\mathrm{Ag}^+/\mathrm{Ag}} = +0.80\ \mathrm{V}$
$1\mathrm{F} = 96500\ \mathrm{C\ mol^{-1}}$ *(2020)*

OR

For the cell reaction,
$\mathrm{Ni}_{(s)}\,|\mathrm{Ni}^{2+}_{(aq)}||\mathrm{Ag}^+_{(aq)}|\mathrm{Ag}_{(s)}$
Calculate the equilibrium constant at 25°C. How much maximum work would be obtained by operation of this cell?

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

(3/5, Delhi 2015C)

18. Calculate the e.m.f. of the following cell at 298K :
$\mathrm{Fe}_{(s)}\,|\,\mathrm{Fe}^{2+}(0.001\ \mathrm{M})\,||\,\mathrm{H}^+(0.01\ \mathrm{M})\,|\,\mathrm{H}_{2(g)}(1\ \mathrm{bar})\,|\,\mathrm{Pt}_{(s)}$
Given that $E^\circ_{\mathrm{cell}} = +0.44\ \mathrm{V}$
[log 2 = 0.3010, log 3 = 0.4771, log 10 = 1]
(Term II, 2021-22) Ev

OR

Calculate emf of the following cell at 25°C:
$\mathrm{Fe}|\mathrm{Fe}^{2+}(0.001\ \mathrm{M})||\mathrm{H}^+(0.01\ \mathrm{M})|\mathrm{H}_{2(g)}(1\ \mathrm{bar})|\mathrm{Pt}_{(s)}$
$E^\circ_{(\mathrm{Fe}^{2+}/\mathrm{Fe})} = -0.44\ \mathrm{V}, E^\circ_{(\mathrm{H}^+/\mathrm{H}_2)} = 0.00\ \mathrm{V}$ *(Delhi 2015)*

19. Calculate ΔG° for the reaction,

$\mathrm{Zn}_{(s)} + \mathrm{Cu}^{2+}_{(aq)} \rightarrow \mathrm{Zn}^{2+}_{(aq)} + \mathrm{Cu}_{(s)}$
Given : E° for $\mathrm{Zn}^{2+}/\mathrm{Zn} = -0.76\ \mathrm{V}$ and
E° for $\mathrm{Cu}^{2+}/\mathrm{Cu} = +0.34\ \mathrm{V}$
$R = 8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $1\ \mathrm{F} = 96500\ \mathrm{C\ mol^{-1}}$.
(3/5, 2020)

20. Calculate e.m.f of the following cell :
$\mathrm{Zn}_{(s)}\,|\,\mathrm{Zn}^{2+}(0.1\ \mathrm{M})\,||\,\mathrm{Ag}^+(0.01\ \mathrm{M})\,|\,\mathrm{Ag}_{(s)}$
Given : $E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.76\ \mathrm{V}, E^\circ_{\mathrm{Ag}^+/\mathrm{Ag}} = +0.80\ \mathrm{V}$
[Given : log 10 = 1] *(3/5, 2020)*

21. Calculate $\Delta_r G^\circ$ and $\log K_c$ for the following reaction.
$\mathrm{Cd}^{2+}_{(aq)} + \mathrm{Zn}_{(s)} \longrightarrow \mathrm{Zn}^{2+}_{(aq)} + \mathrm{Cd}_{(s)}$
Given : $E^\circ_{\mathrm{Cd}^{2+}/\mathrm{Cd}} = -0.403\ \mathrm{V}; E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.763\ \mathrm{V}$
(AI 2019) Ap

22. Zinc rod is dipped in 0·01 M solution of zinc sulphate when temperature is 298 K. Calculate the electrode potential of zinc.

(Given : $E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = = -0{\cdot}76\ \mathrm{V}$; log 10 = 1) *(2019C)* Ev

23. Write the cell reaction and calculate the e.m.f. of the following cell at 298 K.
$\mathrm{Sn}_{(s)}\,|\,\mathrm{Sn}^{2+}(0.004\ \mathrm{M})\,||\,\mathrm{H}^+(0.020\ \mathrm{M})\,|\,\mathrm{H}_{2(g)}(1\ \mathrm{bar})\,|\,\mathrm{Pt}_{(s)}$
(Given : $E^\circ_{\mathrm{Sn}^{2+}/\mathrm{Sn}} = -0.14\ \mathrm{V}$) *(3/5, 2018)* U

24. For the reaction,
$2\mathrm{AgCl}_{(s)} + \mathrm{H}_{2(g)}(1\ \mathrm{atm}) \rightarrow 2\mathrm{Ag}_{(s)} + 2\mathrm{H}^+(0.1\ \mathrm{M}) + 2\mathrm{Cl}^-(0.1\ \mathrm{M})$
$\Delta G^\circ = -43600\ \mathrm{J}$ at 25 °C.
Calculate the e.m.f. of the cell. ($\log 10^{-n} = -n$)
(3/5, 2018)

25. Calculate e.m.f. of the following cell at 298 K.
$2\mathrm{Cr}_{(s)} + 3\mathrm{Fe}^{2+}(0.1\mathrm{M}) \rightarrow 2\mathrm{Cr}^{3+}(0.01\mathrm{M}) + 3\mathrm{Fe}_{(s)}$
Given : $E^\circ_{(\mathrm{Cr}^{3+}/\mathrm{Cr})} = -0.74\ \mathrm{V}, E^\circ_{(\mathrm{Fe}^{2+}/\mathrm{Fe})} = -0.44\ \mathrm{V}$
(Delhi 2016)

26. Calculate E°_{cell} for the following reaction at 298 K.
$2\mathrm{Al}_{(s)} + 3\mathrm{Cu}^{2+}(0.01\mathrm{M}) \rightarrow 2\mathrm{Al}^{3+}(0.01\mathrm{M}) + 3\mathrm{Cu}_{(s)}$
Given : $E_{\mathrm{cell}} = 1.98\ \mathrm{V}$ *(3/5, AI 2016)*

27. Calculate the standard cell potential of the galvanic cell in which the following reaction takes place :
$\mathrm{Fe}^{2+}_{(aq)} + \mathrm{Ag}^+_{(aq)} \rightarrow \mathrm{Fe}^{3+}_{(aq)} + \mathrm{Ag}_{(s)}$
Calculate the $\Delta_r G^\circ$ and equilibrium constant of the reaction.
$\left(E^\circ_{\mathrm{Ag}^+/\mathrm{Ag}} = 0.80\mathrm{V}; E^\circ_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} = 0.77\mathrm{V}\right)$
(3/5, Delhi 2015C) U

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

29. Estimate the minimum potential difference needed to reduce $\mathrm{Al_2O_3}$ at 500°C. The Gibbs energy change for the decomposition reaction,
$\frac{2}{3}\mathrm{Al_2O_3} \rightarrow \frac{4}{3}\mathrm{Al} + \mathrm{O_2}$ is 960 kJ. ($F = 96500\ \mathrm{C\ mol^{-1}}$)
(3/5, Delhi 2014C)

LA (5 marks)

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

$\mathrm{Mg}_{(s)} + \mathrm{Cu}^{2+}(0.01\mathrm{M}) \rightarrow \mathrm{Mg}^{2+}(0.001\mathrm{M}) + \mathrm{Cu}_{(s)}$
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)*

31. Calculate e.m.f and ΔG for the following cell
$\mathrm{Mg}_{(s)}\,|\,\mathrm{Mg}^{2+}(0.001\ \mathrm{M})\,||\,\mathrm{Cu}^{2+}(0.0001\ \mathrm{M})\,|\,\mathrm{Cu}_{(s)}$
$E^\circ_{(\mathrm{Mg}^{2+}/\mathrm{Mg})} = -2{\cdot}37\ \mathrm{V}, E^\circ_{(\mathrm{Cu}^{2+}/\mathrm{Cu})} = +0.34\ \mathrm{V}$
(NCERT, AI 2015)

2.4 Conductance of Electrolytic Solutions

MCQ

32. The unit of molar conductivity is
(a) $\mathrm{S\ cm^{-2}\ mol^{-1}}$ (b) $\mathrm{S\ cm^{2}\ mol^{-1}}$
(c) $\mathrm{S^{-1}\ cm^{2}\ mol^{-1}}$ (d) $\mathrm{S\ cm^{2}\ mol}$ *(2023)*

33. **Assertion (A)** : Conductivity of an electrolyte increases with decrease in concentration.
Reason (R) : Number of ions per unit volume decreases 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 wrong statement.

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

VSA (1 mark)

34. Give reason :
Conductivity of CH_3COOH decreases on dilution. *(1/5, 2018)* U

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

OR

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

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

OR

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

37. Define the following term :
Molar conductivity (Λ_m) *(1/5, Delhi 2015C)*

SA I (2 marks)

38. On diluting two electrolytes 'A' and 'B', then Λ_m of 'A' increases 25 times while that of 'B' increases by 1.5 times. Which of the two electrolytes is strong? Justify your answer graphically. *(2023)*

39. (i) State Kohlrausch's law of independent migration of ions.
(ii) Calculate the degree of dissociation (α) of CH_3COOH if Λ_m and Λ_m° of CH_3COOH are 48 S cm^2 mol^{-1} and 400 S cm^2 mol^{-1} respectively. *(Term II, 2021-22)*

40. The conductivity of 0.001 M acetic acid is 7.8×10^{-5} S cm^{-1}. Calculate its degree of dissociation if Λ_m° for acetic acid is 390 S cm^2 mol^{-1}. *(Term II, 2021-22)* Ap

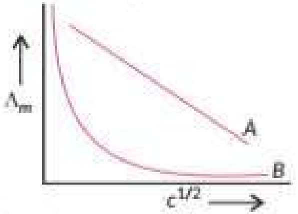
41. In a plot of Λ_m against the square root of concentration ($C^{1/2}$) for strong and weak electrolyte, the value of limiting molar conductivity of a weak electrolyte cannot be obtained graphically. Suggest a way to obtain this value. Also state the related law, if any. *(Term II, 2021-22)* Ev

42. Answer the following questions (Any two) :
(a) Define molar conductivity (Λ_m).
(b) Write the unit of Λ_m.
(c) How does Λ_m vary with concentration? *(Term II,2021-22 C)*

43. Answer the following questions (Any two) :
(a) Why is alternating current used instead of direct current for measuring resistance of an electrolytic solution ?
(b) State Kohlrausch's law of independent migration of ion.
(c) Depict the Galvanic cell in which the following reaction takes place :
$Mg_{(s)} + Cu^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Cu_{(s)}$ *(Term II, 2021-22C)*

44. 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)* Ap

45. 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)* Ev

46. Explain with a graph, the variation of molar conductivity of a strong electrolyte with dilution. *(2019)*

47. 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)*

48. 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)* Cr

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

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

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

52. 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)*

SA II (3 marks)

53. (a) The standard Gibbs energy ($\Delta_r G^\circ$) for the following cell reaction is -300 kJ mol^{-1} :
$Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$

Calculate E°_{cell} for the reaction.
(Given: 1F = 96500 C mol^{-1})

(b) Calculate λ°_m for $MgCl_2$ if λ° values for Mg^{2+} ion and Cl^- ion are 106 S cm^2 mol^{-1} and 76.3 S cm^2 mol^{-1} respectively. *(Term I, 2021-22)*

54. 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 : $\lambda^\circ(H^+)$ = 349.6 S cm^2 mol^{-1} and $\lambda^\circ(CH_3COO^-)$ = 40.9 S cm^2 mol^{-1}]
(Term II, 2021-22C, 3/5, AI 2016)

55. Conductivity of 2×10^{-3} M methanoic acid is 8×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation if Λ°_m for methanoic acid is 404 S cm^2 mol^{-1}. *(2020)*

56. 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)

57. 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)*

58. (a) Following reaction takes place in the cell :
$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$
Calculate Δ_rG° of the reaction..
[Given : $E^\circ_{(Zn^{2+}/Zn)} = -0.76$ V,
$E^\circ_{(Ag^+/Ag)} = 0{\cdot}80$ V, 1 F = 96,500 C mol^{-1}]
(b) How can you determine limiting molar conductivity, (Λ°_m) for strong electrolyte and weak electrolyte? *(2019)*

59. 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 : $\lambda^\circ(K^+)$ = 73.5 S cm^2 mol^{-1} and
$\lambda^\circ(Cl^-)$ = 76.5 S cm^2 mol^{-1}. *(AI 2015)*

60. 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) Ap

LA (4/5 marks)

61. Rahul set up an experiment to find resistance of aqueous KCl solution for different concentrations at 298 K using a conductivity cell connected to a Wheatstone bridge. He fed the Wheatstone bridge with a.c. power in the audio frequency range 550 to 5000 cycles per second. Once the resistance was calculated from null point he also calculated the conductivity κ and molar conductivity Λ_m and recorded his readings in tabular form.

S.No.	Conc. (M)	κ (S cm^{-1})	Λ_m (S cm^2 mol^{-1})
1.	1.00	111.3×10^{-3}	111.3
2.	0.10	12.9×10^{-3}	129.0
3.	0.01	1.41×10^{-3}	141.0

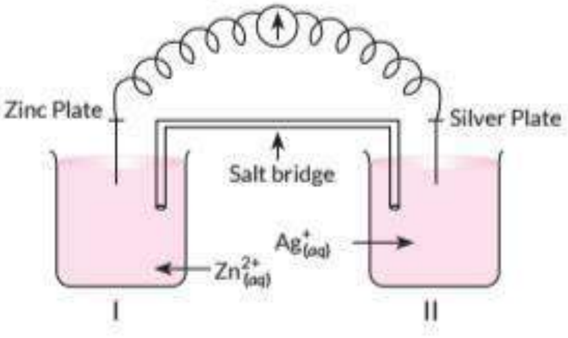
Answer the following questions:

(a) Why does conductivity increase though the conductivity decrease with dilution?
(b) If Λ°_m of KCl is 150.0 S cm^2 mol^{-1}, calculate the degree of dissociation of 0.01 M KCl.
(c) If Rahul had used HCl instead to KCl then would you expect the Λ_m values to be more or less than those per KCl for a given concentration. Justify. *(2023)*

62. **Read the passage given below and answer the questions that follow :**

Oxidation-reduction reactions are commonly known as redox reactions. They involve transfer of electrons from one species to another. In a spontaneous reaction, energy is released which can be used to do useful work. The reaction is split into two half reactions. Two different containers are used and a wire is used to drive the electrons from one side to the other and a voltaic/galvanic cell is created. It is an electrochemical cell that uses spontaneous redox reactions to generate electricity. A salt bridge also connects to the half cells. The reading of the voltmeter gives the cell voltage or cell potential or electromotive force. If E°_{cell} is positive the reaction is spontaneous and if it is negative the reaction is non-spontaneous and is referred to as electrolytic cell. Electrolysis refers to the decomposition of a substance by an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+}. This was first formulated by Faraday in the form of laws of electrolysis.

The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. Conductivity is represented by *k* and it depends upon nature and concentration of electrolyte, temperature etc. A more common term molar conductivity of a solution at a given concentration is conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. Limiting molar conductivity of weak electrolytes cannot be obtained graphically.



(a) Is silver plate the anode or cathode ?
(b) What will happen if the salt bridge is removed ?
(c) When does electrochemical cell behave like an electrolytic cell ?
(d) (i) What will happen to the concentration of Zn^{2+} and Ag^+ when $E_{cell} = 0$.
(ii) Why does conductivity of a solution decreases with dilution ?

OR

(d) 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.

(Term II, 2021-22)

63. (i) The electrical resistance of a column of 0·02 M NaOH solution of diameter 1·40 cm and length 44 cm is $5{\cdot}00 \times 10^3$ ohm. Calculate its resistivity, conductivity and molar conductivity.
(ii) Depict the galvanic cell in which the reaction takes place :
$Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$
Further show :
(i) Which of the electrodes is positively charged ?
(ii) The carriers of the current in the outer circuit.

(2021C) An

64. (a) Represent the cell in which the following reaction takes place :
$2Al_{(s)} + 3Ni^{2+}\,(0{\cdot}1\text{ M}) \rightarrow 2Al^{3+}\,(0{\cdot}01\text{ M}) + 3Ni_{(s)}$
Calculate its emf if $E^\circ_{cell} = 1{\cdot}41$ V.
(b) How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte ? How can you obtain limiting molar conductivity (Λ°_m) for weak electrolyte ? *(2019)*

2.5 Electrolytic Cells and Electrolysis

MCQ

65. Four half reactions I to IV are shown below:
I. $2Cl^- \rightarrow Cl_2 + 2e^-$
II. $4OH^- \rightarrow O_2 + 2H_2O + 2e^-$
III. $Na^+ + e^- \rightarrow Na$
IV. $2H^+ + 2e^- \rightarrow H_2$
Which two of these reactions are most likely to occur when concentrated brine is electrolysed?
(a) I and III (b) I and IV
(c) II and III (d) II and IV *(2023)*

VSA (1 mark)

66. How much charge in terms of Faraday is required to reduce one mol of MnO_4^- to Mn^{2+}? *(2020)* Ev

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

68. 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)* U

69. Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution :
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$, $E^\circ = +0.80$ V
$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$, $E^\circ = 0.00$ V
On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why? *(AI 2017C, 1/2, Delhi 2015)*

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

71. Following reactions occur at cathode during the electrolysis of aqueous copper (II) chloride solution :
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$; $E^\circ = +0.34$ V
$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$; $E^\circ = 0.00$ 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)* Ev

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

SA I (2 marks)

73. (i) What should be the signs (positive/negative) for E°_{cell} and ΔG° for a spontaneous redox reaction occurring under standard conditions?
(ii) State Faraday's first law of electrolysis. *(2023)*

74. 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, $E^\circ_{(1/2O_2/H_2O)} = +1.23$ V)
(2/5, 2020)

75. Predict the products of electrolysis in each of the following :
(a) An aqueous solution of $CuSO_4$ with Pt electrode
(b) An aqueous solution of $AgNO_3$ with Pt electrode
(2020C)

76. How many seconds does it require to reduce 3 moles of Fe^{3+} to Fe^{2+} with 2 A current?
(Given : 1 F = 96500 C mol^{-1}) *(2020C)*

77. Following reactions may occur at cathode and anode during electrolysis of aqueous sodium chloride. What products will be held at anode and cathode? Use given E° values to justify your answer.
Cathode: $Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$ $E^\circ = -2{\cdot}71$ V
$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$ $E^\circ = 0{\cdot}00$ V
Anode: $Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^-$ $E^\circ = +1{\cdot}36$ V
$2H_2O_{(aq)} \rightarrow O_{2(g)} + 4H^+ + 4e^-$ $E^\circ = +1{\cdot}23$ V
(2019) Ap

78. 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)*

79. 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)*

80. 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)*

81. 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)*

SA II (3 marks)

82. When a steady current of 2A was passed through two electrolytic cells *A* and *B* containing electrolytes $ZnSO_4$ and $CuSO_4$ connected in series, 2 g of Cu were deposited at the cathode of cell *B*. How long did the current flow?
What mass of Zn was deposited at cathode of cell *A*?
[Atomic mass : Cu = $63.5\ g\ mol^{-1}$, Zn = $65\ g\ mol^{-1}$; 1F = $96500\ C\ mol^{-1}$] *(2020)* Ev

83. 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)*

84. Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation :
$CrO_{3(aq)} + 6H^+ + 6e^- \rightarrow Cr_{(s)} + 3H_2O$
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)*

85. (a) 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 of the cell reaction.
(Given : $1\ F = 96{,}500\ C\ mol^{-1}$) *(NCERT Intext)*
    (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)*

LA (5 marks)

86. (i) State Kohlrausch's law of independent migration of ions. Write an expression for the limiting molar conductivity of acetic acid according to Kohlrausch's law.
    (ii) 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 : $E^\circ_{Ni^{2+}/Ni} = -0.25\ V$, $E^\circ_{Ag^+/Ag} = +0.80\ V$
$1\ F = 96500\ C\ mol^{-1}$ *(2023)*

2.6 Batteries

VSA (1 mark)

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

SA I (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)* R

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

LA (5 marks)

92. (a) The conductivity of 0·001 mol L^{-1} acetic acid is $4.95 \times 10^{-5}\ S\ cm^{-1}$. Calculate the dissociation constant if Λ°_m for acetic acid is $390.5\ S\ cm^2\ mol^{-1}$.
    (b) Write Nernst equation for the reaction at 25°C :
$2\,Al_{(s)} + 3Cu^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Cu_{(s)}$
    (c) What are secondary batteries? Give an example. *(2019)*

2.7 Fuel Cells

MCQ

93. Which of the following cell was used in Apollo space programme?
(a) Mercury cell (b) Daniell cell
(c) H_2-O_2 Fuel cell (d) Dry cell *(2023)*

VSA (1 mark)

94. Name the cell use in hearing aids and watches. *(2020)* R

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

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

SA I **(2 marks)**

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

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

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 inverters?
   (iv) Which cell does not have long life?

(Delhi 2016) R

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

2.8 Corrosion

VSA **(1 mark)**

101. Using the $E°$ values of A and B predict which is better for coating the surface of iron $\left[E^\circ_{(Fe^{2+}/Fe)} = -0.44\text{ V}\right]$ to prevent corrosion and why?
$E^\circ_{(A^{2+}/A)} = -2.37\text{ V}; E^\circ_{(B^{2+}/B)} = -0.14\text{ V}$

(AI 2016) An

CBSE Sample Questions

2.3 Nernst Equation

SA II **(3 marks)**

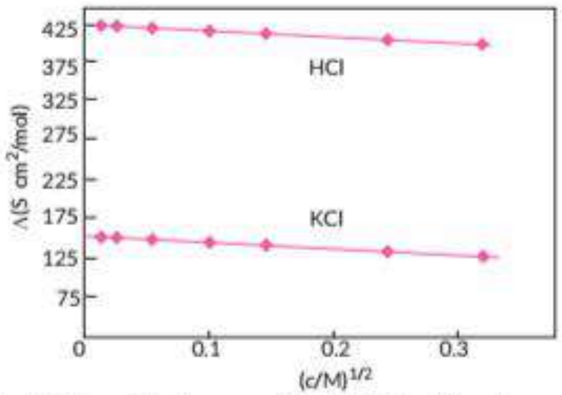
1. Represent the cell in which the following reaction takes place. The value of $E°$ for the cell is 1.260 V. What is the value of E_{cell}?
$2Al_{(s)} + 3Cd^{2+}(0.1\text{ M}) \rightarrow 3Cd_{(s)} + 2Al^{3+}(0.01\text{ M})$

(Term II, 2021-22)

2.4 Conductance of Electrolytic Solutions

MCQ

2. The molar conductivity of CH_3COOH at infinite dilution is 390 S cm^2/mol. Using the graph and given information, the molar conductivity of CH_3COOK will be



(a) 100 S cm^2/mol
(b) 115 S cm^2/mol
(c) 150 S cm^2/mol
(d) 125 S cm^2/mol

(Term-II, 2021-22)

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

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

(a) 350 S cm^2 mol^{-1}
(b) 375.3 S cm^2 mol^{-1}
(c) 390.5 S cm^2 mol^{-1}
(d) 340.4 S cm^2 mol^{-1}

(2020-21) An

SA I **(2 marks)**

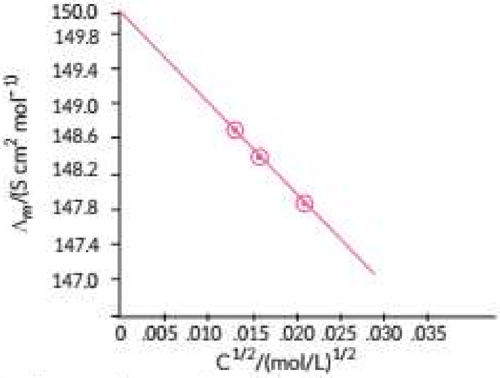
4. Solutions of two electrolytes '*A*' and '*B*' are diluted. The Λ_m of '*B*' increases 1.5 times while that of *A* increases 25 times. Which of the two is a strong electrolyte? Justify your answer. Graphically show the behaviour of '*A*' and '*B*'. *(Term II, 2021-22)*

LA **(5 marks)**

5. (i) State Kohlrausch law.
   (ii) Calculate the emf of the following cell at 298 K :
   $Al_{(s)}|Al^{3+}(0.15\text{ M}) || Cu^{2+}(0.025\text{ M}) | Cu_{(s)}$
   (Given $E^\circ_{(Al3+/Al)} = -1.66$ V, $E^\circ_{(Cu2+/Cu)} = 0.34$ V, log 0.15 = −0.8239, log 0.025 = −1.6020)

(2020-21)

6. (i) On the basis of $E°$ values identify which amongst the following is the strongest oxidising agent?
   $Cl_{2(g)} + 2e^- \rightarrow 2Cl^-;\ E^\circ = +1.36\text{ V},$
   $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O;\ E^\circ = +1.51\text{ V}$
   $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O;$
   $E^\circ = +1.33\text{ V}$
   (ii) The following figure represents variation of (Λ_m) *vs* $\sqrt{C}$ for an electrolyte. Here, Λ_m is the molar conductivity and C is the concentration of the electrolyte.



(a) Define molar conductivity.
(b) Identify the nature of electrolyte on the basis of the above plot. Justify your answer.
(c) Determine the value of Λ_m° for the electrolyte.
(d) Show how to calculate the value of *A* for the electrolyte using the above graph. *(2020-21)*

2.5 Electrolytic Cells and Electrolysis

LA **(5 marks)**

7. (a) Molar conductivity of substance '*A*' is 5.9×10^3 S/m and '*B*' is 1×10^{-16} S/m. Which of the two is most likely to be copper metal and why?
(b) What is the quantity of electricity in Coulombs required to produce 4.8 g of Mg from molten $MgCl_2$? How much Ca will be produced if the same amount of electricity was passed through molten $CaCl_2$? (Atomic mass of Mg = 24 u, atomic mass of Ca = 40 u).
(c) What is the standard free energy change for the following reaction at room temperature? Is the reaction spontaneous?
$Sn_{(s)} + 2Cu^{2+}_{(aq)} \rightarrow Sn^{2+}_{(aq)} + 2Cu^{+}_{(s)}$ *(2022-23)*

2.6 Batteries

LA **(5 marks)**

8. (a) Why does the cell voltage of a mercury cell remain constant during its lifetime?
(b) Write the reaction occurring at anode and cathode and the products of electrolysis of aq KCl.
(c) What is the pH of HCl solution when the hydrogen gas electrode shows a potential of -0.59 V at standard temperature and pressure? *(2022-23)*

2.8 Corrosion

SA I **(2 marks)**

9. Corrosion is an electrochemical phenomenon. The oxygen in moist air reacts as follows:
$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$.
Write down the possible reactions for corrosion of zinc occurring at anode, cathode, and overall reaction to form a white layer of zinc hydroxide. *(2022-23)*

Detailed SOLUTIONS

Previous Years' CBSE Board Questions

1. (c) : 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.*, $\Delta G = -ve$	In it redox reaction is non-spontaneous and takes place only when electrical energy is supplied *i.e.*, $\Delta G = +ve$.

Commonly Made Mistake

- **Electrochemical cell :** Convert chemical energy into electrical energy.
- **Electrolytic cell :** Convert electrical energy into chemical energy.

3. 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.

4. (d): The cell can be represented as :
$Zn \mid Zn^{2+} \parallel Ag^+ \mid Ag$

5. (a): If standard electrode potential of an electrode is greater than zero, then we can infer that its reduced form is more stable as compared to hydrogen gas.

6. (c): For a spontaneous reaction, Gibb's free energy change ΔG must be negative, so E°_{cell} should be positive.
$\Delta G = -nFE^\circ_{cell}$

7. (d): $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
$= +0.80 - (-0.44) = +1.24$ V

8. (b): $Sn_{(s)} \longrightarrow Sn^{2+}_{(aq)} + 2e^-$ ...(i)

$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$ ...(ii)

On multiplying equation (ii) by 2 and adding equation (i) and (ii), we get

$Sn_{(s)} + 2\,Fe^{3+}_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.77 - (-0.14) = +0.91\text{ V}$$

∵ E°_{cell} is positive, so ΔG is −ve, hence spontaneous reaction.

9. $Fe \longrightarrow Fe^{2+} + 2e^-$

$2H^+ + 2e^- \longrightarrow H_2$

$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$

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

$$= 0.44 - \frac{0.0591}{2}\log\left(\frac{0.01}{1}\right)$$

$$= 0.44 + \frac{0.0591}{2} \times 2$$

$E_{cell} = 0.4991\text{ V}$

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

$= 0.40 - (-0.76)$

$= 1.16\text{ V}$

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

$\Delta G^\circ = -2 \times 96500 \times 1.16$

$= -2{,}23{,}880\text{ J mol}^{-1}$

$= -223.880\text{ kJ mol}^{-1}$

11. $$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

or $$E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

(i) When concentration of Cu^{2+} ions is increased, E_{cell} will increase.

(ii) When concentration of Zn^{2+} ions is increased, E_{cell} will decrease.

12. The cell can be written as

$Mg \mid Mg^{2+} \parallel Ag^+ \mid Ag$

According to Nernst equation,

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2}\log\frac{[Mg^{2+}]}{[Ag^+]^2},\text{ At } 25^\circ C$$

Key Points

- Metal|Metal ion (conc.) $\underset{\text{Salt bridge}}{||}$ Metal ion (conc.)|Metal

  By convention the electrode on which oxidation takes place is written on the L.H.S and other electrode on which reduction takes place is written on the R.H.S

13. $2Al_{(s)} + 3Ni^{2+}_{(aq.)} \longrightarrow 2Al^{3+}_{(aq.)} + 3Ni_{(s)}$

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

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

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

$$= 1.41 - \frac{0.0591}{6}\log\frac{(0.001)^2}{(0.1)^3}$$

$$= 1.41 - \frac{0.0591}{6}\log 10^{-3}$$

$$= 1.41 + \frac{0.0591}{6} \times 3 \times 1 = 1.439\text{ V}$$

14. Given : $E^\circ_{cell} = 2.71\text{ V}$

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

$n = 2, \Delta_r G^\circ = ?$

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

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

or $\Delta_r G^\circ = -523030\text{ J mol}^{-1} = -523.03\text{ kJ mol}^{-1}$

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

Here, $n = 2$

Using formula,

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

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

$E^\circ_{cell} = 0.0295\text{ V}$

16. For a general electrochemical reaction,

$aA + bB \longrightarrow cC + dD$

Nernst equation can be written as:

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

Given cell :

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

Cell reaction :

$Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

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

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

$= 0.76 - (0.0295) \times (1) = 0.76 - 0.0295 = 0.73\text{ V}$

17. **At anode :** $Ni \rightarrow Ni^{2+} + 2e^-$

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

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

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

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

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

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

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

$\log K_c = 35.53$

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

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

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

The maximum work that can be obtained = 202.65 kJ.

Answer Tips

- When a spontaneous chemical reaction occurs, the decrease in the free energy, $-\Delta G$, corresponds to the maximum possible quantity of useful work, W_{max}.

18. The cell reaction is

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

$E^\circ_{cell} = 0.0 - (-0.44) = 0.44\ V$

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

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

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

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

Here, $n = 2$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.34 - (-0.76) = 1.1\ V$

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

$$\Delta_r G^\circ = -nFE^\circ_{cell} = -2 \times 1.1 \times 96500 = -212300\ J\ mol^{-1}$$
$$= -212.3\ kJ\ mol^{-1}$$

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

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

Overall reaction : $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

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

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

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

$$= 1.56 - \frac{0.059}{2}\log\frac{0.1}{(0.01)^2} = 1.47\ V$$

21. $E^\circ_{cell} = E^\circ_{right} - E^\circ_{left} = -0.403 - (-0.763) = 0.36\ V$

$\Delta_r G^\circ = -nFE^\circ_{cell} = -2 \times 96500 \times 0.36$

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

Using formula, $\log K_c = \frac{nE^\circ_{cell}}{0.059} = \frac{2 \times 0.36}{0.059} = 12.20$

$K_c = \text{antilog } 12.20 = 1.58 \times 10^{12}$

22. $$E = E^\circ - \frac{0.0591}{n}\log\frac{[M]}{[M^{n+}]}$$

$$= E^\circ - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$$

$$= -0.76 - \frac{0.0591}{2}\log\frac{1}{0.01}$$

$$= -0.76 - \frac{0.0591}{2} \times 2$$

$$= -0.819\ V$$

Key Points

- For pure solids or liquids or gases at one atmospheric pressure, the molar concentration (here [M]) is taken as unity.

23. 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

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

$E^\circ_{cell} = E^\circ_{H^+|H_2} - E^\circ_{Sn^{2+}|Sn} = 0.000\ V - (-0.14\ V) = +0.14\ V$

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

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

$$= E^\circ_{cell} - 0.0296\ (\log 10)$$

$$= E^\circ_{cell} - 0.0296 \times 1 = E^\circ_{cell} - 0.0296$$

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

Key Points

- Remember : $E^\circ_{H^+|H_2} = 0$

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

$$E^\circ_{cell} = -\frac{\Delta G^\circ}{nF} = -\frac{(-43600)}{2 \times 96500} = 0.226\ V$$

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

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

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

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

$$= 0.226 + 0.0591 = 0.2851\ V$$

Answer Tips

- As Cl^- is not participating in the redox reaction so Cl^- ion concentration should be ignored.

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

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

$$E_{cell} = 0.30 - \frac{0.0591}{6}\log\frac{(0.01)^2}{(0.1)^3} = 0.30 + 0.01 = 0.31\ V$$

Answer Tips

- E°_{cell} = Oxidation potential at anode – oxidation potential at cathode

  $= E^\circ_{ox(Anode)} - E^\circ_{ox(Cathode)}$

26. Given cell,

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

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

Using Nernst equation at 298 K

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

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

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

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

$\therefore\quad E^\circ_{\text{cell}} = 1.98 + \frac{0.0591}{3} = 2\text{ V}$

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

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

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

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

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

or $\log K_c = 0.5074$

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

28. The cell reaction can be represented as :

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

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

According to the Nernst equation :

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

$$= 2.71 - \frac{0.0591}{2}\log\frac{0.1}{0.01} = 2.6804\text{ V}$$

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

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

$\Delta G = 960\text{ kJ} = 960000\text{ J}$

Now, $\Delta G = -nFE_{\text{cell}}$

$E_{\text{cell}} = -\frac{\Delta G}{nF} = \frac{-960000}{4\times 96500} = -2.487\text{ V}$

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

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

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

(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.

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

Reactions :

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

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

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

$\therefore\quad n = 2$

Using Nernst equation :

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

For the given cell

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

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

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

Putting in Nernst equation at 298 K

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

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

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

$= -517240\text{ J mol}^{-1} = -517.24\text{ kJ mol}^{-1}$

32. (b): Unit of molar conductivity:

$$\Lambda_m = \frac{\kappa(\Omega^{-1}\text{cm}^{-1})\times 1000(\text{cm}^3\text{L}^{-1})}{\text{Molarity (mol L}^{-1})}$$

$= \Omega^{-1}\text{cm}^2\text{ mol}^{-1}$ or $\text{S cm}^2\text{ mol}^{-1}$.

33. (d)

Key Points

- Conductivity always decrease with decrease in concentration both for weak and strong electrolytes.

34. 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.

35. 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.

36. **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

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$$

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

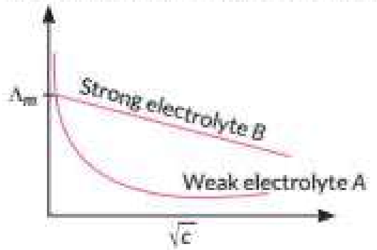
37. **Molar Conductivity :** Molar conductivity of a solution at a volume V is the conductance of all the ions produced from one mole of the electrolyte dissolved in V cm^3 of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole solution is contained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

$\Lambda_m = \kappa V$

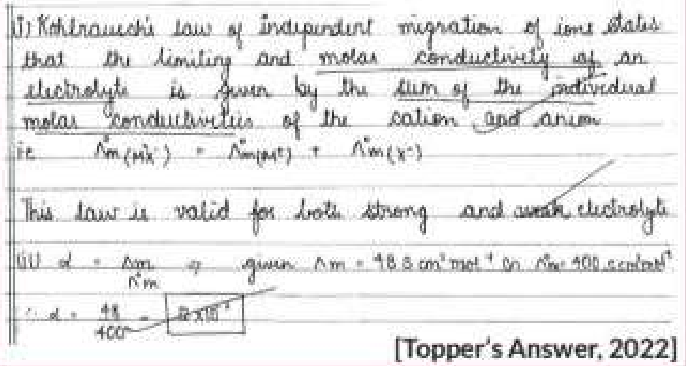
Its units are $\text{S cm}^2\text{ mol}^{-1}$.

38. The molar conductivity (Λ_m) of strong electrolyte increases slowly with dilution as there is no increase in number of ions on dilution because they are already completely dissociated whereas Λ_m for weak electrolyte

increases very rapidly on dilution as the number of ions increase due to increase in dissociation. Hence, *B* is a strong electrolyte and *A* is a weak electrolyte.



39.


(i) Kohlrausch's law of independent migration of ions states that the limiting and molar conductivity of an electrolyte is given by the sum of the individual molar conductivities of the cation and anion
i.e. $\Lambda^\circ_{m(M^+X^-)} = \Lambda^\circ_{m(M^+)} + \Lambda^\circ_{m(X^-)}$

This law is valid for both strong and weak electrolyte

(ii) $\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}$ ∴ given $\Lambda_m = 48\ \text{S cm}^2\ \text{mol}^{-1}$ & $\Lambda^\circ_m = 400\ \text{S cm}^2\ \text{mol}^{-1}$

$\therefore \alpha = \frac{48}{400} = \boxed{12 \times 10^{-2}}$

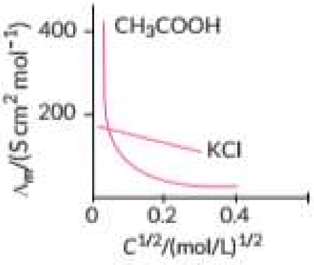
[Topper's Answer, 2022]

40. Given that, $\kappa = 7.8 \times 10^{-5}\ \text{S cm}^{-1}$, $M = 0.001\ \text{M}$
$\Lambda^\circ_m = 390\ \text{S cm}^2\ \text{mol}^{-1}$
We know that,

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{7.8 \times 10^{-5} \times 1000}{0.001} = 78\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{78}{390} = 0.2$$

41. Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations and hence for such electrolytes, the change in Λ_m with dilution is due to increase in the degree of dissociation. This results in increase in the number of ions in the total volume. In case of weak electrolyte, Λ_m increases steeply on dilution at lower concentrations and does not reach a constant value even at infinite dilution. Therefore Λ°_m cannot be obtained by extrapolation of Λ_m to zero concentration.



Λ°_m for such case is obtained by using Kohlrausch law of independent migration of ions. The law 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 electrolytes, *i.e.*, $\Lambda^\circ_m = \upsilon_+ \lambda^\circ_+ + \upsilon_- \lambda^\circ_-$

42. (a) Molar conductivity of a solution at a volume *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.

$\Lambda_m = \kappa V$

(b) Units are $\text{S cm}^2\ \text{mol}^{-1}$.

(c) Molar conductivity increases with decrease in concentration because the total volume, *V* of solution containing one mole of electrolyte also increases.

43. (a) Direct current will cause electrolysis of solution, so more ions will be produced. Hence, we use alternating current instead of direct current.

(b) 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

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

(c) The cell can be represented as :
$Mg \,|\, Mg^{2+} \,||\, Cu^{2+} \,|\, Cu$

44. *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 increase in conductance with dilution, because a strong electrolyte is completely dissociated in solution so the number of ions remain constant.

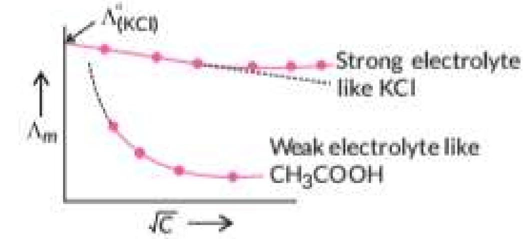
45. (i) Electrolyte *A* is a strong electrolyte while electrolyte *B* is a weak electrolyte.

(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.

46. For a strong electrolyte it is shown by Debye-Huckel Onsager equation as follows :

$\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$



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.

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

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

48. 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.

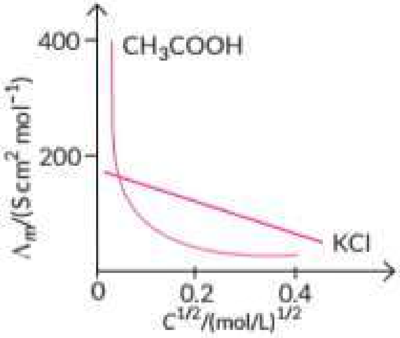
49. The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by κ (kappa).

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

Hence, conductivity of a solution is defined as the conductance of a conductor of 1 cm length and having 1 cm^2 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 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.

Commonly Made Mistake

- For strong electrolyte conductivity decrease with decrease in concentration while molar conductivity increase with increase in concentration.

50. **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

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

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.

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

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

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 temperature : Both increase with increase in temperature as degree of ionisation increases.

52. 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)

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

53. (a) $\Delta G^\circ = nFE^\circ_{cell}$

$$E^\circ_{cell} = \frac{-\Delta G^\circ}{nF} = \frac{300 \times 1000 \text{ J mol}^{-1}}{2 \times 96500 \text{ C mol}^{-1}} = 1.55 \text{ V}$$

(b) $\Lambda^\circ_m(\text{MgCl}_2) = \lambda^\circ_m(\text{Mg}^{2+}) + 2\lambda^\circ_m(\text{Cl}^-)$

$$= 106 \text{ S cm}^2\text{ mol}^{-1} + 2 \times 76.3 \text{ S cm}^2\text{ mol}^{-1}$$
$$= 258.6 \text{ S cm}^2\text{ mol}^{-1}$$

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

Given, $\kappa = 3.905 \times 10^{-5}$ S cm^{-1}
$C = 0.001$ mol L^{-1}

$$\therefore \Lambda_m = \frac{3.905 \times 10^{-5} \times 1000}{0.001} = 39.05 \text{ S cm}^2\text{ mol}^{-1}$$

The degree of dissociation, $\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m} = \dfrac{39.05}{390.5} = 0.1$

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

55. Given : Conductivity, $\kappa = 8 \times 10^{-5}$ S cm^{-1}
Molarity, $C = 0.002$ M $= 0.002$ mol L^{-1}

Using formula, $\Lambda^c_m = \dfrac{1000 \times \kappa}{C}$

$$\Lambda^c_m = \frac{1000 \times 8 \times 10^{-5}}{0.002} = 40 \text{ S cm}^2\text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m} = \frac{40}{404} = 0.099$$

56. (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.

Commonly Made Mistake

- In solid metals, conduction decreases with increase in temperature while in solution conductivity increases with increase in temperature.

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

$R = 5 \times 10^3$ ohm, $M = 0.05$ M

Resistivity, $\rho = R \times \dfrac{A}{l} = 5 \times 10^3 \times \dfrac{0.625}{50}$ ohm cm

$= 62.5$ ohm cm

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

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

$= \dfrac{0.016 \times 1000}{0.05} = 320\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

58. (a) $E^\circ_{\text{cell}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}}$

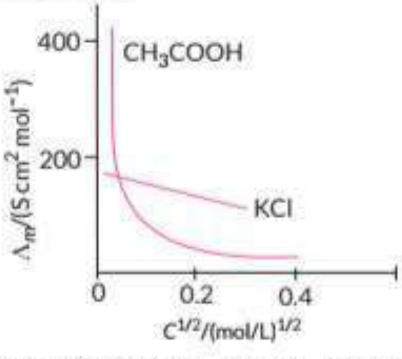
$= 0.80 + 0.76 = 1.56\ \text{V}$

$\Delta_r G^\circ = -nFE^\circ$

$\Delta_r G^\circ = -2 \times 96500 \times 1.56$

$= 301080\ \text{J mol}^{-1} = 301.080\ \text{kJ mol}^{-1}$

(b) For strong electrolytes the plot between Λ_m and $\sqrt{C}$ is a straight line with intercept equal to Λ°_m and slope equal to $-A$. Λ°_m for these can be obtained by extrapolation of Λ_m to zero concentration.



Λ°_m for weak electrolyte cannot be obtained by entrapolaration of graph at zero concentration. Λ°_m for such case is obtained by using Kohlrausch law of independent migration of ions. The law 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 electrolytes, *i.e.*, $\Lambda^\circ_m = \upsilon_+ \lambda^\circ_+ + \upsilon_- \lambda^\circ_-$

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

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

Using formula, $\Lambda^c_m = \dfrac{1000 \times \kappa}{C}$

$\Lambda^c_m = \dfrac{1000 \times 0.0248}{0.20} = 124\ \text{S cm}^2\ \text{mol}^{-1}$

$\alpha = \dfrac{\Lambda^c_m}{\Lambda^\circ_m} = \dfrac{124}{73.5 + 76.5} = 0.82$

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

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

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

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

Conductivity, $\kappa = \dfrac{\text{cell constant}}{R} = \dfrac{129\ \text{m}^{-1}}{520\ \Omega} = 0.248\ \text{S m}^{-1}$

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

$= 1000 \times 0.02\ \text{mol m}^{-3} = 20\ \text{mol m}^{-3}$

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

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

61. (a) 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.

Molar conductivity increases with decrease in concentration because the total volume, V of solution containing one mole of electrolyte also increases.

(b) Degree of dissociation, $\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m}$

Given, $\Lambda^\circ_m = 150.0\ \text{S cm}^2\ \text{mol}^{-1}$

$\Lambda_m = 141.0\ \text{S cm}^2\ \text{mol}^{-1}$

$\therefore \quad \alpha = \dfrac{141}{150} = 0.94$ or 94%

(c) H^+ ion is smaller than K^+ ion. Since, smaller the cation, higher the molar conductivity, hence for the same concentration of HCl and KCl, molar conductivity of HCl is higher than that of KCl.

62. (a) The half cell reactions are :

At anode : $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$

At cathode : $2\text{Ag}^+ + 2e^- \longrightarrow 2\text{Ag}$

So, silver plate is acting as cathode where reduction is taking place.

(b) The function of salt bridge in an electrochemical cell is to maintain electrical neutrality in solutions and prevent voltage drop. If the salt bridge is removed voltage will drop to zero and no current will flow.

(c) If external potential applied becomes greater than E°_{cell} of electrochemical cell then it behaves as an electrolytic cell and the direction of flow of current is reversed.

(d) (i) When E_{cell} is equal to zero, there will be a condition of equilibrium in the cell. So, the concentrations of Zn^{2+} and Ag^+ will become constant.

(ii) Conductivity of the solution decreases with dilution because the number of ions per unit volume that carry the current in solution decreases with dilution.

OR

(d) Given that, $\lambda_m = 138.9\ \text{S cm}^2\ \text{mol}^{-1}$,

Concentration = 1.5 M, $\kappa = ?$

$\lambda_m = \dfrac{\kappa \times 1000}{M} \quad \Rightarrow \quad \kappa = \dfrac{\lambda_m \times M}{1000}$

$$k = \frac{138.9\ \text{S cm}^2\ \text{mol}^{-1} \times 1.5\text{M}}{1000} = 0.208\ \text{S cm}^{-1}$$

63. (i) $C = 0.02$ M

$$r = \frac{d}{2} = \frac{1.40}{2}\ \text{cm} = 0.70\ \text{cm}$$

$l = 44$ cm, $R = 5.00 \times 10^3\ \Omega$

As we know that,

$$R = \rho\frac{l}{A} \Rightarrow 5.00\times10^3 = \rho\times\frac{44}{\pi(0.70)^2}$$

$$\rho = \frac{5.00\times10^3\times3.14\times(0.70)^2\times10^{-2}}{44}$$

$$= 174.8\ \Omega\text{cm}$$

Conductivity, $\kappa = \frac{1}{\rho} = \frac{1}{174.8} = 5.72\times10^{-3}\Omega^{-1}\text{cm}^{-1}$

Molar conductivity,

$$\Lambda_m = \kappa\times\frac{1000}{\text{Molarity}} = \frac{5.72\times1000\times10^{-3}}{0.02} = 2{,}86\ \text{Scm}^2\ \text{mol}^{-1}$$

(ii) $Ni|Ni^{2+}||Ag^+|Ag$

(i) Silver electrode is positively charged.

(ii) Electrons are the carriers of the current in the outer circuit.

64. (a) $2Al + 3Ni^{2+}\ (0.1\ M) \rightarrow 2Al^{3+}\ (0.01\ M) + 3Ni$

$E^\circ_{cell} = 1.41$ V

The cell can be represent as :

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

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

$$= 1.41 - \frac{0.0591}{n}\log\frac{(0.01)^2}{(0.1)^3}$$

$$= 1.41 - \frac{0.0591}{6}\log 10^{-1}$$

$$= 1.41 + \frac{0.0591}{6} = 1.419\ \text{V}$$

(b) For weak electrolytes molar conductivity decrease with increase in concentration. As on low concentration (or on dilution) ionisation increases for weak electrolytes hence molar conductivity increases on dilution.

While the molar conductivity of strong electrolytes increases with increase in concentration as number of ions increases on increasing concentration.

For strong electrolyte, $\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$

Thus Λ_m increase with increase in concentration.

Limiting molar conductivity for weak electrolytes is obtained by using kohlrauhch law of independent migration of ions. The law states that limiting molar conductivity of on electrolyte can be represent as the sum of the individual contributions of an anion and cation of the electrolyte i.e.,

$\Lambda^\circ_m = \nu_+\lambda^\circ_+ + \nu_-\lambda^\circ_-$

65. (b): When concentrated brine *i.e.* aqueous solution of NaCl is electrolysed, products are chlorine at anode and hydrogen at cathode.

At cathode:

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

At anode :

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

66. $\overset{+7}{Mn}O_4^- + 5e^- \longrightarrow Mn^{2+}$

As $5e^-$ are needed to reduce 1 mol of MnO_4^- to Mn^{2+} thus chnage required is 5 Faraday.

Answer Tips

- For calculating charge required calculate number of electrons need for the change.

67. $H_2\overset{-2}{O} \longrightarrow H_2 + \frac{1}{2}\overset{0}{O_2}$,

charge required to oxidised 1 mol of H_2O is 2F
= 2 × 96500 = 193000 C

68. 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 preferred at anode 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.

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

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

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

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

71. 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

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

72. **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 $w \propto I\times t$ $[\because Q = I\times t]$

$w = Z\times I\times t$

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

73. (i) $\Delta G^\circ = -nFE^\circ_{cell}$ (nF = amount of charge passed)

If ΔG is negative, *i.e.* E° is positive then the reaction will be spontaneous.

(ii) According to Faraday's first law of electrolysis, "weight of ions deposited on an electrode of an electrolytic cell is directly proportional to the quantity of electricity passed" *i.e.*,

$w \propto Q$ or $w = ZQ = ZIt$

where, Q = quantity of electricity (in coulombs)

I = current (in amperes), t = time (in second)

Z = electrochemical equivalent of material deposited on the electrode.

74. In aqueous solution, $CuCl_2$ ionises into
$CuCl_2 \rightarrow Cu^{2+} + 2Cl^-$
At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$
At anode : $2Cl^- \rightarrow Cl_2 + 2e^-$

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.

75. (a) $CuSO_{4(aq)} \rightarrow Cu^{2+}_{(aq)} + SO^{2-}_{4(aq)}$

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

At anode : $H_2O_{(l)} \rightarrow \frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e^-$

(b) At the cathode the following reduction reactions compete to take place :
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}\ ;\ E^\circ = 0.80\ V$
$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}\ ;\ E^\circ = 0.00\ V$

The reaction with a higher value of E° takes place at the cathode. Therefore, the deposition of silver will take place. 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.
$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

76. $\underset{1\ \text{mole}}{Fe^{3+}} + \underset{1e^-}{1e^-} \rightarrow Fe^{2+}$

1 mole of Fe^{3+} requires 1 mole of electrons for reduction.
3 moles of Fe^{3+} requires 3 moles of electrons for reduction.

i.e., $Q = 3 \times F$
$Q = 3 \times 96500$
$I = 2A$
$I = \frac{Q}{t}$
$t = \frac{Q}{I} = \frac{289500}{2} = 144750\ s$

77. 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

$$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)};\quad E^\circ = 0{\cdot}00\ V$$

The species that get oxidised at anode is the one having lower value of E°. Thus
$2H_2O \longrightarrow O_{2(g)} + 4H^+ + 4e^-$
should take place but on account of overpotential of oxygen reaction preferred at anode is

$$Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^-;\quad E^\circ = +\,1{\cdot}36\ V$$

78. 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 :

$$\underset{}{Ag^+} + \underset{\substack{1\,F \\ 1 \times 96500\,C}}{1e^-} \rightarrow \underset{\substack{1\,mol \\ 108\,g}}{Ag}$$

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

∴ 1800 C of electricity would deposit

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

79. **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 $w \propto I \times t$ $[\because Q = I \times t]$
$w = Z \times I \times t$
where, Z is a constant of proportionality known as electrochemical equivalent of the substance deposited.
The electrode reaction is $Cu^{2+} + 2e^- \rightarrow Cu$
∴ Quantity of charge required for reduction of 1 mol of $Cu^{2+} = 2F = 2 \times 96500 = 193000\ C$

80. 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,

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

Thus, 2 × 96500 C of electricity produces 58.7 g Ni.
∴ 6000 C of electricity would produce

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

81. (i) At the cathode the following reduction reactions compete to take place :
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}\ ;\ E^\circ = 0.80\ V$
$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}\ ;\ E^\circ = 0.00\ V$

The reaction with a higher value of E° takes place at the cathode. Therefore, the deposition of silver will take place. 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.
$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

(ii) At the cathode, the following reduction reaction occurs to produce H_2 gas.
$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$

At the anode, the following processes are possible :
$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-\ ;\ E^\circ = +\ 1.23\ V$ ...(i)
$2SO^{2-}_{4(aq)} \rightarrow S_2O^{2-}_{8(aq)} + 2e^-\ ;\ E^\circ = +\,1.96\ V$ ...(ii)
For dilute sulphuric acid, reaction (i) is preferred to produce O_2 gas but for concentrated sulphuric acid, (ii) occurs.

82. According to first law of electrolysis,
$w = ZIt$
$w = \frac{Eq.\ wt.}{F} \times It$
$w_{Cu} = 2\ g$
$I = 2\ A$
$2 = \frac{31.75}{96500} \times 2 \times t \Rightarrow t = \frac{96500 \times 2}{2 \times 31.75} = 3040\ sec$
Eq. w.t of $Cu^{2+} = 31.75$

According to second law of electrolysis,

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

$$\frac{w_{Zn}}{2}=\frac{32.5}{31.75}$$

$$w_{Zn}=\frac{32.5\times 2}{31.75}=2.047\text{ g}$$

83. According to Faraday's first law of electrolysis, mass of substance deposited ∝ quantity of electricity passed

$$\Rightarrow\ W=ZQ=\frac{\text{Eq. wt.}}{F}\times Q$$

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

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

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

According to Faraday's second law of electrolysis,

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

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

$$\Rightarrow\ \text{Mass of Zn deposited}=\frac{2.8}{28}\times 32.65=3.265\text{ g}$$

84. 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 first law of electrolysis,

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

$w = ZIt$

$$1.5=\frac{52}{6\times 96500}\times 12.5\times t \Rightarrow t=\frac{6\times 1.5\times 96500}{52\times 12.5}=1336.15\text{ s}$$

85. (a) $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ and $2I^- \longrightarrow I_2 + 2e^-$

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

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

(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

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

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

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

86. (i) 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.

Expression for the limiting molar conductivity of acetic acid is

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

(ii) $E^\circ_{cell}=E^\circ_{cathode}-E^\circ_{anode}=E^\circ_{Ag^+/Ag}-E^\circ_{Ni^{2+}/Ni}$

$= +0.80\text{ V} - (-0.25\text{ V})$

$= 1.05\text{ V}$

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

$= -2 \times 96500 \times 1.05$

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

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

$\Delta G^\circ = -RT\ln K_c = -202650\text{ J mol}^{-1}$

$8.314\text{ J K}^{-1}\text{mol}^{-1} \times 298\text{ K}\ln K_c = 202650\text{ J mol}^{-1}$

$\ln K_c = 81.79$

$2.303\log K_c = 81.79$

$\log K_c = 35.5145$

87. 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 :

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

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 : $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

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

91. 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.

92. (a) $\kappa = 4.95 \times 10^{-5}\text{ S cm}^{-1}$, $M = 0.001$ M

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

We know that

$$\Lambda_m=\frac{\kappa\times 1000}{M}=\frac{4.95\times 10^{-5}\times 1000}{0.001}=49.5\text{ S cm}^2\text{ mol}^{-1}$$

$$\alpha=\frac{\Lambda_m}{\Lambda^\circ_m}=\frac{49.5}{390.5}=0.1267$$

$$K_c=\frac{C\alpha^2}{1-\alpha}=\frac{0.001\times 0.1267\times 0.1267}{(1-0.1267)}=1.82\times 10^{-5}$$

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

(c) The batteries which can be recharged again and again are called as secondary batteries. *e.g.*, lead storage battery.

93. (c) : The H_2–O_2 fuel cell was used for producing electricity in Apollo space programme. The water vapours produced were condensed and added to drinking water supply for astronauts.

94. Mercury cell is used for low current devices like hearing aids and watches.

Key Points

- Mercury cell is used in waters and hearing aids because their potential remains constant throughout their life.

95. The hydrogen oxygen fuel cell was used in Apollo space programme.

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

97. 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.

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

100. (i) It is pollution free.
(ii) It has high efficiency of 70 - 75% and its rate can be controlled.

101. 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 $E^\circ_{(B^{2+}/B)} = (-0.14\ V)$.

CBSE Sample Questions

1. $Al\,|\,Al^{3+}(0.01\ M)\,||\,Cd^{2+}(0.1\ M)\,|\,Cd$ (1/2)

$2Al_{(s)} + 3Cd^{2+}\ (0.1\ M) \rightarrow 3Cd_{(s)} + 2Al^{3+}\ (0.01\ M)$

$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Al^{3+}]^2}{[Cd^{2+}]^3}$ (1/2)

$E_{cell} = 1.26 - \frac{0.059}{6}\log\frac{(0.01)^2}{(0.1)^3}$ (1/2)

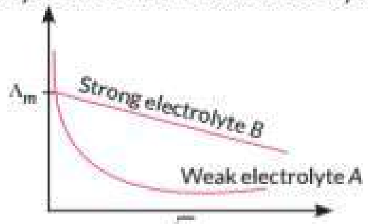
$= 1.26 - \frac{0.059}{6}(-1)$ (1)

$= 1.26 + 0.0098 = 1.269\ V = 1.27\ V$ (1/2)

2. (b): $\Lambda^\circ_{CH_3COOK} = \Lambda^\circ_{CH_3COOH} + \Lambda^\circ_{KCl} - \Lambda^\circ_{HCl}$
$= 390 + 150 - 425 = 115\ S\ cm^2/mol$
(1)

3. (c) : Limiting molar conductivity of CH_3COOH can be calculated as
$\Lambda^\circ_{CH_3COOH} = \lambda^\circ_{CH_3COONa} + \lambda^\circ_{H^+} - \lambda^\circ_{Na^+}$
$= 91 + 349.6 - 50.1$
$= 440.6 - 50.1 = 390.5\ S\ cm^2\ mol^{-1}$ (1)

4. The molar conductivity(Λ_m) of strong electrolyte increases slowly with dilution as there is no increase in number of ions on dilution because they are already completely dissociated whereas Λ_m for weak electrolyte increases very rapidly on dilution as the number of ions increase due to increase in dissociation. Hence, *B* is a strong electrolyte and *A* is a weak electrolyte. (1)



(1)

5. (i) **Kohlrausch's law** : 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. (1)

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

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

(ii) $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}\,;\ E^\circ_{Cu^{2+}/Cu} = 0.34\ V$ (At cathode)
$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-;\ E^\circ_{Al^{3+}/Al} = -1.66\ V$ (At anode)
$2Al_{(s)} + 3Cu^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Cu_{(s)}$ (Overall reaction)
(1/2)

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.34 - (-1.66) = 2.00\ V$ (1/2)

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

$= 2.00 - \frac{0.059}{6}\log\frac{(0.15)^2}{(0.025)^3}$ $(\because n = 6)$ (1)

$= 2.00 - \frac{0.059}{6}(2\log 0.15 - 3\log 0.025)$

$= 2.00 - \frac{0.059}{6}(-1.6478 - (-4.806)) = 1.9689\ V$ (1)

6. (i) MnO_4^- is the strongest oxidising agent because it has maximum positive E° value. (1)

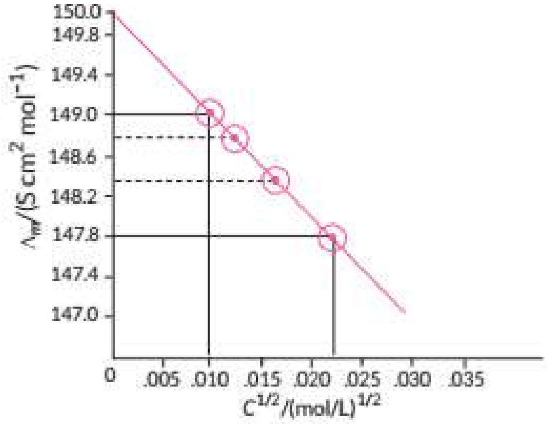
(ii) (a) Molar conductivity of a solution at a dilution *V* is the conductance of all the ions produced from one mole of the electrolyte dissolved in *V* cm^3 of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole solution is contained between them, *i.e.*, $\Lambda_m = \kappa V_m$ (1)

(b) Electrolyte is a strong electrolyte. Molar conductivity (Λ_m) increases slowly with dilution. (1)

(c) $\Lambda_m = \Lambda^\circ_m - AC^{1/2}$ (1)

Λ°_m is equal to intercept on y-axis of the graph.
Therefore $\Lambda^\circ_m = 150\ S\ cm^2\ mol^{-1}$

(d)



$A = -\text{slope} = -(149 - 147.8/0.010 - 0.022)$
$= 100\ S\ cm^2\ mol^{-1}/(mol/L^{-1})^{1/2}$ **(1)**

7. (a) "*A*" is copper metal as metals have high value of conductivity. **(1)**

(b) $Mg^{2+} + 2e^- \longrightarrow Mg$

1 mole of magnesium ions gain 2 moles of electrons or 2*F* to form 1 mole of Mg. 24 g Mg requires 2*F* electricity.

4.8 g Mg requires $2 \times \frac{4.8}{24} = 0.4F = 0.4 \times 96500 = 38600C$

(1)

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

2 F electricity is required to produce 1 mole or 40 g Ca.

0.4 F electricity will produce 8 g Ca. **(1)**

(c) $F = 96500C, n = 2,$

$Sn^{2+}_{(aq)} + 2e^- \longrightarrow Sn_{(s)}; E^\circ - 0.14\ V$

$Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)}; E^\circ = 0.15\ V$

$E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{Anode}$
$= 0.15 - (-0.14) = 0.29\ V$

$\Delta G^\circ = -nFE^\circ_{cell} = 2 \times 96500 \times 0.29 = 55970\ J/mol$ **(1)**

8. (a) 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 lifetime. **(1)**

(b) $KCl_{(aq)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$

Cathode: $H_2O_{(l)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} + OH^-_{(aq)}$ **(1/2)**

Anode: $Cl^-_{(aq)} \longrightarrow \frac{1}{2}Cl_{2(aq)} + e^-$ **(1/2)**

Net reaction: $KCl_{(aq)} + H_2O_{(l)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)} + \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)}$ **(1)**

(c) Given, potential of hydrogen gas electrode = –0.59 V

Electrode reaction: $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

Applying Nernst equation,

$E_{(H^+/H_2)} = E^\circ_{(H^+/H_2)} - \frac{0.059}{n}\log\frac{[H_2]^{1/2}}{[H^+]}$ **(1)**

$E^\circ_{(H^+/H_2)} = 0\ V$
$E_{(H^+/H_2)} = -0.59\ V$
$n = 1$
$[H_2] = 1$ bar
$-0.59 = 0 - 0.059(-\log[H^+])$ **(1/2)**
$-0.59 = -0.059pH$ **(1/2)**
$\therefore$ pH = 10

9. Anode: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ **(1/2)**

Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$ **(1/2)**

Overall: $2Zn_{(s)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Zn^{2+}_{(aq)} + 4OH^-_{(aq)}$

$2Zn_{(s)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2[Zn(OH)_2]_{(ppt.)}$ **(1)**