

LESSON AT A GLANCE

- **Electrochemical cell:** An electrochemical cell is a device that consists of two metallic electrodes dipping in electrolytic solutions which convert chemical energy into electrical energy.
- **Galvanic cell:** In galvanic cell the chemical energy of a spontaneous redox reaction is converted into electrical energy.
- **Electrolysis and Electrolytic cell:** Electrolysis is the production of a chemical reaction by passing an electric current through an electrolyte. In electrolysis, positive ions migrate to the cathode and negative ions to the anode. The device used for electrolysis or the cell in which electrolysis occurs, is called electrolytic cell.
- **Molar Conductivity:** Symbol λ_m . The conductivity of that volume of an electrolyte that contains one mole of solution between electrodes placed one metre apart.

$$\lambda_m = \frac{K}{C}$$

- Molar conductivity of an electrolyte increases with dilution.
- **Kohlrausch Law:** The molar conductivity at infinite dilution, for an electrolyte is equal to the sum of the ionic conductivity of the individual ions.

$$\lambda_m^0 = v_+ \lambda_+^0 + v_- \lambda_-^0$$

- **Batteries:** The term 'battery' is used to represent the arrangement of two or more galvanic cells connected in series. The cell which we employ as a source of electrical energy is basically an electrochemical cell.
- **Corrosion:** Metal is oxidised by loss of electrons to oxygen and formation of oxides.

- **Electrochemistry:** The branch of chemistry which deals with the relationship between chemical energy and electrical energy and how one can be converted into another is known as electrochemistry.
- **Electrode Potential:** The tendency of an electrode to lose or gain electrons is called electrode potential. Since each electrode represents a half cell, therefore, electrode potential is also called potential for half cell.
- **Standard Electrode Potential:** When the concentrations of all the species involved in a half cell is united then the electrode potential is known as standard electrode potential.
- **Cell Potential:** The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrode potential of cathode and anode.
- **Conductance (G):** Conductance is a measure of the ease with which current flows through the conductor. It may be defined as the reciprocal of electrical resistance. It is called the conductance. It is usually represented by G. Thus,

$$G = \frac{1}{R}$$

- **Units:** The units of conductance are reciprocal ohms written as ohm^{-1} or *Siemens denoted by S*. $1 \text{ S} = 1 \text{ } \Omega^{-1}$.
- **Specific Conductance or Simply Conductivity:** The inverse of resistivity is called conductivity (specific conductance). It is represented by the symbol 'k'.
- **Units:** SI unit of conductivity is S m^{-1} or S cm^{-1} .
- **Factors Affecting Conductivity**
 - (i) Depends upon the nature of the material.
 - (ii) Depends upon the temperature and pressure at which the measurement are made.
- **Conductors:** Metals and their alloys which have very large conductivity are known as conductors. Certain non-metals like carbon-black, graphite and some organic polymers are also electronically conducting.
- **Insulators:** Substances like glass, ceramics etc. which do not allow electricity to pass through, *i.e.* having very low conductivity are known as insulators.
- **Semiconductor:** Substances having conductivity between conductors and insulators are called semiconductors and are

are important electronic materials. *For example:* Silicon, doped silicon and gallium are known as semiconductors.

- **Superconductors:** Certain materials having zero resistivity or infinite conductivity are called superconductors. Ceramic materials and mixed oxides are known to show super conductivity at temperatures as high as 150 K.
- **Applications of Kohlrausch Law**
 - Using Kohlrausch Law of independent migration of ions, it is possible to calculate l° for any electrolyte from the l° of individual ions.
 - For weak electrolytes like acetic acid it is possible to determine the value of dissociation constant once we know the λ_m° and λ_m at a given concentration C.
- **Corrosion:** It is a matter of common observation that 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 sulphates etc. is called corrosion.

TEXTBOOK QUESTIONS SOLVED

3.1 Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn

Ans. The desired order is:

Mg, Al, Zn, Fe, Cu, Ag

Hint. A metal with a lower electrode potential would displace another with a higher electrode potential from a solution of its salt. The metals are arranged in the **increasing order** of their electrode potentials.

3.2 Given the standard electrode potentials,

$K^+/K = -2.93V$, $Ag^+/Ag = 0.80 V$,

$Hg^{2+}/Hg = 0.79 V$

$Mg^{2+}/Mg = 2.37 V$, $Cr^{3+}/Cr = -0.74 V$

Arrange these metals in their increasing order of reducing power.

Ans. The required order is:

$Ag < Hg < Cr < Mg < K$

Hint. Lower the electrode potential of a metal, more easily is it oxidising, hence greater is its oxidising power. The

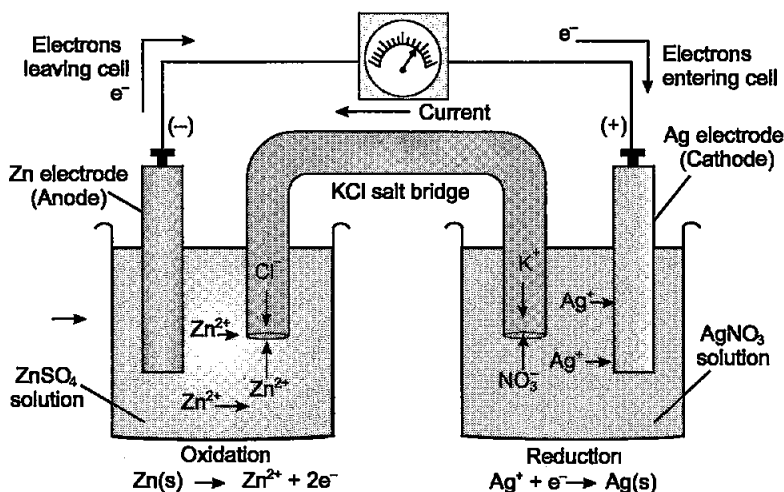
metals are arranged in the decreasing order of their electrode potentials.

3.3 Depict the galvanic cell in which the reaction

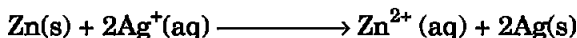
$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show:

- (i) Which of the electrode is negatively charged?
- (ii) The carriers of the current in the cell.
- (iii) Individual reaction at each electrode.

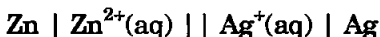
Ans.



Since the reaction is

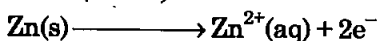


it can be denoted as

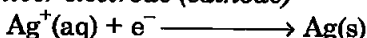


- (i) The negatively charged electrode is the zinc electrode since it is the anode and would act as the sink for electrons lost by zinc atoms.
- (ii) Ions are the carriers of current in the cell, which migrate through the salt bridge. While the cations Zn^{2+} and Ag^+ ions move toward negatively charged zinc electrode. Their corresponding anions move towards positively charged silver electrodes.
- (iii) The reactions occurring at the two electrodes are:

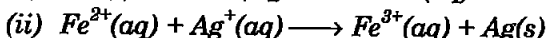
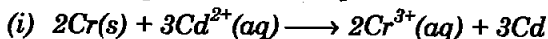
At zinc electrode (anode)



At silver electrode (cathode)



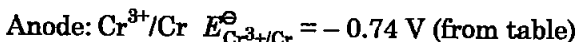
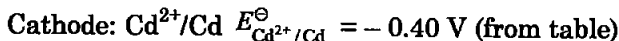
3.4 Calculate the standard cell potentials of galvanic cell in which the following reactions take place:



Calculate the $\Delta_r G^\ominus$ and equilibrium constant of the reactions.

Ans. (i) Cell reaction

(a) E_{cell}^\ominus

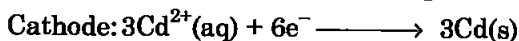
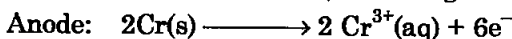


$$E_{\text{cell}}^\ominus = E_{\text{cathode}}^\ominus - E_{\text{anode}}^\ominus$$

$$= -0.40 \text{ V} - (-0.74 \text{ V}) = +0.34 \text{ V.}$$

(b) $\Delta_r G^\ominus$

From electrode reactions (from the given cell reaction)



$$n = 6$$

$$\Delta_r G^\ominus = -nFE_{\text{cell}}^\ominus = -6 \times 96500 \text{ C mol}^{-1} \times 0.34 \text{ V}$$

$$= -196860 \text{ C V mol}^{-1}$$

$$= -196860 \text{ J mol}^{-1} (\because 1 \text{ J} = 1 \text{ CV})$$

$$= -196.86 \text{ kJ mol}^{-1}$$

(c) K

$$\Delta_r G^\ominus = -2.303 RT \log K$$

$$\text{or } \log K = - \frac{\Delta_r G^\ominus}{2.303 RT}$$

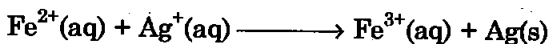
$$= \frac{-196860 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

(Since E^\ominus values used are at 298 K, $T = 298 \text{ K}$)

$$= 34.5014$$

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

(ii) Cell reaction

(a) $E_{\text{cell}}^{\ominus}$ Cathode: Ag^{+}/Ag $E_{\text{Ag}^{+}/\text{Ag}}^{\ominus} = 0.80 \text{ V}$ (from table)Anode: $\text{Fe}^{2+}/\text{Fe}^{3+}$ $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\ominus} = 0.77 \text{ V}$ (from table)

$$\begin{aligned} E_{\text{cell}}^{\ominus} &= E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus} \\ &= 0.80 \text{ V} - 0.77 \text{ V} = 0.03 \text{ V} \end{aligned}$$

(b) $\Delta_r G^{\ominus}$

From electrode reactions (from the given cell reaction)

Anode: $\text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Fe}^{3+}(\text{aq}) + e^{-}$ Cathode: $\text{Ag}^{+}(\text{aq}) + e^{-} \longrightarrow \text{Ag}(\text{s})$

$$n = 1$$

$$\begin{aligned} \Delta_r G^{\ominus} &= -nFE_{\text{cell}}^{\ominus} = (-1) \times (96500 \text{ C mol}^{-1}) \times (0.03 \text{ V}) \\ &= -2895 \text{ C V mol}^{-1} = -2898 \text{ J mol}^{-1} \\ &= -2.895 \text{ kJ mol}^{-1} \end{aligned}$$

(c) K

$$\Delta_r G^{\ominus} = -2.303 RT \log K$$

$$\therefore \log K = -\frac{\Delta_r G^{\ominus}}{2.303 RT}$$

$$= -\frac{-2895 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 0.5074$$

$$K = \text{antilog } 0.5074 = 3.22$$

3.5 Write the Nernst equation and calculate the emf of the following cells at 298 K:

(i) $\text{Mg}(\text{s}) | \text{Mg}^{2+}(0.001 \text{ M}) || \text{Cu}^{2+}(0.0001 \text{ M}) | \text{Cu}(\text{s})$ (ii) $\text{Fe}(\text{s}) | \text{Fe}^{2+}(0.001 \text{ M}) || \text{H}^{+}(1 \text{ M}) | \text{H}_2(\text{g})(1 \text{ bar}) | \text{Pt}(\text{s})$ (iii) $\text{Sn}(\text{s}) | \text{Sn}^{2+}(0.050 \text{ M}) || \text{H}^{+}(0.020 \text{ M}) | \text{H}_2(\text{g})(1 \text{ bar}) | \text{Pt}(\text{s})$ (iv) $\text{Pt}(\text{s}) | \text{Br}_2(\text{l}) | \text{Br}^{-}(0.010 \text{ M}) | \text{H}^{+}(0.030 \text{ M}) | \text{H}_2(\text{g})(1 \text{ bar}) | \text{Pt}(\text{s})$ Ans. (i) $\text{Mg}(\text{s}) | \text{Mg}^{2+}(0.001 \text{ M}) || \text{Cu}^{2+}(0.0001 \text{ M}) | \text{Cu}(\text{s})$

Reactions

Anode: $\text{Mg}(\text{s}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + 2e^{-}$ Cathode: $\text{Cu}^{2+}(\text{aq}) + 2e^{-} \longrightarrow \text{Cu}(\text{s})$ Cell reaction: $\text{Mg}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

$$n = 2$$

Nernst equation:

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

Calculation of E_{cell}

$$\begin{aligned} E_{\text{cell}}^{\ominus} &= E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus} \\ &= E_{\text{Cu}^{2+}/\text{Cu}}^{\ominus} - E_{\text{Mg}^{2+}/\text{Mg}}^{\ominus} \\ &= 0.34 \text{ V} - (-2.37 \text{ V}) \quad (\text{Values from the table}) \\ &= 2.71 \text{ V} \end{aligned}$$

$$n = 2, \frac{2.303 RT}{F} = 0.059 \text{ V at } 298 \text{ K}$$

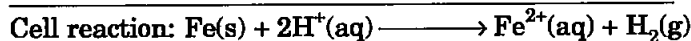
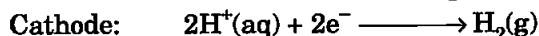
$$[\text{Mg}^{2+}] = 0.001 \text{ M}, [\text{Cu}^{2+}] = 0.0001 \text{ M}$$

Putting in Nernst equation

$$\begin{aligned} E_{\text{cell}}^{\ominus} &= 2.71 \text{ V} - \frac{0.059}{2} \log \frac{0.001}{0.0001} \text{ V} \\ &= 2.71 - 0.0295 \log 10 \text{ V} \\ &= 2.71 - 0.03 = 2.68 \text{ V} \end{aligned}$$



Reactions



$$n = 2.$$

Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{[\text{Fe}^{2+}] \times p_{\text{H}_2}}{[\text{H}^{+}]^2}$$

Calculation of E_{cell}

$$\begin{aligned} E_{\text{cell}}^{\ominus} &= E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus} \\ &= E_{\text{H}^{+}/\text{H}_2}^{\ominus} - E_{\text{Fe}^{2+}/\text{Fe}}^{\ominus} \\ &= 0 - (-0.44) = +0.44 \text{ V (Values from table)} \end{aligned}$$

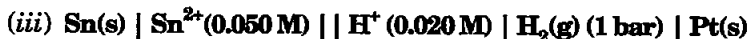
$$[\text{Fe}^{2+}] = 0.001 \text{ M}; [\text{H}^{+}] = 1 \text{ M}; p_{\text{H}_2} = 1 \text{ bar}$$

Putting in Nernst equation

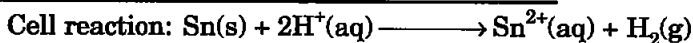
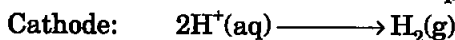
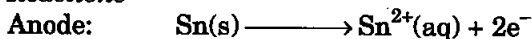
$$\begin{aligned} E_{\text{cell}} &= 0.44 \text{ V} - 0.0295 \log \frac{0.001 \times 1}{1^2} \text{ V} \\ &= 0.44 \text{ V} - 0.0295 \log 10^{-3} \text{ V} \end{aligned}$$

$$= 0.44 \text{ V} - [(0.0295) \times (-3)] \text{ V}$$

$$= 0.44 \text{ V} + 0.0887 \text{ V} = 0.53 \text{ V}$$



Reactions



$$n = 2$$

Nernst equation

$$E_{\text{cell}}^{\ominus} = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}] \times p_{\text{H}_2}}{[\text{H}^+]^2}$$

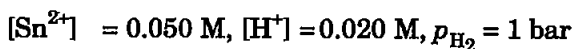
Calculation of E_{cell}

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

$$= E_{\text{H}^+/\text{H}_2}^{\ominus} - E_{\text{Sn}^{2+}/\text{Sn}}^{\ominus}$$

$$= 0 - (-0.14) = 0.14 \text{ V} \quad (\text{Values from table})$$

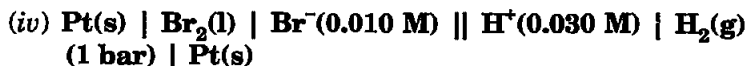
$$n = 2$$



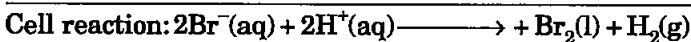
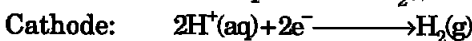
$$E_{\text{cell}} = 0.14 \text{ V} - \frac{0.059}{2} \log \frac{0.05 \times 1}{(0.02)^2} \text{ V}$$

$$= 0.14 \text{ V} - (0.0295 \times 2.0969)$$

$$= 0.14 \text{ V} - 0.062 \text{ V} = 0.078 \text{ V}$$



Reactions



$$n = 2$$

Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{2} \log \frac{p_{\text{H}_2}}{[\text{Br}^-]^2 [\text{H}^+]^2}$$

Calculation of E_{cell}

$$E_{\text{cell}}^{\ominus} = E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus} = E_{\text{H}^+/\text{H}_2}^{\ominus} - E_{\text{Br}^-/\text{Br}_2}^{\ominus}$$

$$= 0 - 1.09 = -1.09 \text{ V} \quad (\text{Values from table})$$

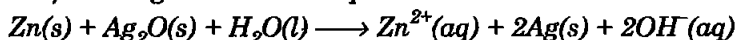
$$n = 2$$

$$[\text{Br}^-] = 0.01 \text{ M}; [\text{H}^+] = 0.02 \text{ M}; p_{\text{H}_2} = 1 \text{ bar}$$

Putting in Nernst equation

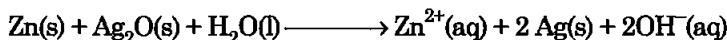
$$\begin{aligned} E_{\text{cell}} &= -1.09 \text{ V} - \frac{0.059}{2} \log \frac{1}{[0.01]^2 [0.03]^2} \text{ V} \\ &= -1.09 \text{ V} - 0.0295 \log 1.111 \times 10^7 \text{ V} \\ &= -1.09 \text{ V} - (0.0295 \times 7.0457) \text{ V} \\ &= -1.09 - 0.208 = -1.298 \text{ V} \end{aligned}$$

3.6 In the button cells widely used in watches and other devices the following reaction takes place:

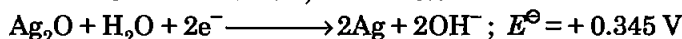
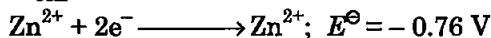


Determine $\Delta_r G^\ominus$ and E^\ominus for the reaction.

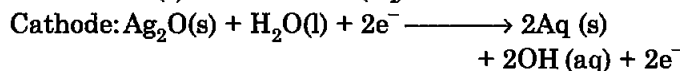
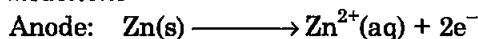
Ans. The cell reaction in button cell:



(i) E_{cell}^\ominus



Reactions



$$n = 2$$

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

$$= E_{\text{Ag}_2\text{O}, \text{H}_2\text{O}/\text{OH}^-, \text{Ag}}^\ominus - E_{\text{Zn}^{2+}/\text{Zn}}^\ominus$$

$$= +0.345 - (-0.76) \text{ V} = 1.105 \text{ V}$$

(ii) $\Delta_r G^\ominus$

$$\Delta_r G^\ominus = -n F E_{\text{Cell}}^\ominus = -2 \times 96500 \text{ C mol}^{-1} \times 1.105 \text{ V}$$

$$= -213.265 \text{ C V mol}^{-1}$$

$$= -213265 \text{ J mol}^{-1} = -213.3 \text{ k J mol}^{-1}$$

3.7 Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Ans. Conductivity of a solution is defined as the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section.

Specific conductivity:

$$\begin{aligned}\kappa &= \frac{1}{\rho} = \frac{1}{\text{ohm cm}} \\ &= \text{ohm}^{-1} \text{ cm}^{-1}\end{aligned}$$

In terms of SI units

$$= \text{Sm}^{-1}$$

Molar conductivity: It is defined as the conducting power of all the ions produced by one gram mole of an electrolyte in a solution and it is denoted by λ_m .

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

where ' κ ' is electrolytic conductivity of solution and ' C ' is concentration of the solution expressed in mol L^{-1}

The unit of $\lambda_m = 1 \text{ S m}^2 \text{ mol}^{-1}$

Variation of conductivity and molar conductivity with concentration: Both conductivity and molar conductivity change with change in concentration of electrolyte. Conductivity always decreases with decrease in concentration both for weak as well as for strong electrolytes. It is because of number of ions per unit volume that carries the current in a solution decrease on dilutions. Molar conductivity increases with decrease in concentration. This is because both number of ions as well as mobility of ions increases with dilution. When concentration approaches zero, the molar conductivity is known as limiting molar conductivity or molar conductivity at infinite dilution.

3.8 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1} . Calculate its molar conductivity.

Ans. $\Lambda_m = \frac{1000 \times \kappa}{CC_m}$

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

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

$$\Lambda_m = \frac{(1000 \text{ cm}^3 \text{ L}^{-1}) \times (0.0248 \text{ S cm}^{-1})}{(0.20 \text{ mol L}^{-1})} = 124 \text{ S cm}^2 \text{ mol}^{-1}$$

3.9 The resistance of a conductivity cell containing 0.001M 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 $0.146 \times 10^{-3} \text{ S cm}^{-1}$?

Ans. Cell constant = $\frac{\text{Conductivity}}{\text{Conductance}} = \text{Conductivity} \times \text{Resistance}$
 $= (0.146 \times 10^{-3} \text{ S cm}^{-1}) \times (1500 \Omega) = 0.219 \text{ cm}^{-1}$

3.10 The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

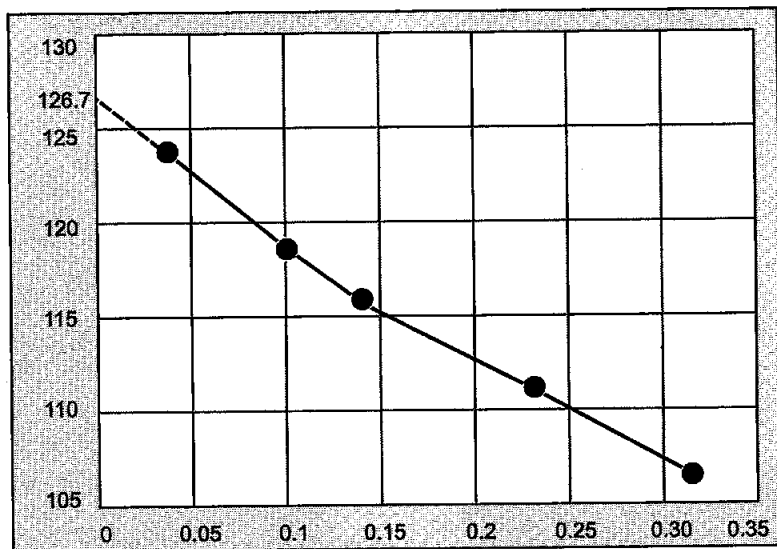
Concentration / M	0.001	0.010	0.020	0.050	0.100
$10^3 \times \kappa / \text{S m}^{-1}$	1.237	11.85	33.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of Λ_m° .

Ans. The conductivity is given in the units S m^{-1} . For conversion into the units S cm^{-1} using the relation.

$$1 \text{ S m}^{-1} = 10^{-2} \text{ S cm}^{-1}$$

Concentration C/M	$\sqrt{C}/M^{1/2}$	$\kappa/\text{S m}^{-1}$	$\kappa/\text{S cm}^{-1}$	$\Lambda_m = \frac{1000 \times \kappa}{C}$ ($\text{S cm}^2 \text{ mol}^{-1}$)
0.001	0.032	1.237×10^{-2}	1.237×10^{-4}	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}}$ = 123.7
0.010	0.100	11.85×10^{-2}	11.85×10^{-4}	$\frac{1000 \times 11.85 \times 10^{-4}}{0.01}$ = 118.5
0.020	0.141	33.15×10^{-2}	33.15×10^{-4}	$\frac{1000 \times 33.15 \times 10^{-4}}{0.02}$ = 115.8
0.050	0.224	55.53×10^{-2}	55.53×10^{-4}	$\frac{1000 \times 55.53 \times 10^{-4}}{0.05}$ = 111.1
0.100	0.316	106.74×10^{-2}	106.74×10^{-4}	$\frac{1000 \times 106.74 \times 10^{-4}}{0.1}$ = 106.7



Λ_m vs \sqrt{C}

Λ_m° = Intercept of the graph on Λ_m axis = 126.7 S cm² mol⁻¹

3.11 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 cm² mol⁻¹, what is its dissociation constant?

Ans. $\Lambda_m = \frac{1000 \times \kappa}{C_m}$

Given: $\kappa = 7.896 \times 10^{-5}$ S cm⁻¹; $C_m = 0.00241$ mol L⁻¹

$$\begin{aligned} \therefore \Lambda_m &= \frac{(1000 \text{ cm}^3 \text{ L}^{-1}) \times (7.896 \times 10^{-5} \text{ S cm}^{-1})}{0.00241 \text{ mol L}^{-1}} \\ &= 32.76 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

The degree of dissociation α is related to molar conductivity

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{32.76}{390.5} = 8 \times 10^{-2} = 0.0839$$

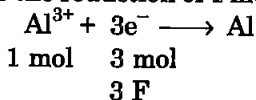
The dissociation constant K_a is related to the degree of dissociation α as

$$K_a = \frac{C \alpha^2}{1 - \alpha} = \frac{0.00241 \times (8.39 \times 10^{-2})^2}{1 - 0.0839} = 1.85 \times 10^{-5}$$

3.12 How much charge is required for the following reductions:

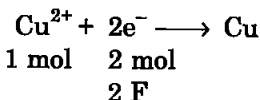
- (i) 1 mol of Al^{3+} to Al?
 (ii) 1 mol of Cu^{2+} to Cu?
 (iii) 1 mol of MnO_4^- to Mn^{2+} ?

Ans. (i) For the reduction of 1 mol of Al^{3+}



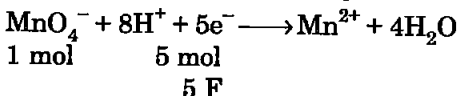
The charge required is 3 F.

(ii) For the reduction of 1 mol of Cu^{2+}



The charge required is 2 F.

(iii) For the reduction of 1 mol of MnO_4^-

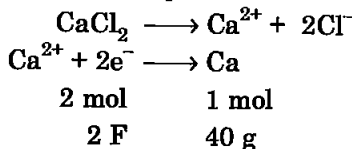


The charge required is 5 F.

3.13 How much electricity in terms of Faraday is required to produce

- (i) 20.0 g of Ca from molten CaCl_2 ?
 (ii) 40.0 g of Al from molten Al_2O_3 ?

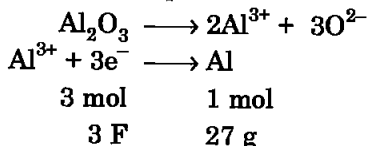
Ans. (i) Reaction for production of Ca from molten CaCl_2



40 g Ca is produced by 2 F charge.

\therefore 20 g Ca would be produced by 1 F charge.

(ii) Reaction for production of Al from molten Al_2O_3 .



27 g Al is produced by 3 F charge.

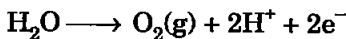
40.0 g Al would be produced by $\frac{3\text{F} \times 40}{27} = 4.44 \text{ F}$

3.14 How much electricity is required in coulomb for the oxidation of

(i) 1 mol of H_2O to O_2 ?

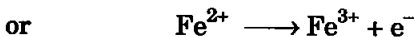
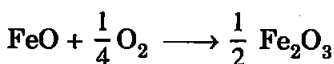
(ii) 1 mol of FeO to Fe_2O_3 ?

Ans. (i) The reaction for the oxidation of 1 mol of H_2O to O_2 is:



Thus one mole H_2O requires 2 F or $2 \times 96500 \text{ C} = 193000 \text{ C}$ of electricity for oxidation.

(ii) The reaction for the oxidation of 1 mol of FeO to Fe_2O_3

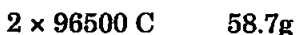
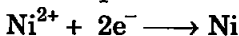


\therefore One mole FeO requires 1 F or 96500 C of electricity for oxidation.

3.15 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Ans. Given: Current, $I = 5.2 \text{ A}$; $t = 20 \times 60 \text{ s}$.

Reaction for deposition of Ni

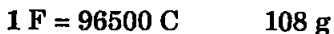
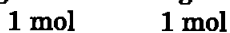
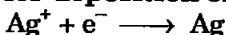


Thus $2 \times 96500 \text{ C}$ of electricity produces 58.7 g Ni

6000 C of electricity would produce $\frac{58.7 \times 6000}{2 \times 96500} = 1.825 \text{ g}$

3.16 Three electrolytic cells A, B, C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

Ans. Reaction for deposition of silver:



\therefore 108 g of silver is deposited by 96500 C of electricity

1.45 g of silver would be deposited by $\frac{96500 \times 1.45}{108} = 1295.6 \text{ C}$

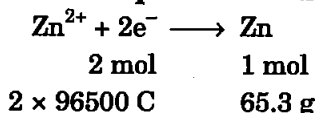
$$Q = 1295.6 \text{ C}$$

$$Q = I \times t$$

Given, current strength $I = 1.5 \text{ A}$

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

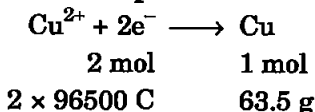
Reaction for deposition of zinc:



Thus $2 \times 96500 \text{ C}$ 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:



Thus $2 \times 96500 \text{ C}$ electricity deposits 63.5 g Cu

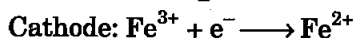
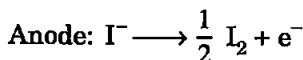
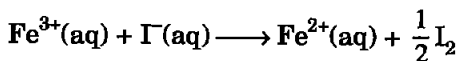
1295.6 C electricity would deposit $\frac{63.5 \times 1295.6}{2 \times 96500} = 0.426 \text{ g Cu}$

3.17 Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:

- $\text{Fe}^{3+}(\text{aq})$ and $\text{I}^{-}(\text{aq})$
- $\text{Ag}^{+}(\text{aq})$ and $\text{Cu}(\text{s})$
- $\text{Fe}^{3+}(\text{aq})$ and $\text{Br}^{-}(\text{aq})$
- $\text{Ag}(\text{s})$ and $\text{Fe}^{3+}(\text{aq})$
- $\text{Br}_2(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$

Ans. (i) **Reaction between $\text{Fe}^{3+}(\text{aq})$ and $\text{I}^{-}(\text{aq})$**

$$E_{\text{Fe}^{3+}, \text{Fe}^{2+}/\text{Pt}}^{\ominus} = +0.77 \text{ V}, E_{\text{I}_2/\text{I}^{-}}^{\ominus} = 0.541 \text{ V}$$



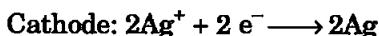
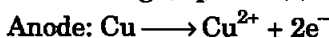
$$E_{\text{cell}}^{\ominus} = E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus}$$

$$= +0.77 - 0.541 = +0.229 \text{ V}$$

Since $E_{\text{cell}}^{\ominus}$ is positive, the reaction is **feasible**.

(ii) **Reaction between Ag^+ (aq) and Cu (s)**

$$E_{\text{Ag}^+/\text{Ag}}^{\ominus} = +0.80 \text{ V} \quad E_{\text{Cu}^{2+}/\text{Cu}}^{\ominus} = 0.34 \text{ V}$$



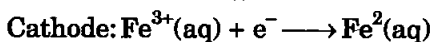
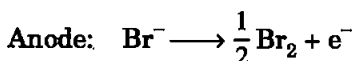
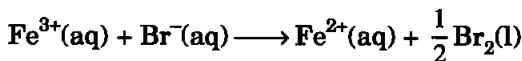
$$E_{\text{cell}}^{\ominus} = E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus}$$

$$= 0.80 - 0.34 = +0.46 \text{ V}$$

Since $E_{\text{cell}}^{\ominus}$ is positive, the reaction is **feasible**.

(iii) **Reaction between Fe^{3+} (aq) and Br^- (aq)**

$$E_{\text{Fe}^{3+}, \text{Fe}^{2+}/\text{Pt}}^{\ominus} = +0.77 \text{ V}; \quad E_{\text{Br}_2/\text{Br}^-}^{\ominus} = 1.09 \text{ V}$$



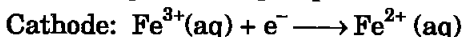
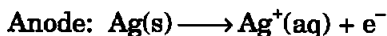
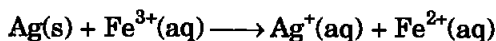
$$E_{\text{cell}}^{\ominus} = E_{\text{cathode}}^{\ominus} - E_{\text{anode}}^{\ominus}$$

$$= +0.77 - 1.09 = -0.32 \text{ V}$$

Since $E_{\text{cell}}^{\ominus}$ is negative, the reaction is **not feasible**,

(iv) **Reaction between Ag (s) and Fe^{3+} (aq)**

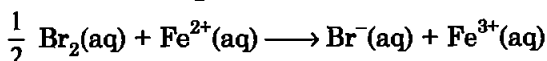
$$E_{\text{Ag}^+/\text{Ag}}^{\ominus} = +0.80 \text{ V}; \quad E_{\text{Fe}^{3+}, \text{Fe}^{2+}/\text{Pt}}^{\ominus} = +0.77 \text{ V}$$



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

$$= +0.77 - 0.80 = -0.03 \text{ V}$$

Since $E_{\text{cell}}^{\ominus}$ is negative, the reaction is **not feasible**.

(v) **Reaction between $\text{Br}_2(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$** 

This reaction is reverse of reaction (iii), Therefore,

$$E_{\text{cell}}^{\ominus} = + 0.32 \text{ V.}$$

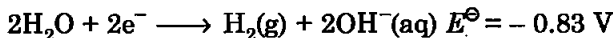
Since the $E_{\text{cell}}^{\ominus}$ is positive, the reaction is feasible.

3.18 Predict the products of electrolysis in each of the following:

- (i) An aqueous solution of AgNO_3 with silver electrodes.
- (ii) An aqueous solution of AgNO_3 with platinum electrodes.
- (iii) A dilute solution of H_2SO_4 with platinum electrodes.
- (iv) An aqueous solution of CuCl_2 with platinum electrodes.

Ans. (i) Electrolysis of aqueous solution of AgNO_3 with silver electrodes

Cathode: Reduction of Ag^+ and H_2O are possible.



Since E^{\ominus} (reduction potential of Ag^+) is greater than that of H_2O , *Ag will be deposited on cathode*

Anode: As silver anode is attacked by NO_3^- ions, it would be oxidised as:



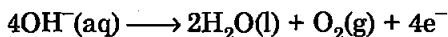
Thus *Ag dissolves from anode.*

(ii) Electrolysis of aqueous solution of AgNO_3 with platinum electrodes

Cathode: Same as above and *Ag will be deposited at cathode.*

Anode: (i) Platinum anode is not attacked by NO_3^- ions.

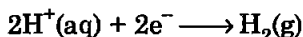
(ii) Out of OH^- and NO_3^- ions, the discharge potential of OH^- is lower and it would be discharged as:



Thus *$\text{O}_2(\text{g})$ is liberated at anode*

(iii) Electrolysis of dil. solution of H_2SO_4 with platinum electrodes

Cathode: Both water and H_2SO_4 furnish H^+ ions which are discharged at the cathode as



and $H_2(g)$ is liberated at cathode.

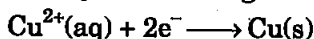
Anode: Water furnishes OH^- and H_2SO_4 furnishes SO_4^{2-} ions. Out of these, the discharge potential of OH^- is lower and these are discharged as



Thus $O_2(g)$ is liberated at anode.

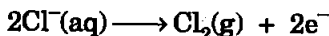
(iv) **Electrolysis of an aqueous solution of $CuCl_2$ with platinum electrodes**

Cathode: $CuCl_2$ furnishes Cu^{2+} ions and H_2O furnishes H^+ ions. Out of these, discharge potential of Cu^{2+} ions is lower hence they are discharged as



Hence *Cu* is deposited at cathode.

Anode: $CuCl_2$ furnishes Cl^- ions and H_2O furnishes OH^- ions. Out of these, discharge potential of Cl^- is lower and these are discharged as:



Thus $Cl_2(g)$ is liberated at anode.

□□□