energy of a **spontaneous redox reaction** is converted into electrical work, whereas in an electrolytic cell, electrical energy is used to carry out a **non-spontaneous redox reaction**. The **standard electrode potential** for any electrode dipping in an appropriate solution is defined with respect to standard electrode potential of **hydrogen electrode** taken as zero. The standard potential of the cell can be obtained by taking the difference of the standard potentials of cathode and anode ($E^{\ominus}_{(cell)} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$). The standard potential of the cells are related to standard Gibbs energy ($\Delta_r G^{\ominus} = -nFE^{\ominus}_{(cell)}$) and **equilibrium constant** ($\Delta_r G^{\ominus} = -RT \ln K$) of the reaction taking place in the cell. Concentration dependence of the potentials of the electrodes and the cells are given by Nernst equation.

The **conductivity**, κ, of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature. **Molar conductivity**, Λ_m, is defined by $= \kappa / c$ where c is the concentration. Conductivity decreases but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolytes while the increase is very steep for weak electrolytes in very dilute solutions. Kohlrausch found that molar conductivity at infinite dilution, for an electrolyte is sum of the contribution of the molar conductivity of the ions in which it dissociates. It is known as **law of independent migration of ions** and has many applications. Ions conduct electricity through the solution but oxidation and reduction of the ions take place at the electrodes in an electrochemical cell. **Batteries** and **fuel cells** are very useful forms of galvanic cell. **Corrosion** of metals is essentially an **electrochemical phenomenon**. Electrochemical principles are relevant to the **Hydrogen Economy**.

Exercises

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.

3.2 Given the standard electrode potentials,

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

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

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

Arrange these metals in their increasing order of reducing power.

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.

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

(i) $2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$

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

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

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

(i) $Mg(s) | Mg^{2+}(0.001M) || Cu^{2+}(0.0001\ M) | Cu(s)$

(ii) $Fe(s) | Fe^{2+}(0.001M) || H^+(1M) | H_2(g)(1bar) | Pt(s)$

(iii) $Sn(s) | Sn^{2+}(0.050\ M) || H^+(0.020\ M) | H_2(g)\ (1\ bar) | Pt(s)$

(iv) $Pt(s) | Br_2(l) | Br^-(0.010\ M) || H^+(0.030\ M) | H_2(g)\ (1\ bar) | Pt(s)$.

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

$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

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

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

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

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 0.001M KCl solution at 298 K is 0.146×10^{-3} S 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
$10^2 \times \kappa$/S m^{-1}	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{½}$. Find the value of Λ_m^0.

3.11 Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity and if Λ_m^0 for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

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+}.

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.

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.

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?

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?

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

(i) $Fe^{3+}(aq)$ and $I^-(aq)$

(ii) Ag^+ (aq) and Cu(s)

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

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

(v) Br_2 (aq) and Fe^{2+} (aq).

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.

Answers to Some Intext Questions

3.5 $E_{(cell)} = 0.91$ V

3.6 $\Delta_r G^\ominus = -45.54\ kJ\ mol^{-1}$, $K_c = 9.62 \times 10^7$

3.9 0.114, 3.67×10^{-4} mol L^{-1}