

CHAPTER 3 : **ELECTROCHEMISTRY**

Teacher and student oriented

Electrochemical Series, Applications of Electrochemical Series, Electrolysis, Electrolysis of Water, Electrolysis of molten NaCl, Electrolysis of molten lead bromide, Electrolysis of aqueous sodium chloride, Electrolysis of aqueous CuSO₄ using Pt electrode (inert or non-attackable electrode), Electrolysis of aqueous CuSO₄ using Cu electrode (attackable electrode), Faraday's first law of electrolysis, Electrochemical Cell, Construction, Salt bridge, Functions of salt bridge, Representation of Electrochemical Cell, Nernst equation, Important relations, Conductors, Types of Conductors, Factors affecting the electrolytic conductance, Some Important Terms related with Conductance, Effect of Dilution on Conductance, The Variation of Molar Conductance with Concentration, Kohlrausch's law, Applications of Kohlrausch's law, Commercial Cells, Corrosion, Factors affecting the Corrosion.

Concept detail

Electrochemical Series: It is the arrangement of different elements in the increasing order of their standard reduction values. **Electrolysis:** It is the process of decomposition of a substance either in molten state or in aqueous solution by passing electricity. **Faraday's first law of electrolysis:** The amount or weight of substances obtained at respective electrodes is directly proportional to the amount or quantity of electricity or charge passed. Mathematically, $w \propto Q$ and $w = Z Q$, where Z is known as electrochemical equivalent. **Faraday's second law of electrolysis:** When same amount of electricity is passed into two different electrolytic solutions connected in series, then weights of substances obtained at respective electrodes are proportional to their equivalent weights. Mathematically, $\frac{W_1}{W_2} = \frac{E_1}{E_2}$.

Electrochemical Cell: It is the device which is used to convert chemical energy into electrical energy. It is an example of indirect redox reaction. **Functions of salt bridge:** (i) It completes the circuit. (ii) It maintains the electrical neutrality of the two half cells. **Nernst equation for electrode potential:**

Consider the following reduction reaction, $M^{n+}(aq) + ne^- \rightarrow M(s)$. The Nernst equation for above reaction is as follow: $E_{\text{electrode}} = E^0_{\text{electrode}} - \frac{2.303 RT}{nF} \log \frac{[M(s)]}{[M^{n+}]}$. **Nernst equation for cell reaction:**

Consider the following cell representation, $A | A^{n+} || B^{n+} | B$. The Nernst equation for above cell is as follow: $E_{\text{cell}} = E^0_{\text{cell}} - \frac{2.303 RT}{nF} \log \frac{[\text{anode}]^x}{[\text{cathode}]^y}$, where x and y are the stoichiometric coefficients in the cell reaction. **Relationship between E^0_{cell} and K, equilibrium constant:** $E^0_{\text{cell}} = \frac{0.0591}{n} \log K$

Relationship between ΔG^0 and E^0_{cell} : $\Delta G^0 = -nFE^0_{\text{cell}}$ **Relationship between ΔG^0 and K:** $\Delta G^0 = -2.303 RT \log K$

Equivalent Conductance: It is the conductance due to all the ions produced by one gram equivalent of an electrolyte in 1000 cm³ solution. It is denoted by λ_e . **Molar Conductance:** It is the conductance due to all the ions produced by one mole of electrolyte in 1000 cm³ solution. It is denoted by λ_M . **Effect of**

Dilution on Conductance: The specific conductance decreases while equivalent and molar conductance increase with the increase in dilution. The decrease in specific conductance is due decrease in number of ions per unit volume. However, the increase in equivalent and molar conductance is due decrease in inter ionic (cation-anion) interactions. **Kohlrausch's law:** At infinite dilution, each ion makes definite

contribution towards molar conductance independent of the nature of other ions present in solution. For an electrolyte A_xB_y which dissociate as follows, $A_xB_y \rightarrow x A^{y+} + y B^{x-}$, the molar conductance is given by the relation, $\lambda_M^\infty(A_xB_y) = x \lambda_M^\infty(A^{y+}) + y \lambda_M^\infty(B^{x-})$. **Commercial Cells:** There are three types of commercial cells, primary cells, secondary cells and fuel cells.

(i) Primary Cells: The primary cells are those electrochemical cells which cannot be recharged. For example, Drycell and Mercury cell.

(ii) Secondary cells: The secondary cells are those electrochemical cells which can be recharged.

For example, lead storage cell or battery and Nickel-Cadmium cell or battery.

(iii) Fuel Cells: Fuel cells are those cells in which chemical energy of the fuel is converted into electrical energy. For example, H_2-O_2 cell. **Corrosion:** It is the process of slow eating away of the metal

by the interaction with water vapor and other gases present in the air. **Factors affecting the Corrosion:**

(i) Position of metal in the electrochemical series. (ii) Presence of impurities. (iii) Uneven surface of the metal.

Protection of Metals from the corrosion: Following methods are used for the protection of metals from corrosion:

- (i) Barrier protection (ii) Sacrificial protection
(iii) Cathodic protection (iv) Using anti rust solution.

Activity

Study the rate of rusting in different seasons.

Instant diagnostic assignment

1. What is the effect of concentration on molar conductivity of electrolytes?
2. Can copper sulphate solution be stored in zinc container? Explain.
3. Consider the reaction; $Cr_2O_7^{2-} + 14 H^+ + 6 e^- \rightarrow 2 Cr^{3+} + 7 H_2O$. What is the quantity of electricity in coulomb needed to reduce 1 mole of $Cr_2O_7^{2-}$?
[$5.79 \times 10^5 C$]
4. How does the concentration of sulphuric acid change in lead storage battery when current is drawn from it?
5. How specific conductance, molar conductance and equivalent conductance does change with the variation of dilution of electrolyte?
6. What is the relation between e.m.f. of cell and equilibrium constant?

Formative assignment

1. Define following: (a) Electrolysis (b) specific conductance (c) Corrosion (d) secondary cell
(d) concentration cell
2. Write short note on following: (a) Nernst equation (b) standard hydrogen electrode
(c) lead storage cell (d) electrolysis of aqueous solution of sodium sulphate
3. The E_{cell}^0 for the reaction, $4 BiO^+(aq) + 3 N_2H_5^+(aq) \rightarrow 4 Bi(s) + 3 N_2(g) + 4 H_2O(l) + 7 H^+$, is 0.55 V at 25°C. Calculate the value of ΔG^0 in kJ/mol.

- A metal wire carries a current of 1 A. How many electrons pass through a point in the wire in 1 second?
- How specific conductance, molar conductance and equivalent conductance does change with the variation of dilution of electrolyte?

Level wise questions

Level – I

- Define molar conductivity and write its S.I. unit.
- Define Kohlrausch's law.
- What is the relation between specific conductance, cell constant and resistance?
- What is corrosion and what is chemical formula of rust?
- What is the effect of concentration on molar conductivity of electrolytes?
- Can copper sulphate solution be stored in zinc container? Explain.

Level – II

- Define following: (a) Electrolysis (b) specific conductance (c) Corrosion (d) secondary cell (d) concentration cell
- Write short note on following: (a) Nernst equation (b) standard hydrogen electrode (c) lead storage cell (d) electrolysis of aqueous solution of sodium sulphate
- The E_{cell}^0 for the reaction, $4 \text{BiO}^+ (\text{aq}) + 3 \text{N}_2\text{H}_5^+ (\text{aq}) \rightarrow 4 \text{Bi} (\text{s}) + 3 \text{N}_2 (\text{g}) + 4 \text{H}_2\text{O} (\text{l}) + 7 \text{H}^+$, is 0.55 V at 25°C. Calculate the value of ΔG^0 in kJ/mol.
- A metal wire carries a current of 1 A. How many electrons pass through a point in the wire in 1 second?
- 0.2864 g of copper was collected on passing a current of 0.5 A for 30 min through a solution of copper sulphate. What is electrochemical equivalent of copper?
- During the electrolysis of an aqueous solution of stannous chloride, 4.48 L of Cl_2 is liberated at anode at S.T.P. Calculate the weight of tin collected at cathode. Atomic weight of tin is 119 amu.

Level – III

- Calculate the value of K for the equilibrium, $2 \text{MnO}_4^- + 6 \text{H}^+ + 5 \text{H}_2\text{C}_2\text{O}_4 \rightarrow 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O} + 10 \text{CO}_2$. Given that $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^0 = +1.51 \text{ V}$ and $E_{\text{CO}_2/\text{C}_2\text{O}_4^{2-}}^0 = -0.49 \text{ V}$.
- Calculate the e.m.f. of the cell, $\text{Fe} | \text{FeSO}_4 (0.1 \text{ M}) || \text{CuSO}_4 (0.01 \text{ M}) | \text{Cu}$. Given that $E_{\text{Fe}/\text{Fe}^{2+}}^0 = +0.44 \text{ V}$ and $E_{\text{Cu}/\text{Cu}^{2+}}^0 = -0.34 \text{ V}$.
- The λ_M^∞ of sodium butyrate = 83, for NaCl = 127 and for HCl = $426 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Calculate the λ_M^∞ of butyric acid.
- For 0.5 N HCOOH solution at 25°C, its molar conductance is $7.36 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ and its molar conductance at infinite dilution is $391 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Calculate the degree of dissociation of HCOOH and its K_a value.

5. Calculate the value of K_c for the following reaction, at 298 K, $2 \text{Fe}^{3+} + \text{Sn}^{2+} \rightleftharpoons 2 \text{Fe}^{2+} + \text{Sn}^{4+}$. From the value of K_c , predict whether Sn^{2+} ions can reduce Fe^{3+} ions to Fe^{2+} or not? Given that $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.771 \text{ V}$ and $E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 = 0.150 \text{ V}$.

Project

Make a memory frame to remember the applications of electrochemical series.