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Electrolytic Conductivity and Kohlrausch's Law

Electrochemistry Overview

Electrochemistry is the branch of chemistry that studies the production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to drive non-spontaneous chemical changes.

Electrolytic Conduction

Electrolytic conduction refers to the flow of electric current through an electrolytic solution due to the movement of ions.

Electrolytes

An electrolyte is a substance that dissociates into ions in solution or molten state, enabling the conduction of electricity. Electrolytes can be classified as:

- **Strong electrolytes:** Completely dissociate into ions (e.g., NaCl, HCl, NaOH).
- **Weak electrolytes:** Partially dissociate into ions (e.g., H_2CO_3, CH_3COOH, HCN).

Degree of Ionisation

The degree of ionisation is the ratio of the number of ions produced to the total number of molecules of the electrolyte.

Resistance and Resistivity

Resistance (R) is the property of a substance that opposes the flow of electric current. It is directly proportional to the length (l) of the conductor and inversely proportional to its cross-sectional area (A):

$$R = \rho \times (l / A)$$

where ρ is the resistivity or specific resistance of the material, measured in ohm-meters (Ω·m) or ohm-centimeters (Ω·cm).

Conductance and Conductivity

Conductance (C) is the ease with which current flows through a conductor and is the reciprocal of resistance:

$$C = 1 / R = A / (\rho \times l)$$

The SI unit of conductance is Siemens (S).

Conductivity (κ) is the reciprocal of resistivity and is given by:

$$\kappa = C \times (l / A)$$

Its SI unit is Siemens per meter (S m^{-1}) or Siemens per centimeter (S cm^{-1}).

Factors Affecting Conductivity

- Nature of the material
- Temperature
- Number of valence electrons per atom or size and solvation of ions

Metallic and Electrolytic Conductance

Metallic conductance arises from free electrons in metals and depends on the metal's nature, structure, valence electrons, and temperature.

Electrolytic conductance arises from ions in solution and depends on the nature of the electrolyte, solvation of ions, solvent viscosity, and temperature.

Viscosity

Viscosity is the resistance of a liquid to flow; lower viscosity means easier flow.

Cell Constant

The cell constant (G) is the ratio of the distance between electrodes (l) to the cross-sectional area (A):

$$G = l / A$$

It depends on the geometry of the electrodes and is expressed in cm^{-1} or m^{-1}.

Molar Conductivity

Molar conductivity (Λ_m) is the conductance of all ions produced by one mole of electrolyte in solution:

$$\Lambda_m = (\kappa / C) \times 1000$$

where κ is conductivity and C is concentration in mol/L. Its SI unit is $S\ m^2\ mol^{-1}$.

Debye-Hückel Equation

For strong electrolytes, molar conductivity varies with concentration as:

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

where Λ°_m is limiting molar conductivity, A is a constant, and C is concentration.

Kohlrausch’s Law of Independent Migration of Ions

At infinite dilution, the limiting molar conductivity of an electrolyte is the sum of the contributions of its individual ions:

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

where ν^+ and ν^- are the number of cations and anions, and λ°_+ and λ°_- are their limiting molar conductivities.

Applications of Kohlrausch’s Law

- Calculating molar conductivities of weak electrolytes at infinite dilution.
- Determining degree of dissociation (α) of weak electrolytes: $\alpha = \Lambda_m / \Lambda^\circ_m$.
- Calculating dissociation constant (K_a) of weak electrolytes:

$$K_a = C\,\alpha^2 / (1 - \alpha) = C\,\Lambda_m^2 / [\Lambda^\circ_m (\Lambda^\circ_m - \Lambda_m)]$$

- Determining solubility of sparingly soluble salts:

$$\text{Solubility} = (\kappa \times 1000) / \Lambda^\circ_m$$

Solved Examples

Example 1

A conductivity cell with 0.1 mol/L KCl solution has resistance 100 Ω. When the concentration changes to 0.02 mol/L, resistance changes to 520 Ω. Given conductivity of 0.1 mol/L KCl is 1.29 S/m, find the conductivity and molar conductivity of 0.02 mol/L KCl solution.

Solution:

Given:

- $R_1 = 100\ \Omega$, $C_1 = 0.1$ mol/L
- $R_2 = 520\ \Omega$, $C_2 = 0.02$ mol/L
- Conductivity at 0.1 mol/L, $\kappa_1 = 1.29$ S/m $= 1.29\ \Omega^{-1}\ m^{-1}$

Calculate cell constant (G):

$G = \kappa_1 \times R_1 = 1.29 \times 100 = 129\ m^{-1} = 1.29\ cm^{-1}$

Calculate conductivity at 0.02 mol/L:

$\kappa_2 = G / R_2 = 1.29 / 520 = 0.00248\ \Omega^{-1}\ cm^{-1} = 2.48 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$

Convert concentration to mol/cm^3:

$C_2 = 0.02\ mol/L = 2 \times 10^{-5}\ mol/cm^3$

Calculate molar conductivity:

$\Lambda_m = \kappa_2 / C_2 = (2.48 \times 10^{-3}) / (2 \times 10^{-5}) = 124\ \Omega^{-1}\ mol^{-1}\ cm^2$

Practice Set

- **Level 1:** Define electrolytic conduction and give examples of strong and weak electrolytes.
- **Level 2:** Explain Kohlrausch’s law and its significance in determining molar conductivity.
- **Level 3:** A conductivity cell has a cell constant of 1.5 cm^{-1}. If the resistance of a 0.05 mol/L solution is 200 Ω, calculate the conductivity and molar conductivity of the solution.

Answer Key

- **Level 1:** Electrolytic conduction is the flow of electric current through an electrolytic solution due to ion movement. Strong electrolytes fully dissociate (e.g., NaCl), weak electrolytes partially dissociate (e.g., CH_3COOH).
- **Level 2:** Kohlrausch's law states that the limiting molar conductivity of an electrolyte is the sum of the contributions of its ions. It helps calculate molar conductivity and degree of dissociation.
- **Level 3:** Conductivity $\kappa = G / R = 1.5 / 200 = 0.0075\ \Omega^{-1}\ cm^{-1}$. Concentration $C = 0.05\ mol/L = 5 \times 10^{-5}\ mol/cm^3$. Molar conductivity $\Lambda_m = \kappa / C = 0.0075 / 5 \times 10^{-5} = 150\ \Omega^{-1}\ mol^{-1}\ cm^2$.

Redox Reactions and Electrochemical Cells

Redox Reactions

A redox reaction involves simultaneous oxidation (loss of electrons) and reduction (gain of electrons).

Galvanic Cell

A galvanic cell converts chemical energy into electrical energy through spontaneous redox reactions. It consists of two electrodes immersed in electrolyte solutions.

Redox Couple

A redox couple consists of the oxidized and reduced forms of a substance involved in a half-reaction.

Daniell Cell

A Daniell cell is a galvanic cell with zinc and copper electrodes in their respective sulfate solutions:

$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$

Cell notation: $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

Salt Bridge

A salt bridge is an inverted U-shaped tube containing a salt solution in agar-agar that completes the circuit, prevents mixing of electrolytes, and maintains electrical neutrality.

Electrode Potential

Electrode potential is the potential difference between an electrode and its solution, measured against the standard hydrogen electrode (SHE) which has zero potential.

Standard Electrode Potential

Standard electrode potential (E°) is the electrode potential measured at 25°C, 1 bar pressure, and 1 M concentration.

Cell Potential and EMF

The cell potential or electromotive force (EMF) is the potential difference between two electrodes when no current flows:

$E_{cell} = E_{cathode} - E_{anode}$

Standard Oxidation Potential

It is the potential when an electrode undergoes oxidation at standard conditions relative to SHE.

Electrochemical Series

Elements arranged in order of increasing electrode potential form the electrochemical series.

Nernst Equation

For non-standard conditions, the electrode potential is given by:

$$E = E^\circ - (RT / nF) \ln Q$$

At 298 K, this simplifies to:

$$E = E^\circ - (0.059 / n) \log Q$$

where Q is the reaction quotient.

Gibbs Energy and Cell Spontaneity

Gibbs free energy change (ΔG) relates to cell potential as:

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

For a spontaneous reaction, ΔG must be negative.

Solved Examples

Example 2

Calculate ΔG° for the reaction:

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Given $E^\circ_{cell} = +1.1$ V.

Solution:

At anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

$n = 2$

$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.1 = -212300$ J/mol $= -212.3$ kJ/mol

Practice Set

- **Level 1:** Define redox reaction and give an example.
- **Level 2:** Explain the function of a salt bridge in a galvanic cell.
- **Level 3:** Calculate the cell potential at 298 K for the reaction where $E^\circ_{cell} = 1.1$ V and the reaction quotient $Q = 0.01$, with $n = 2$.

Answer Key

- **Level 1:** A redox reaction involves simultaneous oxidation and reduction. Example: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$.
- **Level 2:** The salt bridge completes the circuit, prevents mixing of electrolytes, and maintains electrical neutrality by allowing ion flow.
- **Level 3:** $E = E° - (0.059 / n) \log Q = 1.1 - (0.059 / 2) \log 0.01 = 1.1 - 0.0295 \times (-2) = 1.1 + 0.059 = 1.159$ V.

Electrolysis, Batteries, Fuel Cells and Corrosion

Electrolysis

Electrolysis is the decomposition of an electrolyte by passing electric current through its aqueous or molten state in an electrolytic cell.

Faraday’s Laws of Electrolysis

First law: The amount of substance liberated at an electrode is proportional to the quantity of electricity passed.

$m = Z \times I \times t$, where Z is electrochemical equivalent.

Second law: The amounts of different substances liberated by the same quantity of electricity are proportional to their chemical equivalent weights.

$w_1 / E_1 = w_2 / E_2$

Electrolysis Products Dependence

- Physical state of the electrolyte
- Type of electrodes used

Batteries

Batteries are combinations of galvanic cells connected in series to provide electrical energy.

Types of Batteries

- **Primary batteries:** Non-rechargeable, e.g., Leclanche cell, dry cell, mercury cell.
- **Secondary batteries:** Rechargeable, e.g., lead storage battery, nickel–cadmium cell.

Dry Cell (Leclanche Cell)

Consists of zinc container (anode), graphite electrode (cathode), surrounded by manganese dioxide and carbon mixture, with ammonium chloride and zinc chloride paste.

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

At cathode: $MnO_2(s) + NH_4^+(aq) + 2e^- \longrightarrow MnO(OH) + NH_3$

Net reaction: $Zn + NH_4^+ + MnO_2 \longrightarrow Zn^{2+} + MnO(OH) + NH_3$

Lead Storage Battery

Anode: Spongy lead

Cathode: Lead dioxide packed with lead

Electrolyte: 38% aqueous sulfuric acid (H_2SO_4)

Discharge reactions:

Anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

Cathode: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

Overall: $Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$

Recharge reactions reverse the above processes.

Fuel Cells

Fuel cells convert chemical energy from fuels like hydrogen directly into electrical energy without recharging.

Anode reaction: $H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-$

Cathode reaction: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Net reaction: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Corrosion

Corrosion is the slow chemical degradation of metals, such as rusting of iron.

Rusting reactions:

$Fe(s) + 2H^+(aq) + ½\ O_2(aq) \rightarrow Fe^{2+}(aq) + H_2O(l)$

$2Fe^{2+}(s) + ½\ O_2(g) + 2H_2O(l) \rightarrow Fe_2O_3(s) + 4H^+$

$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 \cdot xH_2O$ (rust)

Prevention of Corrosion

- **Barrier protection:** Painting, greasing, electroplating to prevent exposure.
- **Sacrificial protection:** Galvanisation using zinc or aluminium coatings.
- **Alloying:** Combining metals to form corrosion-resistant alloys.

Practice Set

- **Level 1:** State Faraday’s first and second laws of electrolysis.
- **Level 2:** Describe the structure and working of a dry cell.
- **Level 3:** Write the reactions occurring at the anode and cathode during discharge and recharge of a lead storage battery.

Answer Key

- **Level 1:** First law: Amount of substance liberated is proportional to charge passed. Second law: Amounts of substances liberated by same charge are proportional to their chemical equivalents.

- **Level 2:** Dry cell has zinc container as anode, graphite cathode surrounded by MnO_2 and carbon, with NH_4Cl and $ZnCl_2$ paste. Chemical reactions produce electricity.
- **Level 3:** Discharge:
  Anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$
  Cathode: $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$
  Recharge:
  Cathode: $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$
  Anode: $PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

Quick Reference Table

Common Mistakes and Misconceptions

Glossary