Kinetic Molecular Theory Solutions of Electrolytes

Introduction

This module combines two distinct but related areas of physical chemistry: the **Kinetic Molecular Theory (KMT)**, which describes the microscopic behavior of gas particles to explain macroscopic gas laws, and the study of **Solutions of Electrolytes**, which deals with the movement of ions in liquid systems and their ability to conduct electricity.

Understanding these concepts is key to predicting gas properties under various conditions and quantifying the conductivity of ionic solutions.

Learning Objectives

By the end of this module, you will be able to:

- **Discuss** the postulates of KMT and use them to explain ideal gas properties.
- **Apply** KMT equations to calculate molecular speeds, collision frequency, and mean free path.
- **Describe and calculate** quantities used to measure the electrical properties of electrolytic solutions.
- **Discuss** methods for determining ion mobility and transport numbers.
- **Calculate** the degree of ionization and molar solubility using conductivity data.

Key Concepts and Definitions

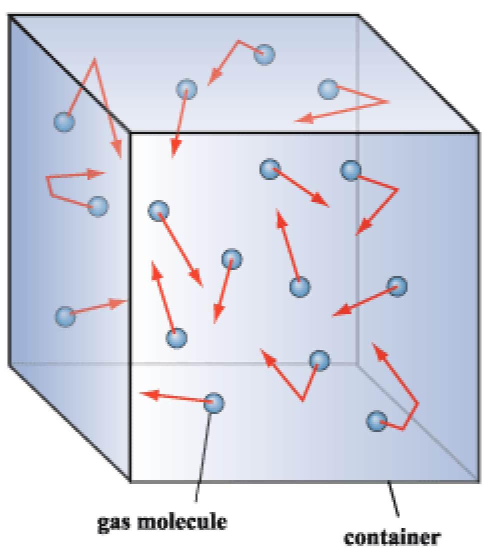
Term	Definition
Kinetic Molecular Theory (KMT)	A theoretical model describing gas behavior based on the motion of tiny, random-moving particles.
Root-Mean-Square Speed	A type of average speed for gas molecules, giving weight to faster molecules.
Mean Free Path (Λ)	The average distance a molecule travels between collisions.
Electrolyte	A substance that produces ions when dissolved in a solvent, making the solution electrically conductive.
Molar Conductivity (Λm)	The conducting power of all the ions produced by one mole of an electrolyte dissolved in a solution.
Transport Number (t+ or t-)	The fraction of the total current carried by a specific ion (cation or anion).

Detailed Discussion

1. Kinetic Molecular Theory of Gases

KMT is based on several key postulates that explain the ideal gas law (PV=nRT):

- **Postulate 1:** Gases consist of large numbers of identical particles (atoms or molecules) that are continuously and randomly moving.
- **Postulate 2:** The volume occupied by the gas particles themselves is negligible compared to the total volume of the container.
- **Postulate 3:** Gas particles exert no attractive or repulsive forces on each other.
- **Postulate 4:** Collisions between particles and the container walls are perfectly elastic (no energy is lost).
- **Postulate 5:** The average kinetic energy of the particles is directly proportional to the absolute temperature (in Kelvin).



2. KMT Equations for Molecular Motion

The random motion of gas molecules can be quantified using the following equations derived from KMT:

Root-Mean-Square Speed:

$$V_{rms} = \sqrt{\frac{3RT}{\underbrace{M}_{\text{Molar mass}}}}$$

Where: R is the ideal gas constant, T is the absolute temperature, and M is the molar mass of the gas (in kg/mol).

Collision Frequency (Z):

Where: d is the molecular diameter, v_{avg} is the average speed, and n is the number density. Collision frequency is the number of collisions per unit time per unit volume.

Mean Free Path (Λ):

$$\lambda = \frac{kT}{\sqrt{2}\,\pi d^2 P},$$

The mean free path is inversely proportional to pressure and molecular size.

3. Electrolytes and Conductivity

The property of a solution to conduct electricity depends on the concentration and mobility of the ions present.

Conductivity (k) and Molar Conductivity (Λm):

Conductivity (k) is the reciprocal of resistivity (rho). For a cell of a fixed geometry, it is related to the measured conductance (G).

Molar Conductivity:

$$\Lambda m = k / c$$

Where: k is the conductivity , and c is the molar concentration (in mol/m^3).

Kohlrausch's Law of Independent Migration of Ions:

At infinite dilution, where inter-ionic attraction is negligible, the total limiting molar conductivity of an electrolyte is the sum of the limiting molar conductivities of its constituent ions:

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu\_\lambda\_^\circ \text{ (or } \Lambda_0 = \lambda_{cation} + \lambda_{anion}$$

Where: v+ and v- are the number of cations and anions per formula unit, and Λcation and Λanion are their respective limiting molar conductivities.

4. Ion Mobility and Transport Number

Ion Mobility (u): Ion mobility is the velocity of an ion per unit electric field.

Ion Mobility:

$$u = v / E$$

Where: v is the ion's velocity, and E is the electric field strength.

Transport Number:

The transport number (t) of an ion is the fraction of the total current carried by that specific ion.

$$t^{+} = I^{+}/(I^{+} + I^{-}) = I^{+}/I_{\text{total}}$$

The transport numbers are generally determined experimentally using methods like the moving boundary method or the Hittorf method.

5. Applications of Conductivity Data

Degree of Ionization (α) for Weak Electrolytes:

For weak electrolytes that only partially dissociate, conductivity can be used to determine the degree of ionization (α):

Degree of Ionization:

$$\alpha = [\text{Ions at Equilibrium}] / [\text{Total Initial Concentration}]$$

Molar Solubility of Sparingly Soluble Salts:

The molar solubility (s) of a sparingly soluble salt (like AgCl) can be calculated directly from the molar conductivity at saturation:

Molar Solubility:

$$s = k / \Lambda m0$$

Where: k is the conductivity of the saturated solution (after subtracting the solvent's conductivity), and Λm0 is the known limiting molar conductivity of the salt.

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