

Kinetic Theory of Gases

CHAPTER OUTLINE

- 14.1 Kinetic-Molecular Theory of Gases
- 14.2 Pressure of an Ideal Gas
- 14.3 Temperature
- 14.4 Distribution of Molecular Speeds in an Ideal Gas
- 14.5 Applications of the Maxwell Distribution
- 14.6 Collisions with a Wall and Effusion
- 14.7 Molecular Collisions and Mean Free Path
- 14.8 The Barometric Formula
- 14.9 The Boltzmann Distribution Law
- 14.10 Heat Capacities of Ideal Polyatomic Gases
- 14.11 Summary

This chapter derives properties of an ideal gas based on a model of the gas as consisting of spherical molecules obeying classical mechanics. Properties derived include the equation of state (Secs. 14.2 and 14.3), the distribution of molecular speeds (Sec. 14.4), the average molecular speed (Sec. 14.5), molecular collision rates, and the average distance traveled between collisions (Sec. 14.7). These properties are important in discussing the rates of gas-phase reactions (Chapters 16 and 22) and in dealing with transport properties (for example, heat flow) in gases (Chapter 15).

14.1 KINETIC-MOLECULAR THEORY OF GASES

Chapters 1 to 12 use mainly a macroscopic approach. Chapter 13 uses both macroscopic and molecular approaches. The remaining chapters use mainly a molecular approach to physical chemistry.

This chapter and several sections of the next discuss the **kinetic-molecular theory of gases** (**kinetic theory**, for short). The kinetic theory of gases pictures a gas as composed of a huge number of molecules whose size is small compared with the average distance between molecules. The molecules move freely and rapidly through space. Although this picture seems obvious nowadays, it wasn't until about 1850 that the kinetic theory began to win acceptance.

Kinetic theory began with Daniel Bernoulli's 1738 derivation of Boyle's law using Newton's laws of motion applied to molecules. Bernoulli's work was ignored for over 100 years. In 1843 John Waterston submitted a paper to the Royal Society of England that correctly developed many concepts of kinetic theory. Waterston's paper was rejected as "nonsense." Joule's experiments demonstrating that heat is a form of energy transfer made the ideas of kinetic theory seem plausible, and from 1848 to 1898, Joule, Clausius, Maxwell, and Boltzmann developed the kinetic theory of gases.

From 1870 to 1910 a controversy raged between the schools of Energetics and Atomism. The Atomists (led by Boltzmann) held that atoms and molecules were real entities, whereas the Energetists (Mach, Ostwald, Duhem) denied the existence of atoms and molecules and argued that the kinetic theory of gases was a mechanical model that imitated the properties of gases but did not correspond to the true structure of matter. [The Freudian-oriented sociologist Lewis Feuer speculates that Mach's opposition to atomism was an unconscious expression of revolt against his father; the shape of atoms unconsciously reminded Mach of testicles, and "a reality deatomized was a projection, we might infer, in which the father himself was unmanhood." (L. Feuer, *Einstein and the Generations of Science*, Basic Books, 1974, p. 39.)]

The attacks on the kinetic theory of gases led Boltzmann to write in 1898: "I am conscious of being only an individual struggling weakly against the stream of time. But it still

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