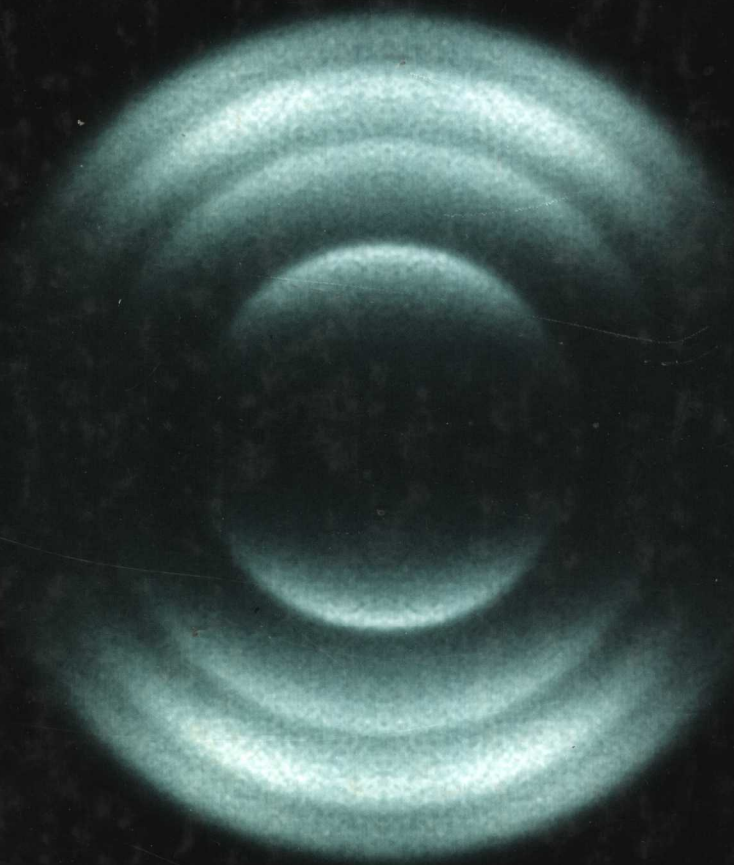


Chemical Kinetics and Reaction Dynamics



Paul L. Houston



Chemical Kinetics and Reaction Dynamics

Paul L. Houston

Cornell University



Boston Burr Ridge, IL Dubuque, IA Madison, WI New York San Francisco St. Louis
Bangkok Bogotá Caracas Kuala Lumpur Lisbon London Madrid Mexico City
Milan Montreal New Delhi Santiago Seoul Singapore Sydney Taipei Toronto

McGraw-Hill Higher Education

A Division of The McGraw-Hill Companies

CHEMICAL KINETICS AND REACTION DYNAMICS

Published by McGraw-Hill, a business unit of The McGraw-Hill Companies, Inc., 1221 Avenue of the Americas, New York, NY 10020. Copyright © 2001 by The McGraw-Hill Companies, Inc. All rights reserved. No part of this publication may be reproduced or distributed in any form or by any means, or stored in a database or retrieval system, without the prior written consent of The McGraw-Hill Companies, Inc., including, but not limited to, in any network or other electronic storage or transmission, or broadcast for distance learning.

Some ancillaries, including electronic and print components, may not be available to customers outside the United States.

This book is printed on acid-free paper.

1 2 3 4 5 6 7 8 9 0 CCW/CCW 0 9 8 7 6 5 4 3 2 1

ISBN 0-07-243537-2

Publisher: *James M. Smith*

Developmental editor: *Spencer J. Cotkin, Ph.D.*

Marketing manager: *Thomas Timp*

Project manager: *Jane E. Matthews*

Production supervisor: *Laura Fuller*

Designer: *K. Wayne Harms*

Cover designer: *Rokusek Design*

Senior photo research coordinator: *Carrie K. Burger*

Supplement producer: *Jodi K. Banowetz*

Compositor: *Lachina Publishing Services*

Typeface: *10.5/12 Times Roman*

Printer: *Courier Westford*

Cover image: Velocity distribution of $O(^1D)$ produced in the photodissociation of ozone at 265 nm. The four rings correspond to production of the sibling $O_2(^1\Delta_g)$ fragment in $v = 0$ (outer right), 1, 2, or 3 (inner ring). The image was taken by Scott Dylewski in the laboratory of Paul L. Houston using the technique described in Section 7.5.5.

Library of Congress Cataloging-in-Publication Data

Houston, Paul L.

Chemical kinetics and reaction dynamics / Paul L. Houston. — 1st ed.

p. cm.

Includes index.

ISBN 0-07-243537-2

1. Chemical kinetics. 2. Chemical reactions. I. Title.

QD502 .H7 2001

541.3'94—dc21

00-064712

CIP

www.mhhe.com

Preface

Chemical Kinetics and Reaction Dynamics is a textbook in modern chemical kinetics. There are two operative words here, *textbook* and *modern*. It is a textbook, not a reference book. While the principal aim of a reference book is to cover as many topics as possible, the principal aim of a textbook is to teach. In my view, a serious problem with modern "textbooks" is that they have lost the distinction. As a consequence of incorporating too many topics, these books confuse their audience; students have a difficult time seeing the forest through the trees. This textbook first aims to teach, and to teach as well as possible, the underlying principles of kinetics and dynamics. Encyclopedic completeness is sacrificed for an emphasis on these principles. I aim to present them in as clear a fashion as possible, using several examples to enhance basic understanding rather than racing immediately to more specialized applications. The more technical applications are not totally neglected; many are included as separate sections or appendices, and many are covered in sets of problems that follow each chapter. But the emphasis is on making this a textbook.

The second operative word is *modern*. Even recently written texts often use quite dated examples. Important aims of this textbook are first to demonstrate that the basic kinetic principles are essential to the solution of modern chemical problems and second to show how the underlying question, "how do chemical reactions occur," leads to exciting, vibrant fields of modern research. The first aim is achieved by using relevant examples in presenting the basic material, while the second is attained by inclusion of chapters on surface processes, photochemistry, and reaction dynamics.

Chemical Kinetics and Reaction Dynamics provides, then, a modern textbook. In addition to teaching and showing modern relevance, any textbook should be flexible enough so that individual instructors may choose their own sequence of topics. In as much as possible, the chapters of this text are self-contained; when needed, material from other sections is clearly referenced. An introduction to each chapter identifies the basic goals, their importance, and the general plan for achieving those goals. The text is designed for several possible formats. Chapters 1, 2, and 3 form a basic package for a partial semester introduction to kinetics. The basic material can be expanded by inclusion of Chapter 4. Chapters 5 through 8 can be included for a full semester course. Taken in its entirety, the text is suitable for a one-semester course at the third-year undergraduate level or above. I have used it for many years in a first-year graduate course.

While rigorous mathematical treatment of the topic cannot and should not be avoided if we are to give precision to the basic principles, the greatest problem students have with physical chemistry is keeping sight of the chemistry while wading through the mathematics. This text endeavors to emphasize the chemistry by two techniques. First, the chemical objectives and the reasons for undertaking the mathematical routes to those objectives are clearly stated; the mathematics is treated as a means to an end rather than an end in itself. Second, the text includes several "conceptual" problems in addition to the traditional "method" problems. Recent research on the teaching of physics has shown that, while students can frequently memorize the recipe for solving particular types of problems, they often fail to develop conceptual intuition.* The first few problems at the end of each chapter are designed as a conceptual self-test for the student.

*I. A. Halloun and D. Hestenes, *Am. J. Phys.* **53**, 1043 (1985); **53**, 1056 (1985); **55**, 455 (1987); D. Hestenes, *Am. J. Phys.* **55**, 440 (1987); E. Mazur, *Opt. Photon. News* **2**, 38 (1992).

The text assumes some familiarity with elementary kinetics at the level of high-school or freshman chemistry, physics at the freshman level, and mathematics through calculus. Each chapter then builds upon this basis using observations, derivations, examples, and instructive figures to reach clearly identified objectives.

I am grateful to Professor T. Michael Duncan for providing some of the problems used in Chapters 2 and 3, to Brian Bocknack and Julie Mueller for assistance with the problems and solutions, to Jeffrey Steinfeld and Joseph Francisco for helpful suggestions, to many outside reviewers of the text, especially Laurie Butler, for good suggestions, and to my wife, Barbara Lynch, for support and tolerance during the long periods when I disappeared to work on the text.

Paul Houston
Ithaca, New York

Introduction

A User's Guide to Chemical Kinetics and Reaction Dynamics

Chemistry is the study of the composition, structure, and properties of substances; of the transformation between various substances by reaction; and of the energy changes that accompany reaction. In these broad terms, *physical* chemistry is then the subbranch of the discipline that seeks to understand chemistry in quantitative and theoretical terms; it uses the tools of physics and mathematics to predict and explain macroscopic behavior on a microscopic level.

Physical chemistry can, in turn, be described by its subfields. Thermodynamics deals primarily with *macroscopic* manifestations of chemistry: the transformations between work and heat, the stability of compounds, and the equilibrium properties of reactions. Quantum mechanics and spectroscopy, on the other hand, deal primarily with *microscopic* manifestations of chemistry: the structure of matter, its energy levels, and the transitions between these levels. The subfield of statistical mechanics relates the microscopic properties of matter to the macroscopic observables such as energy, entropy, pressure, and temperature.

At their introductory level, however, all of these fields emphasize properties at equilibrium. Thermodynamics can be used to calculate an equilibrium constant, but it cannot be used to predict the rate at which equilibrium will be approached. For example, a stoichiometric mixture of hydrogen and oxygen is predicted by thermodynamics to react to water, but kinetics can be used to calculate that the reaction will take on the order of 10^{25} years ($\approx 3 \times 10^{32}$ s) at room temperature, though only 10^{-6} s in the presence of a flame. Similarly, quantum mechanics can do a good job at predicting the spacing of energy levels, but it does not do very well, at least at the elementary level, in providing simple reasons why population of some energy levels will be preferred over others following a reaction. Many reactions produce products in a Maxwell-Boltzmann distribution, but some, such as those responsible for chemical lasers, produce an "inverted" distribution that, over a specified energy range, is characterized by a negative temperature. We would like to have an understanding of why the rate for a reaction can be changed by 38 orders of magnitude, or why a reaction yields products in very specific, nonequilibrium distributions over energy levels.

Questions about the rates of processes and about how reactions take place are the purview of chemical kinetics and reaction dynamics. Because this subfield of physical chemistry is the one most concerned with the "how, why, and when" of chemical reaction, it is a central intellectual cornerstone to the discipline of chemistry.

And yet it is of enormous practical importance as well. Chemical reactions control our environment, our life processes, our food production, and our energy utilization. Understanding of and possible influence over the rates of chemical reactions could provide a healthier environment and a better life, with adequate food and more efficient resource management.

Thus, chemical kinetics is both an exciting intellectual frontier and a field that addresses societal needs as well. At the present time both the intellectual and practical forefronts of chemical kinetics are linked to a rapidly developing new set of instrumental techniques, including lasers that can push our time resolution to 10^{-15} s or detect concentrations at sensitivities approaching one part in 10^{16} , microscopes that can see individual atoms, and computers that can calculate some rate constants more accurately than they can be measured. These techniques are being applied to rate processes in all phases of matter, to reactions in solids, liquids, gases, plasmas, and even at the narrow interfaces between such phases. Never before have we been in such a good position to answer the fundamental question "how do molecules react?"

We begin our answer to this question by examining the motions of gas-phase molecules. What are their velocities, and what controls the rate of collisions among them? In Chapter 1, "Kinetic Theory of Gases," we will see that at equilibrium the molecular velocities can be described by the Boltzmann distribution and that factors such as the size, relative velocity, and molecular density influence the number of collisions per unit time. We will also develop an understanding of one of the central tools of physical chemistry, the distribution function.

We then examine the rates of chemical reactions in Chapter 2, first concentrating on the macroscopic observables such as the order of a reaction and its rate constant, but then examining how the overall rate of a reaction can be broken down into a series of elementary, molecular steps. Along the way we will develop some powerful tools for analyzing chemical rates, tools for determining the order of a reaction, tools for making useful approximations (such as the "steady-state" approximation), and tools for analyzing more complex reaction mechanisms.

In Chapter 3, "Theories of Chemical Reactions," we look at reaction rates from a more microscopic point of view, drawing on quantum mechanics, statistical mechanics, and thermodynamics to help us understand the magnitude of chemical rates and how they vary both with macroscopic parameters like temperature and with microscopic parameters like molecular size, structure, and energy spacing.

Chapter 4, "Transport Properties," uses the velocity distribution developed in Chapter 1 to provide a coherent description of thermal conductivity, viscosity, and diffusion, that is, a description of the movement of such properties as energy, momentum, or concentration through a gas. We will see that these properties are passed from one molecule to another upon collision, and that the mean distance between collisions, the "mean free path," is an important parameter governing the rate of such transport.

Armed with the fundamental material of the first four chapters, we move to four exciting areas of modern research: "Reactions in Liquid Solutions" (Chapter 5), "Reactions at Solid Surfaces" (Chapter 6), "Photochemistry" (Chapter 7), and "Molecular Reaction Dynamics" (Chapter 8).

The material of the text can be presented in several different formats depending on the amount of time available. The complete text can be covered in 12–14 weeks assuming 3 hours of lecture per week. In this format, the text might form the basis of an advanced undergraduate or beginning graduate level course. A more likely scenario, given the pressures of current instruction in physical chemistry, is one in which only the very fundamental topics are covered in detail. **Table 1** shows a flow chart giving the order of presentation and the number of lectures required for the fundamental material; the total number of lectures ranges between 11 and 17.

Of course, if more time is available, the instructor can supplement the fundamental material with selected topics from later chapters. Several suggestions, including the number of lectures required, are given in **Table 2** through **Table 5**.

TABLE 1 Fundamental Sections for a Course in Kinetics

Most Important Sections (Lectures)	Supplemental (Lectures)
1.1–1.6 (3)	
1.7 (1)	4.1–4.8 (3)
2.1–2.5 (4)	2.6 (2)
3.1–3.5 (3)	5.1–5.2 (1)
Total Lectures: 11	Total Lectures: 6

TABLE 2 Reactions in Liquid Solutions

Fundamental (Lectures)	Supplemental (Lectures)	Advanced (Lectures)
5.1–5.3 (2)	5.4 (1)	

TABLE 3 An Introduction to Surface Kinetics

Fundamental (Lectures)	Supplemental (Lectures)	Advanced (Lectures)
6.1–6.3, 6.6 (2)	6.4 (1)	6.5 (1)

TABLE 4 Photochemistry and Atmospheric Chemistry

Fundamental (Lectures)	Supplemental (Lectures)	Advanced (Lectures)
7.1, 7.2 (1)		
7.3.1, 7.3.4 (1)	7.3.2, 7.3.3 (1)	
7.4 (1)		7.5 (2)
Total Lectures: 3	Total Lectures: 2	Total Lectures: 2

TABLE 5 Reaction Dynamics

Fundamental (Lectures)	Supplemental (Lectures)	Advanced (Lectures)
8.1, 8.2, 8.3 (2)	8.4 (1)	
8.5 (2)	8.6 (1)	8.7 (1)
Total Lectures: 4	Total Lectures: 2	Total Lectures: 1

Contents

<i>Preface</i>	<i>xi</i>
<i>Introduction: A User's Guide to Chemical Kinetics</i> <i>and Reaction Dynamics</i>	<i>xiii</i>

Chapter 1 Kinetic Theory of Gases1

1.1	Introduction	1
1.2	Pressure of an Ideal Gas	2
1.3	Temperature and Energy	4
1.4	Distributions, Mean Values, and Distribution Functions	5
1.5	The Maxwell Distribution of Speeds	8
1.5.1	The Velocity Distribution Must Be an Even Function of v	8
1.5.2	The Velocity Distributions Are Independent and Uncorrelated ..	9
1.5.3	$\langle v^2 \rangle$ Should Agree with the Ideal Gas Law	9
1.5.4	The Distribution Depends Only on the Speed	11
1.5.5	Experimental Measurement of the Maxwell Distribution of Speeds	15
1.6	Energy Distributions	17
1.7	Collisions: Mean Free Path and Collision Number	19
1.8	Summary	24
Appendix 1.1	The Functional Form of the Velocity Distribution	25
Appendix 1.2	Spherical Coordinates	26
Appendix 1.3	The Error Function and Co-Error Function	27
Appendix 1.4	The Center-of-Mass Frame	28
	Suggested Readings	30
	Problems	31

Chapter 2 The Rates of Chemical Reactions34

2.1	Introduction	34
2.2	Empirical Observations: Measurement of Reaction Rates	35
2.3	Rates of Reactions: Differential and Integrated Rate Laws	35
2.3.1	First-Order Reactions	37
2.3.2	Second-Order Reactions	40
2.3.3	Pseudo-First-Order Reactions	44
2.3.4	Higher-Order Reactions	47
2.3.5	Temperature Dependence of Rate Constants	48
2.4	Reaction Mechanisms	51
2.4.1	Opposing Reactions, Equilibrium	52
2.4.2	Parallel Reactions	54
2.4.3	Consecutive Reactions and the Steady-State Approximation ...	56

2.4.4	Unimolecular Decomposition: The Lindemann Mechanism . . .	60
2.5	Homogeneous Catalysis	63
2.5.1	Acid-Base Catalysis	63
2.5.2	Enzyme Catalysis	64
2.5.3	Autocatalysis	70
2.6	Free Radical Reactions: Chains and Branched Chains	72
2.6.1	$\text{H}_2 + \text{Br}_2$	72
2.6.2	Rice-Herzfeld Mechanism	73
2.6.3	Branched Chain Reactions: Explosions	74
2.7	Determining Mechanisms from Rate Laws	77
2.8	Summary	81
	Suggested Readings	83
	Problems	83

Chapter 3 Theories of Chemical Reactions 91

3.1	Introduction	91
3.2	Potential Energy Surfaces	92
3.3	Collision Theory	95
3.3.1	Simple Collision Theory	95
3.3.2	Modified Simple Collision Theory	99
3.4	Activated Complex Theory (ACT)	102
3.5	Thermodynamic Interpretation of ACT	109
3.6	Summary	109
	Suggested Readings	111
	Problems	111

Chapter 4 Transport Properties 116

4.1	Introduction	116
4.2	The Functional Form of the Transport Equations	117
4.3	The Microscopic Basis for the Transport Laws	119
4.3.1	Simplifying Assumptions	119
4.3.2	The Molecular Flux	120
4.3.3	The Vertical Distance between Collisions	122
4.3.4	The General Flux Equation	122
4.4	Thermal Conductivity	124
4.5	Viscosity	127
4.6	Diffusion	131
4.7	Time-Dependent Transport	133
4.8	Summary	138
Appendix 4.1	The Poiseuille Formula	139
	Suggested Readings	141
	Problems	141

Chapter 5	Reactions in Liquid Solutions	144
5.1	Introduction	144
5.2	The Cage Effect, Friction, and Diffusion Control	145
5.2.1	The Cage Effect	145
5.2.2	The Langevin Equation	145
5.2.3	A Simple Model for Diffusion Control	148
5.2.4	The Diffusion-Controlled Rate Constant	148
5.3	Reactions of Charged Species in Solution: Ionic Strength and Electron Transfer	152
5.3.1	Reaction Rates and Ionic Strength	153
5.3.2	Electron Transfer Reactions: Marcus Theory	155
5.4	Experimental Techniques	159
5.4.1	The Temperature Jump Technique	159
5.4.2	Ultrafast Laser Techniques	161
5.5	Summary	164
Appendix 5.1	The Langevin Equation and the Mean Squared Displacement	165
Appendix 5.2	Diffusion with an Electrostatic Potential	167
	Suggested Readings	169
	Problems	169
Chapter 6	Reactions at Solid Surfaces	171
6.1	Introduction	171
6.2	Adsorption and Desorption	174
6.2.1	The Langmuir Isotherm	176
6.2.2	Competitive Adsorption	177
6.2.3	Heats of Adsorption	178
6.3	Reactions at Surfaces: Catalysis	179
6.3.1	Unimolecular Surface Reactions	179
6.3.2	Bimolecular Surface Reactions	180
6.3.3	Activated Complex Theory of Surface Reactions	181
6.3.4	The Nature of Surface Catalytic Sites	182
6.4	Surface Diffusion	183
6.5	Advanced Topics in Surface Reactions	185
6.5.1	Temperature-Programmed Desorption	185
6.5.2	Modulated Molecular Beam Methods	187
6.6	Summary	194
Appendix 6.1	Integral Transforms	196
	Suggested Readings	198
	Problems	198

Chapter 7	Photochemistry	204
7.1	Introduction	204
7.2	Absorption and Emission of Light	205
7.3	Photophysical Processes	209
7.3.1	Fluorescence and Quenching	209
7.3.2	Intramolecular Vibrational Energy Redistribution	212
7.3.3	Internal Conversion, Intersystem Crossing, and Phosphorescence	215
7.3.4	Photodissociation	218
7.4	Atmospheric Chemistry	221
7.5	Photodissociation Dynamics	225
7.5.1	The Pump-Probe Technique	226
7.5.2	Laser-Induced Fluorescence	228
7.5.3	Multiphoton Ionization	229
7.5.4	Unimolecular Dissociation	231
7.5.5	Photofragment Angular Distributions	239
7.5.6	Photochemistry on Short Time Scales	244
7.6	Summary	245
	Suggested Readings	248
	Problems	249
Chapter 8	Molecular Reaction Dynamics	257
8.1	Introduction	257
8.2	A Molecular Dynamics Example	258
8.3	Molecular Collisions—A Detailed Look	260
8.4	Molecular Scattering	263
8.4.1	The Center-of-Mass Frame—Newton Diagrams	264
8.4.2	Reactive Scattering: Differential Cross Section for $F + D_2$	270
8.4.3	Elastic Collisions	273
8.4.4	Inelastic Collisions	278
8.5	Potential Energy Surfaces	281
8.5.1	Trajectory Calculations by Classical Mechanics	283
8.5.2	Semiclassical Calculations	286
8.6	Molecular Energy Transfer	289
8.6.1	Translational Energy Transfer	289
8.6.2	Vibrational Energy Transfer	292
8.6.3	Rotational Energy Transfer	296
8.6.4	Electronic Energy Transfer	297
8.7	Molecular Reaction Dynamics—Some Examples	302
8.7.1	Reactive Collisions: Orientation	302
8.7.2	Reactive Collisions: Bond-Selective Chemistry	304

8.7.3	Potential Energy Surfaces from Spectroscopic Information: van der Waals Complexes	305
8.8	Summary	307
	Suggested Readings	309
	Problems	310

	Answers and Solutions to Selected Problems	315
	Index	319

Kinetic Theory of Gases

Chapter Outline

- 1.1 Introduction
 - 1.2 Pressure of an Ideal Gas
 - 1.3 Temperature and Energy
 - 1.4 Distributions, Mean Values, and Distribution Functions
 - 1.5 The Maxwell Distribution of Speeds
 - 1.6 Energy Distributions
 - 1.7 Collisions: Mean Free Path and Collision Number
 - 1.8 Summary
-
- Appendix 1.1 The Functional Form of the Velocity Distribution
 - Appendix 1.2 Spherical Coordinates
 - Appendix 1.3 The Error Function and Co-Error Function
 - Appendix 1.4 The Center-of-Mass Frame

1.1 INTRODUCTION

The overall objective of this chapter is to understand macroscopic properties such as pressure and temperature on a microscopic level. We will find that the pressure of an ideal gas can be understood by applying Newton's law to the microscopic motion of the molecules making up the gas and that a comparison between the Newtonian prediction and the ideal gas law can provide a function that describes the distribution of molecular velocities. This distribution function can in turn be used to learn about the frequency of molecular collisions. Since molecules can react only as fast as they collide with one another, the collision frequency provides an upper limit on the reaction rate.

The outline of the discussion is as follows. By applying Newton's laws to the molecular motion we will find that the product of the pressure and the volume is proportional to the average of the square of the molecular velocity, $\langle v^2 \rangle$, or equivalently to the average molecular translational energy ϵ . In order for this result to be consistent with the observed ideal gas law, the temperature T of the gas must also be proportional to $\langle v^2 \rangle$ or $\langle \epsilon \rangle$. We will then consider in detail how to determine the average of the square of the velocity from a distribution of velocities, and we will use the proportionality of T with $\langle v^2 \rangle$ to determine the Maxwell-Boltzmann distribution of speeds. This distribution, $F(v) dv$, tells us the number of molecules with speeds between v and $v + dv$. The speed distribution is closely related to the distribution of molecular energies, $G(\epsilon) d\epsilon$. Finally, we will use the velocity distribution

to calculate the number of collisions Z that a molecule makes with other molecules in the gas per unit time. Since in later chapters we will argue that a reaction between two molecules requires that they collide, the collision rate Z provides an upper limit to the rate of a reaction. A related quantity λ is the average distance a molecule travels between collisions or the *mean free path*.

The history of the kinetic theory of gases is a checkered one, and serves to dispel the impression that science always proceeds along a straight and logical path.^a In 1662 Boyle found that for a specified quantity of gas held at a fixed temperature the product of the pressure and the volume was a constant. Daniel Bernoulli derived this law in 1738 by applying Newton's equations of motion to the molecules comprising the gas, but his work appears to have been ignored for more than a century.^b A school teacher in Bombay, India, named John James Waterston submitted a paper to the Royal Society in 1845 outlining many of the concepts that underlie our current understanding of gases. His paper was rejected as "nothing but nonsense, unfit even for reading before the Society." Bernoulli's contribution was rediscovered in 1859, and several decades later in 1892, after Joule (1848) and Clausius (1857) had put forth similar ideas, Lord Rayleigh found Waterston's manuscript in the Royal Society archives. It was subsequently published in *Philosophical Transactions*. Maxwell (*Illustrations of Dynamical Theory of Gases*, 1859–1860) and Boltzmann (*Vorlesungen über Gastheorie*, 1896–1898) expanded the theory into its current form.

1.2 PRESSURE OF AN IDEAL GAS

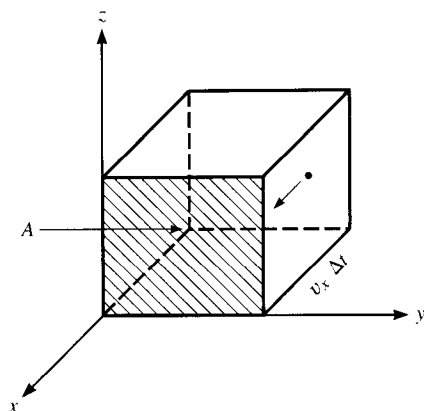
We start with the basic premise that the pressure exerted by a gas on the wall of a container is due to collisions of molecules with the wall. Since the number of molecules in the container is large, the number colliding with the wall per unit time is large enough so that fluctuations in the pressure due to the individual collisions are immeasurably small in comparison to the total pressure. The first step in the calculation is to apply Newton's laws to the molecules to show that the product of the pressure and the volume is proportional to the average of the square of the molecular velocity, $\langle v^2 \rangle$.

Consider molecules with a velocity component v_x in the x direction and a mass m . Let the molecules strike a wall of area A located in the z - y plane, as shown in **Figure 1.1**. We would first like to know how many molecules strike the wall in a time Δt , where Δt is short compared to the time between molecular collisions. The distance along the x axis that a molecule travels in the time Δt is simply $v_x \Delta t$, so that all molecules located in the volume $Av_x \Delta t$ and moving toward the wall will strike it. Let n^* be the number of molecules per unit volume. Since one half of the molecules will be moving toward the wall in the $+x$ direction while the other half will be moving in the $-x$ direction, the number of molecules which will strike the wall in the time Δt is $\frac{1}{2}n^*Av_x\Delta t$.

The force on the wall due to the collision of a molecule with the wall is given by Newton's law: $F = ma = m dv/dt = d(mv)/dt$, and integration yields $F\Delta t = \Delta(mv)$. If a molecule rebounds elastically (without losing energy) when it hits the wall, its momentum is changed from $+mv_x$ to $-mv_x$, so that the total momentum change is $\Delta(mv) = 2mv_x$. Consequently, $F\Delta t = 2mv_x$ for one molecular collision, and $F\Delta t = (\frac{1}{2}n^*Av_x\Delta t)(2mv_x)$ for the total number of collisions. Canceling Δt from both sides and recognizing that the pressure is the force per unit area, $p = F/A$, we obtain $p = n^*mv_x^2$.

^aThe history of the kinetic theory of gases is outlined by E. Mendoza, *Physics Today* **14**, 36–39 (1961).

^bA translation of this paper has appeared in *The World of Mathematics*, J. R. Newman, Ed., Vol. 2 (Simon and Schuster, New York, 1956), p. 774.



■ **Figure 1.1**

All the molecules in the box that are moving toward the z - y plane will strike the wall.

Of course, not all molecules will be traveling with the same velocity v_x . We will learn below how to characterize the distribution of molecular velocities, but for now let us simply assume that the pressure will be proportional to the average of the square of the velocity in the x direction, $p = n^* m \langle v_x^2 \rangle$.^c The total velocity of an individual molecule most likely contains other components along y and z . Since $\mathbf{v} = \hat{i}v_x + \hat{j}v_y + \hat{k}v_z$,^d where \hat{i} , \hat{j} , and \hat{k} are unit vectors in the x , y , and z directions, respectively, $v^2 = v_x^2 + v_y^2 + v_z^2$ and $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$. In an isotropic gas the motion of the molecules is random, so there is no reason for the velocity in one particular direction to differ from that in any other direction. Consequently, $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \langle v^2 \rangle / 3$. When we combine this result with the calculation above for the pressure, we obtain

$$p = \frac{1}{3} n^* m \langle v^2 \rangle. \quad (1.1)$$

Of course, n^* in **equation 1.1** is the number of molecules per unit volume and can be rewritten as nN_A/V , where N_A is Avogadro's number and n is the number of moles. The result is

$$pV = \frac{1}{3} n N_A m \langle v^2 \rangle. \quad (1.2)$$

Since the average kinetic energy of the molecules is $\langle \epsilon \rangle = \frac{1}{2} m \langle v^2 \rangle$, another way to write **equation 1.2** is

$$pV = \frac{2}{3} n N_A \langle \epsilon \rangle. \quad (1.3)$$

Equations 1.2 and **1.3** bear a close resemblance to the ideal gas law, $pV = nRT$. The ideal gas law tells us that the product of p and V will be constant if the temperature is constant, while **equations 1.2** and **1.3** tell us that the product will be constant if $\langle v^2 \rangle$ or $\langle \epsilon \rangle$ is constant. The physical basis for the constancy of pV with $\langle v^2 \rangle$ or $\langle \epsilon \rangle$ is clear from our previous discussion. If the volume is

^cIn this text, as in many others, we will use the notation $\langle x \rangle$ or \bar{x} to mean "the average value of x ."

^dThroughout the text we will use **boldface** symbols to indicate vector quantities and normal weight symbols to indicate scalar quantities. Thus, $v = |\mathbf{v}|$. Note that $\mathbf{v}^2 = \mathbf{v} \cdot \mathbf{v} = v^2$.

increased while the number, energy, and velocity of the molecules remain constant, then a longer time will be required for the molecules to reach the walls; there will thus be fewer collisions in a given time, and the pressure will decrease. To identify **equation 1.3** with the ideal gas law, we need to consider in more detail the relationship between temperature and energy.

1.3 TEMPERATURE AND ENERGY

Consider two types of molecule in contact with one another. Let the average energy of the first type be $\langle \epsilon \rangle_1$ and that of the second type be $\langle \epsilon \rangle_2$. If $\langle \epsilon \rangle_1$ is greater than $\langle \epsilon \rangle_2$, then when molecules of type 1 collide with those of type 2, energy will be transferred from the former to the latter. This energy transfer is a form of heat flow. From a macroscopic point of view, as heat flows the temperature of a system of the type 1 molecules will decrease, while that of the type 2 molecules will increase. Only when $\langle \epsilon \rangle_1 = \langle \epsilon \rangle_2$ will the temperatures of the two macroscopic systems be the same. In mathematical terms, we see that $T_1 = T_2$ when $\langle \epsilon \rangle_1 = \langle \epsilon \rangle_2$ and that $T_1 > T_2$ when $\langle \epsilon \rangle_1 > \langle \epsilon \rangle_2$. Consequently, there must be a correspondence between $\langle \epsilon \rangle$ and T so that the latter is some function of the former: $T = T(\langle \epsilon \rangle)$.

The functional form of the dependence of T on $\langle \epsilon \rangle$ cannot be determined solely from kinetic theory, since the temperature scale can be chosen in many possible ways. In fact, one way to define the temperature is through the ideal gas law: $T = pV/(nR)$. Experimentally, this corresponds to measuring the temperature either by measuring the volume of an ideal gas held at constant pressure or by measuring the pressure of an ideal gas held at constant volume. Division of both sides of **equation 1.3** by nR and use of the ideal gas relation gives us the result

$$T = \frac{pV}{nR} = \frac{2}{3} \frac{N_A}{R} \langle \epsilon \rangle, \quad (1.4)$$

or

$$\langle \epsilon \rangle = \frac{3}{2} kT, \quad (1.5)$$

where k , known as Boltzmann's constant, is defined as R/N_A . Note that since $\langle \epsilon \rangle = \frac{1}{2} m \langle v^2 \rangle$,

$$\langle v^2 \rangle = \frac{3kT}{m}. \quad (1.6)$$

example 1.1

Calculation of Average Energies and Squared Velocities

Objective	Calculate the average molecular energy, $\langle \epsilon \rangle$, and the average squared velocity, $\langle v^2 \rangle$, for a nitrogen molecule at $T = 300$ K.
Method	Use equations 1.5 and 1.6 with $m = (28 \text{ g/mole})(1 \text{ kg}/1000 \text{ g})/(N_A \text{ molecule/mole})$ and $k = 1.38 \times 10^{-23} \text{ J/K}$.
Solution	$\langle \epsilon \rangle = 3kT/2 = 3(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})/2 = 6.21 \times 10^{-21} \text{ J}.$ $\langle v^2 \rangle = \frac{3kT}{m}$