# CHEMICAL KINETICS AND REACTION DYNAMICS

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# 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 Importan	t 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)
Tota	l Lectures: 11	Total Lectures: 6

TABLE 2 Reactions in Liquid Solutions			
Fundamental (I	.ectures)	Supplemental (Lectures)	Advanced (Lectures)
5.1-5.3 (2	2)	5.4 (1)	

TABLE 3	An Intro	roduction to Surface Kinetics		
Fundamental (L	ectures)	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 Reactio	n 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

# 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.

<sup>\*</sup>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).

#### Preface

The text assumes some familiarity with elementary kinetics at the level of highschool 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

# Contents

	Preface
	and Reaction Dynamics xiii
	Errata xvíi
Chapter 1	Kinetic Theory of Gases1
1.1 1.2 1.3 1.4 1.5	Introduction1Pressure of an Ideal Gas2Temperature and Energy4Distributions, Mean Values, and Distribution Functions5The Maxwell Distribution of Speeds81.5.1The Velocity Distribution Must Be an Even Function of v.81.5.2The Velocity Distributions Are Independent and Uncorrelated91.5.3 $$ Should Agree with the Ideal Gas Law91.5.4The Distribution Depends Only on the Speed111.5.5Experimental Measurement of 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
	Suggested Readings
	Problems
Chapter 2	The Rates of Chemical Reactions
2.1	Introduction
2.2	Empirical Observations: Measurement of Reaction Rates
2.3	Rates of Reactions: Differential and Integrated Rate Laws
	2.3.1 First-Order Reactions
	2.3.2 Second-Order Reactions
	2.3.3 Pseudo-First-Order Reactions
	2.3.4 Higher-Order Reactions
	2.3.5 Temperature Dependence of Rate Constants
2.4	Reaction Mechanisms
	2.4.1 Opposing Reactions, Equilibrium
	2.4.2 Parallel Reactions
	2.4.3 Consecutive Reactions and the Steady-State Approximation 56
	¥ 11

Contents
----------

2.5 2.6 2.7 2.8	2.4.4Unimolecular Decomposition: The Lindemann Mechanism60Homogeneous Catalysis632.5.1Acid-Base Catalysis632.5.2Enzyme Catalysis642.5.3Autocatalysis70Free Radical Reactions: Chains and Branched Chains722.6.1 $H_2 + Br_2$ 722.6.2Rice-Herzfeld Mechanism732.6.3Branched Chain Reactions: Explosions74Determining Mechanisms from Rate Laws77Suggested Readings83Problems83
Chapter 3	Theories of Chemical Reactions
3.1	Introduction
3.2	Potential Energy Surfaces
3.3	Collision Theory
	3.3.1 Simple Collision Theory
2.4	3.3.2 Modified Simple Collision Theory
3.4	Thermodynamic Interpretation of ACT
3.5	Summary 109
5.0	Suggested Readings
	Problems
Chapter 4	Transport Properties
4.1	Introduction
4.2	The Functional Form of the Transport Equations
4.3	The Microscopic Basis for the Transport Laws
	4.3.1 Simplifying Assumptions 119
	4.3.2 The Molecular Flux
	4.5.5 The vertical Distance between Confisions 122 A 3.4 The General Flux Equation 122
44	Thermal Conductivity
4.5	Viscosity
4.6	Diffusion
4.7	Time-Dependent Transport
4.8	Summary
Appendix 4.1	The Poiseuille Formula
	Suggested Keadings
	1100/CHIS

vii

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
Chanter 6	Beactions at Solid Surfaces	171
Unapter U		//
6.1	Introduction	171
6.2	Adsorption and Desorption	174
	6.2.1 The Langmuir Isotherm	176
	6.2.2 Competitive Adsorption	
( )	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
	6.5.5 Activated Complex Theory of Surface	101
	6.2.4 The Network of Surface Catalytic Sites	101
6 1	0.3.4 The Nature of Surface Catalytic Sites	182
0.4	Advensed Tenics in Symform Desctions	
0.5	6.5.1 Temperature Programmed Description	
	6.5.2 Modulated Molecular Beam Mathada	
6.6	Summery	
0.0 Annendiv 6 1	Integral Transforms	194 106
Appendix 0.1	Suggested Readings	109
	Problems	108
		190

<u> </u>
( ontonto
COLICIUS

Chapter 7	Photochemistry
7.1	Introduction
7.2	Absorption and Emission of Light
7.3	Photophysical Processes
	7.3.1 Fluorescence and Quenching
	7.3.2 Intramolecular Vibrational Energy Redistribution
	7.3.3 Internal Conversion, Intersystem Crossing,
	and Phosphorescence
	734 Photodissociation
74	Atmospheric Chemistry
7.1	Photodissociation Dynamics
1.5	7.5.1 The Pump-Probe Technique 226
	7.5.1 The Funp-Frobe reeningue
	7.5.2 Last-Induced Fidorescence 220
	7.5.4 Unimplecular Dissociation 231
	7.5.5 Deptofragment Angular Distributions 230
	7.5.6 Photoshamistry on Short Time Scales
76	7.5.0 Photochemistry on Short Time Scales
/.0	Summary
	Suggested Readings
Chantar 9	Problems
Chapter 8	Problems
Chapter 8 8.1	Problems    249      Molecular Reaction Dynamics    257      Introduction    257
Chapter 8 8.1 8.2 8 2	Problems    249      Molecular Reaction Dynamics    257      Introduction    257      A Molecular Dynamics Example    258
<b>Chapter 8</b> 8.1 8.2 8.3	Problems    249      Molecular Reaction Dynamics    257      Introduction    257      A Molecular Dynamics Example    258      Molecular Collisions—A Detailed Look    260
<b>Chapter 8</b> 8.1 8.2 8.3 8.4	Problems       249         Molecular Reaction Dynamics       257         Introduction       257         A Molecular Dynamics Example       258         Molecular Collisions—A Detailed Look       260         Molecular Scattering       263
<b>Chapter 8</b> 8.1 8.2 8.3 8.4	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams264
<b>Chapter 8</b> 8.1 8.2 8.3 8.4	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section
<b>Chapter 8</b> 8.1 8.2 8.3 8.4	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for $F + D_2$ 270
<b>Chapter 8</b> 8.1 8.2 8.3 8.4	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for F + D22708.4.3Elastic Collisions273
<b>Chapter 8</b> 8.1 8.2 8.3 8.4	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for F + D22708.4.3Elastic Collisions2738.4.4Inelastic Collisions278
<b>Chapter 8</b> 8.1 8.2 8.3 8.4 8.4	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for $F + D_2$ 2708.4.3Elastic Collisions2738.4.4Inelastic Collisions278Potential Energy Surfaces281
<b>Chapter 8</b> 8.1 8.2 8.3 8.4 8.5	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for F + D22708.4.3Elastic Collisions2738.4.4Inelastic Collisions278Potential Energy Surfaces2818.5.1Trajectory Calculations by Classical Mechanics283
<b>Chapter 8</b> 8.1 8.2 8.3 8.4 8.5	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for $F + D_2$ 2708.4.3Elastic Collisions2738.4.4Inelastic Collisions278Potential Energy Surfaces2818.5.1Trajectory Calculations by Classical Mechanics2838.5.2Semiclassical Calculations286
<b>Chapter 8</b> 8.1 8.2 8.3 8.4 8.4	Problems       249         Molecular Reaction Dynamics       257         Introduction       257         A Molecular Dynamics Example       258         Molecular Collisions—A Detailed Look       260         Molecular Scattering       263         8.4.1       The Center-of-Mass Frame—Newton Diagrams       264         8.4.2       Reactive Scattering: Differential Cross Section       270         6.4.3       Elastic Collisions       273         8.4.4       Inelastic Collisions       278         Potential Energy Surfaces       281         8.5.1       Trajectory Calculations by Classical Mechanics       283         8.5.2       Semiclassical Calculations       286         Molecular Energy Transfer       289
<b>Chapter 8</b> 8.1 8.2 8.3 8.4 8.5 8.5	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for $F + D_2$ 2708.4.3Elastic Collisions2738.4.4Inelastic Collisions278Potential Energy Surfaces2818.5.1Trajectory Calculations by Classical Mechanics2838.5.2Semiclassical Calculations286Molecular Energy Transfer2892898.6.1Translational Energy Transfer289
<b>Chapter 8</b> 8.1 8.2 8.3 8.4 8.5 8.5	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for $F + D_2$ 2708.4.3Elastic Collisions2738.4.4Inelastic Collisions2738.4.4Inelastic Collisions278Potential Energy Surfaces2818.5.1Trajectory Calculations by Classical Mechanics2838.5.2Semiclassical Calculations2898.6.1Translational Energy Transfer2898.6.2Vibrational Energy Transfer292
<b>Chapter 8</b> 8.1 8.2 8.3 8.4 8.5 8.5	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for $F + D_2$ 2708.4.3Elastic Collisions2738.4.4Inelastic Collisions278Potential Energy Surfaces2818.5.1Trajectory Calculations by Classical Mechanics2838.5.2Semiclassical Calculations286Molecular Energy Transfer289286.38.6.3Rotational Energy Transfer290
<b>Chapter 8</b> 8.1 8.2 8.3 8.4 8.5 8.6	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for $F + D_2$ 2708.4.3Elastic Collisions2738.4.4Inelastic Collisions278Potential Energy Surfaces2818.5.1Trajectory Calculations by Classical Mechanics2838.5.2Semiclassical Calculations2898.6.1Translational Energy Transfer2898.6.2Vibrational Energy Transfer2928.6.3Rotational Energy Transfer2968.6.4Electronic Energy Transfer297
Chapter 8 8.1 8.2 8.3 8.4 8.5 8.5 8.6	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.28.4.2Reactive Scattering: Differential Cross Section for $F + D_2$ 708.4.38.4.4Inelastic Collisions2738.4.4Inelastic Collisions2738.5.1Trajectory Calculations by Classical Mechanics2838.5.2Semiclassical Calculations2898.6.1Translational Energy Transfer2898.6.2Vibrational Energy Transfer2928.6.3Rotational Energy Transfer2928.6.4Electronic Energy Transfer297Molecular Reaction Dynamics—Some Examples302
Chapter 8 8.1 8.2 8.3 8.4 8.5 8.6 8.7	Problems249Molecular Reaction Dynamics257Introduction257A Molecular Dynamics Example258Molecular Collisions—A Detailed Look260Molecular Scattering2638.4.1The Center-of-Mass Frame—Newton Diagrams2648.4.2Reactive Scattering: Differential Cross Section for $F + D_2$ 2708.4.3Elastic Collisions2738.4.4Inelastic Collisions278Potential Energy Surfaces2818.5.1Trajectory Calculations by Classical Mechanics2838.5.2Semiclassical Calculations2898.6.1Translational Energy Transfer2928.6.2Vibrational Energy Transfer2928.6.3Rotational Energy Transfer2968.6.4Electronic Energy Transfer297Molecular Reaction Dynamics—Some Examples3028.7.1Reactive Collisions: Orientation302

ix

Contents

	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  $\epsilon$ . 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

#### Chapter 1 Kinetic Theory of Gases

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  $\lambda$  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.<sup>a</sup> 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.<sup>b</sup> 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  $\Delta t$ , where  $\Delta t$  is short compared to the time between molecular collisions. The distance along the x axis that a molecule travels in the time  $\Delta t$  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  $\Delta t$  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  $\Delta t$ from both sides and recognizing that the pressure is the force per unit area, p = F/A, we obtain  $p = n^*mv_x^2$ .

<sup>&</sup>lt;sup>a</sup>The history of the kinetic theory of gases is outlined by E. Mendoza, *Physics Today* 14, 36–39 (1961). <sup>b</sup>A 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



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,  $p = n^*m < v_x^2 > .^c$  The total velocity of an individual molecule most likely contains other components along y and z. Since  $\mathbf{v} = \hat{i}v_x + \hat{j}v_y + \hat{k}v_z$ ,<sup>d</sup> where  $\hat{i}, \hat{j}$ , and  $\hat{k}$  are unit vectors in the x, y, and z directions, respectively,  $\mathbf{v}^2 = v_x^2 + v_y^2 + v_z^2$  and  $<\mathbf{v}^2 > = < v_x^2 > + < v_y^2 > + < v_z^2 >$ . 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,  $< v_x^2 > = < v_y^2 > = < v_z^2 > = < v^2 > /3$ . When we combine this result with the calculation above for the pressure, we obtain

$$p = \frac{1}{3}n^*m < v^2 >.$$
 (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

$$pV = \frac{1}{3} nN_{\rm A}m < v^2 >.$$
 (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

$$pV = \frac{2}{3}nN_{\rm A} < \epsilon >. \tag{1.3}$$

**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

<sup>&</sup>lt;sup>c</sup>In this text, as in many others, we will use the notation  $\langle x \rangle$  or  $\overline{x}$  to mean "the average value of x."

<sup>&</sup>lt;sup>d</sup>Throughout the text we will use **boldface** symbols to indicate vector quantities and normal weight symbols to indicate scalar quantities. Thus, v = |v|. Note that  $v^2 = v \cdot v = v^2$ .

#### Chapter 1 Kinetic Theory of Gases

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

$$T = \frac{pV}{nR} = \frac{2}{3} \frac{N_{\rm A}}{R} < \epsilon >, \tag{1.4}$$

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

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

$$\langle v^2 \rangle = \frac{3kT}{m}.$$
 (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 $m = (28 \text{ g/mole})(1 \text{ kg/1000 g})/(N_{\text{A}} \text{ molecule/mole})$ and $k = 1.38 \times 10^{-23} \text{ J/K}.$					
Solution	$<\epsilon> = 3kT/2 = 3(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})/2 = 6.21 \times 10^{-21} \text{ J}.$					
	$\langle v^2 \rangle = \frac{3kT}{m}$					

$$= 3 \frac{(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{[(28/6.02 \times 10^{26})]}$$
$$= 2.67 \times 10^5 \text{ (m/s)}^2 = (516 \text{ m/s})^2.$$

To summarize the discussion so far, we have seen from **equation 1.2** that pV is proportional to  $\langle v^2 \rangle$  and that the ideal gas law is obtained if we take the definition of temperature to be that embodied in **equation 1.5**. Since  $\langle \epsilon \rangle = \frac{1}{2}m \langle v^2 \rangle$ , both temperature and pV are proportional to the average of the square of the velocity. The use of an average recognizes that not all the molecules will be moving with the same velocity. In the next few sections we consider the *distribution* of molecular speeds. But first we must consider what we mean by a distribution.

#### 1.4 DISTRIBUTIONS, MEAN VALUES, AND DISTRIBUTION FUNCTIONS

Suppose that five students take a chemistry examination for which the possible grades are integers in the range from 0 to 100. Let their scores be  $S_1 = 68$ ,  $S_2 = 76$ ,  $S_3 = 83$ ,  $S_4 = 91$ , and  $S_5 = 97$ . The average score for the examination is then

$$\langle S \rangle = \frac{S_1 + S_2 + S_3 + S_4 + S_5}{N_{\rm T}} = \frac{1}{N_{\rm T}} \sum_{i=1}^{N_{\rm T}} S_i,$$
 (1.7)

where  $N_{\rm T} = 5$  is the number of students. In this case, the average is easily calculated to be 83.

Now suppose that the class had 500 students rather than 5. Of course, the average grade could be calculated in a manner similar to that in **equation 1.7** with an index *i* running from 1 to  $N_{\rm T} = 500$ . However, another method will be instructive. Clearly, if the examination is still graded to one-point accuracy, it is certain that more than one student will receive the same score. Suppose that, instead of summing over the students, represented by the index *i* in **equation 1.7**, we form the average by summing over the scores themselves, which range in integer possibilities from j = 0 to 100. In this case, to obtain the average, we must weight each score  $S_i$  by the number of students who obtained that score,  $N_i$ :

$$\langle S \rangle = \frac{1}{N_{\rm T}} \sum_{j=0}^{100} S_j N_j.$$
 (1.8)

Note that the definition of  $N_j$  requires that  $\sum N_j = N_T$ . The factor  $1/N_T$  in **equation 1.8** is included for normalization, since, for example, if all the students happened to get the same score  $S_i = S$  then

$$\langle S \rangle = \frac{1}{N_{\rm T}} \sum_{j} S_{j} N_{j} = \frac{S}{N_{\rm T}} \sum_{j} N_{j} = S.$$
 (1.9)

Now let us define the probability of obtaining score  $S_j$  as the fraction of students receiving that score:

$$P_j = \frac{N_j}{N_{\rm T}}.\tag{1.10}$$

#### Chapter 1 Kinetic Theory of Gases

Then another way to write equation 1.8 is

$$\langle S \rangle = \sum_{j} S_{j} P_{j},$$
 (1.11)

where  $\sum_{i} P_{i} = 1$  from normalization.

**Equation 1.11** provides an alternative to **equation 1.7** for finding the average score for the class. Furthermore, we can generalize **equation 1.11** to provide a method for finding the average of *any* quantity,

$$\langle Q \rangle = \sum_{j} P_{j} Q_{j},$$
 (1.12)

where  $P_i$  is the probability of finding the *j*th result.

## example 1.2

#### **Calculating Averages from Probabilities**

Objective	Find the average throw for a pair of dice.
Method	Each die is independent, so the average of the sum of the throws will be twice the average of the throw for one die. Use <b>equation 1.12</b> to find the average throw for one die.
Solution	The probability for each of the six outcomes, 1–6, is the same, namely, 1/6. Factoring this out of the sum gives $\langle T \rangle = (1/6) \Sigma$ $T_i$ , where $T_i = 1,2,3,4,5,6$ for $i = 1-6$ . The sum is 21, so that the average throw for one die is $\langle T \rangle = 21/6 = 3.5$ . For the sum of two dice, the average would thus be 7.

The method can be extended to calculate more complicated averages. Let  $f(Q_j)$  be some arbitrary function of the observation  $Q_j$ . Then the average value of the function f(Q) is given by

$$\langle f(Q) \rangle = \sum_{i} P_{i} f(Q_{i}).$$
 (1.13)

For example, if Q were the square of a score, then

$$\langle S^2 \rangle = \sum_{i} P_i S^2.$$
 (1.14)

Suppose now that the examination is a very good one, indeed, and that the talented instructor can grade it not just to one-point accuracy (a remarkable achievement in itself!) but to an accuracy of dS, where dS is a very small fraction of a point. Let P(S) dS be the probability that a score will fall in the range between S and S +dS, and let dS become infinitesimally small. The fundamental theorems of calculus tell us that we can convert the sum in **equation 1.11** to the integral

$$\langle S \rangle = \int P(S)S \,\mathrm{d}S,$$
 (1.15)

#### Section 1.4 Distributions, Mean Values, and Distribution Functions

or, more generally for any observable quantity,

$$\langle Q \rangle = \int P(Q)Q \,\mathrm{d}Q.$$
 (1.16)

**Equation 1.16** will form the basis for much of our further work. The probability function P(Q) is sometimes called a *distribution function*, and the range of the integral is over all values of Q where the probability is nonzero. Note that normalization of the probability requires

$$\int P(Q) \,\mathrm{d}Q = 1. \tag{1.17}$$

The quantity  $|\psi(x)|^2 dx$  is simply a specific example of a distribution function. Although knowledge of quantum mechanics is not necessary to solve it, you may recognize a connection to the particle in the box in Problem 1.7, which like **Example 1.3** is an exercise with distribution functions.

## example 1.3

#### **Determining Distribution Functions**

- **Objective** Bees like honey. A sphere of radius  $r_0$  is coated with honey and hanging in a tree. Bees are attracted to the honey such that the average number of bees per unit volume is given by  $Kr^{-5}$ , where K is a constant and r is the distance from the center of the sphere. Derive the normalized distribution function for the bees. They can be at any distance from the honey, but they cannot be inside the sphere. Using this distribution, calculate the average distance of a bee from the center of the sphere.
- **Method** First we need to find the normalization constant K by applying equation 1.17, recalling that we have a three-dimensional problem and that in spherical coordinates the volume element for a problem that does not depend on the angles is  $4\pi r^2 dr$ . Then, to evaluate the average, we apply equation 1.16.
- **Solution** Recall that, by hypothesis, there is no probability for the bees being at  $r < r_0$ , so that the range of integration is from  $r_0$  to infinity. To determine K we require

$$\int_{r_0}^{\infty} (Kr^{-5}) \, 4\pi r^2 \, \mathrm{d}r = 1, \qquad (1.18)$$

or

$$4\pi K \int_{r_0}^{\infty} r^{-3} dr = 1 = 4\pi K \left( -\frac{r^{-2}}{2} \right) \Big|_{r_0}^{\infty} = \frac{4\pi K}{2r_0^2}, \qquad (1.19)$$

so that

$$K = \frac{r_0^2}{2\pi}$$

Having determined the normalization constant, we now calculate the average distance:

$$< r > = \int_{r_0}^{\infty} r \left(\frac{r_0^2}{2\pi}\right) r^{-5} 4\pi r^2 \, \mathrm{d}r$$
  
$$= 2r_0^2 \int_{r_0}^{\infty} r^{-2} \, \mathrm{d}r \qquad (1.20)$$
  
$$= 2r_0^2 (-r^{-1}) \Big|_{r_0}^{\infty} = 2r_0^2 \frac{1}{r_0} = 2r_0.$$

#### 1.5 THE MAXWELL DISTRIBUTION OF SPEEDS

We turn now to the distribution of molecular speeds. We will denote the probability of finding  $v_x$  in the range from  $v_x$  to  $v_x + dv_x$ ,  $v_y$  in the range from  $v_y$  to  $v_y + dv_y$ , and  $v_z$  in the range from  $v_z$  to  $v_z + dv_z$  by  $F(v_x, v_y, v_z) dv_x dv_y dv_z$ . The object of this section is to determine the function  $F(v_x, v_y, v_z)$ . There are four main points in the derivation:

- 1. In each direction, the velocity distribution must be an even function of v.
- 2. The velocity distribution in any particular direction is independent from and uncorrelated with the distributions in orthogonal directions.
- 3. The average of the square of the velocity  $\langle v^2 \rangle$  obtained using the distribution function should agree with the value required by the ideal gas law:  $\langle v^2 \rangle = 3kT/m$ .
- 4. The three-dimensional velocity distribution depends only on the magnitude of v (i.e., the speed) and not on the direction.

We now examine these four points in detail.

#### **1.5.1** The Velocity Distribution Must Be an Even Function of *v*

Consider the velocities  $v_x$  of molecules contained in a box. The number of molecules moving in the positive x direction must be equal to the number of molecules moving in the negative x direction. This conclusion is easily seen by examining the consequences of the contrary assumption. If the number of molecules moving in each direction were not the same, then the pressure on one side of the box would be greater than on the other. Aside from violating experimental evidence that the pressure is the same wherever it is measured in a closed system, our common observation is that the box does not spontaneously move in either the positive or negative x direction, as would be likely if the pressures were substantially different. We conclude that the distribution function for the velocity in the x direction, or more generally in any arbitrary direction, must be symmetric; i.e.,  $F(v_x) = F(-v_y)$ . Functions possessing the property that f(x) = f(-x) are called *even functions*, while those having the property that f(x) = -f(-x) are called *odd functions*. We can ensure that  $F(v_{r})$  be an even function by requiring that the distribution function depend on the square of the velocity:  $F(v_r) = f(v_r^2)$ . As shown in Section 1.5.3, this condition is also in accord with the Boltzmann distribution law.<sup>e</sup>

<sup>&</sup>lt;sup>e</sup>Other even functions, for example,  $F = f(v_x^4)$  would be mathematically acceptable, but would not satisfy the requirement of Section 1.5.3.

#### 1.5.2 The Velocity Distributions Are Independent and Uncorrelated

We now consider the relationship between the distribution of x-axis velocities and y- or z-axis velocities. In short, there should be no relationship. The three components of the velocity are independent of one another since the velocities are uncorrelated. An analogy might be helpful. Consider the probability of tossing three honest coins and getting "heads" on each. Because the tosses  $t_i$  are independent, uncorrelated events, the joint probability for a throw of three heads,  $P(t_1 = \text{heads}, t_2 = \text{heads}, t_3 = \text{heads})$ , is simply equal to the product of the probabilities for the three individual events,  $P(t_1 = \text{heads}) \times P(t_2 = \text{heads}) \times P(t_3 = \text{heads}) = \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$ . In a similar way, because the x-, y-, and z-axis velocities are independent and uncorrelated, we can write that

$$F(v_x, v_y, v_z) = F(v_x)F(v_y)F(v_z).$$
 (1.21)

We can now use the conclusion of the previous section. We can write, for example, that  $F(v_x) = f(v_x^2)$  and similarly for the other directions. Consequently,

$$F(v_x, v_y, v_z) = F(v_x)F(v_y)F(v_z) = f(v_x^2)f(v_y^2)f(v_z^2).$$
(1.22)

What functional form has the property that f(a + b + c) = f(a)f(b)f(c)? A little thought leads to the exponential form, since  $\exp(a + b + c) = e^a e^b e^c$ . It can be shown, in fact, that the exponential is the *only* form having this property (see Appendix 1.1), so that we can write

$$F(v_x) = f(v_x^2) = K \exp(\pm \kappa v_x^2),$$
 (1.23)

where K and  $\kappa$  are constants to be determined. Note that although  $\kappa$  can appear mathematically with either a plus or a minus sign, we must require the minus sign on physical grounds because we know from common experience that the probability of very high velocities should be small.

The constant K can be determined from normalization since, using equation 1.17, the total probability that  $v_x$  lies somewhere in the range from  $-\infty$  to  $+\infty$  should be unity:

$$\int_{-\infty}^{\infty} F(v_x) \,\mathrm{d}v_x = 1. \tag{1.24}$$

Substitution of equation 1.23 into equation 1.24 leads to the equation

$$1 = K \int_{-\infty}^{\infty} \exp(-\kappa v_x^2) dv_x = K \left(\frac{\pi}{\kappa}\right)^{1/2},$$
 (1.25)

where the integral was evaluated using **Table 1.1.** The solution is then  $K = (\kappa/\pi)^{1/2}$ .

#### 1.5.3 $\langle v^2 \rangle$ Should Agree with the Ideal Gas Law

The constant  $\kappa$  is determined by requiring  $\langle v^2 \rangle$  to be equal to 3kT/m, as in equation 1.6. From equation 1.16 we find

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 F(v_x) dv_x = \left(\frac{\kappa}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} v_x^2 \exp(-\kappa v_x^2) dv_x.$$
 (1.26)

The integral is a standard one listed in Table 1.1, and using its value we find that

$$\langle v_x^2 \rangle = \frac{1}{2} \left(\frac{\kappa}{\pi}\right)^{1/2} \left(\frac{\pi}{\kappa^3}\right)^{1/2} = \frac{1}{2\kappa}.$$
 (1.27)

#### Chapter 1 Kinetic Theory of Gases

#### TABLE 1.1

#### Integrals of Use in the Kinetic Theory of Gases

$\int_{-\infty}^{\infty} x^{2n} e^{-\beta x^2} \mathrm{d}x = 2 \int_{0}^{\infty} x^{2n} e^{-\beta x^2} \mathrm{d}x$	$\int_{-\infty}^{\infty} x^{2n+1} e^{-\beta x^2} \mathrm{d}x = 0$
$\int_0^\infty e^{-\beta x^2} \mathrm{d}x = \frac{1}{2}\sqrt{\pi}\beta^{-1/2}$	$\int_0^\infty x e^{-\beta x^2} \mathrm{d}x = \frac{1}{2}\beta^{-1}$
$\int_0^\infty x^2 e^{-\beta x^2}  \mathrm{d}x = \frac{1}{2} \sqrt{\pi} \frac{1}{2} \beta^{-3/2}$	$\int_0^\infty x^3 e^{-\beta x^2} dx = \frac{1}{2}\beta^{-2}$
$\int_0^\infty x^4 e^{-\beta x^2}  \mathrm{d}x = \frac{1}{2} \sqrt{\pi} \frac{3}{4} \beta^{-5/2}$	$\int_0^\infty x^5 e^{-\beta x^2} \mathrm{d}x = \beta^{-3}$
$\int_0^\infty x^{2n} e^{-\beta x^2}  \mathrm{d}x = \frac{1}{2} \sqrt{\pi}  \frac{(2n)! \beta^{-(n+1/2)}}{2^{2n} n!}$	$\int_0^\infty x^{2n+1} e^{-\beta x^2}  \mathrm{d}x = \frac{1}{2} (n!) \beta^{-(n+1)}$

As a consequence, the average of the square of the total speed,  $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle$ , is simply

$$\langle v^2 \rangle = \frac{3}{2\kappa}.$$
 (1.28)

From equation 1.6 we have that  $\langle v^2 \rangle = 3kT/m$  for agreement with the ideal gas law, so that  $3kT/m = 3/(2\kappa)$ , or  $\kappa = m/(2kT)$ . The complete one-dimensional distribution function is thus

$$F(v_x) dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp\left(-\frac{1}{2}\frac{mv_x^2}{kT}\right) dv_x.$$
 (1.29)

This equation is known as the one-dimensional Maxwell-Boltzmann distribution for molecular velocities. Plots of  $F(v_x)$  are shown in **Figure 1.2**.

Note that **equation 1.29** is consistent with the Boltzmann distribution law, which states that the probability of finding a system with energy  $\epsilon$  is proportional to  $\exp(-\epsilon/kT)$ . Since  $\epsilon_x = \frac{1}{2}mv_x^2$  is equal to the translational energy of the molecule in the *x* direction, the probability of finding a molecule with an energy  $\epsilon_x$  should be proportional to  $\exp(-\epsilon_x/kT)$ , as it is in **equation 1.29**. In Section 1.5.1 we ensured  $F(v_x)$  to be even by choosing it to depend on the square of the velocity,  $F(v_x) = f(v_x^2)$ . Had we chosen some other even function, say  $F(v_x) = f(v_x^4)$ , the final expression for the one-dimensional distribution would not have agreed with the Boltzmann distribution law.

**Equation 1.29** provides the distribution of velocities in one dimension. In three dimensions, because  $F(v_x, v_y, v_z) = F(v_x)F(v_y)F(v_z)$ , and because  $v^2 = v_x^2 + v_y^2 + v_z^2$ , we find that the probability that the velocity will have components  $v_x$  between  $v_x$  and  $v_x + dv_x$ ,  $v_y$  between  $v_y$  and  $v_y + dv_y$ , and  $v_z$  between  $v_z$  and  $v_z + dv_z$  is given by

$$F(v_x, v_y, v_z) dv_x dv_y dv_z = F(v_x)F(v_y)F(v_z) dv_x dv_y dv_z$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv_x dv_y dv_z.$$
(1.30)





One-dimensional velocity distribution for a mass of 28 amu and two temperatures.

#### 1.5.4 The Distribution Depends Only on the Speed

Note that the right-hand side of **equation 1.30** depends on  $v^2$  and not on the directional property of **v**. When we have a function that depends only on the length of the velocity vector,  $v = |\mathbf{v}|$ , and not on its direction, we can be more precise by saying that the function depends on the *speed* and not on the *velocity*. Since  $F(v_x, v_y, v_z) = f(v^2)$  depends on the speed, it is often more convenient to know the probability that molecules have a speed in a particular range than to know the probability that their velocity vectors will terminate in a particular volume. As shown in **Figure 1.3**, the probability that the speed will be between v and v + dv is simply the probability that velocity vectors will terminate within the volume of a spherical shell between the radius v and the radius v + dv. The volume of this shell is  $dv_x dv_y dv_z = 4\pi v^2 dv$ , so that the probability that speed will be in the desired range is<sup>f</sup>

$$F(v) dv = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) \sin\theta dv d\theta d\phi$$
$$= \int_{\phi=0}^{2\pi} d\phi \int_{\theta=0}^{\pi} \sin\theta d\theta v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv$$
$$= 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv.$$

A more complete description of spherical coordinates is found in Appendix 1.2.

<sup>&</sup>lt;sup>f</sup>An alternate method for obtaining equation 1.31 is to note that  $dv_x dv_y dv_z$  can be written as  $v^2 \sin\theta d\theta d\phi dv$  in spherical coordinates (see Appendix 1.2) and then to integrate over the angular coordinates. Since the distribution does not depend on the angular coordinates, the integrals over  $d\theta$  and  $d\phi$  simply give  $4\pi$  and we are left with the factor  $v^2 dv$ .



#### Figure 1.3

The shell between v and v + dv has a volume of  $4\pi v^2 dv$ . The thickness of the shell here is exaggerated for clarity.



Figure 1.4



$$F(v) dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv.$$
 (1.31)

By analogy to equation 1.29, we will call equation 1.31 the *Maxwell-Boltzmann* speed distribution. Speed distributions as a function of temperature are shown in Figure 1.4.

We often characterize the speed distribution by a single parameter, for example, the temperature. Equivalently, we could specify one of several types of "average" speed, each of which is related to the temperature. One such average is called the *root-mean-squared* (rms) speed and can be calculated from **equation** 

**1.6**:  $c_{\rm rms} \equiv \langle v^2 \rangle^{1/2} = (3kT/m)^{1/2}$ . Another speed is the *mean* speed defined by using equation 1.16 to calculate  $\langle v \rangle$ :

$$\langle v \rangle = \int_0^\infty v F(v) dv$$

$$= \int_0^\infty v 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv = \left(\frac{8kT}{\pi m}\right)^{1/2},$$
(1.32)

where the integral was evaluated using **Table 1.1** as described in detail in **Example 1.4**. Finally, the distribution might also be characterized by the *most probable* speed,  $c^*$ , the speed at which the distribution function has a maximum (Problem 1.8):

$$c^* = \left(\frac{2kT}{m}\right)^{1/2}.$$
 (1.33)

#### Using the Speed Distribution

- **Objective** The speed distribution can be used to determine averages. For example, find the average speed,  $\langle v \rangle$ .
- **Method** Once one has the normalized distribution function, equation 1.16 gives the method for finding the average of any quantity. Identifying Q as the velocity and P(Q) dQ as the velocity distribution function given in equation 1.31, we see that we need to integrate vF(v) dv from limits v = 0 to  $v = \infty$ .

Solution 
$$\langle v \rangle = \int_{0}^{\infty} vF(v) dv = \int_{0}^{\infty} 4\pi v^{3} \left(\frac{a^{3}}{\pi^{3/2}}\right) \exp(-a^{2}v^{2}) dv$$
  
 $= \frac{4}{\sqrt{\pi}} \int_{0}^{\infty} a^{3}v^{3} \exp(-a^{2}v^{2}) dv,$  (1.34)

where  $a \equiv (m/2kT)^{1/2}$ . We now transform variables by letting  $x \equiv av$ . The limits will remain unchanged, and dv = dx/a. Thus the integral in equation 1.34 becomes

$$\frac{4}{a\sqrt{\pi}} \int_0^\infty x^3 \exp(-x^2) dx = \frac{4}{a\sqrt{\pi}} \frac{1}{2}$$

$$= \frac{2}{\sqrt{\pi}} \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{8kT}{\pi m}\right)^{1/2},$$
(1.35)

The molecular speed is related to the speed of sound, since sound vibrations cannot travel faster than the molecules causing the pressure waves. For example, in **Example 1.5** we find that the most probable speed for  $O_2$  is 322 m/s, while the

example 1.4



#### Figure 1.5

Maxwell-Boltzmann speed distribution for a mass of 28 amu and a temperature of 300 K. The vertical lines mark  $c^*$ ,  $\langle v \rangle$ , and  $c_{\rm rms}$ .

speed of sound in O<sub>2</sub> is measured to be 330 m/s. For an ideal gas the speed of sound can be shown to be  $(\gamma kT/m)^{1/2}$ , where  $\gamma$  is the ratio of heat capacities,  $\gamma = C_p/C_V$ . The *Mach number* is defined as the ratio of the speed of an object in a medium to the speed of sound through the same medium, so that when an aircraft "breaks the sound barrier" (or exceeds "Mach 1") it is actually traveling faster than the speed of the molecules in the medium.

Figure 1.5 shows the shape of the distribution function for T = 300 K and the locations of the variously defined speeds.

# example 1.5

Comparison of the Most Probable Speeds for Oxygen and Helium						
Objective	Compare the most probable speed for $O_2$ to that for He at 200 K.					
Method	Use equation 1.33 with $T = 200$ K and $m = 2$ amu or $m = 32$ amu. Note that the relative speeds should be proportional to $m^{-1/2}$ .					
Solution	$c^{*}(\text{He}) = (2kT/m)^{1/2} = [2(1.38 \times 10^{-23} \text{ J K}^{-1})(200 \text{ K})(6.02 \times 10^{23} \text{ amu/g})(1000 \text{ g/kg})/(2 \text{ amu})]^{1/2} = 1290 \text{ m/s}.$ A similar calculation substituting 32 amu for 2 amu gives $c^{*}(O_{2}) = 322 \text{ m/s}.$					
Comment	The escape velocity from the Earth's gravitational field is roughly $v_e = 1.1 \times 10^4$ m/s, only about 10 times the most probable speed for helium. Because the velocity distribution shifts so strongly toward high velocities as the mass decreases, the fraction of helium					



Figure 1.6

Various average speeds as a function of mass for T = 300 K.

atoms having speeds in excess of  $v_e$ , while minuscule (about  $10^{-31}$ ), is still  $10^{475}$  times larger than the fraction of oxygen molecules having speeds in excess of  $v_e$ ! As a consequence, the composition of the atmosphere is changing; much of the helium released during the lifetime of the planet has already escaped into space. A plot of various speeds as a function of mass for T = 300 K is shown in **Figure 1.6**.

#### 1.5.5 Experimental Measurement of the Maxwell Distribution of Speeds

Experimental verification of the Maxwell-Boltzmann speed distribution can be made by direct measurement using the apparatus of **Figure 1.7.** Two versions of the measurement are shown. In **Figure 1.7a**, slits (S) define a beam of molecules moving in a particular direction after effusing from an oven (O). Those that reach the detector (D) must successfully have traversed a slotted, multiwheel chopper by traveling a distance d while the chopper rotated through an angle  $\phi$ . In effect, the chopper selects a small slice from the velocity distribution and passes it to the detector. The speed distribution is then measured by recording the integrated detector signal for each cycle of the chopper as a function of the angular speed of the chopper.

A somewhat more modern technique, illustrated in **Figure 1.7b**, clocks the time it takes for molecules to travel a fixed distance. A very short pulse of molecules leaves the chopper at time t = 0. Because these molecules have a distribution of speeds, they spread out in space as they travel toward the detector, which records as a function of time the signal due to molecules arriving a distance L from the chopper.



#### Figure 1.7

Two methods for measuring the Maxwell-Boltzmann speed distribution.

Analysis of the detector signal from this second experiment is instructive, since it introduces the concept of *flux*. Recall that the distribution F(v) dv gives the fraction of molecules with speeds in the range from v to v + dv; it is dimensionless. If the number density of molecules is  $n^*$ , then  $n^*F(v) dv$  will be the number of molecules per unit volume with speeds in the specified range. The *flux* of molecules is defined as the number of molecules crossing a unit area per unit time. It is equal to the density of molecules times their velocity: flux (number/m<sup>2</sup>/s) = density (number/m<sup>3</sup>) × velocity (m/s).<sup>g</sup> Thus, the flux J of molecules with speeds between v and v + dv is

$$J \,\mathrm{d}v = v n^* F(v) \,\mathrm{d}v. \tag{1.36}$$

We will consider the flux in more detail in Section 4.3.2 and make extensive use of it in Chapter 4.

We now return to the speed measurement. Most detectors actually measure the number of molecules in a particular volume during a particular time duration. For example, the detector might measure current after ionizing those molecules that enter a volume defined by a cross-sectional area of A and a length  $\ell$ . Because molecules with high velocity traverse the distance  $\ell$  in less time than molecules with low velocity, the detection sensitivity is proportional to 1/v. The detector signal S(t) is thus proportional to  $JA\ell dv/v$ , or to  $n^*A\ell F(v) dv$ , where  $n^*$  is the number density of molecules in the oven. Assuming that a very narrow pulse of molecules is emitted from the chopper, the speed measured at a particular time t is simply v = L/t. We must now transform the velocity distribution from a speed distribution to a time distribution. Note that  $dv = d(L/t) = -L dt/t^2$ , and recall from equation 1.31 that  $F(v) dv \propto v^2 \exp(-\beta v^2) dv \propto (1/t^2) \exp(-\beta L^2/t^2)(L/t^2)$ . We thus find that  $S(t) \propto t^{-4} \exp(-\beta L^2/t^2)$ . Figure 1.8 displays an arrival time distribution of helium measured

<sup>&</sup>lt;sup>g</sup>Strictly speaking, the flux, **J**, is a vector, since the magnitude of the flux may be different in different directions. Here, since the direction of the flux is clear, we will use just its magnitude, *J*.



Figure 1.8

Time-of-flight measurements: intensity as a function of flight time. From J. F. C. Wang and H. Y. Wachman, as illustrated in F. O. Goodman and H. Y. Wachman, *Dynamics of Gas-Surface Scattering* (Academic Press, New York, 1976). Figure from "Molecular Beams" in DYNAMICS OF GAS-SURFACE SCATTERING by F. O. Goodman and H. Y. Wachmann, copyright © 1976 by Academic Press, reproduced by permission of the publisher. All rights or reproduction in any form reserved.

using this "time-of-flight" technique. The open circles are the detector signal, while the smooth line is a fit to the data of a function of the form expected for S(t). The best fit parameter gives a temperature of 300 K.

#### 1.6 ENERGY DISTRIBUTIONS

It is sometimes interesting to know the distribution of molecular energies rather than velocities. Of course, these two distributions must be related since the molecular translational energy  $\epsilon$  is equal to  $\frac{1}{2}mv^2$ . Noting that this factor occurs in the exponent of **equation 1.31** and that  $d\epsilon = mv \, dv = (2m\epsilon)^{1/2} \, dv$ , we can convert velocities to energies in **equation 1.31** to obtain

$$G(\epsilon) d\epsilon = 4\pi \left(\frac{2\epsilon}{m}\right) \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{\epsilon}{kT}\right) \frac{d\epsilon}{\sqrt{2m\epsilon}}$$
$$= 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \sqrt{\epsilon} \exp\left(-\frac{\epsilon}{kT}\right) d\epsilon.$$
(1.37)

The function  $G(\epsilon) d\epsilon$  tells us the fraction of molecules which have energies in the range between  $\epsilon$  and  $\epsilon + d\epsilon$ . Plots of  $G(\epsilon)$  are shown in **Figure 1.9**.

The distribution function  $G(\epsilon)$  can be used to calculate the average of any function of  $\epsilon$  using the relationship of **equation 1.16.** In particular, it can be shown as expected that  $\langle \epsilon \rangle = 3kT/2$  (see Problem 1.9).

Let us pause here to make a connection with thermodynamics. In the case of an ideal monatomic gas, there are no contributions to the energy of the gas from internal degrees of freedom such as rotation or vibration, and there is normally very





Energy distributions for two different temperatures. The fraction of molecules for the 300 K distribution having energy in excess of  $\epsilon^*$  is shown in the shaded region.

little contribution to the energy from excitation of electronic degrees of freedom. Consequently, the average energy U of n moles of a monatomic gas is simply  $nN_A$  times the average energy of one molecule of the gas, or

$$U = nN_{\rm A}\frac{3}{2}kT = \frac{3}{2}nRT.$$
 (1.38)

Note that the heat capacity at constant volume is defined as  $C_V = (\partial U/\partial T)_V$ , so that for an ideal monatomic gas we find that

$$C_V = \frac{3}{2}nR.$$
 (1.39)

This result is an example of the *equipartition principle*, which states that each term in the expression of the molecular energy that is quadratic in a particular coordinate contributes  $\frac{1}{2}kT$  to the average kinetic energy and  $\frac{1}{2}R$  to the molar heat capacity. Since there are three quadratic terms in the three-dimensional translational energy expression, the molar heat capacity of a monatomic gas should be 3R/2.

It is sometimes useful to know what fraction of molecules has an energy greater than or equal to a certain value  $\epsilon^*$ . In principle, the energy distribution  $G(\epsilon)$  should be able to provide this information, since the fraction of molecules having energy in the desired range is simply the integral of  $G(\epsilon) d\epsilon$  from  $\epsilon^*$  to infinity, as shown by the hatched region in **Figure 1.9.** In practice, the mathematics are somewhat cumbersome, but the result is reasonable. Let  $f(\epsilon^*)$  be the fraction of molecules with kinetic energy equal to or greater than  $\epsilon^*$ . This fraction is given by the integral

$$f(\epsilon^*) = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \int_{\epsilon^*}^{\infty} \sqrt{\epsilon} \exp\left(-\frac{\epsilon}{kT}\right) d\epsilon.$$
 (1.40)





The fraction of molecules having energy in excess of  $\epsilon^*$  as a function of  $\epsilon^*/kT$ .

Problem 1.10 shows that this integral is given by

$$f(\boldsymbol{\epsilon}^*) = \frac{2}{\sqrt{\pi}} a e^{-a^2} + \operatorname{erfc}(a), \qquad (1.41)$$

where  $a = (\epsilon^*/kT)^{1/2}$  and  $\operatorname{erfc}(a)$  is the co-error function defined in Appendix 1.3. A plot of  $f(\epsilon^*)$  as a function of  $\epsilon^*/kT$  is shown in **Figure 1.10**. Note that for  $\epsilon^* > 3kT$ , the function  $f(\epsilon^*)$  is nearly equal to the first term in **equation 1.41**,  $2\sqrt{(\epsilon^*/\pi kT)}\exp(-\epsilon^*/kT)$ , shown by the dashed line in the figure. Thus, the fraction of molecules with energy greater than  $\epsilon^*$  falls off as  $\sqrt{\epsilon^*}\exp(-\epsilon^*/kT)$ , provided that  $\epsilon^* > 3kT$ .

#### 1.7 COLLISIONS: MEAN FREE PATH AND COLLISION NUMBER

One of the goals of this chapter is to derive an expression for the number of collisions that molecules of type 1 make with molecules of type 2 in a given time. We will argue later that this collision rate provides an upper limit to the reaction rate, since the two species must have a close encounter to react.

The principal properties of the collision rate can be easily appreciated by anyone who has ice skated at a local rink. Imagine two groups of skaters, some rather sedate adults and some rambunctious 13-year-old kids. If there is only one kid and one adult in the rink, then the likelihood that they will collide is small, but as the number of either adults or kids in the rink increases, so does the rate at which collisions

#### Chapter 1 Kinetic Theory of Gases

will occur. The collision rate is proportional to the number of possible kid-adult pairs, which is proportional to the number density of adults times the number density of kids.

But the collision rate depends on other factors as well. If all the skaters follow the rules and skate counterclockwise around the rink at the same speed, then there will be no collisions. More often, the kids will skate at much faster or slower speeds, and they will rarely move uniformly. The rate at which they collide with the adults is proportional to the *relative speed* between the adults and kids.

Finally, consider the dependence of the collision rate on the size of the adults and kids. People are typically about 40 cm wide. What would be the effect of increasing or decreasing this diameter by a factor of 10? If the diameter were decreased to 4 cm, the number of collisions would go down dramatically; if the diameter were increased to 4 m, it would be difficult to move around the rink at all. Thus, simple considerations suggest that the collision rate between molecules should be proportional to the relative speed of the molecules, to their size, and to the number of possible collision pairs.

Let us assume that the average of the magnitude of the relative velocity between molecules of types 1 and 2 is  $\langle v_r \rangle$  and that the molecules behave like hard spheres; there are no attractive forces between them, and they bounce off one another like billiard balls when they collide.<sup>h</sup> Let the quantity *b*, shown in **Figure 1.11**, be defined as the distance of a line perpendicular to the each of the initial velocities of two colliding molecules, one of type 1 and the other of type 2. This distance is often referred to as the *impact parameter*. If the radii of the two molecules are  $r_1$  and  $r_2$ , then, as shown in **Figure 1.11**, a "collision" will occur if the two molecules approach one another so that their centers are within the distance  $b_{max} \equiv r_1 + r_2$ . Thus,  $b_{max}$  is the maximum value of the impact parameter for which a collision can occur. From the point of view of one type of molecule striking a molecule of the other type, the target area for a collision is then equal to  $\pi(r_1 + r_2)^2 = \pi b_{max}^2$ .





A collision will occur if the impact parameter is less than  $b_{\text{max}}$ , the sum of the two molecular radii.

<sup>&</sup>lt;sup>b</sup>We consider only the *relative* velocity between the molecules. Appendix 1.4 shows that the *total* velocity of each molecule can be written as a vector sum of the velocity of the center of mass of the pair of molecules and the relative velocity of the molecule with respect to the center of mass. The forces between molecules depend on the relative distance between them and do not change the velocity of their center of mass, which must be conserved during the collision.



#### Figure 1.12

Molecule 1 sweeps out a cylinder of area  $\pi b_{\text{max}}^2$ . Any molecule of type 2 whose center is within the cylinder will be struck.

Consider a molecule of type 1 moving through a gas with a speed equal to the average magnitude of the relative velocity  $\langle v_r \rangle$ . Figure 1.12 shows that any molecule of type 2 located in a cylinder of volume  $\pi b_{max}^2 \langle v_r \rangle \Delta t$  will then be struck in the time  $\Delta t$ .<sup>i</sup> If the density of molecules of type 2 is  $n_2^*$ , then the number of collisions one molecule of type 1 will experience with molecules of type 2 per unit time is

$$Z_2 = \pi b_{\max}^2 < v_r > n_2^*. \tag{1.42}$$

Of course, for a molecule of type 1 moving through other molecules of the same type,

$$Z_1 = \pi b_{\max}^2 < v_r > n_1^* = \pi d^2 < v_r > n_1^*,$$
 (1.43)

where  $b_{\max}^2$  has been replaced by  $d^2$  since  $r_1 + r_2 = 2r_1 = d$ . The quantity  $\pi b_{\max}^2$  is known as the hard-sphere collision cross section. Cross sections are generally given the symbol  $\sigma$ .

**Equation 1.42** gives the number of collisions per unit time of one molecule of type 1 with a density  $n_2^*$  of molecules of type 2. The *total* number of collisions of molecules of type 1 with those of type 2 per unit time and per unit volume is found simply by multiplying by the density of type 1 molecules:

$$Z_{12} = Z_2 n_1^* = \pi b_{\max}^2 < v_r > n_1^* n_2^*.$$
(1.44)

Note that the product  $n_1^* n_2^*$  is simply proportional to the total number of pairs of collision partners.

By a similar argument, if there were only one type of molecule, the number of collisions per unit time per unit volume is given by

$$Z_{11} = \frac{1}{2} Z_1 n_1^* = \frac{1}{2} \pi b_{\max}^2 < v_r > (n_1^*)^2.$$
(1.45)

The factor of  $\frac{1}{2}$  is introduced for the following reason. The collision rate should be proportional to the number of pairs of collision partners. If there are *n* molecules, then the number of pairs is n(n - 1)/2, since each molecule can pair with n - 1 others and the factor of 2 in the denominator corrects for having counted each pair twice. If *n* is a large number, then we can approximate n(n - 1) as  $n^2$ , and since the number of molecules is proportional to the number density, we see that the number of pairs goes as  $(n_1^*)^2/2$ .

It remains for us to determine the value of the relative speed, averaged over the possible angles of collision and averaged over the speed distribution for each molecule. One way to arrive quickly at the answer for a very specific case is shown in

<sup>&</sup>lt;sup>i</sup>Because of the collisions, the molecule under consideration will actually travel along a zigzag path, but the volume swept out per unit time will be the same.



In a hypothetical collision where two molecules each have a speed equal to the average  $\langle v \rangle$ , the relative velocity between two molecules, averaged over all collision directions, is  $\sqrt{2} \langle v \rangle$ .

**Figure 1.13.** Suppose that the two types of molecules have the same mass, *m*. Let us assume for the moment that we can accomplish the average of the speed distribution by assuming that the two molecules each have a speed equal to the average of their distribution. Since the two molecules are assumed to have the same mass (and temperature), they will also have the same average speed,  $\langle v \rangle$ . We now consider the average over collision angles. If the molecules are traveling in the same direction, then the relative velocity between them will have zero magnitude,  $v_r = 0$ , while if they are traveling in opposite directions along the same line the relative velocity will have a magnitude of  $v_r = 2 < v >$ . Suppose that they are traveling at right angles to one another. In that case, which is representative of the average angle of collision, the relative velocity will have a magnitude of  $v_r = \langle 8kT/\pi m \rangle^{1/2}$ , we find that

$$\langle v_{\rm r} \rangle = \sqrt{2} \langle v \rangle$$
  
=  $\sqrt{2} \left( \frac{8kT}{\pi m} \right)^{1/2} = \left( \frac{8kT}{\pi (m/2)} \right)^{1/2} = \left( \frac{8kT}{\pi \mu} \right)^{1/2},$  (1.46)

where we have introduced the *reduced mass*,  $\mu$ , defined as  $\mu = m_1 m_2/(m_1 + m_2)$ . When the masses  $m_1$  and  $m_2$  are the same,  $\mu = m^2/2m = m/2$ . If the masses are different, then the mean velocities will not be the same, and the simple analysis of **Figure 1.13** is not adequate. However, as shown for the general case in Appendix 1.4 and Problem 1.12, the result for  $\langle v_r \rangle$  is the same as that given in **equation 1.46**. The appendix also shows why the definition of  $\mu$  as  $m_1 m_2/(m_1 + m_2)$  is a useful one.

# example 1.6

#### The Collision Rate of NO with O<sub>3</sub>

**Objective** Find the collision rate of NO with  $O_3$  at 300 K if the abundances at 1 atm total pressure are each 0.2 ppm and if the molecular diameters are 300 and 375 pm, respectively. Reactive collisions between these two species are important in photochemical smog formation.

Method Use equation 1.44, remembering to convert the abundances to number densities at 300 K and calculating the average relative velocity by use of equation 1.46.

**Solution** First find the total number density  $n^*$  at 1 atm:  $n^* = (n/V)N_A = (p/RT)N_A = (1 \text{ atm})(6.02 \times 10^{23} \text{ molec/mole})/[(0.082 \text{ L atm mol}^{-1} \text{ K}^{-1})(300 \text{ K})] = 2.45 \times 10^{22} \text{ molec/L}$ . Next determine the number densities of NO and O<sub>3</sub>, each being the total density times  $0.2 \times 10^{-6}$ :  $n^*(\text{NO}) = n^*(\text{O}_3) = (0.2 \times 10^{-6})(2.45 \times 10^{22}) = 4.9 \times 10^{15} \text{ molec/L}$ . The average relative velocity is  $\langle v_r \rangle = (8kT/\pi\mu)^{1/2} = [8(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})(6.02 \times 10^{23} \text{ amu/g})(1000 \text{ g/kg})/(\pi (48 \times 30/78) \text{ amu})]^{1/2} = 586 \text{ m/s}$ . The average diameter is (300 + 375 pm)/2 = 337.5 pm. Then  $Z_{12} = \pi (337.5 \times 10^{-12} \text{ m})^2$  (586 m/s)(4.9  $\times 10^{15} \text{ molec/L})^2(1 \text{ L}/10^{-3} \text{ m}^3)^2 = 5.0 \times 10^{21} \text{ collisions s}^{-1} \text{ m}^{-3}$ . If every collision resulted in a reaction, this would be the number of reactions per unit second per cubic meter.

A quantity related to  $Z_1$  is the *mean free path*,  $\lambda$ . This is the average distance a molecule travels before colliding with another molecule. If we divide the average speed  $\langle v \rangle$  in meters per second by the collision number  $Z_1$  in collisions per second, we obtain the mean free path in meters per collision:

$$\lambda = \frac{\langle v \rangle}{Z_1} = \frac{\langle v \rangle}{\pi d^2 \sqrt{2} \langle v \rangle n_1^*}$$
  
=  $\frac{1}{\sqrt{2} \pi d^2 n_1^*}$ . (1.47)

Note that the mean free path is inversely proportional to pressure. The mean free path will be important in Chapter 4, where we will see that the transport of heat, momentum, and matter are all proportional to the distance traveled between collisions.

## example 1.7

#### The Mean Free Path of Nitrogen

Objective	Find $Z_1$ and the mean free path of N <sub>2</sub> at 300 K and 1 atm given that the molecular diameter is 218 pm.
Method	Use equation 1.46 to calculate $\langle v_r \rangle$ , equation 1.43 to calculate $Z_1$ , and equation 1.47 to calculate $\lambda$ .
Solution	We start by calculating $\langle v_r \rangle = (8kT/\pi\mu)^{1/2}$ , where $\mu = 28 \times 28/(28 + 28) = 14$ amu.
$\langle v_{\rm r} \rangle = \begin{cases} \frac{8(1.2)}{2} \end{cases}$	$\frac{38 \times 10^{-23} \mathrm{J} \mathrm{K}^{-1})(300 \mathrm{K})(6.02 \times 10^{23} \mathrm{amu/g})(1000 \mathrm{g/kg})}{(3.1415 \times 14 \mathrm{amu})} \begin{cases} 1/2 \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
	= 673  m/s.

Next, we calculate  $Z_1$  noting that the density

$$n_{1}^{*} = \frac{p}{RT} = \frac{(1 \text{ atm})(6.02 \times 10^{23} \text{ molec/mole})}{(0.082 \text{ L atm mole}^{-1} \text{ K}^{-1})(10^{-3} \text{ m}^{3}/\text{L})(300 \text{ K})}$$

$$= 2.45 \times 10^{25} \text{ molec/m}^{3}.$$
(1.49)
Then,  $Z_{1} = \pi (218 \times 10^{-12} \text{ m})^{2} (673 \text{ m/s})(2.45 \times 10^{25} \text{ molec/m}^{3}) =$ 

Then,  $Z_1 = \pi (218 \times 10^{-12} \text{ m})^2 (6/3 \text{ m/s})(2.45 \times 10^{23} \text{ molec/m}^3) = 2.46 \times 10^9 \text{ collision/s}$ . Finally,  $\langle v_r \rangle / (\sqrt{2} Z_1) = (673 \text{ m/s}) / (\sqrt{2} \times 2.46 \times 10^9 \text{ collision/s}) = 1.93 \times 10^{-7} \text{ m}.$ 

#### 1.8 SUMMARY

By considering the pressure exerted by ideal gas molecules on a wall, we determined that, for agreement with the observed ideal gas law, the average energy of a molecule must be given by

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

To learn how to perform averages, we discussed distribution functions of a continuous variable. The average of some observable quantity Q was found to be given by

$$\langle Q \rangle = \int P(Q)Q \,\mathrm{d}Q,$$
 (1.16)

where P(Q) is the distribution function for the quantity Q. We then made the following observations about the molecular speed distribution: (1) the speed distribution must be an even function of v, (2) the speed distribution in any particular direction is independent from and uncorrelated with that in orthogonal directions, (3) the value of  $\langle v^2 \rangle$  must be equal to 3kT/m to agree with the ideal gas law, and (4) the distribution depends only on the magnitude of v. These four considerations allowed us to determine the Maxwell-Boltzmann distribution of speeds:

$$F(v) dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) dv.$$
 (1.31)

Calculations using this distribution gave us an equation for the average speed of a molecule,

$$\langle v \rangle = \left(\frac{8kT}{\pi m}\right)^{1/2},$$
 (1.32)

and the most probable speed,

$$c^* \left(\frac{2kT}{m}\right)^{1/2}.$$
 (1.33)

A simple transformation of variables in the speed distribution led to the Maxwell-Boltzmann energy distribution:

$$G(\epsilon) d\epsilon = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \sqrt{\epsilon} \exp\left(-\frac{\epsilon}{kT}\right) d\epsilon.$$
 (1.37)

Finally, for molecules behaving as hard spheres, we determined the collision rate,

$$Z_1 = \pi b_{\max}^2 < v_r > n_1^*, \tag{1.42}$$
the relative velocity,

$$\langle v_{\rm r} \rangle = \sqrt{2} \langle v \rangle = \left(\frac{8kT}{\pi\mu}\right)^{1/2},$$
 (1.46)

and the mean free path,

$$\lambda = \frac{\langle v \rangle}{Z_1} = \frac{1}{\sqrt{2\pi}d^2 n_1^*}.$$
(1.47)

These concepts form the basis for further investigation into transport properties and chemical reaction kinetics.

# appendix 1.1

#### The Functional Form of the Velocity Distribution

We demonstrate in this appendix that the exponential form used in **equation 1.23** is the only function that satisfies the equation f(a + b + c) = f(a)f(b)f(c). Consider first the simpler equation

$$f(z) = f(a)f(b),$$
 (1.50)

where z = a + b. Taking the derivative of both sides of equation 1.50 with respect to *a* we obtain

$$\frac{\mathrm{d}f(z)}{\mathrm{d}z}\frac{\mathrm{d}z}{\mathrm{d}a} = f'(a)f(b). \tag{1.51}$$

On the other hand, taking the derivative of both sides of equation 1.50 with respect to *b*, we obtain

$$\frac{\mathrm{d}f(z)}{\mathrm{d}z}\frac{\mathrm{d}z}{\mathrm{d}b} = f(a)f'(b). \tag{1.52}$$

Since z = a + b, dz/da = dz/db = 1. Consequently,

$$\frac{df(z)}{dz} = f'(a)f(b) = f(a)f'(b).$$
(1.53)

Division of both sides of the right-hand equality by f(a)f(b) yields

$$\frac{f'(a)}{f(a)} = \frac{f'(b)}{f(b)}.$$
(1.54)

Now the left-hand side of **equation 1.54** depends only on *a*, while the right-hand side depends only on *b*. Since *a* and *b* are independent variables, the only way that **equation 1.54** can be true is if each side of the equation is equal to a constant,  $\pm \kappa$ , where  $\kappa$  is defined as nonnegative:

$$\frac{f'(a)}{f(a)} = \pm \kappa \qquad \qquad \frac{f'(b)}{f(b)} = \pm \kappa. \tag{1.55}$$

Solution of these differential equations using x to represent either a or b leads to

$$\frac{f'(x)}{f(x)} = \pm \kappa \quad \text{or} \quad \frac{\mathrm{d}f(x)}{f(x)} = \pm \kappa \,\mathrm{d}x. \tag{1.56}$$

Integration shows that

$$f(x) = Ke^{\pm\kappa x},\tag{1.57}$$

where K is related to the constant of integration. Equation 1.23 is obtained by replacing x with  $v_x^2$ .

## appendix 1.2

#### **Spherical Coordinates**

Many problems in physical chemistry can be solved more easily using spherical rather than Cartesian coordinates. In this coordinate system, as shown in **Figure 1.14**, a point *P* is located by its distance *r* from the origin, the angle  $\theta$  between the *z* axis and the line from the point to the origin, and the angle  $\phi$  between the *x* axis and the line between the origin and a projection of the point onto the *x*-*y* plane. Any point can be described by a value of *r* between 0 and  $\infty$ , a value of  $\theta$  between 0 and  $\pi$ , and a value of  $\phi$  between 0 and  $2\pi$ . The Cartesian coordinates are related to the spherical ones by the following relationships:  $x = r \sin \theta \cos \phi$ ,  $y = r \sin \theta \sin \phi$ , and  $z = r \cos \theta$ .

The volume element in spherical coordinates can be calculated with the help of **Figure 1.15.** As the variable  $\theta$  is increased for fixed *r*, the position of the point described by  $(r,\theta,\phi)$  moves along a longitudinal line on the surface of a sphere, while if  $\phi$  is increased at fixed *r*, the position of the point moves along a latitudinal line. Starting at a point located at  $(r,\theta,\phi)$ , if *r* is increased by d*r*,  $\theta$  is increased by d $\theta$ , and  $\phi$  is increased by d $\phi$ , then the volume increase is the surface area on the



Spherical coordinates.





The volume element in spherical coordinates.

sphere times the thickness dr (for clarity, the thickness dr is not shown in the diagram). The surface area is given by the arc length on the longitude,  $r d\theta$ , times the arc length on the latitude,  $r \sin \theta d\phi$ . Thus, the volume element is  $dV = r^2 \sin \theta d\theta d\phi dr$ .

# appendix 1.3

#### **The Error Function and Co-Error Function**

It often occurs that we need to evaluate integrals of the form of those listed in **Table 1.1** but for limits less than the range of 0 to infinity. For such evaluations it is useful to define the *error function*:

$$\operatorname{erf}(x) \equiv \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-u^{2}} \mathrm{d}u.$$
 (1.58)

From **Table 1.1** we see that for  $x = \infty$ , the value of the integral is  $\sqrt{\pi/2}$ , so that  $\operatorname{erf}(\infty) = 1$ . Note that if we "complement" the error function by  $2/\sqrt{\pi}$  times the integral from x to  $\infty$ , we should get unity:

$$\frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-u^{2}} du + \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-u^{2}} du = \operatorname{erf}(x) + \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-u^{2}} du$$

$$= \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} e^{-u^{2}} du = 1.$$
(1.59)





Values of the error function.

Consequently, it is also useful to define the co-error function, erfc(x), as the complement to the error function:

$$\operatorname{erfc}(x) \equiv 1 - \operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-u^{2}} du.$$
 (1.60)

Tables of the error function and co-error function are available, but the pervasive use of computers has made them all but obsolete. For calculational purposes, the integrand in equation 1.58 or equation 1.60 can be expanded using a series,

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{(-1)^n x^{2n+1}}{n! (2n+1)},$$
(1.61)

and then the integration can be performed term by term. Figure 1.16 plots erf(x) as a function of x.

## appendix 1.4

#### **The Center-of-Mass Frame**

We show in this appendix that the total kinetic energy of two particles of velocities  $\mathbf{v}_1$  and  $\mathbf{v}_2$  is given by  $\frac{1}{2}\mu v_r^2 + \frac{1}{2}Mv_{com}^2$ , where  $\mathbf{v}_r = \mathbf{v}_2 - \mathbf{v}_1$ , and where  $\mathbf{v}_{com}$ , the vector describing the velocity of the center of mass, is defined by the equation  $(m_1 + m_2)\mathbf{v}_{com} = m_1\mathbf{v}_1 + m_2\mathbf{v}_2$ , and  $M \equiv m_1 + m_2$ . Figure 1.17 shows the vector relationships.



Figure 1.17

Vector diagram for center-of-mass conversion.

The virtue of this transformation is that the total momentum of the system  $\mathbf{p} = m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2$  is also equal to the momentum of the center of mass, defined as  $M \mathbf{v}_{com}$ . Because we assume that no external forces are acting on the system,  $\mathbf{F} = M \mathbf{a}_{com} = (d\mathbf{p}_{com}/dt) = 0$ , so that the momentum of the center of mass does not change during the interaction between the two particles.

Note that since  $(m_1/M) + (m_2/M) = 1$  we can write

 $m_1 \mathbf{v}_1$ 

$$\mathbf{v}_2 - \mathbf{v}_{com} = \left(\frac{m_1}{M} + \frac{m_2}{M}\right) \mathbf{v}_2 - \mathbf{v}_{com}$$
  
=  $\frac{m_1}{M} \mathbf{v}_2 + \frac{m_2}{M} \mathbf{v}_2 - \mathbf{v}_{com}.$  (1.62)

However,

$$m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 = M \mathbf{v}_{\rm com}, \tag{1.63}$$

so that

Consequently,

$$\mathbf{v}_2 - \mathbf{v}_{com} = \frac{m_1}{M} \mathbf{v}_2 - \frac{m_1}{M} \mathbf{v}_1$$
  
=  $\frac{m_1}{M} \mathbf{v}_r$ . (1.64)

 $\frac{m_2\mathbf{v}_2}{M} - \mathbf{v}_{\rm com}.$ 

In a similar way, we find that

$$\mathbf{v}_{\rm com} - \mathbf{v}_1 = \frac{m_2}{M} \mathbf{v}_{\rm r}.$$
 (1.65)

We now note an important point, that the velocities of the particles with respect to the center of mass are just given by the two pieces of the vector  $\mathbf{v}_r$ :  $\mathbf{u}_1 = -(m_2/M)\mathbf{v}_r$ , and  $\mathbf{u}_2 = (m_1/M)\mathbf{v}_r$ , as shown in **Figure 1.18**. Note also that in the moving frame of the center of mass, there is no net momentum for the particles; that is,  $m_1\mathbf{u}_1 + m_2\mathbf{u}_2 = 0$ . This important property enables us to calculate the velocity of one particle in the center-of-mass frame given just the mass and the velocity of the other particle.



#### Figure 1.18

Vector diagram for center-of-mass conversion, showing the relative velocities in the center-ofmass frame for the two particles.

We can rearrange equations 1.64 and 1.65 to get

$$\mathbf{v}_{\rm com} - \frac{m_2}{M} \mathbf{v}_{\rm r} = \mathbf{v}_1,$$

$$\mathbf{v}_{\rm com} + \frac{m_1}{M} \mathbf{v}_{\rm r} = \mathbf{v}_2.$$
(1.66)

The total energy is then

$$\frac{1}{2}m_{1}\mathbf{v}_{1}^{2} + \frac{1}{2}m_{2}\mathbf{v}_{2}^{2} = \frac{1}{2}m_{1}\left(\mathbf{v}_{com} - \frac{m_{2}}{M}\mathbf{v}_{r}\right)^{2} + \frac{1}{2}m_{2}\left(\mathbf{v}_{com} + \frac{m_{1}}{M}\mathbf{v}_{r}\right)^{2}$$

$$= \frac{1}{2}m_{1}\mathbf{v}_{com}^{2} - \frac{2m_{1}m_{2}}{2M}\mathbf{v}_{r}\cdot\mathbf{v}_{com} + \frac{m_{1}m_{2}^{2}}{2M^{2}}\mathbf{v}_{r}^{2}$$

$$+ \frac{1}{2}m_{2}\mathbf{v}_{com}^{2} + \frac{2m_{2}m_{1}}{2M}\mathbf{v}_{r}\cdot\mathbf{v}_{com} + \frac{m_{2}m_{1}^{2}}{2M^{2}}\mathbf{v}_{r}^{2}$$

$$= \frac{1}{2}M\mathbf{v}_{com}^{2} + \frac{m_{1}m_{2}M}{2M^{2}}\mathbf{v}_{r}^{2}$$

$$= \frac{1}{2}Mv_{com}^{2} + \frac{1}{2}\mu\nu_{r}^{2}.$$
(1.67)

It will often be useful to consider collisions in the center-of-mass frame. For example, we will make extensive use of this view in talking about molecular scattering in Section 8.4. Problem 1.12 shows how this result can be used to calculate the average relative velocity.

## suggested readings

- G. G. Hammes, *Principles of Chemical Kinetics* (Academic Press, New York, 1978).
- W. Kauzmann, Kinetic Theory of Gases, Vol. 1, Thermal Properties of Matter, (Benjamin, Reading, MA, 1966)
- E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1938).
- R. D. Present, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1958).
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# problems

- 1.1 Molecules all of mass m and speed v exert a pressure p on the walls of a vessel. If half the molecules are replaced by ones of another type all with mass  $\frac{1}{2}m$  and speed 2v, will the pressure (a) increase, (b) decrease, (c) remain constant?
- 1.2 Suppose the probability of obtaining a score between 0 and 100 on an exam increases monotonically between 0 and 1.00. Is the average score on the exam (a) greater than 50, (b) equal to 50, (c) less than 50?
- 1.3 Suppose some property q of a gas is proportional to  $(0.326 \text{ s}^3 \text{ m}^{-3})v_x^3 + (\pi \text{ s}^9 \text{ m}^{-9})v_y^9$ . What is the average value of q?
- 1.4 Without referring to any formula, decide whether at constant density the mean free path (a) increases, (b) decreases, or (c) stays constant with increasing temperature and explain your answer.
- 1.5 Consider a deck of cards. With aces valued at one and jacks, queens, and kings valued at 11, 12, and 13, respectively, calculate the average value of a card drawn at random from a full deck.
- 1.6 The distribution of the grades S (where  $0 \le S \le 100$ ) for a class containing a large number of students is given by the continuous function P(S) = K(50 |S 50|), where |x| is the absolute value of x and K is a normalization constant. Determine the normalization constant and find out what fraction of the students received grades greater than or equal to 90.
- 1.7 A pair of dancers is waltzing on a one-dimensional dance floor of length L. Since they tend to avoid the walls, the probability of finding them at a position x between walls at x = 0 and x = L is proportional to  $\sin^2(\pi x/L)$ . What is the normalized distribution function for the position of the waltzers? Using this distribution function, calculate the most probable position for the waltzers. Calculate the average position of the waltzers. (*Hint:* The integral of  $y \sin^2 y \, dy$  is  $[y^2/4] - [(y \sin 2y)/4] - [(\cos 2y)/8]$ ; this is also the probability for finding a particle in a box at a particular position.)
- 1.8 By setting the derivative of the formula for the Maxwell-Boltzmann speed distribution equal to zero, show that the speed at which the distribution has its maximum is given by equation 1.33.
- 1.9 Show using equations 1.16 and 1.37 that the average molecular energy is 3kT/2.
- 1.10 Prove equation 1.41 from equation 1.40. Integration can be accomplished by making the following change of variable. Let  $\epsilon = kTx^2$ , so that  $d\epsilon = kT d(x^2)$  and  $\epsilon^{1/2} = (kT)^{1/2}x$ . Substitute these into equation 1.40 and integrate by parts, recalling that since d(uv) = u dv + v du, then  $\int d(uv) = \int u dv + \int v du$ , so that  $\int u dv = (uv)|_{\text{limits}} - \int v du$ , where the notation  $|_{\text{limits}}$  indicates that the product (uv) should be evaluated at the limits used for the integrals.
- 1.11 The Maxwell-Boltzmann distribution may not be quite valid! Calculate the fraction of  $N_2$  molecules having speeds in excess of the speed of light.
- 1.12 The object of this problem is to show more rigorously that  $\langle v_r \rangle = (8kT/\pi\mu)^{1/2}$ , where  $\mu$ , the reduced mass, is defined as  $\mu \equiv m_1 m_2/(m_1 + m_2)$ .

#### Chapter 1 Kinetic Theory of Gases

We have already learned in Appendix 1.4 that the total kinetic energy of two particles is given by  $\frac{1}{2}\mu v_r^2 + \frac{1}{2}Mv_{com}^2$ , where  $\mathbf{v}_r = \mathbf{v}_2 - \mathbf{v}_1$  and  $\mathbf{v}_{com}$ , the center-of-mass velocity vector, is defined by the equation  $(m_1 + m_2)\mathbf{v}_{com} = m_1\mathbf{v}_1 + m_2\mathbf{v}_2$ , and  $M \equiv m_1 + m_2$ .

a. Consider the probability of finding two molecules, one with velocity  $v_1$  and one with velocity  $v_2$ . Using equation 1.30, we see that this probability is given by

$$F(v_{1x})F(v_{1y})F(v_{1z})F(v_{2x})F(v_{2y})F(v_{2z}) dv_{1x} dv_{1y} dv_{1z} dv_{2x} dv_{2y} dv_{2z}$$

$$= \left(\frac{m_1}{2\pi kT}\right)^{3/2} \left(\frac{m_2}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_1 \mathbf{v}_1^2}{2kT}\right) \exp\left(-\frac{m_2 \mathbf{v}_2^2}{2kT}\right)$$

$$\times dv_{1x} dv_{1y} dv_{1z} dv_{2x} dv_{2y} dv_{2z}.$$

Use the result from Appendix 1.4 to show that this probability can also be written as

$$F(v_{rx})F(v_{ry})F(v_{rz})F(v_{comx})F(v_{comy})F(v_{comz})$$

$$\times dv_{rx} dv_{ry} dv_{rz} dv_{comx} dv_{comy} dv_{comz}$$

$$= \left(\frac{m_1}{2\pi kT}\right)^{3/2} \left(\frac{m_2}{2\pi kT}\right)^{3/2} \exp\left(-\frac{M\mathbf{v}_{\rm com}^2}{2kT}\right) \exp\left(-\frac{\mu \mathbf{v}_{\rm r}^2}{2kT}\right)$$

$$\times dv_{rx} dv_{ry} dv_{rz} dv_{comx} dv_{comy} dv_{comz}$$

- b. Now transform the Cartesian coordinates to spherical ones and show by integration over all coordinates that the average relative velocity  $\langle v_r \rangle$  is given by  $(8kT/\pi\mu)^{1/2}$ .
- 1.13 What is the ratio of the probability of finding a molecule moving with the average speed to the probability of finding a molecule moving with three times the average speed? How does this ratio depend on the temperature?
- 1.14 You are caught without an umbrella in the rain and wish to get to your dorm, 1 km away, in the driest possible condition. Should you walk or run? To answer this question, calculate the ratio of the rain drop collisions with your body under the two conditions. Assume that the cross section is independent of direction (i.e., that you are spherical), that you run at 8 m/s, you walk at 3 m/s, and that the rainfall is constant with a velocity of, say, 15 m/s.
- 1.15 Calculate the root-mean-squared deviation of the speed from its mean value:  $[\langle (v \langle v \rangle)^2 \rangle]^{1/2}$ .
- 1.16 Find  $\langle v^4 \rangle$  for a gas of molecular weight *M* at temperature *T*.
- 1.17 A very expensive gas is sold by the molecule, and the price is proportional to the velocity of the individual molecule: price in  $= v/\langle v \rangle$ . If I buy a bulb of these gaseous molecules, what is the average price per molecule, and does the price depend on the temperature of the bulb?

- 1.18 In a group of molecules all traveling in the positive z direction, what is the probability that a molecule will be found with a z-component speed between 400 and 401 m/s if  $m/(2kT) = 5.62 \times 10^{-6} \text{ s}^2/\text{m}^2$ ? (*Hint:* You need to find and normalize a one-dimensional distribution function first!)
- 1.19 We will see in Chapter 3, equation 3.4, that the rate constant for a reaction as a function of temperature is given by the average of  $\sigma(\epsilon_r)v_r$  over the thermal energy distribution  $G(\epsilon_r)$ , where  $\epsilon_r = \frac{1}{2}mv_r^2$  and  $\sigma(\epsilon_r)$  is the energy-dependent cross section for the reaction. The thermal relative kinetic energy distribution  $G(\epsilon_r)$  has the same functional form as the kinetic energy distribution  $G(\epsilon)$  given in equation 1.37, except that all energies  $\epsilon = \frac{1}{2}mv^2$  are replaced by relative kinetic energies  $\epsilon_r = \frac{1}{2}\mu v_r^2$ .
  - a. Suppose that for a particular reaction  $\sigma(\epsilon_r) = c\epsilon_r^2$ , where *c* is a constant. Calculate k(T).
  - b. Suppose that for another reaction  $\sigma(\epsilon_r) = c/\epsilon_r$ ; calculate k(T).

# 2

# The Rates of Chemical Reactions

#### **Chapter Outline**

- 2.1 Introduction
- 2.2 Empirical Observations: Measurement of Reaction Rates
- 2.3 Rates of Reactions: Differential and Integrated Rate Laws
- 2.4 Reaction Mechanisms
- 2.5 Homogeneous Catalysis
- 2.6 Free Radical Reactions: Chains and Branched Chains
- 2.7 Determining Mechanisms from Rate Laws
- 2.8 Summary

#### 2.1 INTRODUCTION

The objective of this chapter is to obtain an empirical description of the rates of chemical reactions on a macroscopic level and to relate the laws describing those rates to mechanisms for reaction on the microscopic level. Experimentally, it is found that the rate of a reaction depends on a variety of factors: on the temperature, pressure, and volume of the reaction vessel; on the concentrations of the reactants and products; and on whether or not a catalyst is present. By observing how the rate changes with such parameters, an intelligent chemist can learn what might be happening at the molecular level. The goal, then, is to describe in as much detail as possible the reaction mechanism. This goal is achieved in several steps. First, in this chapter, we will learn how an overall mechanism can be described in terms of a series of *elementary steps*. In later chapters, we will continue our pursuit of a detailed description (1) by examining how to predict and interpret values for the rate constants in these elementary steps and (2) by examining how the elementary steps might depend on the type and distribution of energy among the available degrees of freedom. In addition to these lofty intellectual pursuits, of course, there are very good practical reasons for understanding how reactions take place, reasons ranging from the desire for control of synthetic pathways to the need for understanding of the chemistry of the Earth's atmosphere.

#### 2.2 EMPIRICAL OBSERVATIONS: MEASUREMENT OF REACTION RATES

One of the most fundamental empirical observations that a chemist can make is how the concentrations of reactants and products vary with time. The first substantial quantitative study of the rate of a reaction was performed by L. Wilhelmy, who in 1850 studied the inversion of sucrose in acid solution with a polarimeter. There are many methods for making such observations: one might monitor the concentrations spectroscopically, through absorption, fluorescence, or light scattering; one might measure concentrations electrochemically, for example, by potentiometric determination of the pH; or one might monitor the total volume or pressure if these are related in a simple way to the concentrations. Whatever the method, the result is usually something like that illustrated in **Figure 2.1**.

In general, as is true in this figure, the reactant concentrations will decrease as time goes on, while the product concentrations will increase. There may also be "intermediates" in the reaction, species whose concentrations first grow and then decay with time. How can we describe these changes in quantitative mathematical terms?

#### 2.3 RATES OF REACTIONS: DIFFERENTIAL AND INTEGRATED RATE LAWS

We define the *rate law* for a reaction in terms of the time rate of change in concentration of one of the reactants or products. In general, the rate of change of the chosen species will be a function of the concentrations of the reactant and product species as well as of external parameters such as the temperature. For example, in **Figure 2.1** the rate of change for a species at any time is proportional to the slope



#### Figure 2.1

Concentration of reactant and product as a function of time.

of its concentration curve. The slope varies with time and generally approaches zero as the reaction approaches equilibrium. The stoichiometry of the reaction determines the proportionality constant. Consider the general reaction

$$aA + bB = cC + dD.$$
(2.1)

We will define the rate of change of [C] as rate = (1/c) d[C]/dt. This rate varies with time and is equal to some function of the concentrations: (1/c) d[C] dt = f([A], [B], [C], [D]). Of course, the time rates of change for the concentrations of the other species in the reaction are related to that of the first species by the stoichiometry of the reaction. For the example presented above, we find that

$$\frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}.$$
(2.2)

By convention, since we would like the rate to be positive if the reaction proceeds from left to right, we choose positive derivatives for the products and negative ones for the reactants.

The equation (1/c) d[C]/dt = f([A],[B],[C],[D]) is called the *rate law* for the reaction. While f([A],[B],[C],[D]) might in general be a complicated function of the concentrations, it often occurs that *f* can be expressed as a simple product of a *rate constant*, *k*, and the concentrations each raised to some power:<sup>a</sup>

$$\frac{1}{c}\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k[\mathrm{A}]^{\mathrm{m}}[\mathrm{B}]^{\mathrm{n}}[\mathrm{C}]^{\mathrm{o}}[\mathrm{D}]^{\mathrm{p}}.$$
(2.3)

When the rate law can be written in this simple way, we define the *overall order* of the reaction as the sum of the powers, i.e., *overall order* q = m + n + o + p, and we define the *order of the reaction* with respect to a particular species as the power to which its concentration is raised in the rate law, e.g., *order with respect to* [A] = m. Note that since the left-hand side of the above equation has units of concentration per time, the rate constant will have units of time<sup>-1</sup> concentration<sup>-(q<sup>-1</sup>)</sup>. As we will see below, the form of the rate law and the order with respect to each species give us a clue to the mechanism of the reaction. In addition, of course, the rate law enables us to predict how the concentrations of the various species change with time.

An important distinction should be made from the outset: the overall order of a reaction cannot be obtained simply by looking at the overall reaction. For example, one might think (mistakenly) that the reaction

$$H_2 + Br_2 \rightarrow 2 HBr$$
 (2.4)

should be second order simply because the reaction consumes one molecule of  $H_2$  and one molecule of  $Br_2$ . In fact, the rate law for this reaction is quite different:

$$\frac{1}{2} \frac{d[HBr]}{dt} = k[H_2][Br_2]^{1/2}.$$
 (2.5)

<sup>&</sup>lt;sup>a</sup>Note that both the rate constant and the Boltzmann constant have the same symbol, k. Normally, the context of the equation will make the meaning of k clear.

Thus the order of a reaction is not necessarily related to the stoichiometry of the reaction; it can be determined only by experiment.

Given a method for monitoring the concentrations of the reactants and products, how might one experimentally determine the order of the reaction? One technique is called the *method of initial slopes*. If we were to keep  $[Br_2]$  fixed while monitoring how the initial rate of [HBr] production depended on the H<sub>2</sub> starting concentration,  $[H_2]_0$ , we would find, for example, that if we doubled  $[H_2]_0$ , the rate of HBr production would increase by a factor of 2. By contrast, were we to fix the starting concentration of H<sub>2</sub> and monitor how the initial rate of HBr appearance rate depended on the Br<sub>2</sub> starting concentration,  $[Br_2]_0$ , we would find that if we doubled  $[Br_2]_0$ , the HBr production rate would increase not by a factor of 2, but only by a factor of  $\sqrt{2}$ . Experiments such as these would thus show the reaction to be first order with respect to H<sub>2</sub> and half order with respect to Br<sub>2</sub>.

While the rate law in its differential form describes in the simplest terms how the rate of the reaction depends on the concentrations, it will often be useful to determine how the concentrations themselves vary in time. Of course, if we know d[C]/dt, in principle we can find [C] as a function of time by integration. In practice, the equations are sometimes complicated, but it is useful to consider the differential and integrated rate laws for some of the simpler and more common reaction orders.

#### 2.3.1 First-Order Reactions

Let us start by considering first-order reactions,  $A \rightarrow$  products, for which the differential form of the rate law is

$$\frac{-\mathbf{d}[\mathbf{A}]}{\mathbf{d}t} = k[\mathbf{A}].$$
(2.6)

Rearrangement of this equation yields

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = -k \,\mathrm{d}t.$$

Let [A(0)] be the initial concentration of A and let [A(t)] be the concentration at time *t*. Then integration yields

$$\int_{[A(0)]}^{[A(t)]} \frac{d[A]}{[A]} = -\int_{0}^{t} k dt,$$

$$\ln \frac{[A(t)]}{[A(0)]} = -kt,$$
(2.7)

or, exponentiating both sides of the equation,

$$[A(t)] = [A(0)]exp(-kt).$$
 (2.8)

**Equation 2.8** is the *integrated rate law* corresponding to the *differential rate law* given in **equation 2.6**. While the differential rate law describes the rate of the reaction, the integrated rate law describes the concentrations.





Decay of [A(t)] for a first-order reaction.

**Figure 2.2** plots the [A(t)]/[A(0)] in the upper panel and the natural log of [A(t)]/[A(0)] in the lower panel as a function of time for a first-order reaction. Note that the slope of the line in the lower panel is -k and that the concentration falls to 1/e of its initial value after a time  $\tau = 1/k$ , often called the *lifetime* of the reactant. A related quantity is the time it takes for the concentration to fall to half of its value, obtained from

$$\frac{[A(t = \tau_{1/2})]}{[A(0)]} = \frac{1}{2}$$
  
= exp(-k\tau\_{1/2}), (2.9)  
$$\tau_{1/2} = \frac{\ln(2)}{k}.$$

The quantity  $\tau_{1/2}$  is known as the *half-life* of the reactant.

An example of a first-order process is the radiative decay of an electronically excited species. Figure 2.3 shows the time dependence of the fluorescence intensity



Figure 2.3

I<sup>\*</sup> fluorescence intensity as a function of time on linear (upper) and logarithmic (lower) scales.

for iodine atoms excited to their  ${}^{2}P_{1/2}$  electronic state, denoted here as I<sup>\*</sup>. The chemical equation is

$$\mathbf{I}^* \xrightarrow{\kappa_{\rm rad}} \mathbf{I} + h\nu, \qquad (2.10)$$

where  $\nu/c = 7603 \text{ cm}^{-1}$ . The deactivation of I\* is important because this level is the emitting level of the iodine laser. Since the reaction is first order,  $-d[I^*]/dt = k_{rad}[I^*]$ . From the stoichiometry of the photon production,  $-d[I^*]/dt$  is also equal to  $d(h\nu)/dt$ , so that  $d(h\nu)/dt = k_{rad}[I^*]$ . Finally, the fluorescence intensity, *I*, is defined as the number of photons detected per unit time,  $I = d(h\nu)/dt$ , so that the intensity is directly proportional to the instantaneous concentration of I\*:  $I = k_{rad}[I^*]$ . The top panel plots *I* as a function of *t*, while the lower panel plots  $\ln(I)$  against the same time axis. It is clear that the fluorescence decay obeys first-order kinetics. The lifetime derived from these data is 126 ms, and the half-life is 87 ms as calculated in **Example 2.1**. The measurement of the radiative decay for I\* is actually quite difficult, and the data in **Figure 2.3** represent only a lower limit on the lifetime. The experimental problem is to keep the I\* from being deactivated by a method other than radiation, for example, by a collision with some other species. This process will be discussed in more detail later, after we have considered second-order reactions.

# example 2.1

The Lifetime and Half-Life of I* Emission		
Objective	Find the lifetime and half-life of I <sup>*</sup> from the data given in <b>Figure</b> 2.3.	
Method	First determine the rate constant $k_{\rm rad}$ . Then the lifetime is simply $\tau = 1/k_{\rm rad}$ , while the half-life, given in <b>equation 2.9</b> , is $\tau_{1/2} = \ln(2)/k_{\rm rad}$ .	
Solution	The slope of the line in the bottom half of <b>Figure 2.3</b> can be determined to be $-7.94 \text{ s}^{-1}$ . Thus, the lifetime is $1/(7.94 \text{ s}^{-1}) = 126 \text{ ms}$ , and the half-life is $\ln(2)/(7.94 \text{ s}^{-1}) = 87 \text{ ms}$ .	

#### 2.3.2 Second-Order Reactions

Second-order reactions are of two types, those that are second order in a single reactant and those that are first order in each of two reactants. Consider first the former case, for which the simplest overall reaction is

$$2 \text{ A} \rightarrow \text{products},$$
 (2.11)

with the differential rate law<sup>b</sup>

$$\frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}]^2.$$
(2.12)

Of course, a simple method for obtaining the integrated rate law would be to rearrange the differential law as

$$\frac{-\mathbf{d}[\mathbf{A}]}{[\mathbf{A}]^2} = k \,\mathrm{d}t \tag{2.13}$$

and to integrate from t = 0 when [A] = [A(0)] to the final time when [A] = [A(t)]. We would obtain

$$\frac{1}{[A(t)]} - \frac{1}{[A(0)]} = kt.$$
 (2.14)

However, to prepare the way for more complicated integrations, it is useful to perform the integration another way by introducing a change of variable. Let x be defined as the amount of A that has reacted at any given time. Then [A(t)] = [A(0)] - x, and

$$\frac{-d[A]}{dt} = \frac{dx}{dt} = k([A(0)] - x)^2.$$
 (2.15)

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<sup>&</sup>lt;sup>b</sup>The alert student might notice that we have omitted the  $\frac{1}{2}$  on the left-hand side of the equation, amounting to a redefinition of the rate constant for the reaction. The reason for temporarily abandoning our convention is so that second-order reactions of the type  $2 A \rightarrow$  products and those of the type  $A + B \rightarrow$  products will have the same form.





Variation of concentration with time for a second-order reaction of the type  $2 \text{ A} \rightarrow \text{products}$ .

Rearrangement gives

$$\frac{\mathrm{d}x}{([\mathrm{A}(0)] - x)^2} = k \,\mathrm{d}t,\tag{2.16}$$

and integration yields

$$\int_{0}^{x} ([A(0)] - x)^{-2} dx = k \int_{0}^{t} dt,$$

$$([A(0)] - x)^{-1} |_{0}^{x} = kt,$$

$$\frac{1}{[A(0)] - x} - \frac{1}{[A(0)]} = kt,$$

$$\frac{1}{[A(t)]} - \frac{1}{[A(0)]} = kt.$$
(2.17)

Note that the same answer is obtained using either method.

**Equations 2.14** and **2.17** suggest that a plot of 1/[A(t)] as a function of time should yield a straight line whose intercept is 1/[A(0)] and whose slope is the rate constant k, as shown in **Figure 2.4**.

#### Diels-Alder Condensation of Butadiene, a Second-Order Reaction

**Objective** Butadiene,  $C_4H_6$ , dimerizes in a Diels-Alder condensation to yield a substituted cyclohexene,  $C_8H_{12}$ . Given the data on the 400-K gas phase reaction below, show that the dimerization occurs as a second-order process and find the rate constant.

Time (s)	Total Pressure (torr)
0	626
750	579
1,500	545
2,460	510
3,425	485
4,280	465
5,140	450
6,000	440
7,500	425
9.000	410
10,500	405

- **Method** According to **equation 2.14**, when the reciprocal of the reactant pressure,  $P(C_4H_6)$ , is plotted as a function of time, a second-order process is characterized by a linear function whose slope is the rate constant. The complication here is that we are given the *total* pressure rather than the *reactant* pressure as a function of time. The reactant pressure is related to the total pressure through the stoichiometry of the reaction  $2 C_4H_6 \rightarrow C_8H_{12}$ . Let 2x be the pressure of  $C_4H_6$  that has reacted; then  $P(C_8H_{12}) = x$ , and  $P(C_4H_6) = P_0 2x$ , where  $P_0$  is the initial pressure. The total pressure is thus  $P_{tot} = P(C_4H_6) + P(C_8H_{12}) = P_0 x$ , or  $x = P_0 P_{tot}$ . Consequently,  $P(C_4H_6) = P_0 2(P_0 P_{tot}) = 2P_{tot} P_0$ .
- **Solution** A plot of  $1/(2P_{tot} P_0)$  versus time is shown in **Figure 2.5.** A least-squares fit gives the slope of the line as  $k = 3.8 \times 10^{-7} \text{ s}^{-1}$  torr<sup>-1</sup>. Recalling that 1 torr = (1/760) atm and assuming ideal gas



Plot of reciprocal  $C_4H_6$  pressure as a function of time for the Diels-Alder condensation of butadiene.

behavior, we can express k in more conventional units:  $k = (3.8 \times 10^{-7} \text{ s}^{-1} \text{ torr}^{-1}) \times (760 \text{ torr/1 atm}) \times (82.06 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (400 \text{ K}) = 9.48 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Thus,  $-d[A]/dt = (9.48 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1})[A]^2$ .

We now turn to reactions that are second order overall but first order in each of two reactants. The simplest reaction of this form is

$$A + B \rightarrow \text{products},$$
 (2.18)

with the differential rate law

$$\frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}].$$
(2.19)

Consider a starting mixture of A and B in their stoichiometric ratio, where [A(0)] = [B(0)]. Then, again letting x be the amount of A (or B) that has reacted at time t, we see that [A(t)] = [A(0)] - x and that [B(t)] = [B(0)] - x = [A(0)] - x, where the last equality takes into account that we started with a stoichiometric mixture. Substituting into the differential rate law we obtain

$$\frac{dx}{dt} = k([A(0)] - x)^2,$$
(2.20)

just as in the case for the reaction  $2A \rightarrow$  products. The solution is given by equation 2.17, and a similar equation could be derived for 1/[B(t)].

Suppose, however, that we had started with a nonstoichiometric ratio,  $[B(0)] \neq [A(0)]$ . Substitution into the differential rate law would then yield

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k([A(0)] - x)([B(0)] - x), \qquad (2.21)$$

or

or

$$\frac{\mathrm{d}x}{([A(0)] - x)([B(0)] - x)} = k \,\mathrm{d}t. \tag{2.22}$$

This equation can be integrated by using the method of partial fractions. We rewrite equation 2.22 as (see Problem 2.15)

$$\frac{\mathrm{d}x}{[B(0)] - [A(0)]} \left[ \frac{1}{[A(0)] - x} - \frac{1}{[B(0)] - x} \right] = k \,\mathrm{d}t. \tag{2.23}$$

Integrating, we find

$$\frac{1}{[B(0)] - [A(0)]} \int_{x=0}^{x} \left[ \frac{1}{[A(0)] - x} - \frac{1}{[B(0)] - x} \right] dx = \int_{t=0}^{t} k \, dt, \quad (2.24)$$

$$\frac{1}{[B(0)] - [A(0)]} \left\{ \left[ -\ln([A(0)] - x) \right] - \left[ -\ln([B(0)] - x] \right\} \right|_{0}^{x} = kt, \quad (2.25)$$

$$\ln \frac{\{[B(0)] - x\}[A(0)]]}{[B(0)]\{[A(0)] - x\}} = \{[B(0)] - [A(0)]\}kt,$$
(2.26)

$$\ln \frac{[\mathbf{B}][\mathbf{A}(0)]}{[\mathbf{A}][\mathbf{B}(0)]} = \{ [\mathbf{B}(0)] - [\mathbf{A}(0)] \} kt.$$
(2.27)

Thus, a plot of the left-hand side of equation 2.27 versus t should thus give a straight line of slope  $\{[B(0)] - [A(0)]\}k$ .

#### 2.3.3 Pseudo-First-Order Reactions

It often occurs for second-order reactions that the experimental conditions can be adjusted to make the reaction appear to be first order in one of the reactants and zero order in the other. Consider again the reaction

$$A + B \rightarrow \text{products},$$
 (2.28)

with the differential rate law

$$\frac{-\mathrm{dA}}{\mathrm{dt}} = k[\mathrm{A}][\mathrm{B}]. \tag{2.29}$$

We have already seen that the general solution for nonstoichiometric starting conditions is given by **equation 2.27.** Suppose, however, that the initial concentration of B is very much larger than that of A, so large that no matter how much A has reacted the concentration of B will be little affected. From the differential form of the rate law, we see that

$$\frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = -k[\mathrm{B}]\mathrm{d}t, \qquad (2.30)$$

and, if [B] = [B(0)] is essentially constant throughout the reaction, integration of both sides yields

$$\ln\left[\frac{[\mathbf{A}(t)]}{[\mathbf{A}(0)]}\right] = -k[\mathbf{B}(0)]t,$$
(2.31)

or

$$[A(t)] = [A(0)]exp\{-k[B(0)]t\}.$$
(2.32)

Note that this last equation is very similar to equation 2.8, except that the rate constant k has been replaced by the product of k and [B(0)]. Incidentally, it is easy to verify that equation 2.32 can be obtained from the general solution for nonstoic-chiometric second-order reactions equation 2.27 in the limit when [B(0)] >> [A(0)] (Problem 2.16).

Pseudo-first-order reactions are ubiquitous in chemical kinetics. An example illustrates their analysis. Figure 2.6 shows the decay of the concentration of excited



#### Figure 2.6

Variation of I<sup>\*</sup> concentration with time for various starting concentrations of NO(v = 0).

 $I({}^{2}P_{1/2})$  atoms, here again called I<sup>\*</sup>, following their relaxation by NO(v = 0) to the ground  $I({}^{2}P_{3/2})$  state, here called simply I:

$$I^* + NO(v = 0) \rightarrow I + NO(v > 0).$$
 (2.33)

Note that in this process the electronic energy of I<sup>\*</sup> is transferred to vibrational excitation of the NO; this type of process is often referred to as  $E \rightarrow V$  transfer.<sup>c</sup> In this experiment, the I<sup>\*</sup> concentration was created at time zero by pulsed-laser photodissociation of I<sub>2</sub>, I<sub>2</sub> +  $h\nu \rightarrow I^*$  + I, and the I<sup>\*</sup> concentration was monitored by its fluorescence intensity. Because the initial concentration of I<sup>\*</sup> is several orders of magnitude smaller than the concentration of NO(v = 0), the latter hardly varies throughout the reaction, so the system can be treated as pseudo-first-order. Consequently, the data in **Figure 2.6** are plotted as ln of I<sup>\*</sup> fluorescence intensity versus time; a straight line is obtained for each initial concentration of NO(v = 0). It is clear that the slope becomes steeper with increasing NO(v = 0) concentration, as predicted by **equation 2.32.** The value of k can be determined from the variation as roughly 3.9 × 10<sup>3</sup> s<sup>-1</sup> torr<sup>-1</sup>, or  $1.2 \times 10^{-13}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>, as shown in **Example 2.3**.

<sup>&</sup>lt;sup>c</sup>The data in the figure are taken from A. J. Grimley and P. L. Houston, *J. Chem. Phys.* **68**, 3366–3376 (1978). A review of this type of process appears in P. L. Houston, "Electronic to Vibrational Energy Transfer from Excited Halogen Atoms," in *Photoselective Chemistry*, Part 2, J. Jortner, Ed., (J. Wiley & Sons, New York, 1981), 381–418 (1981).

# *example 2.3*

<b>Evaluation</b> o	f Rate Constant for Pseudo-First-Order Reaction
Objective	Evaluate the second-order rate constant from the data shown in <b>Figure 2.6</b> given the slopes of the lines as $-0.627 \times 10^{-2}$ for 1.6 torr, $-0.213 \times 10^{-1}$ for 5.5 torr, and $-0.349 \times 10^{-1}$ for 9.0 torr, all in units of $\mu$ s <sup>-1</sup> .
Method	From equation 2.31 we see that the slope of $\ln([A(t)]/[A(0)])$ versus <i>t</i> should be the negative of the rate constant times the starting pressure of the constant component. Thus, <i>k</i> should be given by the negative of the slope divided by the pressure of the constant component.
Solution	For the three points given, $k = (0.00627/1.6) = 3.92 \times 10^{-3}$ , $k = (0.0213/5.5) = 3.87 \times 10^{-3}$ , and $k = (0.0349/9.0) = 3.88 \times 10^{-3}$ . The average is $3.89 \times 10^{-3}$ in units of $\mu$ s <sup>-1</sup> torr <sup>-1</sup> , or $(3.89 \times 10^{-3} \mu$ s <sup>-1</sup> torr <sup>-1</sup> ) $\times (10^6 \mu$ s)/(1 s) = $3.89 \times 10^3 \text{s}^{-1}$ torr <sup>-1</sup> .
Comment	A better method for solution would be to plot the negative of the slopes as a function of the pressure of the constant component and to determine the best line through the points. Such a plot is shown in <b>Figure 2.7</b> . The slope of the line is equal to $k[B(0)]$ over $[B(0)]$ , i.e., the slope is equal to the rate constant. If the kinetic scheme is correct, the intercept of the line should be zero. A positive intercept would indicate deactivation of I <sup>*</sup> by some other process or species, for example radiative decay or deactivation by the remaining $I_2$ precursor.
0.04	
(B(0))/ <sup>478-1</sup>	
.0.0 = <i>k</i> [	
0.0	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
F F	Figure 2.7
Figure	showing alternative analysis of pseudo-first-order reaction.

#### Section 2.3 Rates of Reactions: Differential and Integrated Rate Laws

Second-order rate constants are reported in a variety of units. As we have just seen, the units most directly related to the experiment are (time<sup>-1</sup> pressure<sup>-1</sup>), for example, s<sup>-1</sup> torr<sup>-1</sup>. However, reporting the rate constant in these units has the disadvantage that at different temperatures the rate constant is different both because of the inherent change in the constant with temperature and because the pressure changes as the temperature changes. The use of time<sup>-1</sup> density<sup>-1</sup> for rate constant units avoids this complication; the density is usually expressed either as molecules/cm<sup>3</sup> or in moles/L. At any given temperature, of course, the two sets of units can be related. For example, at 300 K, the ideal gas law can be used to determine that 1 torr is equivalent to  $3.22 \times 10^{16}$  molecules cm<sup>-3</sup>. Thus, the rate constant for I<sup>\*</sup> + NO(v = 0)  $\rightarrow$  I + NO(v > 0) listed above as  $3.9 \times 10^3$  s<sup>-1</sup> torr<sup>-1</sup> is equivalent to  $(3.9 \times 10^3 \text{ s}^{-1} \text{ torr}^{-1}) = 1.2 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ , which in turn is equivalent to  $(1.2 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})(6.02 \times 10^{23} \text{ molec}/\text{mole}) = 7.2 \times 10^{10} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ .

#### 2.3.4 Higher-Order Reactions

For higher-order reactions, integration of the differential rate law equation becomes more complicated. For example, in an overall reaction

$$2 A + B \rightarrow \text{products},$$
 (2.34)

where the differential rate law is

$$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A]^{2}[B],$$
(2.35)

the integrated rate expression for a nonstoichiometric starting mixture is

$$\frac{1}{[A(0)] - 2[B(0)]} \left[ \frac{1}{[A(0)]} - \frac{1}{[A]} \right] + \frac{1}{[[A(0)] - 2[B(0)]]^2} \ln \frac{[A][B(0)]}{[A(0)][B]}$$
$$= \frac{1}{2} kt.$$
(2.36)

However, such higher-order reactions usually take place under conditions where the concentration of one of the species is so large that it can be regarded as constant. An example might be the recombination of O atoms:  $O + O + O_2 \rightarrow 2 O_2$ . Under conditions where  $[O_2] >> [O]$ , the third-order process becomes pseudo-second-order, and the integrated rate expression is simply related to expressions already derived. For example, in the reaction  $2A + B \rightarrow$  products, for large [B(0)] the integrated rate expression is simply **equation 2.14** with *k* replaced by *k*[B(0)]. Alternatively, the reaction might become pseudo-first-order (see Section 2.3.3), as would be the case for  $O + O_2 + O_2 \rightarrow O_2 + O_3$  with  $O_2$  in excess. The differential rate law is  $-d[O]/dt = k[O_2]^2[O]$ . If the concentration of  $O_2$  is very nearly constant throughout the reaction, the integrated rate law is an expression similar to **equation 2.8** or **equation 2.14** for the limiting cases when either [A(0)] or [B(0)] is very large, respectively (Problem 2.17).

#### Chapter 2 The Rates of Chemical Reactions

#### 2.3.5 Temperature Dependence of Rate Constants

The temperature dependence of the reaction rate, like the order of the reaction, is another empirical measurement that provides a basis for understanding reactions on a molecular level. Most rates for simple reactions increase sharply with increasing temperature; a rule of thumb is that the rate will double for every 10 K increase in temperature. Arrhenius<sup>d</sup> first proposed that the rate constant obeyed the law

$$k = A \exp\left(-\frac{E_{\rm a}}{RT}\right),\tag{2.37}$$

where A is a temperature-independent constant, often called the preexponential factor, and  $E_a$  is called the activation energy. The physical basis for this law will be discussed in more detail in the next chapter, but we can note in passing that for a simple reaction in which two molecules collide and react, A is proportional to the number of collisions per unit time, and the exponential factor describes the fraction of collisions that have enough energy to lead to reaction.

The temperature dependence of a wide variety of reactions can be fit by this simple Arrhenius law. An alternate way of writing the law is to take the natural logarithm of both sides:

$$\ln k = \ln A - \frac{E_{\rm a}}{RT}.$$
(2.38)

Thus, a plot of  $\ln k$  as a function of 1/T should yield a straight line whose slope is  $-E_a/R$  and whose intercept is  $\ln A$ . Such a plot is shown in **Figure 2.8** for the reaction of hydrogen atoms with O<sub>2</sub>, one of the key reactions in combustion.

Plots such as these have been used to determine the "Arrhenius parameters," A and  $E_a$  for a wide number of reactions. A selection of Arrhenius parameters is provided for first-order reactions in **Table 2.1** and for second-order reactions in **Table 2.2**.<sup>e</sup>

The Arrhenius form of the rate constant allows us to calculate the rate constant  $k_2$  at a new temperature  $T_2$ , provided that we know the activation energy and the rate constant  $k_1$  at a specific temperature,  $T_1$ . Since the Arrhenius A parameter is independent of temperature, subtraction of the Arrhenius form **equation 2.38** for  $k_1$ ,  $\ln k_1 = \ln A - E_a/RT_1$ , from that for  $k_2$ ,  $\ln k_2 = \ln A - E_a/RT_2$ , yields

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right].$$
 (2.39)

Example 2.4 illustrates the use of equation 2.39.

<sup>&</sup>lt;sup>d</sup>Svante August Arrhenius was born in Uppsala, Sweden, in 1859 and died in Stockholm in 1927. He is best known for his theory that electrolytes are dissociated in solution. He nearly turned away from chemistry twice in his career, once as a undergraduate and once when his Ph.D. thesis was awarded only a "fourth class," but his work on electrolytic solutions was eventually rewarded with a Nobel Prize in Chemistry in 1903. His paper on activation energies was published in *Z. physik. Chem.* **4**, 226 (1889).

<sup>&</sup>lt;sup>e</sup>Data taken from *NIST Chemical Kinetics Database Version 4.0*, W. Gary Mallard et al., Chemical Kinetics Data Center, National Institute of Standards and Technology, Gaithersburg, MD 20899. The database covers thermal gas-phase kinetics and includes over 15,800 reaction records for over 5700 reactant pairs and a total of more than 7400 distinct reactions. There are more than 4000 literature references through 1990.





TABLE 2.1

Arrhenius plot of the reaction  $H + O_2 \rightarrow OH + O$ . The data are taken from H. Du and J. P. Hessler, J. Chem. Phys **96**, 1077 (1992).

n -

Phase	Reactions		
Reaction	$A(s^{-1})$	$E_{\rm a}/R$ (K)	Range (K)
$CH_3CHO \rightarrow CH_3 + HCO$	$3.8 imes10^{15}$	39,500	500-2,000
$C_2H_6 \rightarrow CH_3 + CH_3$	$2.5 imes10^{16}$	44,210	200-2,500
$O_3 \rightarrow O_2 + O$	$7.6 imes10^{12}$	12,329	383-413
$HNO_3 \rightarrow OH + NO_2$	$1.1  imes 10^{15}$	24,000	295-1,200
$\rm CH_3OH \rightarrow \rm CH_3 + \rm OH$	$6.5 imes10^{16}$	46,520	300-2,500
$\rm N_2O \rightarrow N_2 + O$	$6.1  imes 10^{14}$	28,210	1,000-3,600
$\rm N_2O_5 \rightarrow \rm NO_3 + \rm NO_2$	$1.6  imes 10^{15}$	11,220	200–384
$C_2H_5 \rightarrow C_2H_4 + H$	$2.8 imes10^{13}$	20,480	250-2,500
$\rm CH_3NC \rightarrow \rm CH_3CN$	$3.8  imes 10^{13}$	19,370	393–600
$H_2S \rightarrow SH + H$	$6.0 imes10^{14}$	40,820	1,965–19,700
$cyclopropane \rightarrow propene$	$2.9 imes10^{14}$	31,410	897-1,450
cyclobutane $\rightarrow 2 C_2 H_4$	$2.3 \times 10^{15}$	30,490	891–1,280

**Arrhenius Parameters for Some First-Order Gas** 

49

Gas Flase Reactions			
Reaction	$A \ (\text{cm}^3 \ \text{mol}^{-1} \ \text{s}^{-1})$	$E_{\rm a}/R$ (K)	Range (K)
$CH_3 + H_2 \rightarrow CH_4 + H$	$6.7 imes10^{12}$	6,250	300-2,500
$CH_3 + O_2 \rightarrow CH_3O + O$	$2.4 imes10^{13}$	14,520	298-3,000
$F + H_2 \rightarrow HF + H$	$8.4 imes10^{13}$	500	200-300
$H + H_2O \rightarrow OH + H_2$	$9.7  imes 10^{13}$	10,340	250-3,000
$H + CH_4 \rightarrow CH_3 + H$	$1.9 imes10^{14}$	6,110	298-2,500
$H + O_2 \rightarrow OH + H$	$1.4 imes10^{14}$	8,000	250-3,370
$H + NO \rightarrow OH + N$	$1.3 imes10^{14}$	24,230	1,750-4,500
$H + N_2O \rightarrow N_2 + OH$	$7.6 imes10^{13}$	7,600	700-2,500
$H + CO_2 \rightarrow CO + OH$	$1.5 imes10^{14}$	13,300	300-2,500
$H + O_3 \rightarrow O_2 + OH$	$8.4 imes10^{13}$	480	220-360
$O + H_2 \rightarrow OH + H$	$5.2 imes10^{13}$	5,000	293-2,800
$O + CH_4 \rightarrow OH + CH_3$	$1.0 imes10^{14}$	5,090	298-2,575
$O + NO_2 \rightarrow NO + O_2$	$3.9 imes10^{12}$	-120	230-350
$O + C_2 H_2 \rightarrow products$	$3.4  imes 10^{13}$	1,760	195-2,600
$O + O_3 \rightarrow O_2 + O_2$	$7.5 imes10^{12}$	2,140	197-2,000
$O + C_2 H_4 \rightarrow products$	$9.5 imes10^{12}$	946	200-2,300
$OH + H_2 \rightarrow H + H_2O$	$4.6 imes10^{12}$	2,100	200-450
$OH + CH_4 \rightarrow H_2O + CH_3$	$2.2 imes10^{12}$	1,820	240-300
$OH + O \rightarrow O_2 + H$	$1.4  imes 10^{13}$	-110	220-500

 TABLE 2.2
 Arrhenius Parameters for Some Second-Order

 Gas Phase Reactions
 Feature

# example 2.4

Relationship between the Rate Constants at Two Temperatures		
Objective	Given that the rate constant for the $H + O_2 \rightarrow OH + O$ reaction is $4.7 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 1000 K and that the activation energy is 66.5 kJ/mol, determine the rate constant at 2000 K.	
Method	Use equation 2.39 with $k_1 = 4.7 \times 10^{10}$ and $E_a = 66.5$ .	
Solution	$\ln(k_2/4.7 \times 10^{10}) = -(66.5 \text{ kJ mol}^{-1}/8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times \{(1/2000 \text{ K}) - (1/1000 \text{ K})\}; \ln k_2 = \ln(4.7 \times 10^{10}) - 8000 \times \{0.0005 - 0.001\} = 24.6 + 4.00 = 28.6; k_2 = \exp(28.6) = 2.64 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$	
Comment	An alternative method would be to determine A from the equation $k_1 = A \exp(-E_a/RT)$ with $E_a = 66.5$ kJ/mol; then one could use the Arrhenius parameters to determine the rate constant at the new temperature. Note from <b>Figure 2.8</b> that 2000 K is at the edge of the graph, where $\log_{10}k_2 \approx 12.42$ , or $k_2 = 2.63 \times 10^{12}$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> , in good agreement with the rate determined by the first method.	

At this point, a word of caution is necessary. Not all reactions obey the simple Arrhenius form. For example, a recent review<sup>f</sup> of the measured rate constants for the OH + CO  $\rightarrow$  H + CO<sub>2</sub> reaction in the temperature range from 300 to 2000 K recommends  $k(T) = (3.25 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1})(T^{1.5})\exp(+250/T)$ . Note that the preexponential factor is not independent of temperature, and that the "activation energy" is negative. We will see in the next chapter why the Arrhenius preexponential factor might depend on temperature. For reactions with very low activation energies, such as this one where there is no barrier to formation of an HOCO complex, the rate of the reaction might actually go down with increasing temperature, because at high temperatures, the two species might not stay in one another's vicinity long enough for the attractive force between them to draw them together. Thus, many reactions may exhibit a more complicated dependence of k on T than given by the simple Arrhenius form.

#### 2.4 REACTION MECHANISMS

As we have seen in the example of the  $Br_2 + H_2$  reaction, equation 2.5, many rate laws do not have the form that might be supposed from the overall stoichiometry. The value of the rate law, in fact, is that it gives us a clue to what might be happening on the molecular level. Here we start to leave empiricism and try to account for our experimental observations on a more chemical and microscopic level. What could be the behavior of the molecules that would lead to the observed macroscopic measurements? We postulate that the macroscopic rate law is the consequence of a *mechanism* consisting of *elementary steps*, each one of which describes a processe that takes place on the microscopic level. Three types of microscopic processes account for essentially all reaction mechanisms: these are *unimolecular*, *bimolecular*, and *termolecular* reactions. As we will see, for such elementary steps the order of the reaction is equal to the molecularity; i.e., a unimolecular reaction follows first-order kinetics, a bimolecular reaction follows second-order kinetics, and a termolecular reaction follows third-order kinetics.

Unimolecular reactions involve the reaction of a single (energized) molecule:

$$A \rightarrow \text{products.}$$
 (2.40)

Since the number of product molecules produced per unit time will be proportional to the number of A species, d[products]/dt = -d[A]/dt = k[A], so the order of this unimolecular reaction is unity; i.e., unimolecular reactions are first order. We have already seen an example of such a unimolecular process, namely the first-order radiative decay of excited iodine atoms discussed in Section 2.3.1 and **Example 2.1.** 

Bimolecular reactions involve the collision between two species:

$$A + B \rightarrow \text{products.}$$
 (2.41)

Since the number of products per unit time will be proportional to the number of collisions between A and B, the rate of this bimolecular reaction should be proportional to the product of the concentrations of A and B (see Section 1.7): d[products]/dt = k[A][B]. Consequently, bimolecular reactions follow second-order kinetics.

<sup>&</sup>lt;sup>f</sup>D. L. Baulch, C. J. Cobos, R. A. Cox, C. Esser, P. Frank, Th. Just, J. A. Kerr, M. J. Pilling, J. Troe, R. W. Walker, and J. Warnatz, *J. Phys. Chem. Ref. Data* **21**, 411 (1992).

Termolecular reactions are encountered less frequently than unimolecular or bimolecular reactions, but they are important at high pressures or in condensed phases. A termolecular reaction is one that requires the collision of three species:

$$A + B + C \rightarrow \text{products.}$$
 (2.42)

By a simple extension of our arguments in Chapter 1, the number of termolecular collisions will be proportional to the product of the concentrations of A, B, and C, so that termolecular reactions follow third-order kinetics.

One might well wonder how often three molecules could converge from separate directions to a single point in space.<sup>g</sup> In fact, most termolecular reactions can reasonably be viewed as two consecutive bimolecular collisions. The termolecular process might start with a "sticky" bimolecular collision, one in which the collision pair, say A and B, remain in close proximity for a finite period. If the pair is struck during this period by the third species, then products are formed; if not, then the reactants A and B separate. Whether one regards the overall process as two bimolecular collisions or as a termolecular one depends, in part, on the length of time that A and B spend together. If the time is no longer than, say, 1–100 vibrational periods, the current practice is to call the process a termolecular one. Whether one regards what happens as two bimolecular collisions or as one termolecular collision, the overall process will be proportional to the product of the pressures of the three species, i.e., third order.

In summary, we see that unimolecular processes follow first-order kinetics, bimolecular processes follow second-order kinetics, and termolecular processes follow third-order kinetics. In general, *the order of an elementary process is equal to its molecularity*, but this statement is true only for elementary processes and not necessarily for an overall process consisting of several elementary steps. We now proceed to combine elementary steps into mechanisms so as to determine the overall reaction and its order.

#### 2.4.1 Opposing Reactions, Equilibrium

Perhaps the most rudimentary "mechanism" is a reaction that can proceed either in the forward or reverse direction. For simplicity, we consider opposing first-order elementary reactions,  $A \rightleftharpoons B$ , with rate constants  $k_1$  in the forward direction and  $k_{-1}$  in the reverse direction. The differential rate law for the reaction is

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A] - k_{-1}[B].$$
 (2.43)

If the initial concentrations of A and B are [A(0)] and [B(0)], respectively, then [A(t)]=[A(0)] - x and [B(t)] = [B(0)] + x, where x is the concentration of A that has reacted to B at any time.

Before demonstrating by integration that A and B approach their equilibrium values exponentially, we digress for a moment to state two important principles. The first is the *principle of microscopic reversibility*, which, as noted by Tolman,<sup>h</sup> is a consequence of the time-reversal symmetry of classical or quantum mechanics. Consider a system that has reached some final state from an initial one by some path. If all the molecular momenta (internal and translational) are reversed, the system will return by

<sup>&</sup>lt;sup>g</sup>Extension of this argument immediately suggests why higher-than-termolecular processes are never observed.

<sup>&</sup>lt;sup>h</sup>R. C. Tolman, *Phys. Rev.* 23, 699 (1924); *The Principles of Statistical Mechanics*, Clarendon Press, Oxford, p. 163.

the same path to its initial state. A macroscopic manifestation of this principle is called the *principle of detailed balance:* in a system at equilibrium, any process and its reverse proceed at the same rate. Although the principle of detailed balance is most powerful when applied to multiequation equilibria, it is still useful in the simple system under study, where it implies that at equilibrium  $k_1A_e = k_{-1}B_e$ , where  $A_e$  and  $B_e$  are the equilibrium concentrations. A proof of this relationship between the forward and reverse rates follows from the fact that, at equilibrium, the concentrations of the species do not change. Hence, d[A]/dt = d[B]/dt = 0 when  $[A] = A_e$  and  $[B] = B_e$ , so that the left-hand side of **equation 2.43** is zero, and  $k_1A_e = k_{-1}B_e$ . Note also that, since the equilibrium constant for the reaction is  $K_e = B_e/A_e = k_1/k_{-1}$ , the principle of detailed balance also tells us that the equilibrium constant for opposing first-order reactions will be equal to the ratio of the forward and reverse rate constants.

Returning to the integration of **equation 2.43**, we rewrite the equation in terms of the single variable *x*:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1([A(0)] - x) - k_{-1}([B(0)] + x).$$
(2.44)

However, since  $A_e = [A(0)] - x_e$  and  $B_e = [B(0)] + x_e$ , we can rewrite equation 2.44 by substituting for [A(0)] and [B(0)]:

$$\frac{dx}{dt} = k_1(A_e + x_e - x) - k_{-1}(B_e - x_e + x), \qquad (2.45)$$

or

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \{ (k_1 \mathrm{A}_{\mathrm{e}} - k_{-1} \mathrm{B}_{\mathrm{e}}) + k_1 (x_{\mathrm{e}} - x) + k_{-1} (x_{\mathrm{e}} - x) \}$$
  
=  $(k_1 + k_{-1}) (x_{\mathrm{e}} - x).$  (2.46)

For this last equality, we have used the fact that  $k_1 A_e = k_{-1} B_e$ . Rearrangement gives

$$\frac{\mathrm{d}x}{x_{\mathrm{e}} - x} = (k_1 + k_{-1})\mathrm{d}t.$$
 (2.47)

Integrating both sides, we find

$$-\int_{0}^{x} d \ln(x_{e} - x) = (k_{1} + k_{-1}) \int_{0}^{t} dt,$$
 (2.48)

or

$$-\ln\frac{x_{\rm e}-x}{x_{\rm e}} = (k_1 + k_{-1})t.$$
 (2.49)

Exponentiation of both sides gives

$$x = x_{e} \{ 1 - \exp[-(k_{1} + k_{-1})t] \},$$
(2.50)

or, after subtracting both sides from [A(0)],

$$[A(t)] = A_e + x_e \exp[-(k_1 + k_{-1})t].$$
(2.51)

Thus, [A(t)] starts at  $A_e + x_e = [A(0)]$  and decreases to  $A_e$  exponentially with a rate constant equal to the sum of the forward and reverse rates. Similarly, [B(t)] starts at  $B_e - x_e = [B(0)]$  and increases to  $B_e$  exponentially with the same rate constant.





Concentrations as a function of time for opposing reactions.

These relationships are shown in **Figure 2.9.** Of course, in the limit where the forward rate constant is much larger than the reverse,  $k_1 >> k_{-1}$ , the completed reaction produces nearly all B. Consequently,  $A_e = 0$  and  $x_e = [A(0)]$ , so that **equation 2.51** reduces to  $[A(t)] = [A(0)]\exp(-k_1 t)$ , which is simply **equation 2.8**.

For opposing second-order reactions, the mathematics is somewhat more complicated, but the general result is the same in the limit when  $x_e$  is small: the system will approach equilibrium exponentially with a rate constant equal to the sum of the rate constants for the forward and reverse reactions. We will return to this result when considering temperature-jump techniques for measuring fast reaction rates in solution in Chapter 5.

#### 2.4.2 Parallel Reactions

A common occurrence in real systems is that a species can react by more than one pathway. Consideration of such parallel reactions provides insight into the phenomenon of competition and clears up some common misconceptions. For simplicity we will model the parallel reactions as competing first-order processes:

$$A \xrightarrow{k_1} B,$$

$$A \xrightarrow{k_2} C.$$
(2.52)

The differential equations describing the parallel reactions are

$$\frac{d[A]}{dt} = -k_1[A] - k_2[A] = -[k_1 + k_2][A],$$

$$\frac{d[B]}{dt} = k_1[A],$$

$$\frac{d[C]}{dt} = k_2[A].$$
(2.53)

The solution to the first of these equations, for a starting concentration of [A(0)], is obtained by straightforward integration:

$$[A(t)] = [A(0)] \exp\{-[k_1 + k_2]t\}.$$
(2.54)

Substitution of this equation for A into the second differential equation leads to

$$\frac{d[B]}{dt} = k_1[A(0)] \exp\{-[k_1 + k_2]t\},\$$

$$\int_{[B]=0}^{[B(t)]} d[B] = k_1[A(0)] \int_0^t \exp\{-[k_1 + k_2]t\} dt,$$

$$[B(t)] = \frac{k_1}{k_1 + k_2} [A(0)] [1 - \exp\{-[k_1 + k_2]t\}].$$
(2.55)

A similar equation can be derived for [C(t)]:

$$[C(t)] = \frac{k_2}{k_1 + k_2} [A(0)][1 - \exp\{-[k_1 + k_2]t\}].$$
 (2.56)

There are two important points to note in comparing **equations 2.55** and **2.56**. First, both B and C rise exponentially with a rate constant equal to  $[k_1 + k_2]$ , as shown schematically in **Figure 2.10**. The reason for this behavior is that the rates of production of both B and C depend on the concentration of A, which decreases exponentially with a rate constant equal to the sum  $[k_1 + k_2]$ . Second, the ratio of products, sometimes called the *branching ratio*, is  $[B(t)]/[C(t)] = k_1/k_2$  at all times. Thus, while the magnitude of [B] relative to [C] is constant and not generally unity, the time constant  $[k_1 + k_2]$  with which each concentration approaches its final value is the same for both [B] and [C]. The situation is analogous to a bucket of water, A, leaking through two holes of different sizes. Buckets B and C collect the leaks. Of course, the relative amount of water collected in buckets B and C will depend on the ratio of the areas of the two holes, but the level of water in either bucket will rise toward its final value with the same rate, a rate equal to the rate at which water disappears from bucket A.

Parallel reactions are often encountered; we have already seen an example. The data of **Figure 2.3** and **Example 2.1** clearly show that one mechanism for deactivation of I<sup>\*</sup> is radiative decay. On the other hand, the data of **Figure 2.6** and **Example 2.3** show that I<sup>\*</sup> can also be deactivated by collision with NO. In this second example, we actually monitor the I<sup>\*</sup> concentration by its fluorescence intensity, so clearly both radiative decay and collisional decay are occurring in parallel. The





solution for the fluorescence intensity *I*, analogous to **equation 2.54**, is  $\ln(I/I_0) = -(k_{rad} + k[NO])t$ . However, for the NO pressures used,  $k[NO] >> k_{rad}$ , so that little error was made in **Example 2.3**. For example, the branching ratio for decay by radiation versus decay by collision in 1.6 torr of NO is  $k_{rad}/(k[NO]) = (7.94 \text{ s}^{-1})/[(3.9 \times 10^{-3} \,\mu\text{s}^{-1} \,\text{torr}^{-1})(1.6 \,\text{torr})] = 1.27 \times 10^{-3}$ ; i.e., nearly all of the deactivation is caused by collisions. However, the radiation is still important—it enables us to monitor the deactivation!

#### 2.4.3 Consecutive Reactions and the Steady-State Approximation

Another common mechanism, which also leads to the important *steady-state approximation*, involves consecutive reactions. An example is the sequence of first-order processes

$$A \xrightarrow{k_1} B, \qquad (2.57)$$

$$B \xrightarrow{\kappa_2} C, \qquad (2.58)$$

for which the differential equations are

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_1[\mathrm{A}], \qquad (2.59)$$

$$\frac{\mathrm{d}[\mathbf{B}]}{\mathrm{d}t} = k_1[\mathbf{A}] - k_2[\mathbf{B}], \qquad (2.60)$$

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_2[\mathrm{B}]. \tag{2.61}$$

The goal of our study of this mechanism is to develop a method, called the steadystate approximation, that we can use to simplify the analysis of consecutive reactions. To see the limitations of this approximation, we must first look at the exact solution for the simple system above. We assume that the initial concentration of A is [A(0)] and that [B(0)] = [C(0)] = 0. Integration of the first of these three differential equations then gives the time dependent concentration of A:

$$[A] = [A(0)]exp(-k_1t).$$
(2.62)

Substitution of this solution into equation 2.60 yields the differential equation

$$\frac{d[B]}{dt} = k_1[A(0)]e^{-k_1 t} - k_2[B].$$
(2.63)

The solution to this equation, as can be verified by direct differentiation (Problem 2.18),  $is^i$ 

$$\mathbf{B}(t) = \frac{k_1}{k_2 - k_1} [\mathbf{A}(0)](e^{-k_1 t} - e^{-k_2 t}).$$
(2.64)

Finally, since by mass balance [A(0)] = [A] + [B] + [C],

$$[C] = [A(0)] - [B] - [A]$$
  
=  $[A(0)] \left\{ 1 - \frac{k_1}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}] - e^{-k_1 t} \right\}.$  (2.65)

While the mathematical complexity of this solution may at first seem daunting, this exact solution will enable us to see how to make some very useful and simplifying approximations. We first consider the case when  $k_1$  is much larger than  $k_2$ . From the scheme in **equations 2.57** and **2.58**, we can see that in this limit the reaction A  $\rightarrow$  B occurs first and goes nearly to completion before the reaction B  $\rightarrow$  C takes place. Thus, we expect that nearly all the A is converted to the intermediate B before any appreciable conversion of B to C occurs. Indeed, in the limit of  $k_1 >> k_2$ , **equation 2.64** reduces to

$$[\mathbf{B}(t)] = [\mathbf{A}(0)](e^{-k_2 t} - e^{-k_1 t}).$$
(2.66)

Because  $k_1 >> k_2$ , the second term in the parentheses rapidly approaches zero while the first term is still near unity. Consequently, the concentration of the intermediate B rapidly reaches a value nearly equal to [A(0)], and then during most of the reaction B decays slowly according to [B(t)] = [A(0)]exp( $-k_2t$ ).

The exact solution for  $k_1 = 10k_2$  is shown in **Figure 2.11.** The situation is analogous to three buckets located above one another. Imagine that the top bucket has a large hole and leaks into the second, which itself leaks through a much smaller hole into a third. Water placed in the first bucket would thus flow rapidly into the second bucket, from which it would then leak slowly into the third.

A more instructive limit for the consecutive reactions is when  $k_2 >> k_1$ . In this case, the water leaks out of the middle bucket faster than it comes in, so one might

 $<sup>^{</sup>i}$ A solution of this differential equation by the method of Laplace transformation is described in Appendix 6.1.



#### Figure 2.11

Concentrations in a consecutive reaction when  $k_1 = 10k_2$ .

guess that the water level in this bucket never rises very high. Indeed, in the limit when  $k_2 >> k_1$ , the solution for [B] given by equation 2.64 reduces to

$$[\mathbf{B}(t)] = \frac{k_1}{k_2} [\mathbf{A}(0)] (e^{-k_1 t} - e^{-k_2 t}).$$
(2.67)

Since  $k_2 >> k_1$ , the second term in the parentheses rapidly approaches zero, while the first term is still close to unity. Consequently, the concentration of B rapidly approaches  $(k_1/k_2)[A(0)]$  and then decays more slowly according to  $[B] = (k_1/k_2)[A(0)]\exp(-k_1t)$ . Because  $k_1/k_2$  is very small, the maximum concentration of B is much less than [A(0)]. Figure 2.12 shows the exact concentrations for  $k_2 = 10k_1$ .

We now come to the major point of this section. It would be extremely tedious if we had to integrate the differential equations whenever we encountered a set of consecutive reactions. Fortunately, in most situations there is an easier method. Consider again the case illustrated in **Figure 2.12**, for which  $k_2 >> k_1$ . After an initial transient rise, called the *induction period*, the concentration of B is very close to  $[B] \approx (k_1/k_2)[A(0)]\exp(-k_1t) = (k_1/k_2)A$ . Rearrangement of this last expression yields  $k_2[B] \approx k_1[A]$ , or, after inserting this approximation into **equation 2.60**, we find that d[B]/dt  $\approx 0$ . Recall that B is the "intermediate" in the consecutive reaction, and that, because  $k_1/k_2$  is small, its concentration is always much less than [A(0)]. The steady-state approximation can then be summarized as follows:

After an initial induction period, the concentration of any intermediate species in a consecutive reaction can be calculated by setting its time derivative equal to zero, provided that the concentration of the intermediate is always small compared to the starting concentrations.

The first qualifier, "after an initial induction period," reminds us that [B] has to build up before the approximation can hold, as shown in **Figure 2.12.** The second qualifier, "provided that the concentration of the intermediate is always small," is equivalent to stating that  $k_2 >> k_1$ .





Concentrations in consecutive reaction when  $k_2 = 10k_1$ .

Having obtained results for the consecutive reactions via the difficult method of integration, it is instructive to see how easily the solution could have been obtained using the steady-state approximation. If we had set d[B]/dt = 0 in **equation 2.60**, we would have found immediately that  $[B] = (k_1/k_2)[A]$ . Since the concentration of A as a function of time is obtained easily as the solution to **equation 2.59**, we would have readily found that  $[B] = (k_1/k_2)[A(0)]\exp(-k_1t)$ . Finally, **equation 2.65** gives [C] as [A(0)] - [A] - [B]. Alternatively, [C] can be found by inserting the solution for [B] into **equation 2.61** and then integrating. In the sections that follow, we will make extensive use of the steady-state approximation.

## example 2.5

#### **Destruction of Stratospheric Ozone as Determined by** Using the Steady-State Approximation

**Background** The balance of ozone in the stratosphere is of critical concern because this molecule absorbs ultraviolet light that would be harmful to life at Earth's surface. The principal production mechanism for ozone is recombination of O atoms with  $O_2$ . The principal destruction mechanism is that given below. There is increasing concern over alternative destruction mechanisms involving molecules introduced into the stratosphere by human activity. These will be discussed in detail in Section 7.4.

**Objective** Determine the destruction rate of ozone in the following mechanism, which is very similar to the Lindemann mechanism:

 $O_3 + M \rightleftharpoons_{k_{-1}}^{k_1} O_2 + O + M$  $O_3 + O \xrightarrow{k_2} 2 O_2$ 

**Method** First, determine the rate law for the destruction of ozone, i.e., an expression for  $-d[O_3]/dt$ . Then use the steady-state approximation to solve for the concentration of the intermediate, O. Finally, substitute the O atom concentration into the ozone rate law and simplify.

**Solution** The rate law for the destruction of ozone is

$$\frac{-d[O_3]}{dt} = k_1[O_3][M] - k_{-1}[O_2][O][M] + k_2[O_3][O].$$

The steady-state equation for [O] is

$$\frac{d[O]}{dt} = 0 = k_1[O_3][M] - k_{-1}[O_2][O][M] - k_2[O_3][O].$$

Some algebra can be avoided by subtracting these two to obtain

$$\frac{-\mathrm{d}[\mathrm{O}_3]}{\mathrm{d}t} = 2k_2[\mathrm{O}_3][\mathrm{O}].$$

Solution of the steady-state equation gives

$$[\mathbf{O}] = \frac{k_1[\mathbf{O}_3][\mathbf{M}]}{k_2[\mathbf{O}_3] + k_{-1}[\mathbf{O}_2][\mathbf{M}]}$$

Substitution of this equation into the simplified ozone destruction equation gives the final answer:

$$\frac{-d[O_3]}{dt} = \frac{2k_2k_1[M][O_3]^2}{k_2[O_3] + k_1[O_2][M]}$$

**Comment** Note that at high values of the pressure, [M] will be large enough so that the second term in the denominator will be large compared to the first. The result will then simplify to  $-d[O_3]/dt = (2k_2k_1/k_{-1}) \cdot [O_3]^2/[O_2]$ .

#### 2.4.4 Unimolecular Decomposition: The Lindemann Mechanism

As an example of the use of the steady-state approximation, we consider in detail the mechanism of unimolecular decomposition. The overall reaction is  $A \rightarrow \text{prod-}$ ucts, and under high-pressure conditions the rate law is  $-d[A]/dt = k_{ap}[A]$ , where  $k_{ap}$  is the apparent rate constant. A question that begs an answer is how the A molecules obtain enough energy to decompose. The matter was debated vigorously in
the early 1900s.<sup>j</sup> It was F. A. Lindemann who first suggested in 1922<sup>k</sup> that the reactants obtained the necessary energy from collisions. In its simplest form, the mechanism he proposed is shown below:

$$A + M \xleftarrow[k_{-1}]{k_{-1}} A^* + M,$$

$$A^* \xrightarrow{k_2} P.$$
(2.68)

In these equations P stands for the products and M represents any molecule that can energize A by collision; M might be A itself, or it might be a nonreactive molecule in which the reactant is mixed.

The overall rate of the reaction is -d[A]/dt, or equivalently by d[P]/dt:

$$-\frac{d[A]}{dt} = \frac{d[P]}{dt} = k_2[A^*].$$
 (2.69)

Since A<sup>\*</sup> is an intermediate in the mechanism, it will be useful to apply the steadystate approximation:

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] = 0.$$
 (2.70)

Here, the time dependence of  $A^*$  is equal to a production term,  $k_1[A][M]$ , and two destruction terms,  $k_{-1}[A^*][M]$  and  $k_2[A^*]$ . We can then solve this last equation for the steady-state concentration of  $A^*$  to obtain

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2}.$$
(2.71)

Substitution of this last equation into equation 2.69 yields the solution

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [A] [M]}{k_{-1} [M] + k_2}.$$
(2.72)

Recall that use of the steady-state approximation assumes that the concentration of the intermediate is small compared to the concentration of the starting material. This assumption is almost always valid for the system under consideration. Rearrangement of **equation 2.71** shows that  $[A^*]/[A]$  is much smaller than unity when  $k_1[M]/(k_{-1}[M] + k_2) << 1$ . However, even if  $k_2$  were zero, this last expression would still be satisfied since  $k_1/k_{-1}$  is simply the equilibrium constant for the first reaction, and this equilibrium constant must be smaller than unity because  $A^*$ has much more energy than A. In addition, for  $A^*$  of sufficiently high energy,  $k_2$  is usually very rapid, so that the inequality  $k_1[M]/(k_{-1}M + k_2) << 1$  is ensured.

Having convinced ourselves that the steady-state approximation is valid for the Lindemann mechanism, equation 2.68, it is instructive to examine the solution, equation 2.72, under two limiting conditions. Let us first consider the "high-pressure

<sup>&</sup>lt;sup>j</sup>For an interesting discussion of the history of this problem, see J. I. Steinfeld, J. S. Francisco, and William L. Hase, *Chemical Kinetics and Dynamics,* 2nd ed. (Prentice-Hall, Englewood Cliffs, NJ, 1999), Section 11.3.

<sup>&</sup>lt;sup>k</sup>F. A. Lindemann, Trans. Faraday Soc. 17, 598 (1922).

### Chapter 2 The Rates of Chemical Reactions

limit," for which  $k_{-1}[M] >> k_2$ . In this limit, the denominator of **equation 2.72** can be approximated by its first term, and division of numerator and denominator by [M] gives  $d[P]/dt = (k_2k_1/k_{-1})[A]$ . Thus, in this limit the [M] cancels and the reaction is first order. Physically, in the high-pressure limit A\* is rapidly being created and destroyed, and only a small fraction goes on to form products.

In the "low-pressure" limit, when  $k_{-1}[M] << k_2$ , the second term in the denominator of **equation 2.72** dominates, and  $d[P]/dt = k_1[A][M]$ . In this limit the reaction is second order. Physically, in this limit most of the A<sup>\*</sup> that is formed lasts long enough to react to form P, and very little gets deactivated.

This behavior is shown in **Figure 2.13**, which plots a theoretical curve on a loglog plot for the apparent first-order rate constant, defined by  $k_{ap} \equiv (1/[A]) d[P]/dt$ , as a function of [M] for the isomerization of *cis*-but-3-ene to *trans*-but-2-ene. The log-log plot is necessary to show both extremes in pressure. In the high-pressure limit, we have seen that  $d[P]/dt = (k_2k_1/k_{-1})[A]$  so that  $\log(k_{ap})$  should be a constant. At high pressures, the apparent rate constant is, indeed, found to be constant, but below about 10<sup>6</sup> torr the apparent rate constant is linearly proportional to pressure. This is because, in the low-pressure limit  $d[P]/dt = k_1[A][M]$  so that  $\log(k_{ap})$ should be equal to  $\log(k_1[M])$ ; i.e., it should vary linearly with  $\log[M]$ , as observed in the plot. An important practical application of the Lindemann mechanism is given in **Example 2.5**.

The high-pressure result for the Lindemann mechanism also illustrates an important point about the temperature dependence of the overall rate constant in complex reactions. In the high-pressure limit d[P]/dt =  $k_{ap}[A] = (k_2k_1/k_{-1})[A]$ . Thus, the temperature dependence of the overall rate constant  $k_{ap}$  depends on how  $k_1$ ,  $k_{-1}$ , and  $k_2$ depend on temperature. Suppose that each of the rate constants for the elementary processes can be expressed in Arrhenius form:  $k_i = A_i \exp(-E_i/kT)$ . Simple multiplication and division of exponentials shows that



Figure 2.13

Theoretical dependence of the Lindemann apparent rate constant with pressure for the isomerization of *cis*-but-2-ene.

# 3

# Theories of Chemical Reactions

### **Chapter Outline**

- 3.1 Introduction
- 3.2 Potential Energy Surfaces
- 3.3 Collision Theory
- 3.4 Activated Complex Theory (ACT)
- 3.5 Thermodynamic Interpretation of ACT
- 3.6 Summary

### 3.1 INTRODUCTION

The goal of this chapter is to provide a theoretical basis for understanding and predicting reaction rates. We begin by considering an encounter between two gasphase reactants, and we assume that on the microscopic level, the outcome and rate of the reaction are determined by the forces acting between atoms making up the reactants. We would like to know what those forces are, or equivalently, what the potential is, since the force is simply proportional to the slope of the potential,  $F_x = -dV/dx$ . Because we will rarely be able to know the potential in complete detail, it will also be of interest to determine which of its features are most responsible for determining the reaction rate, or conversely, which features are determined most accurately by measuring the reaction rate.

Two simple theories of reaction rates will be considered in detail: collision theory and activated complex theory. Both of these theories make approximations about the potential energy function controlling the reaction, and both theories relate the rate constant to simple features of the potential energy function. In its simplest form, collision theory concentrates primarily on the barrier to reaction, while activated complex theory includes not only the barrier but also some information about the "width" of the channel leading from reactants to products. Our goal here will be to explore these general properties of the potential energy function and to learn what approximations are made in these simple theories of reaction rates. We leave

### Chapter 3 Theories of Chemical Reactions

until Chapter 8, Molecular Reaction Dynamics, the question of how more detailed investigations can provide closer approximations to the potential energy function. A thermodynamic formulation of activated complex theory will provide us with an association between the entropy change between reactants and activated complexes and the orientational requirements for reaction.

### 3.2 POTENTIAL ENERGY SURFACES

Consider the reaction between two species having a total of N atoms. For any fixed geometry of these nuclei, quantum mechanics can in principle be used to calculate the energy of the system. What will be of interest in our attempt to calculate reaction rates is the way in which this energy varies with geometry. We first determine the number of coordinates on which the energy depends.

In general, the position of each nucleus can be described by three coordinates, so the position of all atoms relative to an arbitrary origin of the coordinate system can be described by 3N coordinates. However, if we assume that no forces act on the system other than the forces between the atoms, then the potential energy of the system depends on the relative coordinates between the atoms but neither on the position of the system as a whole nor on its overall orientation. Since three coordinates describe the position of the system as a whole and three (two for a linear system) describe its orientation, the potential energy of the system in the absence of external forces is a function of 3N - 6 variables (3N - 5 for linear systems). Thus, if the coordinates are called  $q_i$ , we have  $V = V(q_1, q_2, \ldots, q_k)$ , where k = 3N - 6 for nonlinear or 3N - 5 for linear systems.

Even for a very simple reaction involving just three atoms,  $A + BC \rightarrow AB + C$ , we see that in the general case the potential energy will be a function of  $3 \times 3 - 6 = 3$  coordinates. We would like to picture the energy as a function of these coordinates. If one dimension is used to describe the energy, then a complete description of the way in which V varies with the three coordinates would require a four-dimensional figure, one not easily visualized by inhabitants of three-dimensional space. A way to circumvent this deficiency of human perception is to hold all but two of the coordinates at fixed values and to plot V as a function of those two coordinates.

For example, in the well-studied hydrogen atom exchange reaction,  $D + H_2 \rightarrow$  HD + H,<sup>a</sup> if we constrain all three atoms to be collinear, then the resulting potential energy diagram looks like that in **Figure 3.1**. A somewhat different way of viewing it is from the top, as in **Figure 3.2** where each contour line represents a change in energy of 0.2 eV.

Of course, for nonlinear angles between the three atoms, the potential surface would look different—for example, like that in **Figure 3.3** for a D–H–H angle of 40°. Note that the barrier to reaction is higher than that in **Figure 3.2**.

Returning to **Figure 3.2**, we consider the path of an exchange reaction. In the "entrance" valley on the lower left side of the figure, the H–H distance is small, given by the equilibrium distance for an  $H_2$  molecule, and the D–H distance is large; these conditions describe the reactants. In this valley, motion along the H–H

<sup>&</sup>lt;sup>a</sup>The potential is described in A. J. C. Varandas, F. B. Brown, D. G. Truhlar, C. A. Mead, and N. C. Blais, J. Chem. Phys. **86**, 6258 (1987); D. G. Truhlar and C. J. Horowitz, J. Chem. Phys. **68**, 2466 (1978); J. Chem. Phys. **71**, 1514 (1979).





Potential energy surface for the collinear reaction  $D + H_2 \rightarrow DH + H$ .





Contour diagram of the collinear  $D + H_2 \rightarrow DH + H$  reaction.

coordinate corresponds to vibration of the  $H_2$ , whereas motion along the D–H coordinate represents the approach of the D and  $H_2$  reactants. In the "exit" valley on the upper right side of the figure, the D–H distance is small and the H–H distance is large; these conditions describe the products. In this valley, motion along the D–H coordinate corresponds to vibration of the H–D product, whereas motion along the H–H coordinate corresponds to the separation of the H and D–H products. The saddle point on the contour diagram, marked by a  $\ddagger$ , is called the *activated complex* and is the highest point along the minimum energy path separating the reactants from





Contour diagram of the potential for  $D + H_2 \rightarrow DH + H$  where the D-H-H angle is fixed at 40°.

the products. A typical reaction path would proceed from the valley on the lower left over the saddle point and into the valley on the upper right. We define the "reaction coordinate" as the minimum energy path along which the reaction can take place. Suppose for the moment, as is the case for  $D + H_2$ , that the collinear approach of the atoms is the one of least potential energy. Then the reaction coordinate would simply be given by the dashed line in **Figure 3.2.** If we straighten out this line and plot the energy at each point as a function of the position along the reaction coordinate, then for a generic A + BC reaction we obtain the familiar picture for a chemical reaction given in **Figure 3.4**.

Even when the reaction involves several atoms, the reaction coordinate can always be viewed as the minimum energy path for the reaction along the valley of *some* two-dimensional contour map. However, because several coordinates may be changing at once in order to minimize the energy, the "distance" along the reaction path may not correspond to an easily visualized change in geometry. Thus, while the ordinate of **Figure 3.4** is a well-defined energy axis, the units along the abscissa are usually omitted.

We define the configuration of atoms at the geometry corresponding to the highest energy along the reaction path as the *activated complex*, usually denoted by a double dagger, e.g., ABC<sup>‡</sup>. The difference in energy between the zero-point energy of the reactants and that of the activated complex is called the *threshold* energy,  $\epsilon^*$ , while the difference in energy between the zero-point energy of the reactants and products is  $\Delta\epsilon$  for the reaction. Recall that the zero-point energy of an ensemble of atoms is  $\epsilon_{zp} \equiv \Sigma_2^1 h \nu_i$ , where the sum is over all vibrational frequencies  $\nu_i$ .

In principle, of course, it should also be possible to calculate from quantum mechanics the detailed potential energy surface. And, in principle, as noted in the introduction, a detailed knowledge of the potential energy surface should be all that



### Figure 3.4



we need to determine the rate constant. In practice, however, most systems are sufficiently complicated that neither of these steps is straightforward; drastic approximations are often needed, even using modern computational techniques. The philosophy of simple theories of reaction rates is to avoid these complicated calculations by concentrating on a few key features of the potential surface and by learning how these affect the rate. Simple collision theory, to be considered next, concentrates exclusively on the threshold energy  $\epsilon^*$ . Activated complex theory, to be considered in Section 3.4, considers as well how the "width" or structure of the potential energy valley changes as reactants proceed through the activated complex.

### 3.3 COLLISION THEORY

### 3.3.1 Simple Collision Theory

The simplest theory of chemical reactions, already partially developed in Chapter 1, makes use of only one parameter of the potential energy surface, the height of the barrier to reaction,  $\epsilon^*$ . The method of presentation is in three steps. First we draw on the results of Chapter 1 to show that the rate constant as a function of energy is  $k(\epsilon_r) = \sigma(\epsilon_r)v_r$ , where  $\sigma(\epsilon_r)$  is an energy-dependent cross section and  $v_r$  is the relative velocity at energy  $\epsilon_r$ . Next we argue from a simple model that the functional dependence of the cross section on energy should be  $\sigma(\epsilon_r) = \pi b_{\max}^2(1 - \epsilon^*/\epsilon_r)$ , where  $\epsilon^*$  is a minimum energy needed for reaction and  $\epsilon_r$  is the collision energy. Finally, we obtain the dependence of the rate constant on temperature, k(T), by averaging  $k(\epsilon_r)$  over the energy distribution.

To develop this theory we return to **equation 1.44**, the equation for the collision rate between two dissimilar species, repeated here:

$$Z_{12} = \pi b_{\max}^2 v_r n_1^* n_2^*, \tag{3.1}$$

### Chapter 3 Theories of Chemical Reactions

where  $b_{\text{max}} = r_1 + r_2$  is the sum of the hard-sphere molecular radii and  $v_r$  is the relative velocity. This equation tells us that the collision rate,  $Z_{12}$ , is equal to a cross section, here  $\pi b_{\text{max}}^2$  for hard-sphere collisions, times the relative velocity and the product of molecular densities. To account for the fact that not all collisions will lead to reaction, we need to modify what we mean by the cross section. We suppose that the cross section for a reactive collision will not be a constant  $\pi b_{\text{max}}^2$  but rather will depend on the relative energy of the collision. (We recall from Chapter 1 that the energy corresponding to the motion of the center of mass is conserved, so that the only energy available for overcoming a barrier to reaction is the *relative* energy.) Only collisions with enough relative energy will react. Let us recognize the relative energy dependence of the cross section by writing it as  $\sigma(\epsilon_r)$ . For reactions at a particular relative energy  $\epsilon_r$  corresponding to a relative velocity  $v_r$ , we can rewrite **equation 3.1** as reaction rate  $= k(\epsilon_r)n_1^*n_2^*$ , where  $k(\epsilon_r) = \sigma(\epsilon_r)v_r$  is the rate constant for reaction at  $\epsilon_r = \frac{1}{2}\mu v_r^2$ .

We now model the reactants as spheres and assume that a reaction will occur only if the energy, when evaluated using the relative velocity along the line between the centers of the spheres, exceeds a particular value,  $\epsilon^*$ . It seems a reasonable assumption even for spherical reactants that glancing collisions for a given velocity will be less effective in causing reaction than head-on collisions. Parameterization of the cross section in terms of the energy calculated from the velocity along the line of centers is one way to incorporate this assumption into our model.

**Figure 3.5** helps in deriving the functional dependence of  $\sigma(\epsilon_r)$  on  $\epsilon_r$ . For simplicity, we suppose that one sphere is standing still and that the other is approaching it with relative velocity  $v_r$  at impact parameter *b*. The figure shows that the velocity along the line of centers is  $v_{lc} = v_r \cos \alpha$ , where  $\alpha$  is the angle indicated in the figure. The value of  $\cos \alpha$  is also related to *b* and the distance  $b_{max}$  along the line of centers by  $\sin \alpha = b/b_{max}$ . The energy associated with motion along the line of centers is then  $\epsilon_{lc} = \frac{1}{2}\mu v_{lc}^2 = \frac{1}{2}\mu v_r^2 \cos^2 \alpha = (\frac{1}{2}\mu v_r^2)(1 - \sin^2 \alpha) = \epsilon_r (1 - b^2/b_{max}^2)$ , where  $\epsilon_r$  is the relative translational energy and  $\mu$  is the reduced mass of the two reactants.

Returning to the assumption that  $\epsilon_{lc} > \epsilon^*$  for reaction, we assert that the probability for reaction,  $P(\epsilon_r, b)$ , is unity when  $\epsilon_{lc} = \epsilon_r(1 - b^2/b_{max}^2) > \epsilon^*$  and zero otherwise. The cross section for the reaction is calculated by averaging over the impact parameter b. Figure 3.6 shows a narrow annulus of area = (circumference) × (width) =  $(2\pi b) \times (db)$ . If the probability of reaction in this annulus and for energy



### Figure 3.5

Simple model for obtaining energy dependence of the reaction cross section.



Figure 3.6

The average probability is the integral of  $P(\epsilon_r, b)$  over b weighted by the area of the corresponding annulus.

 $\epsilon_{\rm r}$  is  $P(\epsilon_{\rm r},b)$ , then the average probability is simply the integral of  $P(\epsilon_{\rm r},b)$  over the possible values of b, from b = 0 to  $b = \infty$ , each weighted by the area of the appropriate annulus.

$$\sigma(\epsilon_{\rm r}) = \int_0^\infty P(\epsilon_{\rm r}, b) 2\pi b \, db,$$

$$= \int_0^{b'} P(\epsilon_{\rm r}, b) 2\pi b \, db,$$
(3.2)

where b' is the impact parameter above which  $P(\epsilon_r, b) = 0$ . Note that if the probability were unity for all impact parameters up to  $b_{\text{max}}$ , the integral would simply give the hard-sphere cross section  $\pi b_{\text{max}}^2$ . But the requirement  $\epsilon_{\text{lc}} = \epsilon_r(1 - b^2/b_{\text{max}}^2) > \epsilon^*$  for  $P(\epsilon_r, b) = 1$  implies  $(b')^2 < b_{\text{max}}^2(1 - \epsilon^*/\epsilon_r)$ , so that the range of integration is from 0 to b', where  $(b')^2 = b_{\text{max}}^2(1 - \epsilon^*/\epsilon_r)$ . The integral is easily evaluated to yield  $\sigma(\epsilon_r) = \pi b_{\text{max}}^2(1 - \epsilon^*/\epsilon_r)$ , provided of course that the relative energy  $\epsilon_r$  exceeds  $\epsilon^*$ ; i.e.,  $\sigma(\epsilon_r) = 0$  when  $\epsilon_r \leq \epsilon^*$ .

The solid line in **Figure 3.7** (plotted against the left and lower axes) shows the energy dependence of  $\sigma(\epsilon_r)$  in this simple model. When  $\epsilon_r >> \epsilon^*$ , the reaction occurs for nearly every hard-sphere collision, and  $\sigma(\epsilon_r) \approx \pi b_{max}^2$ . The cross section drops rapidly to zero as  $\epsilon_r \rightarrow \epsilon^*$ . For reference, the points in this figure (plotted against the right and top axes) give experimental measurements of the  $\sigma(\epsilon_r)$  for the H + D<sub>2</sub> reaction. The functional form of the solid line, while not exact, can be seen to be in qualitative agreement with the actual cross sections.

Given the above functional form for  $\sigma(\epsilon_r)$ , we now calculate k(T) by averaging over the Boltzmann energy distribution in **equation 1.37** and repeated here:

$$G(\boldsymbol{\epsilon}_{\mathrm{r}})\,\mathrm{d}\boldsymbol{\epsilon}_{\mathrm{r}} = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \sqrt{\boldsymbol{\epsilon}_{\mathrm{r}}} \exp\left(-\frac{\boldsymbol{\epsilon}_{\mathrm{r}}}{kT}\right)\,\mathrm{d}\boldsymbol{\epsilon}_{\mathrm{r}}.$$
(3.3)

From equation 1.16, we know that the average of any quantity is the integral of that quantity times the distribution function of the variable on which it depends,  $\langle Q \rangle = \int QP(Q) \, dQ$ . Here, the quantity we want to average is the reactive rate constant at a particular energy,  $k(\epsilon_r) = \sigma(\epsilon_r)v_r$ . Thus,  $k(T) = \int k(\epsilon_r)G(\epsilon_r) \, d\epsilon_r = \int \sigma(\epsilon_r)v_r G(\epsilon_r) \, d\epsilon_r$ .



### Figure 3.7

Dependence of reaction cross section on energy for the simple collision model. The solid line plotted against the bottom and left axes shows the prediction of the simple model. Data for  $H + D_2$  are shown as points plotted against the top and right axes. The points with error bars are experimental results taken from K. Tsukiyama, B. Katz, and R. Bersohn, *J. Chem. Phys.* 84, 1934 (1986), while the triangles are from the classical trajectory calculations of N. C. Blais and D. G. Truhlar, *J. Chem. Phys.* 83, 2201 (1985), and the crosses are experimental points taken from R. A. Brownsword, M. Hillenkamp, T. Laurent, H.-R. Volpp, J. Wolfrum, R. K. Vatsa, and H.-S. Yoo, *J. Phys. Chem.* 101, 6448 (1997).

$$k(T) = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \int_0^\infty \sigma(\epsilon_r) v_r \sqrt{\epsilon_r} \exp\left(-\frac{\epsilon_r}{kT}\right) d\epsilon_r.$$
 (3.4)

We now substitute for  $\sigma(\epsilon_r)$  and  $v_r$ , noting that  $\frac{1}{2}\mu v_r^2 = \epsilon_r$  so that  $v_r = (2\epsilon_r/\mu)^{1/2}$ .

$$k(T) = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \int_{\epsilon^*}^{\infty} \pi b_{\max}^2 \left(1 - \frac{\epsilon^*}{\epsilon_r}\right) \sqrt{\frac{2\epsilon_r}{\mu}} \sqrt{\epsilon_r} \exp\left(-\frac{\epsilon_r}{kT}\right) d\epsilon_r$$
$$= 2\pi^2 b_{\max}^2 \left(\frac{1}{\pi kT}\right)^{3/2} \left(\frac{2}{\mu}\right)^{1/2} \int_{\epsilon^*}^{\infty} [\epsilon_r - \epsilon^*] \exp\left(-\frac{\epsilon_r}{kT}\right) d\epsilon_r \qquad (3.5)$$
$$= \pi b_{\max}^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2} \int_{\epsilon^*}^{\infty} \frac{[\epsilon_r - \epsilon^*]}{kT} \exp\left(-\frac{\epsilon_r}{kT}\right) \frac{d\epsilon_r}{kT}.$$

If we premultiply the integral by  $\exp(-\epsilon^*/kT)$ , multiply the integrand by  $\exp(+\epsilon^*/kT)$ , and transform variables by letting  $x \equiv [\epsilon_r - \epsilon^*]/(kT)$ , we obtain

$$k(T) = \pi b_{\max}^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2} \exp\left(-\frac{\epsilon^*}{kT}\right) \int_{\epsilon^*}^{\infty} \frac{[\epsilon_r - \epsilon^*]}{kT} \exp\left(-\frac{\epsilon_r - \epsilon^*}{kT}\right) \frac{d\epsilon_r}{kT}$$
$$= \pi b_{\max}^2 \left(\frac{8kT}{\pi\mu}\right)^{1/2} \exp\left(-\frac{\epsilon^*}{kT}\right) \int_{0}^{\infty} x \exp(-x) dx.$$
(3.6)

The integral in equation 3.6 can be shown to be unity either by integration by parts or by substitution of  $x = y^2$  and use of Table 1.1. The result is thus

$$k(T) = \pi b_{\max}^2 v_r \exp\left(-\frac{\epsilon^*}{kT}\right), \qquad (3.7)$$

where  $v_r = (8kT/\pi\mu)^{1/2}$  is the average relative velocity.

This surprisingly simple result can be interpreted (and remembered!) as follows. The quantity  $\pi b_{\max}^2 v_r$  is simply the rate constant for hard-sphere collisions and is equal to the average of the cross section times the relative velocity. The Boltzmann factor  $\exp(-\epsilon^*/kT)$  can be interpreted as the fraction of collisions that provide energy greater than  $\epsilon^*$ . The reaction rate constant is thus simply the rate constant for hard-sphere collisions times the fraction of those collisions with enough energy to react. This hand-waving "derivation" could have bypassed the calculus of **equations 3.1** through **3.7**, but would not have introduced the key ideas of the probability of reaction and the cross section. These ideas are necessary to extend simple collision theory to incorporate the modifications described below and in Chapter 8. A summary of the key steps in the derivation we pursued is given in **Figure 3.8**.

Before extending the theory, we note that the result in **equation 3.7** is very similar to the Arrhenius form,  $k = A \exp(-E_a/kT)$ , except that since  $v_r$  depends weakly on *T* the activation energy  $E_a$  is not exactly equal to  $\epsilon^*$ . For our purposes, we will take the threshold energy  $\epsilon^*$  to be equal to the activation energy  $E_a$ , although Problem 3.10 shows that they differ slightly. Finally, we note that although this development of collision theory has assumed that the energy necessary to overcome the barrier to reaction comes from the relative translational energy of the reactants, it is also possible to develop a theory in which the energy comes from the internal vibrational energy of the reactants. The final result is the same as that given in **equation 3.7**.

### 3.3.2 Modified Simple Collision Theory

Simple collision theory suffers, however, in that it usually overestimates the absolute magnitude of k. The reason is that for most reactions, the reactants must have favorable orientations for reaction, even when the collision supplies sufficient energy along the line of centers. We have already seen in comparing Figure 3.2





Summary of the key steps in the derivation of k(T) from  $P(\epsilon_r, b)$ .

### Chapter 3 Theories of Chemical Reactions

with **Figure 3.3** that the theoretically determined threshold energy for the D + H<sub>2</sub> reaction depends on the angle of D atom approach; the barrier to reaction is much higher for an approach angle of 40° than for the collinear approach. Direct experiments testing reactivity as a function of approach angle confirm the importance of orientation. For example, Richard Bernstein and coworkers determined that the reaction Rb + CH<sub>3</sub>I  $\rightarrow$  RbI + CH<sub>3</sub> proceeds only if the attacking Rb atom approaches the I end of CH<sub>3</sub>I within a cone of about 127°; attack within 53° of the CH<sub>3</sub> end gives a nonreactive collision (a more complete description is provided in Section 8.7.1).<sup>b</sup> While most reactions are neither as well understood theoretically as D + H<sub>2</sub> nor as well studied experimentally as the Rb + CH<sub>3</sub>I reaction, it is certain that orientation plays a quite general role in determining the magnitude of the rate constant. For this reason, simple collision theory is often modified by including a so-called *steric factor*, *p*, with *p* < 1, to account for the orientation requirement:

$$k(T) = p\pi b_{\max}^2 v_r \exp\left(-\frac{\epsilon^*}{kT}\right).$$
(3.8)

Example 3.1 illustrates how collision theory might be used to estimate the value of p.

# example 3.1

f the Steric Factor <i>p</i>	
Consider the reaction $CH_3 + H_2 \rightarrow CH_4 + H$ . Assuming that the cross-sectional areas ( $\sigma = \pi r^2$ ) of $CH_3$ and $H_2$ are 4.0 and 2.7 > $10^{-19}$ m <sup>2</sup> , respectively, use collision theory to calculate the steri factor <i>p</i> at 300 K given that the measured preexponential factor i $6.7 \times 10^{12}$ cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> .	
Use equation 3.8 recognizing that $b_{\text{max}} = r_{\text{CH3}} + r_{\text{H2}}$ and that the preexponential factor is simply $A = p \pi b_{\text{max}}^2 v_{\text{r}}$ .	
i) Calculate $\pi b_{\max}^2$ :	
$r_{\rm CH_3} = \left(\frac{4.0 \times 10^{-19} \mathrm{m}^2}{\pi}\right)^{1/2}$	
$= 3.6 \times 10^{10} \mathrm{m}, \tag{3.9}$	
$r_{\rm H_2} = \left(\frac{2.7 \times 10^{-19}}{\pi}\right)^{1/2} = 2.9 \times 10^{-10} \mathrm{m},$	
$b_{\rm max} = (3.6 + 2.9) \times 10^{-10} \mathrm{m},$	

<sup>&</sup>lt;sup>b</sup>See D. H. Parker, K. K. Chakravorty, and R. B. Bernstein, J. Phys. Chem. 85, 466 (1981) and S. E. Choi and R. B. Bernstein, J. Chem. Phys. 83, 4463 (1985); also R. D. Levine and R. B. Bernstein, Molecular Reaction Dynamics and Chemical Reactivity (Oxford University Press, New York, 1987), p. 56.

so that

$$\pi b_{\text{max}}^2 = \pi (6.5 \times 10^{-10} \,\text{m})^2 = 1.3 \times 10^{-18} \,\text{m}^2$$

ii) Calculate  $v_r$ :

$$\mu = \frac{(15 \text{ amu})(2 \text{ amu})}{(15 + 2 \text{ amu})}$$
  
= 1.76 amu,  
$$v_{\rm r} = \left(\frac{8kT}{\pi\mu}\right)^{1/2}$$
(3.10)  
$$= \left[\frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}{\pi 1.76/(6.02 \times 10^{23} \times 1000)}\right]^{1/2}$$
  
= 1900 m/s.

iii) Calculate *p*:

$$p = \frac{A}{\pi b_{\max}^2 v_r}$$

$$= \frac{(6.7 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1})(10^{-6} \text{ m}^3/\text{cm}^3)}{(1.3 \times 10^{-18} \text{ m}^2/\text{molecule})(1900 \text{ m/s})(6.02 \times 10^{23} \text{ molecule/mol})}$$

$$= \frac{6.7 \times 10^6}{1.49 \times 10^9}$$

$$= 4.5 \times 10^{-3}.$$
(3.11)

The steric factor p clearly does little more than embody our ignorance of the details of the reaction into a single factor. For many reactions, p is found to lie in the range from 0.001 to 0.1, reflecting the range of probabilities that the reactants will be in the correct configuration for reaction. A somewhat more sophisticated account of the orientation dependence of reactions has recently been introduced<sup>c</sup> and is described below.

The basic assumption of the modification is that the threshold energy depends on orientation. Suppose not only that the energy along the line of centers needs to be above some minimum energy  $\epsilon^*$  for reaction, but also that the minimum energy

<sup>&</sup>lt;sup>c</sup>This extension of collision theory was proposed independently by I. W. M. Smith [*Kinetics and Dynamics of Elementary Gas Reactions* (Butterworths, Boston, 1980), pp. 78 ff; *J. Chem. Ed.* **59**, 9 (1982)] and by R. D. Levine and R. B. Bernstein [*Chem. Phys. Lett.* **105**, 467 (1984)]. As pointed out by Levine [*J. Phys. Chem.* **94**, 8872 (1990)], both are similar to an earlier formulation by H. Pelzer and E. Wigner [*Z. Phys. Chem. B* **15**, 445 (1932)], as described in H. Johnston, *Gas Phase Reaction Rate Theory* (Ronald Press, New York, 1966). A more advanced version is given by A. Miklavc, M. Perdih, and I. W. M. Smith, *Chem. Phys. Lett.* **241**, 415 (1995).



### Figure 3.9

Simple model for a modified collision theory, one for which the effective activation energy depends on angle of approach.

depends on the orientation of one reactant with respect to another. In simple terms, suppose, as shown in **Figure 3.9** that the sphere representing one of the reactants has a "hot spot" toward reactivity at angle  $\gamma = 0$  but that the reactivity falls off as the hot spot is rotated away from the point of impact. A simple model embodying this idea is to assume that the energy along the line of centers needs to be bigger than  $\epsilon^* + \epsilon'(1 - \cos \gamma)$ . When  $\gamma$  is zero, the effective threshold energy is simply  $\epsilon^*$ , but the effective threshold energy rises to  $\epsilon^* + \epsilon'$  for  $\gamma = 90^\circ$  and reaches  $\epsilon^* + 2\epsilon'$  for  $\gamma = 180^\circ$ . Following the argument above, we require  $\epsilon_{lc} \ge \epsilon^* + \epsilon(1 - \cos \gamma)$ , where  $\epsilon_{lc}$  is still given by  $\epsilon_r(1 - b^2/b_{max}^2)$ . Problem 3.7 outlines the solution, which, when compared to **equation 3.8**, shows that *p* can be identified as  $kT/\epsilon'$ . Reasonable values of  $\epsilon'$  are in the range from 10 to 1000 kT, so this modified collision theory finds values of *p* in the range 0.001–0.1, in fair agreement with experiment.

Note that the modified (and improved) collision theory achieves better agreement with experiment by incorporating one more feature of the potential energy function into the model. In this case, the additional feature is the way in which the barrier to reaction increases as the angle between the reactants is varied; in other words, the additional feature is the "width" of the barrier. We will see below that activated complex theory incorporates a similar parameter, although in a different manner.

### 3.4 ACTIVATED COMPLEX THEORY (ACT)

While simple collision theory models the potential energy surface with only the threshold energy  $\epsilon^*$ , activated complex theory goes somewhat beyond this naive view, but only by one step. As we will see, the additional feature of the surface incorporated by ACT is related to the "width" or structure of the reaction channel leading over the activation barrier. In this sense, it is similar to the modified collision theory just described, but the development of ACT provides new insights into the meaning of the preexponential factor.

We start by modeling the chemical reaction by the following scheme:

$$A + B \xrightarrow{k_1} AB^{\ddagger} \xrightarrow{k_2}$$
 products, (3.12)

where A and B each might represent some collection of atoms. Under the steadystate assumption, we can write the overall rate of the reaction as

$$\frac{\mathrm{d}[\mathrm{products}]}{\mathrm{d}t} = k_2[\mathrm{AB}^{\ddagger}]$$

$$= k_2 \frac{k_1}{k_{-1} + k_2} [A][B]$$
(3.13)  
$$\approx k_2 \frac{k_1}{k_{-1}} [A][B],$$

where the last equation was obtained by assuming that  $k_2 \ll k_{-1}$ .

What remains is to express the combination of rate constants  $k_2k_1/k_{-1}$  in terms of properties of the reactants and the potential energy surface. We start with the ratio  $k_1/k_{-1}$  and recognize that this ratio is simply the equilibrium constant for the "reaction"  $A + B \implies AB^{\ddagger}$ . From statistical mechanics, we know that an equilibrium constant can be written as the ratio of partition functions per unit volume, but we must be careful to take into account the offset in energy between the zero-point energies of the reactants and that of the activated complex. Thus, if we denote the partition function per unit volume for the activated complex by  $q^{\ddagger}$  and the product of the partition functions per unit volume for the reactants by  $q_A q_B$ , then  $k_1/k_{-1}$  is equal to  $q^{\ddagger}/q_A q_B$  and the rate of the reaction becomes

$$\frac{\mathrm{d}[\mathrm{products}]}{\mathrm{d}t} = k_2 \frac{q^{\ddagger}}{q_\mathrm{A}q_\mathrm{B}} \exp\left(-\frac{\epsilon^*}{kT}\right) [\mathrm{A}][\mathrm{B}], \qquad (3.14)$$

where each partition function per unit volume depends on temperature and gives the number of states available to the system at that temperature. The factor  $\exp(-\epsilon^*/kT)$  accounts for the offset in energy,  $\epsilon^*$ , between the zero points of the reactants and that of the activated complex. This offset is shown in **Figure 3.10**.

A reminder about the physical interpretation of partition functions may help to clarify the meaning of **equation 3.14.** The partition function is simply a number which describes how many states are available to the system at a given temperature; it is defined as  $z \equiv \sum \exp(-\epsilon_n/kT)$ , where the sum is over all states *n* of the system, each with energy  $\epsilon_n$ . If the system were a single quantum particle in a



Reaction coordinate

### Figure 3.10

The energy  $\epsilon^*$  in ACT is the difference in energy between the zero points of the reactants and the activated complex.

### Chapter 3 Theories of Chemical Reactions

one-dimensional box, for example, the possible states of the system are at the energies  $\epsilon_n = n^2 h^2 / 8mL^2$ , where *h* is Planck's constant, *m* is the mass of the particle, and *L* is the length of the box. For a particle in a one-dimensional box, Problem 3.8 shows that this sum is  $(2\pi m kT)^{1/2} L/h$ . If, instead, the particle is translating freely in a *three*-dimensional box of volume *V*, the partition function is  $z_t = (2\pi m kT)^{3/2} V/h^3$ , where the subscript t denotes that this is the translational contribution to the partition function. For this example, the quantity required in **equation 3.14** is the partition function per unit volume:  $q_t = z_t/V = (2\pi m kT)^{3/2}/h^3$ .

Of course, if a particle has vibrational and rotational degrees of freedom, more states will be available at a given temperature. For independent degrees of freedom, the partition function for a single particle is simply the product of the partition functions for each type of motion:  $z = z_t \times z_r \times z_v \times z_e$ , where the additional subscripts denote rotation, vibration, and electronic motion, respectively. Partition functions for these degrees of motion are summarized in **Table 3.1.** At this stage, we will simply use the listed results. Note that only the translational partition function depends on volume.

It is clear from equation 3.14 that the overall rate constant for the bimolecular reaction  $A + B \rightarrow$  products is  $k = k_2(q^{\dagger}/q_Aq_B)\exp(-\epsilon^*/kT)$ . The partition functions  $q_A$  and  $q_B$  can be calculated with the aid of **Table 3.1.** We then have left two tasks—to determine  $k_2$  and to learn how to calculate  $q^{\ddagger}$ .

The rate constant  $k_2$  describes the unimolecular decomposition rate of AB<sup>‡</sup> going to products. We will take the approach that the rate of AB<sup>‡</sup> decomposition is simply equal to the frequency of vibration of the complex along the path of the reaction coordinate, denoted  $\nu^{\ddagger}$ . Thus, the complex decomposes to products on every vibration, and the reaction rate simplifies to

$$k(T) = v^{\ddagger} \frac{q^{\ddagger}}{q_{\rm A} q_{\rm B}} \exp\left(-\frac{\epsilon^*}{kT}\right).$$
(3.15)

There are admittedly two predicaments with this approach. First, it is difficult to imagine a vibrational frequency along a coordinate for which the potential energy function is not bound. We will see shortly, however, that the frequency  $\nu^{\ddagger}$ actually cancels in the final result. Furthermore, Problem 3.9 shows that the same final result is obtained if the motion is treated as a translation rather than a vibration. Second, we have assumed in our model leading to **equation 3.13** that the

### TABLE 3.1 Partition Functions for Molecular Degrees of Freedom

Type of Motion	Partition Function	Order of Magnitude
Translational, three-dimensional, per unit volume	$z_t/V = (2\pi m kT)^{3/2}/h^3$	$10^{24} \text{ cm}^{-3}$
Rotational, linear molecule	$z_{\rm r} = 8\pi^2 I k T / h^2 \sigma$	10 <sup>2</sup>
Rotational, nonlinear molecule	$z_r = [\pi^{1/2} (8\pi^2 kT)^{3/2} / h^3 \sigma] \times (I_A I_B I_C)^{1/2}$	10 <sup>3</sup>
Vibrational, each degree of freedom, measured		
from the lowest (zero point) vibrational level	$z_{\rm v} = [1 - \exp(-h\nu/kT)]^{-1}$	1 (high $\nu$ )
	· - · · ·	10 (low $\nu$ )
Electronic	$z_{\rm e} = \sum g_i \exp(-\epsilon_i^{\rm e}/kT)$	1

Notes: *I* is the moment of inertia;  $\nu$  is the vibrational frequency;  $\epsilon_i^{e}$  are the electronic energy levels,  $g_i$  is the degeneracy, and  $\sigma$  is a symmetry number (e.g.,  $\sigma = 2$  for a homonuclear diatomic molecule).

decomposition of the complex is slow enough not to perturb the equilibrium  $A + B \rightleftharpoons AB^{\ddagger}$ , yet we are now assuming that  $AB^{\ddagger}$  decomposes on every vibration. Despite this apparent contradiction, a more careful examination, somewhat beyond the level of this text,<sup>d</sup> shows that for  $\epsilon^* > 3kT$  the approximations are still valid, partly because the overall rate is small compared to  $\nu^{\ddagger}$  under these conditions.

We now separate the partition function  $q^{\ddagger}$  into two factors, a partition function for the vibration along the reaction coordinate,  $z_v^{\ddagger}$ , and a partition function for the remaining degrees of freedom,  $q^{\ddagger'}$ , where the prime notation reminds us that the latter partition function is missing one degree of freedom (the vibration). According to **Table 3.1**,  $z_v^{\ddagger}$ , can be calculated as

$$z_{\nu}^{\ddagger} = \frac{1}{1 - \exp(-h\nu^{\ddagger}/kT)}$$

$$\approx \frac{1}{1 - [1 - (h\nu^{\ddagger}/kT)]}$$

$$= \frac{kT}{h\nu^{\ddagger}},$$
(3.16)

where the approximation uses only the first two terms in the Taylor expansion of the exponential since the frequency  $\nu^{\ddagger}$  is assumed to be small. Substitution of equation 3.16 into equation 3.15 gives

$$k(T) = \frac{kT}{h} \frac{q^{\sharp'}}{q_{\rm A} q_{\rm B}} \exp\left(-\frac{\epsilon^*}{kT}\right).$$
(3.17)

Note that the ambiguous frequency  $\nu^{\ddagger}$  cancels in this final result. Example 3.2 illustrates how equation 3.17 can be used to estimate rate constants.

\_\_\_example 3.2

### Estimating Rate Constant Orders of Magnitude with ACT

**Objective** Estimate the order of magnitude of the room-temperature rate constant for a reaction in which an atom and a heteronuclear diatomic molecule react through a nonlinear activated complex; leave the answer as a factor times  $\exp(-\epsilon^*/kT)$ .

Method Use equation 3.17 and the third column of Table 3.1.

**Solution** The nonlinear activated complex of three atoms has three translational degrees of freedom, three rotational degrees of freedom, and 3N - 6 = 3 vibrational degrees of freedom. One of these, the asymmetric stretch, is the reaction coordinate; the symmetric stretch is usually a high frequency while the bend is a low

<sup>&</sup>lt;sup>d</sup>P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley-Interscience, London, 1972), Section 4.12.

frequency. Thus, we may estimate  $q^{\dagger'} \approx (10^{24} \text{ cm}^{-3})(10^3)(10) = 10^{28} \text{ cm}^{-3}$ . The partition function for the atom has only translational contributions:  $q_A \approx 10^{24} \text{ cm}^{-3}$ . The partition function for the diatom has three translational, two rotational, and one (probably high-frequency) vibrational degree of freedom:  $q_B \approx (10^{24} \text{ cm}^{-3}) \cdot (10^2)(1) = 10^{26} \text{ cm}^{-3}$ . Recalling that  $kT/h \approx 6 \times 10^{12} \text{ s}^{-1}$  at room temperature, we find that  $k \approx (6 \times 10^{12} \text{ s}^{-1})(10^{28} \text{ cm}^{-3})/[(10^{24} \text{ cm}^{-3})(10^{26} \text{ cm}^{-3})]\exp(-\epsilon^*/kT) = (6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \exp(-\epsilon^*/kT)$ .

Equation 3.17 is sometimes written as

$$k(T) = \frac{kT}{h} K^{\dagger \prime}, \qquad (3.18)$$

where

$$K^{\dagger \prime} \equiv \frac{q^{\dagger \prime}}{q_{\rm A} q_{\rm B}} \, \exp\!\left(-\frac{\epsilon^*}{kT}\right) \tag{3.19}$$

is a sort of equilibrium constant describing the ratio of activated complexes (less one degree of freedom along the reaction coordinate) to reactants.

Let us step back from equation 3.17 for a moment to consider its physical meaning. The factor of kT/h, equal to  $6.25 \times 10^{12} \text{ s}^{-1}$  at room temperature, is the frequency at which the reactants attempt to get to the activated complex. The factors  $q^{\dagger'}/(q_A q_B)\exp(-\epsilon^*/kT)$  determine the ratio of the number of states available to the activated complex (less one degree of freedom) divided by the number of states available to the reactants. The reaction rate is just the frequency times this ratio, since we have assumed that the activated complexes proceed to products on every vibration along the reaction coordinate.

Note that each of the three partition functions in the ratio  $q^{\pm'/}(q_A q_B)$  has units of volume<sup>-1</sup>, so that the units of the rate constant for this bimolecular reaction are volume per second (per molecule), as required. The Boltzmann factor  $\exp(-\epsilon^*/kT)$  accounts for the difference in energy between the activated complex and the reactants; if the zero of energy had been the same for each of these species, this factor would have been unnecessary.

A view from the reactants' point of view of two possible A + B reactions is shown in **Figure 3.11**, where only one of the possible modes of vibration perpendicular to the reaction path is shown in each panel. Two colliding molecules would find it easier to react on the potential energy surface of **Figure 3.11A** rather than that of **Figure 3.11B**. The reason is that the vibrational levels are more closely spaced on the "wider" potential energy function, so that more states of the activated complex are accessible at any given temperature in this case. The reaction rate should depend both on the threshold energy and on the "width" of the channel leading over the barrier. Note, however, that the "width" in most reactions is multidimensional, so that it is really more accurate to refer to the "structure" of the activated complex state or, even better, to the partition function for the activated complex; for an activated complex with  $N \ge 3$ , there are 3N - 6 - 1 degrees of freedom perpendicular to the reaction coordinate. For example, in a triatomic activated complex, there are 9 - 7 = 2 perpendicular degrees of freedom. The





The reactants' view of two possible reactions.

asymmetric stretching motion of the triatomic system  $(A \rightarrow \leftarrow B - C \rightarrow)$  is the reaction coordinate, while the symmetric stretch ( $\leftarrow A - B - C \rightarrow$ ) and the bending vibration ( $\downarrow A - B^{\uparrow} - C \downarrow$ ) are the two orthogonal vibrational modes.

A connection between ACT and simple collision theory can be made calculating the ACT rate constant for the reaction of two atoms of average diameter  $b_{\text{max}}$ . As one might hope, the resulting expression, derived in **Example 3.3**, is exactly that calculated by collision theory, given in **equation 3.7**. We remarked in Section 3.3.2 that the steric factor, p, was typically less than unity. Activated complex theory gives an explicit formula for p; it is equal to the ratio between the value of  $q^{\dagger'}/(q_A q_B)$  for the reaction under consideration and the value of  $q^{\dagger'}/(q_A q_B)$  for a reaction between two atoms whose average diameter is equal to that of the reactants under consideration.

It should be noted that ACT is not restricted to bimolecular reactions. Returning to **equation 3.17**, we could write the temperature-dependent rate of a unimolecular reaction as

$$k(T) = \frac{kT}{h} \frac{q^{\dagger'}}{q_{\rm A}} \exp\left(-\frac{\epsilon^*}{kT}\right).$$
(3.20)

Of somewhat more interest is to ask what the rate for unimolecular reaction would be if all the reactant molecules had the same energy. The answer involves a somewhat

### Chapter 3 Theories of Chemical Reactions

more complex calculation that we will postpone until Section 7.5.4 when we discuss unimolecular reactions in more detail. However, the final result is reasonably simple:

$$k_{a}(E^{*}) = \frac{W(E^{+})}{hN^{*}(E^{*})},$$
 (3.21)

where  $k_a(E^*)$  is the rate constant for unimolecular decay of molecules with energy  $E^*$ ,  $W(E^+)$  is the number of vibrational states of the activated complex accessible at that same total energy, and  $N^*(E^*)$  is the density of states (the number per unit energy interval) of the reactant at energy  $E^*$ . The energy  $E^+$  is equal to  $E^* - E_0$ , where  $E_0$  is the activation energy. Note that since  $hN^*(E^*)$  has units of time and since  $W(E^*)$  is dimensionless,  $k_a(E^*)$  has units of s<sup>-1</sup>, as required for a first-order reaction.

## example 3.3

### ACT Calculation of the Reaction Rate of Two Atoms

- **Objective** Show that the ACT rate constant for the reaction of two atoms whose average diameter is  $b_{\text{max}}$  gives the same result as collision theory, equation 3.7.
- **Method** Use equation 3.17 with column 2 of Table 3.1. Note  $q^{\ddagger'}$  is the partition function of the activated complex, but without the degree of freedom corresponding to the reaction coordinate. For the reaction of two atoms, the reaction coordinate corresponds to the vibration of the diatomic activated complex.
- **Solution** The exponential factors,  $\exp(-\epsilon^*/kT)$ , are the same for ACT and collision theory, so that our task is to show that the pre-exponential factor in ACT,  $(kT/h)(q^{\ddagger'}/q_Aq_B)$ , is equivalent to the preexponential factor in **equation 3.7**. Using **Table 3.1** and recalling that the moment of inertia in this case is  $\mu b_{max}^2$ , we find that the ACT pre-exponential factor is

$$\frac{kT}{h}\frac{q^{\dagger\prime}}{q_{\rm A}q_{\rm B}} = \frac{kT}{h}\frac{[2\pi(m_{\rm A}+m_{\rm B})kT/h^2]^{3/2}[2IkT/\hbar^2]}{[2\pi m_{\rm A}kT/h^2]^{3/2}[2\pi m_{\rm B}kT/h^2]^{3/2}}$$

$$= \frac{kT}{h} \frac{[2lkT/\hbar^{2}]}{[2\pi(m_{\rm A}m_{\rm B}/(m_{\rm A} + m_{\rm B}))kT/\hbar^{2}]^{3/2}}$$
(3.22)  
$$= \frac{kT}{h} \frac{[2(\mu b_{\rm max}^{2})kT/\hbar^{2}]}{[2\pi\mu kT/\hbar^{2}]^{3/2}} = \frac{(kT)^{1/2}(2\pi)^{1/2}2b_{\rm max}^{2}}{\mu^{1/2}}$$
$$= \left(\frac{8kT}{\pi\mu}\right)^{1/2} \pi b_{\rm max}^{2} = v_{\rm r}\pi b_{\rm max}^{2}.$$

This is just the result of equation 3.7.

108

### 3.5 THERMODYNAMIC INTERPRETATION OF ACT

We now return to **equation 3.18** to provide a thermodynamic interpretation of the rate constant. If we identify the equilibrium constant with a Gibbs free energy through the relationship  $-RT \ln K^{\ddagger \prime} = \Delta G^{\ddagger}$  then **equation 3.18** can be rewritten as

$$k(T) = \frac{kT}{h} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right), \qquad (3.23)$$

where  $\Delta G^{\ddagger}$  is the change in Gibbs free energy in going from the reactants to the activated complex. Of course,  $\Delta G^{\ddagger}$  can be written in terms of the enthalpy and entropy changes between the reactants and the activated complex:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T \Delta S^{\ddagger}, \qquad (3.24)$$

so that equation 3.23 becomes

$$k(T) = \frac{kT}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{H^{\ddagger}}{RT}\right).$$
 (3.25)

Recalling that  $\Delta H = \Delta (E + pV) = \Delta E + (\Delta n)RT$  for an ideal gas and that for our reaction  $A + B \rightleftharpoons (AB)^{\ddagger}$  the value of  $\Delta n$  is -1, we see that  $\Delta H^{\ddagger} = \Delta E^{\ddagger} - RT$ , where  $\Delta E^{\ddagger}$  is the activation energy in going from reactants to activated complexes and can be identified as the activation energy  $E_{a}$ . Thus,

$$k(T) = \exp(1)\frac{kT}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{E_{a}}{RT}\right).$$
 (3.26)

When compared to the Arrhenius expression  $k = A \exp(-E_a/RT)$ , we find that the preexponential factor is identified as

$$A = \exp(1)\frac{kT}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right).$$
(3.27)

The point of this exercise is to identify the Arrhenius preexponential factor with an entropy of activation, the entropy change in going from reactants to the activated complex. For a bimolecular reaction, of course,  $\Delta S^{\ddagger}$  is always a negative quantity, since two reactants must come together into a necessarily more ordered state before they can react. If the activated complex needs to be even more "ordered" than just two spheres in contact, then the entropy of activation will be correspondingly more negative, and the preexponential factor and reaction rate constant will become smaller. A more "ordered" activation complex is one for which, in collision theory, the steric factor is smaller than 1, or one for which, in activated complex theory, there are few accessible states of the complex.

### 3.6 SUMMARY

The main point of this chapter was to show how two simple theories, collision theory and activated complex theory, can be used to estimate rate constants. We started by noting that the rate constant could be calculated if we knew the potential energy surface for the reaction. In most cases, however, this surface is known only approximately. Which of its features is most important in determining the rate constant? Simple collision theory concentrates on the difference between the zero-point energies of

### Chapter 3 Theories of Chemical Reactions

the activated complex and the reactants,  $\epsilon^*$ . It assumes that reaction occurs every time a collision provides an energy along the line between the centers of the reactants greater than  $\epsilon^*$ . The derivation of the collision theory rate constant starts with evaluation of the reaction probability as a function of energy and impact parameter,  $P(\epsilon_r,b)$ , averages this over impact parameter to obtain the cross section for reaction at a particular energy,  $\sigma(\epsilon_r)$ , and then averages the energy-dependent rate constant  $k(\epsilon_r) = \sigma(\epsilon_r)v$  over the thermal distribution of collision energies. The result is

$$k(T) = \pi b_{\max}^2 v_r \exp\left(-\frac{\epsilon^*}{kT}\right), \qquad (3.7)$$

where  $v_r = (8kT/\pi\mu)^{1/2}$  is the average relative velocity. A hand-waving derivation of this result is that the rate constant is simply the hard-sphere collision rate,  $\pi b_{\max}^2 v_r$ , times the fraction of collisions,  $\exp(-\epsilon^*/kT)$ , that provide energy greater than  $\epsilon^*$ .

Simple collision theory overestimates the rate constant because it fails to take into account the fact that the reactants must be oriented properly for reaction even when the collision energy is sufficient to overcome the threshold energy. We can modify the theory by incorporating a steric factor, p, with p < 1 to account for the orientation requirement. Then,

$$k(T) = p\pi b_{\max}^2 v_r \exp\left(-\frac{\epsilon^*}{kT}\right).$$
(3.8)

Consideration of the simple model illustrated in **Figure 3.9** leads to the conclusion that  $p = kT/\epsilon'$ , where  $\epsilon'$  describes the way in which the energy required for reaction varies with the angular orientation of the reactants. Thus, this modified collision theory improves on the simple model by incorporating one more feature of the potential energy surface in addition to the threshold energy  $\epsilon^*$ .

Activated complex theory also improves on the simple model by incorporating information about the "width" of the barrier over the saddle point. The essential assumption of the theory is that the reactants are at equilibrium with activated complexes, so that the equilibrium constant can be used to calculate the overall rate for the reaction,  $k_2[AB^{\ddagger}] = k_2 K^{\ddagger}[A][B]$ . The concepts of statistical mechanics are used to show that

$$k(T) = \frac{kT}{h} \frac{q^{\sharp'}}{q_{\rm A}q_{\rm B}} \exp\left(-\frac{\epsilon^*}{kT}\right).$$
(3.17)

In this equation, the quantities q are partition functions that describe the number of states accessible at the temperature of interest. They can be evaluated using **Table 3.1.** For a unimolecular reaction taking place at a particular temperature, the corresponding equation is simply

$$k(T) = \frac{kT}{h} \frac{q^{\sharp'}}{q_A} \exp\left(-\frac{\epsilon^*}{kT}\right).$$
(3.20)

If all the reactants have the same energy  $E^*$ , then the equation simplifies to

$$k_{\rm a}(E^*) = \frac{W(E^+)}{hN^*(E^*)},$$
 (3.21)

where  $W(E^+)$  is the number of states of the activated complex and  $N^*(E^*)$  is the density of states of the reactant.

By realizing that the equilibrium constant between reactants and activated complexes can be expressed in terms of a free energy of activation,  $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ , we found that the Arrhenius preexponential factor, *A*, can be related to the entropy change in proceeding from the reactants to the activated complex.

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## problems

- 3.1 For a nonlinear system of 5 atoms, on how many coordinates does the potential energy depend?
- 3.2 For simple collision theory, at what energy is the cross section most dependent on energy?
- 3.3 The thermal rate constant is the average of (a) the reaction probability over impact parameter, (b) the reaction probability over the thermal energy distribution, (c) the reaction cross section over the thermal energy distribution, or (d) the energy-dependent rate constant over the thermal energy distribution. (Specify which.)
- 3.4 The steric factor p depends on (a) the angular dependence of the reaction probability, (b) the requirements for the reactants to be in a particular orientation, (c) a ratio of partition functions, (d) the entropy of activation, or (e) more than one of the above. (Specify which.)
- 3.5 When activated by collision, the molecule  $Br-CH_2-CH_2-CH_2-CH_3$  can eliminate either HBr or Br. Which reaction will have the higher Arrhenius A parameter? Why?
- 3.6 The partition function (a) specifies the number of states below a certain energy, (b) is proportional to a volume in phase space, (c) specifies the number of states accessible at a certain energy, (d) more than one of the above. (Specify which.)
- 3.7 The condition for reaction, given the modified collision theory assumptions of Section 3.3.2 and **Figure 3.9**, is that  $\epsilon_{lc} \ge \epsilon^* + \epsilon'(1 \cos \gamma)$ , where  $\epsilon_{lc}$  is equal to  $\epsilon_r(1 b^2/b_{max}^2)$ . For  $\epsilon_r > \epsilon^*$ , this equation defines a maximum angle

### Chapter 3 Theories of Chemical Reactions

 $\gamma_{\text{max}}$  for which reaction can occur:  $1 - \cos \gamma_{\text{max}} = [\epsilon_r (1 - b^2 / b_{\text{max}}^2) - \epsilon^* / \epsilon'$ . The probability for reaction  $P(\epsilon_r, b)$  is then just the surface area of a sphere of radius  $b_{\text{max}}$  for which  $\gamma \le \gamma_{\text{max}}$ :

$$P(\epsilon_{\rm r},b) = \frac{\int_{0}^{\gamma_{\rm max}} 4\pi b_{\rm max}^2 \sin \gamma \, d\gamma}{4\pi b_{\rm max}^2}$$
$$= 1 - \cos \gamma_{\rm max}$$
$$= [\epsilon_{\rm r}(1 - b^2/b_{\rm max}^2) - \epsilon^*]/\epsilon$$

By integrating this value for  $P(\epsilon_r, b)$  over  $2\pi b \, db$ , calculate  $\sigma(\epsilon_r)$ . Then average this cross section over the thermal distribution to show that k(T) is equal to  $(kT/\epsilon')$  times the result for simple collision theory. Note that this theory predicts that the steric factor should increase with temperature. The result is reasonable, since the range of angles for which reaction can occur should increase with increasing temperature.<sup>e</sup>

3.8 Recalling that the energy levels for a particle of mass *m* in a one-dimensional box of length *L* are given by  $\epsilon_n = n^2 h^2 / (8mL^2)$  and that the partition function is defined as  $q = \sum \exp(-\epsilon_n/kT)$ , show that for this system is  $q = (2\pi m kT)^{1/2}L/h$ . Hint:

$$\sum_{n=1}^{\infty} \exp(-n^2 \alpha^2) \approx \int_0^{\infty} \exp(-n^2 \alpha^2) \,\mathrm{d}n.$$

- 3.9 In equation 3.15, we assumed that the rate  $k_2$  at which the activated complexes decompose to products was equal to a vibrational frequency  $\nu^{\ddagger}$ . Although the vibrational frequency cancels in the final analysis, it might appear disturbing to associate a vibrational frequency with motion over a saddle point. In this problem, we consider the motion over the saddle point to be a translation. Let the activated complex be defined as the set of geometries along a length on the reaction coordinate equal to  $\delta$ . This length, about 0.1 nm, is arbitrary, since we will see that it, like the vibrational frequency, cancels in the final analysis. If the average translational velocity along the reaction coordinate is  $\langle v \rangle$ , then the rate of crossing is just  $k_2 = \langle v \rangle/2\delta$ , where the factor of 2 is introduced because half of the transition complexes will be moving in the forward direction. For motion in one dimension the average velocity is  $\langle v \rangle = (2kT/\pi m^{\ddagger})^{1/2}$ , where  $m^{\ddagger}$  is the mass of the activated complex. Starting from equation 3.14, substitute for  $k_2$  and write  $q^{\ddagger}$  as the product of a translational partition function  $q_t^{\ddagger}$  (in one dimension) and the partition function for the remaining degrees of freedom  $q^{\pm'}$  to derive the result in equation 3.17.
- 3.10 The activation energy  $E_a$  can be defined from the Arrhenius expression as

$$E_{\rm a} = kT^2 \, \frac{\partial \ln k(T)}{\partial T}$$

<sup>&</sup>lt;sup>e</sup>For further discussion of this effect, see R. D. Levine, Chem. Phys. Lett. 175, 331 (1990).

a. Use equation 3.7 to show that

$$E_{\rm a}=\frac{1}{2}kT+\epsilon^*.$$

- b. What is the percent error in taking  $E_a = \epsilon^*$  for each of the first three reactions of **Table 2.2** where T is taken to be at the middle of the applicable range?
- 3.11 a. Use simple collision theory to calculate the Arrhenius A factor for the elementary reaction NO +  $O_3 \rightarrow NO_2 + O_2$ . Reasonable values for the molecular radii are 0.14 nm for NO and 0.20 nm for  $O_3$ . Assume T = 300 K.
  - b. The experimental A factor for this reaction is  $1.0 \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>. What is the value of the steric factor p?
- 3.12 Consider a unimolecular decomposition that proceeds via the Lindemann mechanism:

$$A + A \xrightarrow{k_1} A^* + A,$$
$$A^* \xrightarrow{k_2} 2 B.$$

The reactant A may also be activated by a collision with a product molecule B:

$$A + B \xrightarrow{\kappa_3} A^* + B$$

Use collision theory to calculate the relative magnitudes of  $k_1$  and  $k_3$ . You may assume that the two reactions have the same threshold energy. (*Hint:* What is a reasonable assumption about the relative volumes of B and A?)

3.13 The reaction  $F + H_2 \rightarrow H + HF$  is the rate-limiting elementary step in the overall reaction  $H_2 + F_2 \rightarrow 2$  HF. This latter process is the key reaction in the HF chemical laser. The reaction proceeds through a transition state:

 $H_2 + F \rightleftharpoons (HHF)^{\ddagger} \rightarrow H + HF.$ 

Suppose that the activated complex is linear. Some properties of the reactants and the activated complex are given in **Table 3.2.** The threshold energy is estimated to be  $\epsilon^* = 6.6$  kJ mol<sup>-1</sup>.

Properties in the F + H<sub>2</sub> Reaction (Problem 3.13)

	H <sub>2</sub>	F	(HHF) <sup>‡</sup>
$\sigma (10^{-19} \text{ m}^2)$	2.7	1.8	
$I (10^{-47} \text{ kg m}^2)$	0.46		7.43
$\nu (10^{13} \text{ s}^{-1})$	13.19		12.02
			1.19
			1.19
Electronic degeneracy	1	4	4

- a. Use collision theory to calculate the preexponential factor and the rate constant for the reaction at 298 K. Compare your answer to the experimental result of  $A = 2 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ .
- b. Use activated complex theory to calculate the rate constant for the reaction at 298 K. Assume that the electronic degeneracy for F and for the activated complex is 4.
- 3.14 Use activated complex theory to determine the temperature dependence of the Arrhenius preexponential factors for the following three gas-phase reactions
  - a.  $O + N_2 \rightarrow NO + N$
  - b.  $OH + H_2 \rightarrow H_2O + H$
  - c.  $CH_3 + CH_3 \rightarrow C_2H_6$

In other words, for  $A \propto T^n$ , find *n* for each equation. You may assume that the activated complex is linear for reaction (a) and nonlinear for reactions (b) and (c). Further, you may assume that  $h \ll kT$  and that the electronic degeneracies are unity.

- 3.15 A theorem by Tolman states that the activation energy for a reaction is the difference between the average energy of those molecules that react and the average energy of all the molecules:  $E_a = \langle E_r \rangle \langle E \rangle$ .
  - a. Show for a general reaction of cross section  $\sigma(\epsilon_r)$  that the rate constant is

$$k(T) = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \left(\frac{2}{\mu}\right)^{1/2} \int_0^\infty \epsilon_r \sigma(\epsilon_r) \exp\left(-\frac{\epsilon_r}{kT}\right) d\epsilon_r.$$

- b. Recalling that  $E_a = kT^2 \partial \ln k(T)/\partial T$ , prove Tolman's theorem.
- The objective of this problem is to see how isotopic substitution might affect 3.16 the rate of a chemical reaction. For simplicity, we consider the case when the substitution is made at the atom whose motion is most nearly along the reaction coordinate; the effect on the rate constant is called the *primary* kinetic isotope effect. A simple example might be to compare the dissociation  $RH \rightarrow R + H$  to the dissociation  $RD \rightarrow R + D$ . The origin of the effect is due to the fact that different isotopic species have different zero-point vibrational frequencies, both in the ground state and, to a lesser extent, in the excited state. We recall from quantum mechanics that the vibrational frequency in the harmonic oscillator approximation is  $\nu = (1/2\pi)(k_{\rm fc}/\mu)^{1/2}$ , where  $k_{\rm fc}$  is the force constant for the vibration and  $\mu$  is the reduced mass of the vibrating masses. An approximation to the primary kinetic isotope effect can be calculated by assuming that there is no difference in zero point energies between the two isotopic species in the activated complex and that both species have the same Arrhenius A factor. The justification for this approximation is that the stretching motion, for example, R-H or R-D, is not bound if it is along the reaction coordinate. (To be sure, there will be some zeropoint energy difference for the bending motion in the activated complex, but for this crude approximation we will assume it to be negligible. There will

also be some difference in the A factor, but assuming no symmetry number difference, this difference will also be small.) Since the zero-point energy for the hydrogen system,  $\frac{1}{2}h\nu_{\rm H}$ , lies higher than the zero-point energy for the deuterium system,  $\frac{1}{2}h\nu_{\rm D}$ , the former system will have a lower activation energy than the latter by the difference between these two zero points.

- a. Given that the higher of the two ground-state vibrational frequencies is known (as v<sub>H</sub>), derive a formula for the ratio of the two rate constants, k<sub>light</sub>/k<sub>heavy</sub>.
  b. Typical frequencies for hydrogen stretches are given as follows (in
- b. Typical frequencies for hydrogen stretches are given as follows (in cm<sup>-1</sup>): C–H; 2900; OH; 3300; NH; 3100; SH; 2600. Calculate  $k_{\rm H}/k_{\rm D}$  at room temperature for reactions involving motion of the hydrogen or deuterium along the reaction coordinate.

# 4

# **Transport Properties**

### **Chapter Outline**

- 4.1 Introduction
- 4.2 The Functional Form of the Transport Equations
- 4.3 The Microscopic Basis for the Transport Laws
- 4.4 Thermal Conductivity
- 4.5 Viscosity
- 4.6 Diffusion
- 4.7 Time-Dependent Transport
- 4.8 Summary

Appendix 4.1 The Poiseuille Formula

### 4.1 INTRODUCTION

The goal of this chapter is to understand such properties as thermal conductivity, viscosity, and diffusion on a microscopic level. For gases, we can attain this understanding by application of the kinetic theory developed in the last chapter. Although an exact treatment is mathematically cumbersome, simple physical ideas can be used to derive approximate formulas that have the correct dependence on molecular parameters and differ from the exact formulas only by numerical constants of order unity. Thus, our approach focuses on the underlying physics of the process rather than on obtaining exact results.

The outline of the approach is as follows. After briefly discussing the general functional form of the transport equations, we will make four simplifying assumptions that will enable us to easily apply kinetic theory to transport phenomena in gases. The basic theme is that the properties transported, namely, energy, momentum, or concentration, are carried by the motions of molecules. We know something about this motion from our discussions of the Maxwell-Boltzmann distribution. The first step in a general treatment of transport is to calculate the flux of molecules, i.e., the number of molecules that cross an area per unit time. The second step is to calculate how far the molecules travel in a particular direction between collisions. This distance is clearly related to the mean free path, but it is slightly different.

The third step is to combine these two results to calculate a transport equation for an arbitrary property carried by the gas molecules. We will see that the transport always moves the property in a direction opposite to a gradient, or spatial derivative, in the property, and that the proportionality constant is related to the mean velocity of the molecules, the mean free path, and other properties of the molecules. For gradients that are independent of time, it is then relatively straightforward to apply the general equation in turn to thermal conductivity, where energy is transported; to viscosity, where momentum is transported; and to diffusion, where the molecules themselves are transported. For gradients that are not constant in time, the treatment is somewhat more complex but can again be understood using a simple model, as shown in the final section of this chapter.

### 4.2 THE FUNCTIONAL FORM OF THE TRANSPORT EQUATIONS

The principal features of all transport equations can be appreciated by considering the flow of a liquid through a tube. **Figure 4.1** displays the important parameters. For the liquid under consideration and for a particular choice of diameter, the tube has an inherent conductivity *C*. Suppose that a pressure differential  $\Delta p = p_2 - p_1 > 0$  is placed across the tube so as to force the liquid to flow from left to right. We expect from common experience that the rate of liquid volume that crosses a unit area oriented perpendicular to the flow will depend linearly on both the pressure differential and the conductivity. The flow of a quantity per unit time per unit area is called the *flux* and has dimensions of (quantity) s<sup>-1</sup> m<sup>-2</sup>. In this case, the quantity is the volume of liquid and the linear proportionalities can be expressed by the equation

$$J_z = -C \frac{\partial p}{\partial z},\tag{4.1}$$

an equation known as Poiseuille's law. In the example above,  $\partial p/\partial z$  is simply  $-\Delta p/\ell$  and is called the *gradient* of the pressure. Strictly speaking, since the gradient can have different values in different directions, **equation 4.1** should be written in vector form:  $\mathbf{J} = -C\nabla p$ , where  $\nabla$  is the vector  $\mathbf{i}\partial/\partial x + \mathbf{j}\partial/\partial y + \mathbf{k}\partial/\partial z$  and  $\mathbf{i}$ ,  $\mathbf{j}$ , and  $\mathbf{k}$  are unit vectors in the x, y, and z directions, respectively. To keep the notation simple, we will focus on the z component of the flux, while remembering that similar equations can be written for the other directions. Note in **equation 4.1** that the gradient  $\partial p/\partial z$  is negative since the pressure decreases as z increases, but that the flux is positive because of the negative sign incorporated in **equation 4.1**.



### Figure 4.1

The flow of liquid through a tube.

### Chapter 4 Transport Properties

TABLE 4.1 Transport Equations

Quantity Transported	Equation	Name
Fluid	$J_z = -C(\partial p/\partial z)$	Poiseuille's law
Heat (thermal conductivity)	$J_z = -\kappa(\partial T/\partial z)$	Fourier's law
Momentum	$J_z = -\eta (\partial v_x / \partial z)$	Viscosity
Particles (diffusion)	$J_{z} = -D(\partial n^{*}/\partial z)$	Fick's law
Electrical charge	$\tilde{J_{z}} = -(1/\rho)(\partial \phi/\partial z)$	Ohm's law

From dimensional analysis we see that the units of the conductivity C are volume  $s^{-1} m^{-1}$  pressure<sup>-1</sup>. While we note here that C is inversely proportional to the viscosity, we defer discussion of the relationship between the conductivity and molecular properties until Section 4.5.

All transport equations have the form of equation 4.1; the only differences involve the form of the gradient and the quantity that flows counter to the gradient. The examples of greatest interest are described in Table 4.1.

In the case of thermal conductivity, the quantity carried is heat or energy, and it is carried in the direction opposite to the temperature gradient; i.e., heat flows in the positive z direction if the temperature decreases as z increases. The proportionality constant,  $\kappa$ , is called the coefficient of thermal conductivity. Similarly, in the case of diffusion, the quantity carried is the particle itself, and it is carried counter to a density gradient. The proportionality constant, D, is called the diffusion coefficient. Viscosity is at first a bit confusing. The quantity carried is the x component of momentum, but it is carried in the z direction against a gradient of momentum, as discussed in detail in Section 4.5. The proportionality constant is called the viscosity coefficient. Ohm's law concerns the transport of electricity through a conductor against a gradient in electrical potential, as discussed in **Example 4.1**.

# example 4.1

Ohm's Law	
Objective	Determine Ohm's law for the flux of electrons through a wire, given that its conductivity is $1/\rho$ ( $\rho$ is called the resistivity) and that the potential decrease across the wire is V volts per m. Show that the result leads to the common form of Ohm's law: $V = IR$ .
Method	The charge flux will have the units of charge per cross-sectional area of the wire per second. It should be proportional to the con- ductivity of the wire and to the gradient of the electrical potential that pushes the electrons along the wire.
Solution	Since the electrons flow from a region of high potential $\phi$ to one of low potential, the gradient in the direction of flow is negative; the potential decreases with increasing z, where z is the direction of electron flow. Assuming a linear variation in voltage across the wire, the gradient is thus $\partial \phi/\partial z = -V/\ell$ , where $\ell$ is the length of

the wire. The flux of electrons is thus  $J_z = -(1/\rho)(\partial \phi/\partial z)$ . Writing the flux of electrons as the current, *I*, per unit area and substituting for the gradient, we obtain  $I/A = V/\rho \ell$ , or V = IR, where  $R = \rho \ell/A$  is the resistance of the wire.

**Comment** The units of *I* are amperes (one coulomb of charge per second), while the units of *R* are ohms. A 1-volt drop in potential across a resistance of one ohm causes a current flow of 1 ampere. The units of the resistivity,  $\rho$ , are ohm m.

### 4.3 THE MICROSCOPIC BASIS FOR THE TRANSPORT LAWS

### 4.3.1 Simplifying Assumptions

It is clear from **Table 4.1** that the transport laws all have the same basic form, namely that the flux of some quantity is proportional to and in the opposite direction of a gradient. In the case of transport in gases, the explanation of this common form is based on the kinetic theory outlined in Chapter 1. As realized very early by Maxwell and by Boltzmann and later expanded by Enskog and by Chapman,<sup>a</sup> the property transported by the flux must be transported by the individual particles comprising the gas, namely, by molecules subject to the Maxwell-Boltzmann distribution law. In the case of thermal conductivity, the property carried is the energy,  $\epsilon = mv^2/2$ . In the case of viscosity, the property carried is the momentum  $mv_{y}$ . Diffusion involves the flux of the molecules themselves. While a rigorous theory of transport properties involves both complicated mathematics and physics, the basic form of the answer can be derived from kinetic theory and a few simple assumptions. We will follow this latter route, recognizing that while we expect to capture the basic taste of the argument, the seasoning of our dishes may not be perfect. Most of the equations we derive will show the correct dependence on molecular parameters but will have numerical factors that are not guite correct.

We make the following simplifying assumptions: (1) the molecules behave as rigid spheres with no attractive forces; (2) they all travel with the same speed, equal to the average speed  $\langle v \rangle$ , and traverse the same distance, equal to the mean free path  $\lambda$ , between collisions; (3) the molecules taken collectively have an isotropic angular distribution; and (4) each collision results in complete equilibrium with respect to the interchange of the property q which is being transported.

The first assumption is obviously a drastic oversimplification, since we know that it is the forces, both attractive and repulsive, between gas molecules that account for the deviations from ideal gas behavior. The second assumption is more than merely a matter of convenience. It is certainly easier to deal with the average behavior rather than performing each calculation as a function of velocity and finally integrating over the velocity distribution. But this procedure hides the fact that some of the properties we want to transport depend on velocity, q = q(v), so that the rate of transport of this

<sup>&</sup>lt;sup>a</sup>D. Enskog, *Kungliga Svenska Vetenskapsakademiens Handlingar* **63**, No. 4 (1922) (in German); S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases* (Cambridge University Press, Cambridge, England, 1939).

### Chapter 4 Transport Properties

property is proportional to vq(v). By considering only the average velocity we are in effect replacing  $\langle vq(v) \rangle$  by  $\langle v \rangle \langle q(v) \rangle$ , an approximation whose accuracy depends on the exact nature of the distributions. The third assumption turns out to be particularly weak. When molecules collide, they do not completely forget their original direction of motion, so their motion in the presence of a gradient is not likely to be isotropic. The approximation ignores the fact that the gradient affects the velocity distribution. The fourth assumption is likewise a source of error. It may be true for transfer of infinitesimal amounts of the property q per collision, but it will certainly fail when the gradients become large. In view of these approximations, it should be no surprise that the derivations below will introduce incorrect numerical factors. Nonetheless, the essential physical picture is unchanged by these approximations; the property q is carried by molecules whose motions over a wide range of conditions are not too different from those predicted by kinetic theory.

We begin by considering gradients that are stable in time; i.e., gradients that are established by some external means so that the transport of heat, momentum, or concentration does not change the gradient with time. For example, we might hold the ends of a tube of gas at fixed, but different, temperatures by using two large heat baths. Heat would then be transferred through the gas from one bath to another without appreciably changing the gradient.

In the remainder of this section we will first develop an equation for the molecular flux. We will then use this equation to determine two quantities: the flux of a property through a plane and the vertical distance between planes where collisions have occurred. We will finally develop a general flux equation that can be used in subsequent sections to relate the coefficients of thermal conductivity, viscosity, and diffusion to molecular properties such as diameter, speed, heat capacity, and mass.

### 4.3.2 The Molecular Flux

The first step in a microscopic explanation for transport properties is to recognize that, if molecules are carrying the quantity in question across a unit area in a unit time, we need to know the rate at which the molecules themselves cross the area. **Equation 1.30** and **Figure 4.2** can help in this exercise. How many molecules cross the area *A* in the indicated plane per unit time? We treat the problem in spherical coordinates,



Figure 4.2

The flux of molecules through a plane.

where v ranges from 0 to  $\infty$ ,  $\theta$  from 0 to  $\pi$ , and  $\phi$  from 0 to  $2\pi$ . The relationship between spherical and Cartesian coordinates is discussed in Appendix 1.2. Consider for each possible value of v,  $\theta$ , and  $\phi$  a cylinder of slant height  $v\Delta t$  tilted at angles  $\theta$ and  $\phi$  with respect to the *z* axis, where the slant height is chosen so that all molecules within the cylinder with velocities centered on v,  $\theta$ , and  $\phi$  will cross area *A* in the time  $\Delta t$ . The volume of the cylinder depends both on the slant height,  $v\Delta t$ , and on  $\cos \theta$ :  $V = Av\Delta t \cos \theta$ . The number of molecules crossing *A* in  $\Delta t$  is then given simply as the number of molecules in the cylindrical volume times the probability that a molecule will have a velocity v centered on angles  $\theta$  and  $\phi$ . The number of molecules in the volume is  $n^*V = n^*Av\Delta t \cos \theta$ , while the probability of having the given velocity is  $(m/2\pi kT)^{3/2} \times \exp(-mv^2/2kT)v^2\sin \theta \, d\theta \, d\phi \, dv$ .<sup>b</sup> Thus,

number = 
$$n^* A v \Delta t \cos \theta \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) v^2 \sin \theta \, d\theta \, d\phi \, dv.$$
 (4.2)

The number of molecules in the cylinder with velocities centered on  $(v,\theta,\phi)$  that cross a unit area of the plane in a unit time is then the flux distribution function:

$$J(v,\theta,\phi)v^{2}\sin\theta \,d\theta \,d\phi \,dv = \frac{\text{number}}{A\Delta t}$$

$$= n^{*}v^{3} \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^{2}}{2kT}\right)\cos\theta \sin\theta \,d\theta \,d\phi \,dv.$$
(4.3)

**Equation 4.3** is evidently a distribution function giving the probability that a molecule with a speed in the range  $v \rightarrow v + dv$  and direction in the range  $\theta \rightarrow \theta + d\theta$ ,  $\phi \rightarrow \phi + d\phi$  will pass through the plane in a unit time. We can use it to calculate two important quantities.

We would first like to know the flux of molecules  $J_z$  that cross the plane from below regardless of their velocity and direction. To find this quantity, we simply need to integrate **equation 4.3** over all the variables, but the range of integration for  $\theta$  should be from 0 to  $\pi/2$  (see **Figure 4.2**) since we want only those molecules moving upward through the plane. Thus,

$$J_z = n^* \int_0^\infty \int_{0}^{2\pi} \int_0^{\pi/2} v^3 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right) \cos\theta \sin\theta \, d\theta \, d\phi \, dv.$$
 (4.4)

The integration over v (with an additional factor of  $4\pi$ ) was performed in equation 1.31: the answer here is simply  $1/(4\pi < v >)$ . The integration over  $\phi$  gives a factor of  $2\pi$ . Thus,

$$J_{z} = n^{*} \frac{1}{4\pi} < v > 2\pi \int_{0}^{\pi/2} \cos \theta \sin \theta \, d\theta$$
  
=  $n^{*} \frac{1}{2} < v > \int_{0}^{\pi/2} \sin \theta \, d(\sin \theta) = n^{*} \frac{1}{2} < v > \left[\frac{\sin^{2} \theta}{2}\right]_{0}^{\pi/2},$  (4.5)

or

<sup>&</sup>lt;sup>b</sup>Note that integration of the probability over the angles would give a factor of  $4\pi$ , so that the probability would be identical to that given in equation 1.31.

Chapter 4 Transport Properties

$$J_z = \frac{1}{4} n^* < v >, \tag{4.6}$$

where we recall from Chapter 1 that  $\langle v \rangle = (8kT/\pi m)^{1/2}$ , where *m* is the mass of the gas molecules. This important equation gives the flux of molecules in a particular direction. Of course, for an isotropic gas, the flux of molecules has the same value in any direction, a conclusion that is clear from the fact that the right-hand side of **equation 4.6** does not depend on direction.

Suppose now that the molecules each carry an amount q of some property. Then the flux of that property will be simply the flux of molecules times the amount of the property each carries. In particular, for the +z direction,

$$J_{z} = \frac{1}{4} < v > n^{*}q.$$
 (4.7)

### **4.3.3** The Vertical Distance between Collisions

The next question we consider is the distance in the z direction traveled by the average molecule between collisions. Although the total average distance is the mean free path  $\lambda$ , the distance in the z direction will be somewhat shorter, since molecules with positive z component velocities move at a variety of angles  $\theta$  with respect to the z axis. The second result that we will derive from **equation 4.3** is that the average z distance between collision planes is  $2\lambda/3$ .

Let the slant length of the cylinder in **Figure 4.2** be  $v\Delta t = \langle v \rangle / Z_1 = \lambda$ . Then the vertical distance between the indicated plane and the plane in which the molecule last had its collision is  $\lambda \cos \theta$ . We wish to find the average of this quantity. Since **equation 4.3** gives the flux probability, the average of  $\lambda \cos \theta$  will simply be

$$<\lambda\cos\theta> = \frac{\int\lambda\cos\theta J(v,\theta,\phi)\,\mathrm{d}\tau}{\int J(v,\theta,\phi)\,\mathrm{d}\tau}$$

$$= \lambda \frac{\int_{0}^{\pi/2}\cos^{2}\theta\sin\theta\,\mathrm{d}\theta}{\int_{0}^{\pi/2}\cos\theta\sin\theta\,\mathrm{d}\theta} = \lambda \frac{\left[\frac{\cos^{3}\theta}{3}\right]_{0}^{\pi/2}}{\left[\frac{\cos^{2}\theta}{2}\right]_{0}^{\pi/2}} = \frac{2}{3}\lambda,$$
(4.8)

where the volume element abbreviated as  $d\tau$  is equal to  $v^2 \sin \theta \, d\theta \, d\phi \, dv$  and where the integral in the denominator is used for normalization. Consequently, we see that the average distance traveled in the z direction between collisions is  $2\lambda/3$ .

### 4.3.4 The General Flux Equation

To calculate the flux of the property q it is convenient to consider a plane located perpendicular to the direction of the gradient. Let the gradient be in the z direction, and let the plane be located at the arbitrary position  $z_0$ . As shown schematically in **Figure 4.3**, we calculate the net flux into the plane at  $z_0$  as the flux due to the



### Figure 4.3

Transport between layers separated by the mean free path.

upward motion of molecules that made their last collision in the plane at  $z_0 - 2\lambda/3$ and due to the downward motion of molecules that made their last collision in the plane at  $z_0 + 2\lambda/3$ . From **equation 4.7**, the flux from a plane at z is given by  $J_z = \frac{1}{4}n^*q < v >$ , where  $n^*$ , q, and < v > are evaluated at the position z. While assumption 2 enables us to treat < v > as constant, in principle both  $n^*$  and q can vary between planes. Introducing temporarily the notation  $\rho_q(z)$  as  $n^*q$  evaluated at location z, the upward flux of the property q is then given by  $J_{+z} = \frac{1}{4} < v > \rho_q(z_0 - 2\lambda/3)$ , where  $\rho_q(z_0 - 2\lambda/3)$  is the value of  $\rho_q = n^*q$  for upward traveling molecules that had their last collision in the plane at  $z_0 - 2\lambda/3$ . Similarly, the downward flux of the property is given by  $J_{-z} = \frac{1}{4} < v > \rho_q(z_0 + 2\lambda/3)$ . The net flux in the upward direction is then

$$J_{z} = J_{+z} - J_{-z}$$

$$= \frac{1}{4} < v > \left[ \rho_{q} \left( z_{0} - \frac{2\lambda}{3} \right) - \rho_{q} \left( z_{0} + \frac{2\lambda}{3} \right) \right].$$
(4.9)

If the gradient is constant or if its change is small over dimensions corresponding to the mean free path, then we may approximate  $\rho_q(z_0 \pm 2\lambda/3)$  by the first two terms in a Taylor series expansion about the position  $z_0$ :<sup>c</sup>

$$\rho_q \left( z_0 \pm \frac{2\lambda}{3} \right) \approx \rho_q(z_0) \pm \frac{2\lambda}{3} \left( \frac{\partial \rho_q}{\partial z} \right).$$
(4.10)

Substitution of equation 4.10 into equation 4.9 and replacement of  $\rho_q$  by  $n^*q$  yields

<sup>&</sup>lt;sup>c</sup>The Taylor series expansion for  $y(x_0 + \Delta x)$  is given as  $y(x_0 + \Delta x) = y(x_0) + \Delta x(dy/dx) + \frac{1}{2}(\Delta x)^2$  $(d^2y/dx^2) + \cdots$ , where the derivatives are evaluated at  $x = x_0$ . If (dy/dx) is nearly constant over the range of  $\Delta x$ , then  $(d^2y/dx^2)$  will be small and only the first few terms in the expansion will be needed.

$$J_{z} = \frac{1}{4} \langle v \rangle \left[ -\frac{4\lambda}{3} \left( \frac{\partial (n^{*}q)}{\partial z} \right) \right]$$
  
=  $-\frac{1}{3} \langle v \rangle \lambda \frac{\partial (n^{*}q)}{\partial z}.$  (4.11)

**Equation 4.11** will form the basis for much of our further discussion. At this point it is worthwhile to make two comments. First, the result does not depend on having a gradient that is independent of position. If the gradient is constant everywhere in space, then equations 4.10 and 4.11 are exact, but even if the gradient changes as a function of position, equation 4.11 will give an excellent approximation to the flux through the plane at  $z_0$  as long as the change in the gradient is small over distances within roughly one mean free path of  $z_0$ . Second, equation 4.11 suggests that a nonzero flux will result from either a gradient in the molecular density,  $n^*$ , or a gradient in the property q, or both. In our discussions of thermal conductivity and viscosity below, we will assume that there is no net movement of the molecules; that only the property  $q = \epsilon$  for thermal conductivity or  $q = mv_x$  for viscosity changes with position. In this case, since the number density does not change with position, we see that  $\partial(n^*q) = n^*\partial q$ . In the case of diffusion, however, the property in flux is the number density itself, so q = 1 and  $\partial(n^*q) = \partial n^*$ .

### 4.4 THERMAL CONDUCTIVITY

A fundamental observation in the development of the second law of thermodynamics is that heat flows from a hot body to a cold one. The phenomenological description of this flow was discussed in Section 4.2 and is embodied in the equation called Fourier's law:  $J_z = -\kappa (\partial T/\partial z)$ , where  $J_z$  is the flux of heat (energy) in the z direction and  $\kappa$  is the coefficient of thermal conductivity. Since the units of the flux are energy per area per time, we see that Fourier's law has dimensions (J m<sup>-2</sup> s<sup>-1</sup>) =  $\kappa$  (K m<sup>-1</sup>), or that the dimensions of  $\kappa$  are (J m<sup>-2</sup> s<sup>-1</sup>)/(K m<sup>-1</sup>) = J m<sup>-1</sup> s<sup>-1</sup> K<sup>-1.d</sup> Since 1 J of energy per second is also equal to 1 watt of power, alternative units for  $\kappa$  are W m<sup>-1</sup> K<sup>-1</sup>. **Table 4.2** gives some values for  $\kappa$ .

TABLE 4.2	Thermal Conductivity Coefficients, $\kappa$ , for Various Substances at 273 K and 1 atm	
	Substance	$\kappa (J m^{-1} s^{-1} K^{-1})$
	Cu	400
	Fe	80
	He	0.144
	Ar	0.0162
	N <sub>2</sub>	0.0237
	$\tilde{H_2}$	0.174
	$O_2$	0.0240
	$CO_2$	0.0142
	CH <sub>4</sub>	0.0300

<sup>d</sup>Kappa,  $\kappa$ , is used here for the thermal conductivity coefficient and should not be confused with the isothermal compressibility coefficient, which sometimes also uses this symbol.
## *example 4.2*

#### The Heat Flow through Fiberglass Insulation

Objective	Calculate the rate of heat loss through a wall insulated with fiber- glass. Let the wall be 3 m $\times$ 4 m, ignore the conductivity of any other wall materials, and take the thickness of the insulation to be 15 cm, the temperature difference between the inside and outside of the wall to be 10 K, and the coefficient of thermal conductivity for fiberglass to be 5 $\times$ 10 <sup>-2</sup> W m <sup>-1</sup> K <sup>-1</sup> .
Method	According to Fourier's law, the flux of energy is given by $J_z = -\kappa (\partial T/\partial z)$ . The flux is the heat per unit time, so that the total heat loss in watts (joules per second) is the area times the flux: $AJ_z$ .
Solution	The gradient is $-(10 \text{ K})/(0.15 \text{ m})$ , so that the total heat loss is $(3 \text{ m} \times 4 \text{ m})(5 \times 10^{-2} \text{ W m}^{-1} \text{ s}^{-1})(10 \text{ K})/(0.15 \text{ m}) = 40 \text{ W}.$

Of course, thermal conductivity is not the only method for heat transport. Heat is also transferred by radiation, as from the sun to Earth, or by convection, as in winds that move weather fronts. In our consideration of thermal conductivity, we will separate these processes and analyze the flow of heat (energy) in the absence of net movement of either photons or matter. To be sure, even in conduction the heat is transported by the movement of particles, usually by the motion of molecules, but, in metals, also by the motion of electrons. However, we will assume that there is no *net* molecular motion in conductivity. Thus, the conducted heat moves like the baton in a relay race; it is passed from one particle to another. This view is true, and the macroscopic equations valid, for heat flow through solids, liquids, or gases. In the latter case, however, we can easily come to a microscopic understanding of the coefficient of thermal conductivity.

The kinetic theory that we have developed describes the collisions that provide the opportunity for gases to exchange energy, so that **equation 4.11** should predict the essential features of thermal conductivity in gases, subject to the simplifying assumptions made in the last section. The property transported by the molecules is their energy,  $\epsilon$ , and by assumption 4, this energy is equilibrated at every collision. If we assume no net motion of the molecules, then  $\partial(n^*q) = n^*\partial q$ . If the energy per mole is  $q = U/N_A = \epsilon$ , **equation 4.11** then becomes

$$J_{z} = -\frac{1}{3}n^{*}\lambda \langle v \rangle \left(\frac{\partial \epsilon}{\partial z}\right).$$
(4.12)

Recalling from Chapter 1, Section 1.6, that  $(\partial U/\partial T)_v = C_v$ , the constant volume molar heat capacity, we write the gradient  $(\partial \epsilon/\partial z)$  as

$$\frac{\partial \epsilon}{\partial z} = \frac{1}{N_{\rm A}} \frac{\partial U}{\partial z}$$

$$= \frac{1}{N_{\rm A}} \frac{\partial U}{\partial T} \frac{\partial T}{\partial z}$$

$$= \frac{C_{\rm V}}{N_{\rm A}} \frac{\partial T}{\partial z}.$$
(4.13)

#### Chapter 4 Transport Properties

Thus,

$$J_{z} = -\frac{1}{3}n^{*}\lambda < v > \frac{C_{v}}{N_{A}} \left(\frac{\partial T}{\partial z}\right).$$
(4.14)

Comparison of equation 4.14 with Fourier's law yields

$$\kappa = \frac{1}{3}n^*\lambda \langle v \rangle \frac{C_{\rm V}}{N_{\rm A}}.$$
(4.15)

This expression for the thermal conductivity coefficient may be simplified by using equation 1.47, repeated here for use with a single component so that  $n_2^* = n^*$  and  $b_{max} = d$ , the molecular diameter:

$$\lambda = \frac{1}{\sqrt{2\pi}d^2n^*}.$$
(4.16)

Substitution of equation 4.16 into equation 4.15 yields

$$\kappa = \frac{\langle v \rangle C_{\rm V}}{3\sqrt{2\pi}d^2 N_{\rm A}}.\tag{4.17}$$

Note that the result for  $\kappa$  is independent of pressure because the  $n^*$  dependence in the general expression for the flux and the  $1/n^*$  dependence of the mean free path exactly cancel one another. A qualitative explanation for the cancellation is that, while there are fewer molecules crossing a given area per unit time at low pressure, they travel a longer distance between collisions. Although it is found experimentally that  $\kappa$  is independent of pressure over most pressures of interest, this independence breaks down at very high pressures where the molecules no longer behave like an ideal gas and at very low pressures where the mean free path reaches macroscopic dimensions. In the latter case, truncation of the Taylor expansion used in **equation 4.10** is no longer valid after two terms. At extremely low pressures, the mean free path is limited only by collision at the cold surface or the hot surface, and the thermal conductivity coefficient is then directly proportional to  $n^*$ .

It is important to comment that the heat capacity for a real molecule is larger than that for a monatomic ideal gas:  $C_V > 3R/2$ . The reason, of course, is that real molecules have rotational and vibrational degrees of freedom in addition to translational ones. While many vibrational motions are of high enough frequency not to contribute to the heat capacity, the rotational degrees of freedom contribute *R* per mole for diatomic molecules and 3R/2 per mole for polyatomic ones.

## example 4.3

The Thermal	Conductivity Coefficient of N <sub>2</sub> at 273 K and 1 atm
Objective	Estimate the thermal conductivity coefficient of $N_2$ at 1 atm and 273 K, given that the molecular diameter of $N_2$ is 370 pm.
Method	Use equation 4.17 recalling that $C_{\rm V} \approx 5R/2$ .
Solution	First calculate $\langle v \rangle = (8kT/\pi m)^{1/2}$ :

$$= (8kT/\pi m)^{1/2}$$

$$= \left\{ \frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(273 \text{ K})(6.02 \times 10^{23} \text{ amu/g})(1000 \text{ g/kg})}{[3.1415 (28 \text{ amu})]} \right\}^{1/2}$$

$$= 454 \text{ m/s}$$
(4.18)
Then evaluate  $C_V = 5R/2 = 5(8.314 \text{ J mol}^{-1} \text{ K}^{-1})/2 = 20.8 \text{ J}$ 
mol<sup>-1</sup> K<sup>-1</sup>.
Finally,
$$\kappa = \frac{(454 \text{ m/s})(20.8 \text{ J/mol})}{3\sqrt{2}\pi(6.02 \times 10^{23} \text{ molec/mol})(370 \times 10^{-12} \text{ m})^2}$$

$$= 8.59 \times 10^{-3} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}.$$
Comment
Note that the information that the pressure is 1 atm is irrelevant to the solution. Since we used approximations in arriving at equation 4.17 and in evaluating the heat capacity, the answer is not exactly equal to the measured value listed in Table 4.2.

#### 4.5 VISCOSITY

Most people are familiar with the viscous drag of water impeding a swimmer or air impeding a plane. What are the causes of these forces and how can we understand them at a molecular level? Consider two plates of area A separated by a distance in the z direction and immersed in a fluid, as shown in **Figure 4.4.** If the upper plate is drawn through the fluid with a velocity  $v_x$  while the lower plate is stationary, then there will be a force exerted on the lower plate in the x direction due to the frictional



Figure 4.4

The viscous force on a stationary plate exerted by a moving one.

#### Chapter 4 Transport Properties

drag of the fluid; an equivalent force in the negative x direction will have to be applied to hold the lower plate stationary. The force transmitted downward to the stationary plate will be proportional to the area A and is given by Newton's law of viscosity:  $F_x = -\eta A(\partial v_x/\partial z)$ , where the constant  $\eta$  is called the coefficient of viscosity. From Newton's law we recall that F = ma = dp/dt, where p is the momentum, so that the force transferred per unit area is the same as momentum transferred per unit time per unit area, or momentum flux. Thus, the gradient in velocity (or the proportional gradient in momentum) between the two plates causes a flux of momentum that is transmitted by the fluid. Note that, while the momentum and force are in the x direction, the *flux* of momentum is in the z direction:  $J_z = F_x/A = -\eta(\partial v_x/\partial z)$ .

The units of the flux are momentum per second per area or, equivalently, force per area, so that the flux equation has dimensions (force/area) =  $\eta$  (distance/time)/distance. Thus, the units of  $\eta$  are (force/area)/(1/time) or N m<sup>-2</sup> s. A pascal of pressure is also a N m<sup>-2</sup>, so that equivalent units for  $\eta$  are Pa s. In older texts, one often encounters the cgs unit for  $\eta$  called a poise; 1 poise = 1 dyne cm<sup>-2</sup> s = 1 gm cm<sup>-1</sup> s<sup>-1</sup> = 0.1 N m<sup>-2</sup> s.

**Table 4.3** provides some viscosity coefficient data for a few materials. Note that both liquids and gases obey the macroscopic viscosity equation. We will focus first on gases and return to the frictional forces in liquids later in this chapter.

In the case of gases and under the assumptions listed in Section 4.3.1, the transfer of momentum must be described by the general flux equation 4.11, with  $q = mv_x$ . We again assume that there is no net transport of molecules, so that  $\partial(n^*q) = n^* \partial q$ . Substitution of  $q = mv_x$  leads to

$$U_z = -\frac{1}{3}n^* < v > \lambda m \left(\frac{\partial v_x}{\partial z}\right), \qquad (4.20)$$

so that

$$\eta = \frac{1}{3} n^* \langle v \rangle \lambda m. \tag{4.21}$$

Note that since  $\lambda$  is proportional to  $1/n^*$ , the viscosity coefficient will be independent of pressure. This prediction was one of the early triumphs of the kinetic theory

#### TABLE 4.3 Viscosity Coefficients at 273 K for Various Substances

 Substance	η (Pa s)	
Glycerol	0.95	
Olive oil	0.08	
Water, liquid, 298 K	$0.9  imes 10^{-3}$	
Не	$18.8  imes 10^{-6}$	
$\mathbf{H}_2$	$8.4  imes 10^{-6}$	
Ar	$22.2  imes 10^{-6}$	
<b>O</b> <sub>2</sub>	$19.2  imes 10^{-6}$	
$\tilde{CO_2}$	$13.8  imes 10^{-6}$	
$\mathbf{N}_2$	$16.6  imes 10^{-6}$	
NH <sub>3</sub>	$9.2 \times 10^{-6}$	
CH <sub>4</sub>	$10.3 \times 10^{-6}$	

of gases. An alternative formulation of equation 4.21 recognizes that the density  $\rho$ is equal to the product of the number density  $n^*$  and the mass m, so that

$$\eta = \frac{1}{3}\rho < v > \lambda. \tag{4.22}$$

Again, while the numerical factors in these equations are incorrect, the functional form is correct. However, little is gained by using the correct hard-sphere numbers since real molecules do not behave like hard spheres.

Equations 4.21 and 4.22 provide a convenient method for estimation of molecular diameters. Substitution of equation 4.16 into equation 4.21, for example, leads to

$$\eta = \frac{\frac{1}{3}n^* < v > m}{\sqrt{2}\pi d^2 n^*},$$
(4.23)

or

$$d = \left(\frac{\langle v \rangle m}{3\sqrt{2}\pi\eta}\right)^{1/2}.$$
(4.24)

Example 4.4 illustrates this calculation.

#### **Finding Molecular Diameters from Viscosity Coefficients**

Objective Given that the viscosity coefficient for argon at 298 K is 22.2 imes $10^{-6}$  Pa s, calculate its molecular diameter.

Method Use equation 4.24 after calculating  $\langle v \rangle$ .

Solution First, calculate  $\langle v \rangle = (8kT/\pi m)^{1/2}$ :

$$= (8kT/\pi m)^{1/2}$$

$$= \left[\frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})(6.02 \times 10^{23} \text{ amu/g})(1000 \text{ g/kg})}{(\pi 40 \text{ amu})}\right]^{1/2}$$
  
= 397 m/s. (4.25)

= 397 m/s.

Then calculate d:

$$d = \left[\frac{\langle v \rangle m}{(3\sqrt{2}\pi\eta)}\right]^{1/2}$$
  
=  $\left[\frac{(397 \text{ m/s})(40 \text{ amu})}{3\sqrt{2}\pi(6.02 \times 10^{23} \text{ amu/g})(1000 \text{ g/kg})(22.2 \times 10^{-6} \text{ N s m}^{-2})}\right]^{1/2}$   
= 299 pm. (4.26)

#### Chapter 4 Transport Properties

Although there are other methods for measuring the viscosity coefficient of a fluid, one convenient technique is to determine the volume of the fluid that passes by a unit area of a tubing per unit time; i.e., the volume flux. We have already seen in the opening section of this chapter that this flux is proportional to the product of the pressure gradient and a conductivity coefficient:  $J_z = -C(\partial p/\partial z)$ , where C depends on the nature of the fluid and the size of the tubing. The dependence on the nature of the fluid comes about because, while the fluid has a finite velocity in the center of the tube, the molecules in contact with the edges of the tube must have zero velocity. Consequently, C should be inversely proportional to the viscosity coefficient of the fluid. A detailed calculation shows that  $C = a^2/8\eta$ , where a is the radius of the tube. The volume of liquid passing through the tube per unit time is given simply by the volume flux times the area of the tube:  $J_z A = dV/dt = -CA(\partial p/\partial z) = -(\pi a^4/8\eta)(\partial p/\partial z)$ . This last expression, whose complete derivation is given in Appendix 4.1, is perhaps the most useful form of the *Poiseuille formula* describing the laminar flow of a liquid:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = -\frac{\pi a^4}{8\eta} \left(\frac{\partial p}{\partial z}\right). \tag{4.27}$$

It enables determination of the viscosity coefficient from a measurement of the rate of volume change. An alternative form of the Poiseuille formula is obtained by multiplying both sides of **equation 4.27** by the liquid's density,  $\rho$ :

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -\frac{\pi a^4 \rho}{8\eta} \left(\frac{\partial p}{\partial z}\right). \tag{4.28}$$

Using the P	oiseuille Formula	
Objective	Find the viscosity coefficient of a liquid flowing through a tub 0.1 cm in radius and 50 cm in length. When the pressure dro across the tube is 0.1 atm, the volume of liquid emerging from th tube is 1 cm <sup>3</sup> /s.	
Method	Since we know the flow rate and the pressure gradient, we can use Poiseuille's formula, <b>equation 4.27</b> , to calculate the viscosity coefficient.	
<b>Solution</b> The flow rate is $dV/dt = 1 \text{ cm}^3 \text{ s}^{-1} = 10^{-6} \text{ m}^3 \text{ s}^{-1}$ . T gradient is $(0.1 \text{ atm})/(0.50 \text{ m}) = 0.2 \text{ atm m}^{-1}$ . The Poiseuille formula, $\eta$ is		
	$\eta = rac{(\pi r^4/8)(\partial p/\partial z)}{(\mathrm{d} V/\mathrm{d} t)}$	
	$=\frac{\pi(0.001 \text{ m})^4(0.2 \text{ atm/m})(101.3 \times 10^3 \text{ Pa/1 atm})}{8(10^{-6} \text{ m}^3 \text{ s}^{-1})} $ (4.29)	
	$= 7.96 \times 10^{-3} \mathrm{Pa}\mathrm{s}.$	
	The liquid might very well be olive oil (See Table 4.3).	

While **equations 4.27** and **4.28** are useful for liquids, where the density is rather insensitive to pressure, for gases the density changes dramatically with pressure:  $\rho = Mp/RT$ , where *M* is the molecular weight of the gas. Substitution for  $\rho$  and recognition that n = m/M gives

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{\pi a^4}{8\eta RT} \left( p \frac{\partial p}{\partial z} \right). \tag{4.30}$$

Because the number of moles of gas crossing any area per unit time, dn/dt, is constant, it must also be true that p(dp/dz) is a constant. If we call the constant *B*, then p dp = Bdz. Integration gives  $p^2 = 2Bz + C$ . Applying this equation to pressures  $p_1$  at  $z_1$  and  $p_2$  at  $z_2$  yields two equations:  $p_1^2 = 2Bz_1 + C$  and  $p_2^2 = 2Bz_2 + C$ , where *C* is a constant of integration. Subtraction gives  $B = (p_2^2 - p_1^2)/2(z_2 - z_1)$ , so that for gases

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{\pi r^4}{16\eta RT} \left(\frac{p_2^2 - p_1^2}{z_2 - z_1}\right).$$
(4.31)

#### 4.6 **DIFFUSION**

Anyone whose nose is in working order can attest to the fact that diffusion is an important process. The kitchen smells that woke us in the morning as children or the fragrance from an opened bottle of perfume reach us even if there are no convective currents in a room. The mixing process is spontaneous, but the rate of interdiffusion of two substances has yet to be discussed. Experimental observation shows that diffusion in fluids against a gradient obeys Fick's law, whose form is by now quite familiar:  $J_z = -D(\partial n^*/\partial z)$ , where  $J_z$  is the flux of molecules,  $(\partial n^*/\partial z)$  is the gradient in number density, and D is the diffusion coefficient. Dimensionally, the equation is (number time<sup>-1</sup> area<sup>-1</sup>) =  $D \times (\text{number/volume})/\text{distance}$ , so that the dimensions of D are thus distance<sup>2</sup> per unit time, or  $m^2 s^{-1}$ . Because the diffusion of one substance into another can depend on the properties of each substance, it will be useful to add subscripts to D. Let  $D_{12}$  be the coefficient describing the diffusion of type 1 into molecules of type 2 and let  $D_{11}$  be the diffusion coefficient for diffusion of molecules of type 1 into other molecules of the same type. One might well wonder how the latter coefficient could be measured; indeed, it cannot. But  $D_{11}$  can be approached quite closely by studying the diffusion of one isotope of a substance in another isotope of the same substance. Table 4.4 lists some typical diffusion coefficients.

TABLE 4.4	Diffusion Coefficients at 273 K and 1 atm for Various Substances		
	Substances	$D_{11}$ or $D_{12}$ (m <sup>2</sup> s <sup>-1</sup> )	
	$H_2-H_2$	$1.5 \times 10^{-4}$	
	$O_2 - O_2$	$1.9 imes10^{-5}$	
	$N_2 - N_2$	$1.5  imes 10^{-5}$	
	$CO_2$ - $CO_2$	$1.0 imes10^{-5}$	
	Xe–Xe	$5.0 imes10^{-6}$	
	$O_2 - N_2$	$1.8  imes 10^{-5}$	
	O <sub>2</sub> -CO <sub>2</sub>	$1.4 imes10^{-5}$	

example 4.6

## The Number of $O_2$ Molecules Crossing an Area per Second While Diffusing through $N_2$

Objective	Find the number of $O_2$ molecules diffusing through $N_2$ molecules and crossing a 0.2 m <sup>2</sup> area at 273 K if the concentration gradient is 40 torr per centimeter and the diffusion coefficient is that given in <b>Table 4.4</b> .
Method	Use the diffusion equation, $J_z = -D(\partial n^*/\partial z)$ , to calculate the flux. The number crossing the given area is then the flux times the area.
Solution	The diffusion coefficient for O <sub>2</sub> -N <sub>2</sub> is $D = 1.8 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ . Since $p = nRT/V$ , we can convert the pressure gradient to a number density gradient by dividing the pressure by <i>RT</i> . The gradient is thus calculated to be $\frac{\partial n^*}{\partial z}$
$=\frac{(40 \text{ torr/cm})(1)}{100000000000000000000000000000000000$	$\frac{\text{atm}/760 \text{ torr})(100 \text{ cm}/\text{m})(6.02 \times 10^{23} \text{ molecules mole}^{-1})(10^{3} \text{ L/1 m}^{3})}{(0.082 \text{ L atm mole}^{-1} \text{ K}^{-1})(273 \text{ K})}$
= $1.42 \times 10^{26} (\text{molecules/m}^3) \text{m}^{-1}$ .	
	Thus, the flux is $J_z = -(1.8 \times 10^{-5} \text{ m}^2 \text{ s}^{-1})[1.42 \times 10^{26} \text{ (molecules/m}^3) \text{ m}^{-1}]$
	$= -2.55 \times 10^{21} \text{ molecules s}^{-1} \text{ m}^{-2}. $ (4.33)
	The number crossing the area of 0.2 m <sup>2</sup> per unit time is then the flux times the area, or $(0.2 \text{ m}^2)(2.55 \times 10^{21} \text{ molecules s}^{-1} \text{ m}^{-2}) = 5.10 \times 10^{20} \text{ molecules/s}.$

Like thermal conductivity and viscosity, diffusion in gases can be understood by the application of kinetic theory. In this case, however, we must focus on the motion of the molecules themselves. Because their number density changes with position we cannot bring  $n^*$  out of the differential  $\partial(n^*q)$  in **equation 4.11**, and because it is the molecules themselves that are being transported, q = 1 and the flux is the flux of molecules. **Equation 4.11** then becomes

$$J_{z} = -\frac{1}{3} < v > \lambda \left(\frac{\partial n^{*}}{\partial z}\right), \qquad (4.34)$$

and comparison with Fick's first law,  $J_z = -D(\partial n^*/\partial z)$ , shows that

$$D = \frac{1}{3} \langle v \rangle \lambda. \tag{4.35}$$

As might be expected from the severity of the approximations made in Section 4.3.1, the numerical factor in equation 4.35 is incorrect, even for hard spheres, but our understanding of the underlying science is enhanced little by correcting it. It is worth noting, however, that the value of the mean free path depends on whether we are considering the diffusion of a molecule of type 1 into other molecules of type 1 or into molecules of another type, 2. For so-called selfdiffusion, the mean free path is given by equation 4.16, since this equation describes how far a molecule travels before colliding with another of the same type. For one molecule of type 1 diffusing through molecules of type 2, however, we must review the derivation of presented in Section 1.7 just prior to equation 1.47. If the mean free path for a type 1 molecule in molecules of the same type is  $\lambda = \overline{c}/Z_1$ , then the mean free path for a type 1 molecule in molecules of type 2 should be  $\lambda = \bar{c}/Z_2 = \bar{c}/[\pi b_{\max}^2 v_r n_2^*]$ . Note that although the calculation of  $\bar{c}$ involves the mass of molecules of type 1, the calculation of  $v_r$  involves the reduced mass. Furthermore,  $b_{max}$  is the average of the diameters of molecules of type 1 and 2. Thus, the mean free path will depend on the properties of both types of molecules. In real systems, molecules of type 1 will diffuse both through others of the same type and through those of type 2, so that the mean free path is somewhat more complicated than that in either of the above calculations; it depends inversely on the total number density, not just on the number density of type 2 molecules.

#### Calculating the Diffusion Coefficient for N<sub>2</sub>

Objective	Approximate the diffusion coefficient of $N_2$ in $N_2$ at 300 K and 1 atm given that the molecular diameter is 218 pm (see Example 1.7).
Method	Use equation 4.35, noting that under these conditions we have calculated in Example 1.7 the mean free path of N <sub>2</sub> as $3.87 \times 10^{-7}$ m and the average velocity as 673 m/s.
Solution	$D = (1/3)v\lambda = (1/3)(673 \text{ m/s})(3.87 \times 10^{-7} \text{ m}) = 8.68 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}.$
Comment	That this value is higher than that listed in <b>Table 4.4</b> is due only partly to the fact that $v$ and $\lambda$ are higher at 300 K than at 273 K. Because we have made several simplifying approximations, equation 4.35 is not expected to be numerically accurate.

#### 4.7 TIME-DEPENDENT TRANSPORT

We have assumed in the preceding sections that the gradient of temperature, momentum, or concentration was steady in time. For example, in the case of diffusion we see from  $J_z = -D(\partial n^*/\partial z)$  that if the gradient of concentration is steady in time then the flux of particles will also be steady. We now address the situation in which the gradient changes in time, as it might, for example, if a drop of one material were introduced into another or if heat were momentarily applied to one end of a rod of conductive material. In both cases we see that the gradient is large immediately after the perturbation, but that the diffusion of molecules or the flow of heat tends to cause the gradient to diminish as time progresses.

example 4.7

#### Chapter 4 Transport Properties

To be able to describe these processes, we introduce a notation that recognizes that the flux can depend both on position and on time, J = J(z,t). The time dependent flux can be related to the gradient by considering two surfaces of area A separated by a distance  $\Delta z$ , as shown in **Figure 4.5.** Suppose that molecules are diffusing in the positive z direction. What is the change of concentration in the volume  $A\Delta z$  per unit time? The concentration is increased by the number of molecules that flow into the volume from below. Because J(z,t) is the number of molecules per unit time per unit area that cross the plane located at z, the change in concentration is given by J(z,t) times A divided by the volume:  $\partial n^*(z,t)/\partial t = J(z,t)A/A\Delta z = J(z,t)/\Delta z$ , where the dependence of  $n^*$  on z and t is made clear by the notation  $n^*(z,t)$ . Similarly, the concentration is decreased by the molecules that flow out of the volume to regions above; the change is given by  $\partial n^*(z,t)/\partial t = -J(z + \Delta z, t)A/A\Delta z = -J(z + \Delta z, t)/\Delta z$ . Thus, the net rate of concentration change is

$$\frac{\partial n^*(z,t)}{\partial t} = \frac{J(z,t) - J(z + \Delta z, t)}{\Delta z}$$
(4.36)

In the limit when  $\Delta z$  is very small, the quantity on the right-hand side of **equation** 4.36 is simply  $-\partial J(z,t)/\partial z$ , so that

$$\frac{\partial n^*(z,t)}{\partial t} = -\frac{\partial J(z,t)}{\partial z}.$$
(4.37)

At any time t, however, the flux is related to the number density gradient, as we have seen in the previous section:

$$J(z,t) = -D \frac{\partial n^*(z,t)}{\partial z}.$$
 (4.38)



The change in flux with time.

If we take the partial derivative of both sides of equation 4.38 with respect to z, we obtain

$$\frac{\partial J(z,t)}{\partial z} = -D \frac{\partial^2}{\partial z^2} n^*(z,t).$$
(4.39)

Finally, using equation 4.37 we see that equation 4.39 can be rewritten as

$$\frac{\partial n^*(z,t)}{\partial t} = D \frac{\partial^2}{\partial z^2} n^*(z,t).$$
(4.40)

Equation 4.40 is known as the *time-dependent diffusion equation* or as Fick's second law.

Consider the diffusion of N molecules that start at  $z = z_0$  at t = 0 in the crosssectional area A of a tube of infinite length. How will this distribution change in space as a function of time? The solution to **equation 4.40**, as shown in Problem 4.16, is

$$n^{*}(z,t) = \frac{N}{A} \frac{1}{2\sqrt{\pi Dt}} \exp\left[-\frac{(z-z_{0})^{2}}{4Dt}\right].$$
 (4.41)

Figure 4.6 displays the concentration profile predicted by equation 4.41 for different values of *Dt*. With increasing time, the concentration spreads over larger distances. In fact, if we normalize the right-hand side of equation 4.41 (which amounts to multiplication by A/N) we will obtain a function that gives the probability that a molecule will be found at a position z at a time t. This function is thus a distribution function for the position at a particular time, and we can use it to calculate average positions. Of course, because the distribution function is symmetric around  $z_0$ , the average distance that a molecule has traveled from that position after a time t is zero.



#### Figure 4.6

Plot of  $n^*(z,t)$  following diffusion from a starting condition where all molecules are at z = 0 at t = 0.

#### Chapter 4 Transport Properties

It is useful, however, to calculate the root-mean-squared distance,  $z_{\rm rms} = \langle (z - z_0)^2 \rangle^{1/2}$ . Using **Table 1.1** to evaluate the integral, this distance is given by

$$[z_{\rm rms}]^2 = \int_{-\infty}^{\infty} (z - z_0)^2 \frac{1}{2\sqrt{\pi Dt}} \exp\left[-\frac{(z - z_0)^2}{4Dt}\right] dz$$
  
=  $\frac{1}{2\sqrt{\pi Dt}} 2\frac{1}{4}\sqrt{\pi} (4Dt)^{3/2}$  (4.42)  
=  $2Dt$ .

so that

$$z_{\rm rms} = (2Dt)^{1/2}.$$
 (4.43)

We thus see that the root-mean-squared distance that a molecule diffuses is proportional to the square root of the diffusion coefficient and to the square root of the time.

example 4.8

The rms Distance Traveled by a Molecule in a Day			
Objective	Find the rms distance that a molecule of naphthalene travels by diffusion in 1 day through the atmosphere assuming the diffusion coefficient is $1.5 \times 10^{-6}$ m <sup>2</sup> s <sup>-1</sup> . Naphthalene is the principal component in moth balls.		
Method	Use <b>example 4.43</b> , but recognize that this is a three-dimensional problem and not merely a one-dimensional one.		
Solution	Note that the square of the distance from the center of a three- dimensional object is $r^2 = x^2 + y^2 + z^2$ , so that $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3 \langle z^2 \rangle$ . One day is (24 hr)(60 min/hr)(60 s/min) = 8.64 × 10 <sup>4</sup> s. Thus $(z_{\rm rms})^2 = (2Dt)$ or $(r_{\rm rms})^2 = (6Dt) = [6(1.5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1})(8.64 \times 10^4 \text{ s})] = 0.78 \text{ m}^2$ or $r_{\rm rms} = 0.88 \text{ m}$ .		
Comment	Note that molecules do not travel far in a day by diffusion. Convection is more often the mode of transport.		

We can gain some physical insight into diffusion by considering a process known as the *one-dimensional random walk*. Consider a molecule constrained to move in the z direction in steps of length  $\ell$ , and suppose that after each step the molecule has no memory of which direction it traveled in previous steps; its choice of direction for the next step is completely random. On average, what will be the rootmean-squared position of the molecule with respect to its original position after it has taken N steps?

While this problem can be solved mathematically in closed form, the solution is somewhat complex (see Problem 4.18). It is far easier to write a simple computer program to predict the position. Given a position of  $z_i$  after the *i*th step, the position after the (i + 1)th step is given by

$$z_{i+1} = z_i + \ell \operatorname{sign}[\operatorname{RND}() - 0.5],$$
 (4.44)

where RND() is a random number between 0 and 1 and sign[] is a function that is equal to +1 if the argument is nonnegative and -1 otherwise.

**Figure 4.7** displays the results of six random walks starting at a position  $z_0$ . Note that the positions of the particles spread out with increasing number of steps. If we run, say, 1000 trajectories we can compute an accurate average for the root-mean-squared displacement from  $z_0$  as a function of the number of steps. This average for a typical calculation is shown in **Figure 4.8**, which demonstrates that the root-mean-squared displacement in units of  $\ell$  is equal to the square root of the number of steps.



Figure 4.7

Random walks: the position as a function of the number of steps for six one-dimensional random walks.



#### Figure 4.8

Root-mean-squared distance traveled as a function of the square root of the number of steps for a one-dimensional random walk.

#### Chapter 4 Transport Properties

What we learn from this computer experiment (or from the more rigorous closed-form solution derived in Problem 4.18) is that molecular diffusion is just like a random walk in one dimension. Let the total time for N steps be equal to N times the average time per step,  $\tau$ :  $t = N\tau$  or  $N = t/\tau$ . The observation from our computer experiment is that  $(z_{\rm rms})^2 = N\ell^2$ , or  $(z_{\rm rms})^2 = \ell(\ell/\tau)t$ . The expression

$$z_{\rm rms} = (\ell^2 t / \tau)^{1/2}$$
(4.45)

is known as the *Einstein-Smoluchowski* equation.<sup>e</sup> We can interpret it as follows. Note that  $\ell/\tau = \langle v \rangle$ , the average velocity, so that  $z_{\rm rms} = [\ell \langle v \rangle t]^{1/2}$ . If we take the step size in the z direction to be that calculated in **equation 4.8**, we find that  $z_{\rm rms} = [(2/3)\lambda \langle v \rangle t]^{1/2}$ , or, using **equation 4.35**,  $z_{\rm rms} = [2Dt]^{1/2}$ . This last equation is exactly what we have calculated in **equation 4.43**.

In retrospect, it should come as no surprise that the one-dimensional random walk agrees with our diffusion calculation. Assumption 4 in Section 4.3.1 made the approximation that complete equilibrium is attained after every collision. When applied to the motion of molecules, this assumption means that there should be no preferential direction for the velocity after any collision. Thus, the assumption that leads to **equation 4.43** and the assumption of a random walk are equivalent. Both are slightly in error when compared to the real situation, but both capture the essential physical situation.

#### 4.8 SUMMARY

By assuming that the motion of molecules is responsible for the transport of properties such as heat, momentum, and concentration in gases, we have found how the constants  $\kappa$ ,  $\eta$ , and D in the flux equations for these properties depend on microscopic molecular properties. The relationships were found by making four simplifying assumptions in Section 4.3.1 and by treating the motion of molecules using the kinetic theory developed in Chapter 1. We found that the flux of molecules across a surface is given by

$$J_z = \frac{1}{4} n^* < v >$$
 (4.6)

and that the average vertical distance between collisions is  $2\lambda/3$ . Armed with these equations, we showed that when the gradient is constant in time, the flux of a property q in the vertical direction is given by

$$J_z = -\frac{1}{3} \langle v \rangle \lambda \frac{\partial (n^* q)}{\partial z}.$$
(4.11)

Use of this equation with q equal to  $\epsilon$ ,  $p_x$ , or 1 gave equations for the following coefficients:

Thermal Conductivity:

$$\kappa = \frac{1}{3}n^*\lambda < v > \frac{C_V}{N_A} = \frac{ C_V}{3\sqrt{2}\pi d^2 N_A},$$
(4.17)

<sup>&</sup>lt;sup>e</sup>A. Einstein, Ann. d. Physik 17, 549 (1905); 19, 371 (1906); M. v. Smoluchowski, Ann. d. Physik 21, 756 (1906).

Viscosity:

$$\eta = \frac{1}{3}n^* \langle v \rangle \lambda m, \qquad (4.21)$$

and Diffusion:

$$D = \frac{1}{3} \langle v \rangle \lambda. \tag{4.35}$$

It is important to remember that, although these equations capture the essential features of transport properties, the numerical coefficients are not quite correct. Those seeking more accurate formulas are referred to one of the texts listed in the reading list at the end of this chapter.

When the gradient is not constant in time we found, using diffusion as an example, that the derivative of the quantity with time was proportional to the second derivative of the quantity in space:

$$\frac{\partial n^*(z,t)}{\partial t} = D \frac{\partial^2}{\partial z^2} n^*(z,t).$$
(4.40)

For a starting condition in which all the molecules have a specified z component at time zero, the root-mean-squared distance traveled as a function of time is given by

$$z_{\rm rms} = (2Dt)^{1/2}.$$
 (4.43)

Diffusion of molecules in a gas is analogous to a one-dimensional random walk.

## appendix 4.1

#### The Poiseuille Formula

Consider the flow of a fluid through a cylindrical tube of radius a whose axis is coincident with the x direction and which is subject to a pressure gradient along its length. The velocity of the fluid will be a function of the radial position r from the center of the tube. Molecules at r = a will be in contact with the surface of the tube and will have zero velocity in the x direction, while those in the center of the tube at r = 0 will have the largest velocity. The volume V of fluid passing a cross-sectional area of the tube per unit time is given by integrating the area of coaxially concentric shells of thickness dr times the velocity in each shell:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \int_{0}^{a} v_{x}(r)(2\pi r) \,\mathrm{d}r, \qquad (4.46)$$

where  $2\pi r dr$  is the area of the shell and  $v_x(r)$  is the velocity in the x direction as a function of r. To perform the integration, we first need to determine  $v_x(r)$ .

To evaluate the radial dependence of the velocity, consider a small cylindrical volume element of the fluid coaxial with the x axis, as shown in **Figure 4.9**. The cross-sectional area of the cylinder is  $\pi r^2$ , and the length is dx. The pressure on the left side of the volume is p, while that on the right side is p - dp. When the pressure differential is constant in time, the velocity of the fluid through the cylinder will be constant; its acceleration will be zero. From Newton's law, zero acceleration



#### Figure 4.9

The force due to the pressure differential is equal and opposite to the force due to the viscous drag.

means that the total force on the fluid is zero. A fluid in the volume will thus accelerate its flow in the +x direction until the force in the -x direction due to its viscous drag is exactly equal to the force due to the pressure differential. The force due to the pressure differential is the area times dp:  $F_{+x} = \pi r^2 dp$ . The force in the -x direction can be calculated from the flux of momentum in the r direction,  $J_r = -\eta(\partial v_x/\partial r)$ , so that  $F_{-x} = J_r A = -\eta(\partial v_x/\partial r) 2\pi r dx$ , where  $A = 2\pi r dx$  is the surface area of the outside of the cylinder. Thus

$$\pi r^{2} dp = -\eta 2\pi r dx \frac{\partial v_{x}}{\partial r},$$

$$\frac{\partial v_{x}}{\partial r} = -\frac{r}{2\eta} \frac{dp}{dx}.$$
(4.47)

This equation can be integrated to give

$$v_x = -\frac{r^2}{4\eta}\frac{\mathrm{d}p}{\mathrm{d}x} + C, \qquad (4.48)$$

where C, the constant of integration, can be evaluated by the boundary condition that the velocity is zero at the wall of the cylinder:  $v_x(a) = 0$ . The result is

$$v_x = -\frac{a^2 - r^2}{4\eta} \frac{\mathrm{d}p}{\mathrm{d}x}.$$
(4.49)

Figure 4.10 shows the velocity distribution predicted by equation 4.49.



#### Figure 4.10

The velocity distribution of a fluid in a cylindrical tube.

We now substitute equation 4.49 into equation 4.46 and integrate:

$$\frac{dV}{dt} = \int_{0}^{a} \frac{a^{2} - r^{2}}{4\eta} \frac{dp}{dx} (2\pi r) dr$$

$$= \frac{2\pi}{4\eta} \frac{dp}{dx} \left[ \frac{a^{2}r^{2}}{2} - \frac{r^{4}}{4} \right]_{0}^{a}$$

$$= \frac{\pi a^{4}}{8\pi} \frac{dp}{dx}.$$
(4.50)

This last equation is simply the Poiseuille formula given in equation 4.27 with the pressure gradient in the x direction rather than the z direction.

### suggested readings

- R. S. Berry, S. A. Rice, and J. Ross, *Physical Chemistry* (Wiley, New York, 1980).
- J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
- W. Kauzmann, Kinetic Theory of Gases (W. A. Benjamin, New York, 1967).
- E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1938).
- L. B. Loeb, *The Kinetic Theory of Gases* 3rd ed. (Dover, New York, 1961).
- F. R. W. McCourt, J. J. M. Beenakker, W. E. Köhler, and I. Kuscer, *Non-equilibrium Phenomena in Polyatomic Gases* (Clarendon Press, Oxford, 1990), Chapter 6.
- R. D. Present, *Kinetic Theory of Gases* (McGraw-Hill, New York, 1958).

## problems

- 4.1 The coefficient of viscosity does not depend on the number of molecules per unit volume. Explain why not.
- 4.2 The transport coefficients  $\kappa$ ,  $\eta$ , and D all increase as the square root of the temperature, and decrease as the square of the average molecular diameter. Explain why without reference to any formula. Of the three transport coefficients,  $\kappa$  and D vary as  $1\sqrt{m}$ , whereas  $\eta$  varies as  $\sqrt{m}$ . Why?
- 4.3 The rate of a certain surface catalyzed reaction is proportional to the rate at which molecules hit the surface. The rate will increase with an increase in which of the following properties? (a) the mass of the molecules, (b) the velocity of the molecules, (c) the heat capacity of the molecules, (d) the number density of the molecules, (e) the area of the surface.
- 4.4 Consider a thought experiment in which horses are transported by molecules and suppose that the number of horses is proportional to the number of bushels of oats: H = kO. The transport coefficient relating the flux of horses to the gradient of oats depends on which of the following parameters? (a) the weight of the horse, (b) the velocity of the molecule, (c) the proportionality constant k, (d) the mean free path, (e) the speed of the horse.

#### Chapter 4 Transport Properties

- 4.5 Why is the coefficient of thermal conductivity larger for helium than that for argon? Why is the coefficient of thermal conductivity for  $N_2$  larger than that for argon?
- 4.6 The viscosity coefficient of  $O_2$  is greater than that of  $CO_2$ . Which molecule has the greater molecular diameter?
- 4.7 How does the root-mean-squared distance traveled by a diffusing molecule vary with temperature? (a) not at all, (b) increases (c) decreases. How does it vary with pressure? (a) not at all, (b) increases, (c) decreases.
- 4.8 Two bugs each execute a one-dimensional random walk with the same step size, but the second bug takes steps twice as often as the first. After a given time the second bug will be (a) twice as far from the origin as the first, (b)  $\sqrt{2}$  times as far, (c) the same distance.
- 4.9 In a tube of infinite length, consider the diffusion of molecules that start at  $z = z_0$  at  $t = t_0$ . The concentration of molecules at a location different than  $z_0$  (a) increases monotonically with time, (b) stays the same, (c) decreases monotonically, (d) increases then decreases, or (e) decreases then increases.
- 4.10 If thermal conductivity is independent of number density, why is it advantageous to evacuate the region between the walls of a dewar flask?
- 4.11 The thermal conductivity of silver is about 4 J K<sup>-1</sup> cm<sup>-1</sup> s<sup>-1</sup>. Calculate the heat flow in watts through a silver disk 0.1 cm in thickness and having 2 cm<sup>2</sup> area if the temperature difference between the two sides of the disk is 10 K.
- 4.12 The heat capacity of  $N_2$  is about 20 J K<sup>-1</sup> mol<sup>-1</sup> and its diffusion coefficient is  $1.5 \times 10^{-5}$  m<sup>2</sup> s<sup>-1</sup>. How much heat will be conducted in 1 s across a 1-cm space between two parallel plates 2 m<sup>2</sup> in area if the plates differ in temperature by 5 K and the space between the plates is filled with nitrogen at 1 atm and 300 K? You may assume that the ideal gas law holds under these conditions.
- 4.13 a. Calculate the coefficient of thermal conductivity for nitrogen at 303 K. Assume that  $\pi d^2$  for N<sub>2</sub> is  $7 \times 10^{-20}$  m<sup>2</sup> and  $C_{vm} = (5/2)R$ .
  - b. In a double glazed window the panes are separated by 5 cm. What is the rate of heat transfer in watts from a warm room at 323 K to the cold exterior at 283 K through a window of area 1 m<sup>2</sup>? Assume that air has the coefficient of thermal conductivity calculated in part (a).
  - c. To approximately what pressure in torr would one have to evacuate the space between the two windows before  $\kappa$  would be decreased appreciably for the value calculated in part (a)?
- 4.14 The self-diffusion coefficient of CO is  $D = 1.75 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  at 273 K and 1 atm. The density of CO under these conditions is 1.25 kg m<sup>-3</sup>. Calculate the molecular diameter.
- 4.15 The heat capacity of N<sub>2</sub> is 20.9 J K<sup>-1</sup> mol<sup>-1</sup>, and its viscosity at room temperature is  $1.7 \times 10^{-4}$  poise (1 poise = 1 g cm<sup>-1</sup> s<sup>-1</sup>). How much heat will be conducted in 1 s across a 1-mm space between two parallel plates 10 cm × 10 cm in size if the plates differ in temperature by 5 K and if the space between the plates is filled with N<sub>2</sub> at 1 atm?
- 4.16 Show by direct differentiation that equation 4.41 is the solution to equation 4.40.

- 4.17 Write and test a computer program to verify the general result, presented in **Figure 4.8**, that the root-mean-squared distance traveled in a onedimensional random walk is proportional to the square root of the number of steps.
- 4.18 The computer experiment on the random walk showed that the root-meansquared distance traveled in a random walk is proportional to the square root of the number of steps taken. This result can be shown more rigorously by consideration of the following problem.
  - a. Suppose a drunken sailor leaves a bar at closing time and executes a onedimensional random walk in the z direction along the sidewalk. Enumerate all the possible sequences of steps for which, after six steps each of length  $\ell$ , she could be at distances  $-6\ell$ ,  $-4\ell$ ,  $-2\ell$ , 0,  $2\ell$ ,  $4\ell$ , or  $6\ell$ from the doorway of the bar.
  - b. Show that the probabilities obtained in part (a) agree with the following formula, which can be used to calculate the absolute value of the sailor's distance from the bar:

$$P(z) = \frac{n!}{[1/2(n+s)]! [1/2(n-s)]! 2^n},$$

where *n* is the number of steps,  $s = z/\ell$ , and N! = N(N - 1)(N - 2)...(1).

c. A very accurate approximation to N! for large N is given by *Stirling's* approximation:

$$\ln N! = \left(N + \frac{1}{2}\right) \ln N - N + \ln(2\pi)^{1/2}$$

Use this approximation to show that

$$P(z) = \left(\frac{2}{\pi n}\right)^{1/2} \exp\left(-\frac{s^2}{2n}\right).$$

[*Hint*: You will need to approximate  $\ln(1 + x) \approx x - x^2/2$ .]

d. Substitute  $s = z/\ell$ , and let the number of steps *n* be given by the total time divided by the time per step:  $n = t/\tau$ , to show that

$$P(z,t) = \left(\frac{2\tau}{\pi t}\right)^{1/2} \exp\left(-\frac{z^2\tau}{2t\ell^2}\right).$$

e. Finally, compare the above equation with equation 4.41, letting  $z_0 = 0$ , to derive the Einstein-Smoluchowski relationship, equation 4.45.

# Reactions in Liquid Solutions

#### **Chapter Outline**

- 5.1 Introduction
- 5.2 The Cage Effect, Friction, and Diffusion Control
- 5.3 Reactions of Charged Species in Solution: Ionic Strength and Electron Transfer
- 5.4 Experimental Techniques
- 5.5 Summary

Appendix 5.1 The Langevin Equation and the Mean Squared Displacement

Appendix 5.2 Diffusion with an Electrostatic Potential

#### 5.1 INTRODUCTION

Our goal in this chapter is to see what fundamental differences there may be between reactions in the gas phase and reactions in liquid solutions. We will see that, in most cases, the rate for a reaction in solution once the reactants have come together is comparable to that for the same reaction in the gas phase, but that the solution may control the rates at which the reactants come together or products separate. In some cases, the solvent influences the reaction by providing a "cage" around the reactants and products. In other instances, particularly when the reaction involves charge displacement, the solvent may influence the reaction by differentially stabilizing the reactants, products, or the transition state. Finally, some reactions in solution occur on a very short time scale, so we will briefly investigate several experimental approaches to measuring their rate constants.

In comparing a reaction in solution to the same reaction in the gas phase, we often find that the mechanism of the reaction is the same and that the magnitude of the rate constant is quite similar. These facts may at first seem surprising, since gasphase reactions are based on individual *bimolecular* collisions, whereas the density in solution is so high that an individual reactant is usually in direct contact with more than one other molecule. Why then should the simple bimolecular picture be correct? The answer is that most reactions in solution do not involve the solvent, and that the rate of bimolecular encounters between two reactants is not appreciably different in solution than in the gas phase. A typical concentration in solution, say  $4 \times 10^{-2}$  molar, corresponds to a high but not unreasonable concentration in the gas phase, approximately 1 atm, so that for reactions where the solvent is not one of the reactants, the rate of the reaction in solution is typically within an order of magnitude of the rate in the gas phase. Of course, for reactions where the solvent is a reactant, or for reactions involving solvated ions, the rate is obviously much different in solution. For the most part, however, the solvent is simply something that crowds the reactants.

#### 5.2 THE CAGE EFFECT, FRICTION, AND DIFFUSION CONTROL

#### 5.2.1 The Cage Effect

The difference then between a reaction in the gas phase and one in solution is much like the difference between a romantic encounter on an empty beach and one on a crowded dance floor. The romance of closeness is not appreciably changed by the surrounding solvent of dancers, but it is more difficult to find one another in a crowd, and correspondingly difficult to separate once the dance has ended. The solvent tends to slow the rate of approach of the reactants, so that they must diffuse toward one another through the solution, but it also keeps them together for many "collisions" once they come in contact. This latter phenomenon is often referred to as the *cage effect*.

How difficult is it for products to escape the solvent cage? In an interesting experiment a molecular beam of  $I_2^-$  surrounded by a varying number of CO<sub>2</sub> solvent molecules was subjected to a pulse of laser light. The light dissociates the  $I_2^$ to  $I + I^-$ , but in a large enough cage of CO<sub>2</sub> molecules the I and I<sup>-</sup> cannot escape one another. When they recombine, the energy released, about 167 kJ/mol, is dissipated by evaporation of CO<sub>2</sub> molecules from the cluster, so that a smaller cluster with  $I_2^-$  at its core is detected. On the other hand, if the cage is small enough, the product I and I<sup>-</sup> can separate from one another, so that the cluster of  $I_2^{-}(CO_2)_n$ breaks up into two smaller clusters, one containing I- and one containing I. By measuring the size of  $I_2^-$  and  $I^-$  containing product clusters, Papanikolas et al. were able to determine the branching ratio of caged versus uncaged products. Figure 5.1 displays the fraction of dissociations that underwent recombination due to the cage effect as a function of the size of the starting cluster. Whereas 6 CO<sub>2</sub> molecules do not form a large enough cage to contain the dissociated products,  $16 \text{ CO}_2$  molecules cause complete caging. The fraction of caged products increases roughly linearly for cluster sizes between 6 and 16 CO<sub>2</sub> molecules.

If it takes only 16 solvent molecules to cage products having 167 kJ/mol, one can easily imagine that a reactant pair, having much less initial translational energy, will be held by the cage for an appreciable number of bimolecular collisions. How can we describe in simple terms the forces in solution that are responsible for the cage effect?

#### 5.2.2 The Langevin Equation

We consider a particle undergoing collisions in a liquid. Unlike the motion in a gas, the motion of liquid molecules cannot be presented in a closed-form solution. The mean free path, so useful in describing transport properties in gases, is undefined







From J. M. Papanikolas, J. R. Gord, N. E. Levinger, D. Ray, V. Vorsa, and W. C. Lineberger, J. Phys. Chem. 95, 8028 (1991).

in a liquid. Indeed, the concept of a "collision" loses meaning when solvent molecules are constantly in interaction with their neighbors. Transport properties still follow the macroscopic description outlined in Chapter 4, but the microscopic description cannot be described in terms of binary collisions. However, the situation is not quite as intractable as one might expect, since with so many interactions it becomes relatively easy to describe the average behavior. This is the approach taken at the turn of the century by Paul Langevin for the motion of a Brownian particle in a solution.

Langevin's model for a macroscopic Brownian particle in solution is that, whatever the particle's initial velocity, its average velocity decreases to zero with time because of the frictional forces in the fluid. To be sure, the particle is continually buffeted by collisions with the molecules of the fluid, but on average these collisions are random. The equation of motion for the Brownian particle is thus written as

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = -\zeta v + f(t), \qquad (5.1)$$

where v is the velocity of the particle, m is its mass,  $\zeta$  is a coefficient of friction, and f(t) is a function that represents the random forces on the particle due to collisions with the fluid.

Suppose we average over an ensemble of Brownian particles. The ergodic hypothesis of statistical mechanics assures us that such an average is equivalent to an average over time. On average, the forces on the ensemble of Brownian particles must vanish:

$$\langle f(t) \rangle = 0, \tag{5.2}$$

so that averaging both sides of equation 5.1 gives

$$m\frac{\mathrm{d}\langle v\rangle}{\mathrm{d}t} = -\zeta\langle v\rangle. \tag{5.3}$$

The solution to this equation is found by straightforward integration:

$$\langle v \rangle = \langle v \rangle_0 \exp\left(-\frac{\zeta}{m}t\right),$$
 (5.4)

where  $\langle v \rangle_0$  is the initial average velocity. We see that the velocity decays exponentially with a time constant equal to  $m/\zeta$ . This process of velocity decay is called *dissipation* and describes how the directed velocity is transferred to the molecules of the fluid.

Appendix 5.1 demonstrates that the Langevin equation, equation 5.1, can be solved to show that for times long compared to  $m/\zeta$  the mean squared displacement of a macroscopic Brownian particle is given by

$$\langle x^2 \rangle = \frac{2kT}{\zeta}t.$$
 (5.5)

Note that under these conditions, the Brownian particle suffers many collisions with the medium, and its mean squared displacement is determined by the friction coefficient  $\zeta$ .

We now make a connection with our previous study of diffusion in Chapter 4. We write a version of equation 4.43 for motion in the x direction as

$$x_{\rm rms} = (2Dt)^{1/2}, \tag{5.6}$$

and then combine equation 5.5 with equation 5.6 by noting that  $x_{\rm rms} = \langle x^2 \rangle^{1/2}$ :

$$\frac{2kT}{\zeta}t = 2Dt,$$

$$D = \frac{kT}{\zeta}.$$
(5.7)

It is thus clear that for motion in a liquid the diffusion coefficient is inversely proportional to the friction coefficient.

Further insight comes from the work of Stokes, who showed that the frictional force on a spherical particle of radius a moving through a fluid is

$$F = -\zeta v = -6\pi\eta a v, \tag{5.8}$$

where  $\eta$  is the coefficient of viscosity. Thus,  $\zeta = 6\pi \eta a$ , and

$$D = \frac{kT}{6\pi\eta a}.$$
 (5.9)

These equations remind us that, for motion in a liquid, higher viscosity coefficients are equivalent to higher friction coefficients and give rise to lower diffusion coefficients. It thus becomes clear that the forces that prevent particles from moving freely in a fluid are the viscous or frictional forces. It is these forces that are responsible for the cage effect, which we recall can hold reactants together for a number of collisions.

If the rate of reaction between a pair of molecules is high enough, it is possible that the frictional forces responsible for the cage effect will hold the reactant pair together long enough that nearly every encounter between the pair will lead to reaction. Under such circumstances, the rate of the reaction is controlled not by the rate constant for an individual reactive collision between the pair of reactants, but rather by the rate at which they can encounter one another by diffusion. Reactions of this type are called *diffusion-controlled* reactions.

#### Chapter 5 Reactions in Liquid Solutions

#### 5.2.3 A Simple Model for Diffusion Control

Since the rate of a reaction in solution is controlled partly by how fast the reactants encounter one another and partly by how fast they react once they make their encounter, we consider a mechanism for reaction in solution composed of the following steps:

$$A + B \xrightarrow[k_{esc}]{k_{esc}} AB$$

$$AB \xrightarrow[k_{r}]{k_{r}} P,$$
(5.10)

where A and B are the reactants in solution, P represents the products,  $k_{enc}$  is the rate at which A and B encounter one another,  $k_{esc}$  is the rate at which the products escape the solvent cage, and  $k_r$  is the rate at which they react when within the cage. The steady-state solution to this reaction sequence, which is very similar to the Michaelis-Menten and Lindemann mechanisms (Chapter 2), is simply

$$\frac{\mathrm{d}[\mathbf{P}]}{\mathrm{d}t} = \frac{k_{\mathrm{r}}k_{\mathrm{enc}}}{k_{\mathrm{esc}} + k_{\mathrm{r}}} [\mathrm{A}][\mathrm{B}].$$
(5.11)

Note that when the rate of reaction within the cage,  $k_r$ , is very slow compared to the escape rate, then the first reaction will basically be at equilibrium, so that the overall rate of the reaction will be given by  $(k_{enc}/k_{esc})k_r$ . On the other hand, when the reaction within the cage is very fast compared to the escape rate, then the rate of the overall reaction is controlled by the rate at which the reactants encounter one another. Under such conditions, the reaction rate is called diffusion controlled, since the rate is limited by the rate at which reactants can diffuse toward one another. We will see below that for neutral particles this rate is proportional to the sum of the diffusion coefficients for A and B through the solvent and to the radius of the cage,  $R: k_{enc} = 4\pi R(D_A + D_B)$ . For oppositely charged reactants, say A<sup>+</sup> reacting with B<sup>-</sup>, there is an additional multiplicative factor due to the mutual electrostatic attraction.

#### 5.2.4 The Diffusion-Controlled Rate Constant

We have seen in Section 5.2.1 that the solvent cage can have a substantial influence on reaction rates in solution. When the reaction within the cage is very fast compared to the escape rate, then the rate of the overall reaction is controlled by the rate at which the reactants encounter one another. Under such conditions, the reaction rate is called diffusion controlled, and it is now of interest to develop an expression for the overall rate of such reactions. Consider a simple model for this diffusioncontrolled limiting rate constant in which species A reacts with species B every time the two approach one another to within their contact distance R, the sum of their two radii, as shown in **Figure 5.2**.

We now briefly generalize to three dimensions the treatment of diffusion in Chapter 4. In three dimensions, the flux is related to the *gradient* of the concentration:  $J = -D\nabla c$ , where J is a three-dimensional vector, and  $\nabla$  is called the gradient operator. In Cartesian coordinates,  $\nabla = \mathbf{i}(\partial/\partial x) + \mathbf{j}(\partial/\partial y) + \mathbf{k}(\partial/\partial z)$ , with  $\mathbf{i}, \mathbf{j}$ , and  $\mathbf{k}$  as unit vectors in the x, y, and z directions. In spherical coordinates,  $\nabla = \mathbf{a}_r(\partial/\partial r) + \mathbf{a}_{\theta}(1/r)(\partial/\partial \theta) + \mathbf{a}_{\phi}(1/r\sin\theta)(\partial/\partial\phi)$ , with  $\mathbf{a}_r, \mathbf{a}_{\theta}$ , and  $\mathbf{a}_{\phi}$  as unit vectors in the r,  $\theta$ , and  $\phi$  directions.





In a diffusion-controlled reaction every reactant B that approaches to within a radius R of A will react. Reaction causes a gradient in [B] that gives rise to a flux of B toward A.

Returning to **Figure 5.2**, since reaction will deplete the concentration of B around each A, the reaction itself will establish a concentration gradient, and this gradient will cause molecules of type B to flow toward those of type A. Let  $A(r,\theta,\phi)$  represent the spatially dependent concentration of A, and let  $B(r,\theta,\phi)$  represent the spatially dependent concentration of B. The three-dimensional vector representing the flux  $J_{A-B}$  of reactants A and B toward one another is equal to the flux of B toward A due to concentration gradient,

$$-\boldsymbol{J}_{\mathrm{B}} = D_{\mathrm{B}} \nabla B(r, \theta, \phi), \qquad (5.12)$$

plus the flux of A toward B due to concentration gradient,

$$-J_{\rm A} = D_{\rm A} \nabla A(r, \theta, \phi), \qquad (5.13)$$

so that

$$\boldsymbol{J}_{\mathrm{A-B}} = -(\boldsymbol{J}_{\mathrm{A}} + \boldsymbol{J}_{\mathrm{B}}) = (\boldsymbol{D}_{\mathrm{A}} + \boldsymbol{D}_{\mathrm{B}}) \nabla \boldsymbol{B}(\boldsymbol{r}, \boldsymbol{\theta}, \boldsymbol{\phi}). \tag{5.14}$$

In this last equation, we have assumed quite reasonably that  $\nabla A(r,\theta,\phi) = \nabla B(r,\theta,\phi)$ , since the gradients in the two reactants are caused by the same effect, namely, the fact that A molecules around B are depleted by reaction and vice versa. Note that the gradient  $\nabla B(r,\theta,\phi)$  is positive, so that our choice of sign gives that the flux  $J_{A-B}$  is also positive, as it should be.

Suppose that we have a mixture of reactants but that we prevent them from reacting. Their concentrations will then be the bulk, equilibrium concentrations; that is,  $B(r,\theta,\phi) = [B]$  and  $A(r,\theta,\phi) = [A]$ , where  $B(r,\theta,\phi)$  and  $A(r,\theta,\phi)$  are the spatially dependent concentrations and [B] and [A] are the bulk ones, which we will assume to be constants. Now we imagine that the reaction is suddenly turned on. The concentration of A in the vicinity of B will decrease, and vice versa, so that a concentration gradient is formed. But after a short time, steady state will be approached, so that the flux of A and B toward one another will be constant. The

#### Chapter 5 Reactions in Liquid Solutions

concentrations  $A(r,\theta,\phi)$  and  $B(r,\theta,\phi)$  at any position will also be constant. Under the assumption that every encounter leads to reaction, the flux of A and B toward one another will equal to the flux of products. Thus, at steady state

$$J_{\text{rxn}} = J_{\text{A-B}} = (D_{\text{A}} + D_{\text{B}})\nabla B(r,\theta,\phi)$$
  
= constant. (5.15)

Now let us consider the steady-state mathematical solution. Following arguments that exactly parallel those in Section 4.7 (see equation 4.40), we find that

$$\frac{\partial B(r,\theta,\phi)}{\partial t} = -\nabla J_{A-B}(t) = (D_A + D_B)\nabla^2 B(r,\theta,\phi).$$
(5.16)

We wish a solution to the rate constant for which the concentrations of A and B at any position are fixed in time, so that, at equilibrium,  $\partial B(r,\theta,\phi)/\partial t = 0$ .

The coordinates most appropriate for considering the motion of the A–B pair are spherical coordinates, since the gradient in concentration and (we assume) the gradient in electrical potential depend only on the distance between the pair. Thus,  $B(r,\theta,\phi) = B(r)$ . In spherical coordinates the operator  $\nabla^2$ , called the Laplacian, is given by

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial^2\theta} + \frac{1}{r^2}\cot(\theta)\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}.$$
 (5.17)

Substituting equation 5.17 into equation 5.16 and recognizing that B(r) depends only on r and that  $\partial B(r)/\partial t = 0$ , we find that the solution for B(r) needs to obey the equation

$$\frac{\partial B}{\partial t} = (D_{\rm A} + D_{\rm B}) \left( \frac{\partial^2 B(r)}{\partial r^2} + \frac{2}{r} \frac{\partial B(r)}{\partial r} \right)$$
  
= 0. (5.18)

The solution to this equation, as may be readily verified by substitution, is

$$B(r) = \frac{c_1}{2r} + c_2,$$
 (5.19)

where the constants  $c_1$  and  $c_2$  must still be determined from the boundary conditions. When the distance between A and B is sufficiently large, i.e., as  $r \to \infty$ , B(r) must approach its bulk concentration, [B]. Thus, we find that  $c_2 = [B]$ .

To evaluate  $c_1$ , let us calculate the concentration of B at the distance R equal to the sum of the two radii. To do this, we examine in more detail the gradient caused by the reaction. Consider the flux of B into of a sphere of radius r centered on a particular reactant of type A, as shown in **Figure 5.2.** Every B flowing into the sphere eventually reacts with A at a distance R, where the concentration of B is B(R). Thus, the rate of the reaction is then just the flux of B, in number per time per area, times the area of the sphere times concentration of A:

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_{\mathrm{r}}[\mathrm{A}]B(R) = \boldsymbol{J}_{\mathrm{rxn}}4\pi r^{2}[\mathrm{A}], \qquad (5.20)$$

where [P] is the concentration of products,  $k_r$  is the phenomenological rate constant we wish to determine (see Section 5.2.3), and  $4\pi r^2$  is the area of the sphere around A at a distance *r*. Combination of **equations 5.15** and **5.20** leads to

$$k_{\rm r}[{\rm A}]B(R) = [{\rm A}]4\pi r^2 (D_{\rm A} + D_{\rm B}) \frac{{\rm d}B(r)}{{\rm d}r}.$$
 (5.21)

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Section 5.2 The Cage Effect, Friction, and Diffusion Control

In this equation [A] is constant (equal to the macroscopic concentration), B(R) is constant (to be determined) and B(r) denotes how the microscopic concentration of B varies with distance. Division of both sides of the equation by  $[A]r^2$  and multiplication by dr yields

$$k_{\rm r}B(R)\frac{{\rm d}r}{r^2} = 4\pi(D_{\rm A}+D_{\rm B}){\rm d}B(r).$$
 (5.22)

Finally, integration of both sides over dr from r = R to  $r = \infty$  gives

$$k_{\rm r}B(R)\int_{R}^{\infty} \frac{1}{r^2} \, \mathrm{d}r = 4\pi (D_{\rm A} + D_{\rm B})\int_{R}^{\infty} \, \mathrm{d}[B(r)],$$
$$\frac{k_{\rm r}B(R)}{R} = 4\pi (D_{\rm A} + D_{\rm B})[B(r = \infty) - B(r = R)],$$

or

$$B(R)\left[\frac{k_{\rm r}}{R} + 4\pi(D_{\rm A} + D_{\rm B})\right] = 4\pi(D_{\rm A} + D_{\rm B})[{\rm B}],$$

$$B(R) = \frac{[{\rm B}]}{1 + \frac{k_{\rm r}}{4\pi(D_{\rm A} + D_{\rm B})R}}.$$
(5.23)

In this last equation, we have used the fact that  $B(r = \infty)$  is just the bulk concentration [B]. Comparison of the last line of this equation with equation 5.19 leads, after some algebra, to the conclusion that

$$c_{1} = \frac{-2R[B]}{1 + \frac{4\pi(D_{A} + D_{B})R}{k_{r}}},$$
(5.24)

but we will have little use for this equation now that the last line of equation 5.23 gives us an expression for B(R). Substitution of this solution for B(R) into equation 5.20 gives

$$\frac{d[P]}{dt} = \frac{k_{\rm r}}{1 + \frac{k_{\rm r}}{4\pi (D_{\rm A} + D_{\rm B})R}} [A][B].$$
(5.25)

Thus, when  $k_r >> 4\pi (D_A + D_B)R$ , the overall rate constant for the reaction is given by

$$k = 4\pi (D_{\rm A} + D_{\rm B})R.$$
 (5.26)

We see that the rate constant, k, is then completely controlled by the encounter rate,  $k_{enc}$ , defined in Section 5.2.3; i.e., it is controlled by diffusion. In this limiting case, the reaction occurs instantly when the reactants approach to within their average diameter *R*. Example 5.1 illustrates the utility of equation 5.26.

# example 5.1

Calculating Diffusion-Controlled Rate Constants		
Objective	Given that the diffusion coefficient of many species in aqueous solution is on the order of $10^{-9}$ m <sup>2</sup> /s, calculate the diffusion limited rate constant for a pair of reactants whose average diameter is 2.0 nm.	
Method	Use equation 5.26.	
Solution	The rate constant should be $k = 4\pi (D_A + D_B)R$ , with $D_A \approx D_B$ and $R = 2.0$ nm. Thus, $k = 4\pi (2 \times 10^{-9} \text{ m}^2/\text{s})(2.0 \times 10^{-9} \text{ m/molecule})(10^6 \text{ cm}^3/\text{m}^3)(6.02 \times 10^{23} \text{ molecule/mol}) = 3.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = (3.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}) (1 \text{ L/1000 cm}^3) = 3.0 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}.$	

**Equation 5.26** provides the diffusion-controlled rate constant in the case when the reactants are uncharged. When the reactants are ionic, the situation is somewhat more complicated because, in addition to the concentration gradient caused by reaction, there is also a concentration gradient caused by the attraction or repulsion of charged particles. A detailed examination, discussed in Appendix 5.2, shows that

$$k = 4\pi (D_{\rm A} + D_{\rm B})\beta, \tag{5.27}$$

where

$$\beta = \frac{1}{\int_{R}^{\infty} \frac{e^{U(r)/kT}}{r^2} dr},$$
(5.28)

and U(r) is the potential of interaction between the ionic reactants. Note that when U(r) = 0, the integration in **equation 5.28** can be performed to yield  $\beta = R$ , and we recover **equation 5.26** from **equation 5.27**. In general, this potential will be given for charged particles by  $U(r) = z_A z_B e^2/\epsilon r$ , where  $\epsilon$  here refers to the dielectric constant of the solution,  $z_A$  and  $z_B$  are the integer charges on the ions, and e is the magnitude of the charge on an electron. The integration in **equation 5.28** then shows that

$$3 = \frac{-z_{\rm A} z_{\rm B} r_0}{1 - \exp(z_{\rm A} z_{\rm B} r_0/R)},$$
(5.29)

where  $r_0 = e^2/\epsilon kT$  and is equal to about 0.7 nm in water at 25°C.

#### 5.3 REACTIONS OF CHARGED SPECIES IN SOLUTION: IONIC STRENGTH AND ELECTRON TRANSFER

As discussed in the Introduction to this chapter, most rate constants in solution are similar to those for the corresponding reaction in the gas phase, except when the rate of the reaction is limited by how fast the reactants can diffuse through the solution. Another situation for which the solution-phase rate constant can differ substantially from the gas-phase rate is when the reactants or the activated complex interact strongly with the solvent. An example of such interaction is the electrostatic stabilization of ionic reactants or complexes by the solvent. Two situations will be considered. In the first, we will examine the effect on the rate constant of additional ions in the solution, and we will find that the rate constant is influenced by the *ionic strength* of the solution. In the second situation we will see that even a neutral solvent can influence the reaction rate if the energy of solvation is substantially different for the reactants and products. An example of this second effect is when the reaction involves an electron transfer, either from one molecule to another or between two different sites on the same molecule. As the reaction proceeds, a dielectric solvent must rearrange its structure to attain the minimum energy, and this solvent reorganization will have an influence on the rate constant. How the rate constant varies with the solvent reorganization energy is the subject of Marcus theory, which we will briefly develop.

We consider first the influence on reactions of solutions with high ionic strength.

#### 5.3.1 Reaction Rates and Ionic Strength

It is well known that any ion in solution is stabilized by being surrounded by an ionic "atmosphere" of oppositely charged particles; this effect forms the physical basis of the Debye-Hückel theory.<sup>a</sup> The stabilization increases with the square root of the ionic strength,  $I_c = \frac{1}{2} \sum c_i z_i^2$ . The question we approach in this section is how to modify activated complex theory to account for the electrostatic interaction between reactants or activated complexes and the ions in solution.

Our discussion of activated complex theory in Section 3.4 has assumed that the equilibrium constant between reactants and products can be written simply in terms of a ratio of concentrations. However, we know from our study of thermodynamics that equilibrium constants are actually related to activities rather than concentrations. To modify the ACT, we return to the fundamental assumptions in ACT embodied in equation 3.13, d[products]/dt =  $k_2$ [AB<sup>‡</sup>]. If we now write the equilibrium constant for A + B  $\Longrightarrow$  AB<sup>‡</sup> in terms of activities we obtain

$$K^{\ddagger} = \frac{a^{\ddagger}}{a_{\mathrm{A}}a_{\mathrm{B}}} = \frac{\gamma^{\ddagger}}{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}} \frac{[\mathrm{AB}^{\ddagger}]}{[\mathrm{A}][\mathrm{B}]},$$
(5.30)

so that

$$\frac{\mathrm{d}[\mathrm{products}]}{\mathrm{d}t} = k_2[\mathrm{AB}^{\ddagger}] = k_2 \frac{\gamma_{\mathrm{A}} \gamma_{\mathrm{B}}}{\gamma^{\ddagger}} K^{\ddagger}[\mathrm{A}][\mathrm{B}]$$

$$= \frac{\gamma_{\mathrm{A}} \gamma_{\mathrm{B}}}{\gamma^{\ddagger}} k_2 \frac{k_1}{k_{-1}} [\mathrm{A}][\mathrm{B}].$$
(5.31)

The overall rate constant in **equation 5.31** differs from that in our previous equation **equation 3.13** only by the multiplicative factor  $\gamma_A \gamma_B / \gamma^{\ddagger}$ . Let  $k_0$  be the rate constant when all activity coefficients are equal to unity; in other words, let  $k_0$  be the rate constant we have already evaluated by ACT. Then when the activity coefficients are not equal to unity, the rate constant should be given as

$$k = k_0 \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}}, \qquad (5.32)$$

<sup>&</sup>lt;sup>a</sup>Peter Debye was awarded the Nobel Prize in Chemistry in 1936 for his contributions to the understanding of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases.

#### Chapter 5 Reactions in Liquid Solutions

or

$$\log_{10}k = \log_{10}k_0 - \log_{10}\gamma^{\ddagger} + \log_{10}\gamma_A + \log_{10}\gamma_B.$$
 (5.33)

For reactions in ionic solutions at low enough concentrations, we might reasonably assume that the Debye-Hückel limiting law is valid:

$$\log_{10}\gamma_i = -Az_i^2 I_c^{1/2}, \tag{5.34}$$

where  $z_i$  is the charge on the species involved in the reaction,  $I_c$  is the ionic strength, and A is a constant equal to 0.50 (L/mol)<sup>1/2</sup> for water at 25°C. Substitution of equation 5.34 into equation 5.33 and realization that  $z^{\ddagger} = z_A + z_B$  lead to

$$\log_{10} k = \log_{10} k_0 - A[z_A^2 + z_B^2 - (z_A + z_B)^2] I_c^{1/2}$$
  
=  $\log_{10} k_0 + 2A z_A z_B I_c^{1/2}.$  (5.35)

Note that equation 5.35 predicts that the logarithm of the rate constant should vary linearly with the square root of the ionic strength. In addition, reactions between ions of like charge should have rate constants that increase with  $I_c^{1/2}$ , whereas those between ions of unlike charge should decrease. This behavior is illustrated in Figure 5.3.



#### Figure 5.3

Effect of increasing ionic strength on the rate constant for reaction between ions of varying charges. Values of  $z_A$ ,  $z_B$  are indicated.

The physical basis for these effects can be grasped by considering the change in apparent activation energy with increasing ionic strength. When unlike ions form an activated complex, the complex is less charged than the reactants and is thus less stabilized by increasing ionic strength than the reactants; the apparent activation energy increases so that the rate constant decreases. When like ions form an activated complex, on the other hand, the complex has a higher charge than the reactants and is more stabilized by increasing ionic strength; the apparent activation energy decreases and the rate constant increases. This behavior of the rate constant with ionic strength is often called the *primary salt effect*.

#### 5.3.2 Electron Transfer Reactions: Marcus Theory

Another situation in which the solvent can have a profound influence on the rate constant occurs when the energy of solvation differs substantially for reactants and products. This situation occurs frequently in electron transfer reactions, since as the electron moves from the donor site to the acceptor site the structure of the solvent must adjust to accommodate the new charge distribution. Since all oxidation-reduction reactions in solution involve the transfer of an electron, the determination of the rate constant for electron transfer reactions is an extremely important chemical problem. This problem has been considered in detail by Marcus,<sup>b</sup> and we develop here a simplified derivation of his results.<sup>c</sup> It can be shown that the more complete derivation gives the same answer in the limit when the distance between donor and acceptor sites never becomes too small.

The overall reaction that we would like to consider can be symbolized by the following scheme:

$$D + A \rightleftharpoons (DA) \rightleftharpoons (D^+A^-) \rightleftharpoons D^+ + A^-,$$

where the species in parentheses represent having the donor and acceptor at a distance short enough so that the electron can be transferred, and (DA) and  $(D^+A^-)$ represent this "contact pair" before and after transfer. In many oxidation-reduction reactions, the overall rate constant is limited by the rate for the electron transfer, so we will concentrate on this step of the process. In some cases, D and A are different sites on the same molecule, so that, again, the overall rate constant is determined by the rate of the electron transfer.

Consider an electron located on the donor molecule, which itself is surrounded by a number of solvent molecules. The energy of the electron will depend on the nuclear positions of all the atoms in the donor and solvent molecules, so that there will in general be 3N - 6 nuclear coordinates, where N is the total number of atoms. Under the assumption that the electron moves much more rapidly than the nuclei, the energy of the system can be adequately approximated by calculating the electronic energy for a each possible nuclear configuration. We now imagine how this energy varies along a particular coordinate, one of the 3N - 6 coordinates. The coordinate we will choose to examine is the reaction coordinate, the one whose nuclear displacements would lead along a minimum energy path from the nuclear configuration of (DA) to that of  $(D^+A^+)$ .

<sup>&</sup>lt;sup>b</sup>R. Marcus, J. Chem. Phys. 24, 966 (1956); ibid., 24, 979 (1956); ibid. 26, 867 (1957); ibid. 26, 872 (1957); *Disc. Farad. Soc.* 29, 21 (1960); J. Phys. Chem. 63, 853 (1963); J. Chem. Phys. 38, 1858 (1963); ibid., 39, 1734 (1963); ibid., 43, 679 (1965).

<sup>&</sup>lt;sup>c</sup>I am grateful to Prof. A. C. Albrecht for providing this derivation and to M. Stimson for bringing it to my attention.

#### Chapter 5 Reactions in Liquid Solutions



#### Figure 5.4

Energy dependence as a function of reaction coordinate for electron on donor or acceptor.

When the electron is on the donor, the energy will be a minimum at a particular location along the reaction coordinate; let us arbitrarily label this as position zero along that coordinate, as shown in Figure 5.4. The parabolic curve labeled "donor" shows how the energy of the system might vary with displacement when the electron is on the donor. If the electron were on the acceptor, the energy of the system would be different; its minimum will in general be at a different location, say x'', along the reaction coordinate, and the energy of the minimum will differ from that of the donor by  $\Delta G^0$ , the free energy of the reaction. Note that, as drawn in the figure,  $\Delta G^0$  is negative (the products are more stable than the reactants), so that the positive energy difference between the minima of the two parabolas is  $-\Delta G^0$ . The parabolic curve labeled "acceptor" shows how the energy of the system might vary with displacement when the electron is on the acceptor. If we assume, as did Marcus, that the coupling between the donor and acceptor electronic energy states is weak, then the energy of the transition state will be given by the point of intersection between the two curves. The key to determining the rate constant for the reaction is to find the value of  $\Delta G^+$  in the figure. From equation 3.23, we know that the rate for the process is given simply by  $k_{\rm ET}(T) = (kT/h)\exp(-\Delta G^+/kT)$ .

We now suppose that the curves describing how the energy changes with position along the reaction coordinate can be approximated by parabolas, both for the donor and for the acceptor; i.e., we will assume that  $E = x^2$  for both parabolas.<sup>d</sup> It can be shown that this approximation is equivalent to the full theory developed by Marcus in the limit when the donor and acceptor sites are not too close together. Let us label by x' the reaction coordinate position where the donor and acceptor parabola intersect. From the point of view of the donor curve, the value of  $\Delta G^+$  is simply  $\Delta G^+ = x'^2$ . Let us also define  $E_{\rm m} = x''^2$  as the value, relative to its minimum, of the

<sup>&</sup>lt;sup>d</sup>Actually, we need only assume that  $E \propto x^2$ ; e.g.,  $E = Cx^2 = (\sqrt{C}x)^2$ . The arguments given in the text are then appropriate provided that we then transform variables so that the reaction coordinate, now already plotted in arbitrary units, is plotted in units of  $\sqrt{C}$  times the current arbitrary unit.

acceptor parabola at the location of the minimum energy for the donor. This energy, called the *reorganization energy*, is the energy required to reorganize the nuclei of the acceptor and its surrounding solvent into the configuration of the donor and its surrounding solvent in the absence of back transfer of the electron. We now calculate the energy of the intersection point for the two parabola above the minimum energy for the acceptor. As measured from the bottom of the acceptor parabola, this energy is  $-\Delta G^0 + \Delta G^+ = (x'' - x')^2 = x''^2 - 2x'x'' + x'^2$ . Substituting  $\Delta G^+$  for  $x'^2$  and  $E_{\rm m}$  for  $x''^2$ , we obtain

$$-\Delta G^{0} + \Delta G^{+} = E_{m} - 2x'x'' + \Delta G^{+},$$
  

$$2x'x'' = E_{m} + \Delta G^{0},$$
  

$$x' = \frac{E_{m} + \Delta G^{0}}{2x''},$$
  

$$\Delta G^{+} = x'^{2} = \frac{(E_{m} + \Delta G^{0})^{2}}{4x''^{2}}.$$
  
(5.36)

Finally, noting again that  $E_{\rm m} = x'^2$ , we obtain the final result for  $G^+$ :

$$\Delta G^{+} = \frac{(E_{\rm m} + \Delta G^{0})^{2}}{4E_{\rm m}}.$$
(5.37)

The rate constant for the electron transfer reaction is thus

$$k_{\rm ET}(T) = \frac{kT}{h} \exp\left(-\frac{(E_{\rm m} + \Delta G^0)^2}{4E_{\rm m}kT}\right).$$
 (5.38)

The form of equation 5.38 makes an interesting prediction about the rate constant for the reaction. If  $E_{\rm m}$  is large and  $\Delta G^0$  is positive or just slightly negative, then  $(E_{\rm m} + \Delta G^0)$  will be positive and the rate constant will be relatively small. Figure 5.5 shows the positions of the parabolic curves for the same value of  $E_{\rm m}$  (the same displacement between the two parabolas) and for values of  $\Delta G^0$  ranging from positive in panel (A) to increasingly negative values in panels (B)-(D). In panel (A)  $\Delta G^0 > 0$ , while in panel (B)  $\Delta G^0 < 0$ ; both panels have  $E_{\rm m} + \Delta G^0 > 0$ . Thus, the rate should be small for panel (A) and a little larger for panel (B). As  $\Delta G^0$  becomes increasingly and the state of the state o increasingly negative, eventually  $(E_{\rm m} + \Delta G^0)$  will become zero, and the rate constant will become a maximum; this situation is shown in panel (C) of the figure. If  $\Delta G^0$  becomes even more negative, then  $E + \Delta G^0$  will be negative and its square will again increase. Equation 5.38 predicts that the rate constant will then actually *decrease* with increasing free energy change,  $-\Delta G^0$ . The reason why is shown in panel (D) of the figure, where it can be seen that the activation energy for the electron transfer reaction has now increased. The region of free energy change over which the rate constant decreases as the reaction releases more free energy is called the "Marcus inverted region."

That a rate constant should decrease with increasing exothermicity was quite counterintuitive at the time Marcus put forth his model, and the existence of the Marcus inverted region was in doubt for nearly thirty years until G. Closs, J. R. Miller, and their coworkers reported the confirming set of experiments.<sup>e</sup> The results of their measurements are shown in **Figure 5.6**, which plots the logarithm of the

<sup>&</sup>lt;sup>e</sup>J. R. Miller, L. T. Calcaterra, G. L. Closs, J. Am. Chem. Soc. **106**, 3047 (1984); G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Penfield, and J. R. Miller, J. Phys. Chem. **90**, 3673 (1986); G. L. Closs and J. R. Miller, Science **240**, 440 (1988).



#### Figure 5.5

Intersecting donor and acceptor parabolas for increasingly negative values of  $\Delta G^0$  going from panels (A) to (D). Note that activation energy for the reaction is a minimum in panel (C), but that it increases in going from (C) to (D).



#### Figure 5.6

Intramolecular electron transfer rate constants as a function of free energy change. The transfer occurs from biphenyl anions to the eight acceptors attached at A in the structure shown. From G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Penfield, and J. R. Miller, *J Phys. Chem.* **90**, 3673 (1986). Reprinted with permission from *The Journal of Physical Chemistry*. Copyright 1986 American Chemical Society. energy transfer rate constant versus  $-\Delta G^0$  for a series of molecules consisting of a donor group separated from various acceptor groups by a rigid spacer molecule. By varying the composition of the acceptor and measuring the rate of electron transfer following pulse radiolysis to produce the radical anion, the authors were able to see how the electron transfer rate varied with increasing  $-\Delta G^0$ . As shown in the figure, the rate did indeed decrease with increasing  $-\Delta G^0$  in accordance with the Marcus theory (solid line). Similar experiments were performed by other groups.<sup>f</sup> While the Marcus theory is now the accepted standard for electron transfer reactions,<sup>g</sup> it should be noted that this important area of chemistry is still one of active research.

#### 5.4 EXPERIMENTAL TECHNIQUES

It should come as no surprise that some reactions in solution are very rapid. Reactions involving oppositely charged ions, reactions in which the solvent participates as a reactant, or reactions involving the motion of light particles such as protons or electrons might reasonably be expected to proceed quickly. For such rapid processes, which often occur more rapidly than the reactants can be mixed, special methods are necessary to determine reaction rate constants.

#### 5.4.1 The Temperature Jump Technique

One method pioneered in the 1950s by Manfred Eigen and his coworkers<sup>h</sup> is a relaxation technique. In this method, the reactants start already mixed and in equilibrium with the products. Some property of the system that affects the equilibrium constant, for example the temperature or pressure, is then suddenly changed, and the concentration of a reactant or product is monitored as it changes to achieve its new equilibrium value. Figure 5.7 displays a typical apparatus for the so-called temperature jump version of the experiment. A power supply (PS) charges a capacitor (C) to a high voltage. A triggered spark gap (G) then discharges the voltage through a cell, simultaneously starting the sweep of an oscilloscope and heating the reactant/product mixture by a few degrees Kelvin. A light source (L) supplies a frequency absorbed by one of the reactants or products, and this frequency is resolved by a monochromator (M), detected by a photomultiplier tube (PMT) and its intensity displayed on the oscilloscope. The resulting waveform is then analyzed to obtain the kinetic information. The best time resolution of such relaxation techniques is typically in the 100-ns regime. Table 5.1 gives a few protonation and deprotonation rates measured by this technique.

How is the observed signal in this experiment related to the rate constants for the forward and reverse reactions? For simplicity, we first consider an opposing first-order reaction,  $A \rightleftharpoons B$ . Immediately after the perturbation, the concentrations of A and B are each displaced from their new equilibrium values by an amount we

<sup>&</sup>lt;sup>6</sup>M. P. Irvine, R. J. Harrison, M. A. Strahand, and G. S. Beddard, *Ber. Bunsenges. Phys. Chem.* **89**, 226 (1985); M. P. Irvine, R. J. Harrison, G. S. Beddard, P. Leighton, and J. K. M. Sanders, *Chem. Phys.* **104**, 315 (1986).

<sup>&</sup>lt;sup>g</sup>R. Marcus won the 1992 Nobel Prize in Chemistry for his original work in this area.

<sup>&</sup>lt;sup>h</sup>M. Eigen, *Disc. Farad. Soc.* 17, 195 (1954). Eigen shared the 1967 Nobel Prize in Chemistry for his work in this area.



#### Figure 5.7

Schematic of apparatus used for temperature jump experiment.

TABLE 5.1	Protonation and Deprotonation Rates Measured by
	Relaxation Techniques

Reaction	$k_{\rm f}({ m M}^{-1}~{ m s}^{-1})$	$k_{\rm r}({\rm s}^{-1})$	
$H^+ + OH^- \rightarrow H_2O$	$1.3  imes 10^{11}$	$2.6  imes 10^{-5}$	
$H^+ + NH_3 \rightarrow NH_4^+$	$4.3  imes 10^{10}$	24	
$OH^- + HCO_3^- \rightarrow H_2O + CO_3^-$	$6.1 imes10^9$	$1.4 imes10^2$	
$OH^- + HPO^{-2}_4 \rightarrow H_2O + PO^{-2}_4$	$2  imes 10^9$	$3 imes 10^2$	

will call  $x_e$ . We have already seen in **equation 2.51** of Section 2.4.1 that a system of opposing reactions displaced from equilibrium will relax exponentially with a time dependence given by the sum of the forward and reverse rate constants:  $A(t) = A_e + x_e \exp[-(k_1 + k_{-1})t]$ . Thus, by measuring the relaxation rate and knowing the equilibrium constant, which is simply the ratio of the forward and reverse rate constants, one can determine the rate constants separately.

For second-order or more complex reactions, the time dependence will be somewhat more complicated than that for the first-order reaction above, but for small displacements the system will relax exponentially toward equilibrium with a time dependence determined by the sum of the forward and reverse rate constants, each perhaps multiplied by a reactant or product equilibrium concentration. For example, Problem 5.3 shows that for the system  $A + B \rightleftharpoons C$  the result for the relaxation of A is  $A(t) = A_e + x_e \exp\{-[k_f(A_e + B_e) + k_r]t\}$ . Example 5.2 shows how this result can be used to determine the rate constants for  $H^+ + OH^- \oiint H_2O$ .

#### **Calculating Rate Constants from a Relaxation Experiment**

**Objective** Find the forward and reverse rate constants for the recombination reaction  $OH^- + H^+ \Longrightarrow H_2O$  given that the equilibrium constant at 25°C for the reaction written in this direction is  $K_e = [H_2O]/([H^+][OH^-]) = 0.51 \times 10^{16} \text{ M}^{-1}$ . The OH<sup>-</sup> concentration is
observed to change from its original value to its new equilibrium value at this temperature exponentially with a time constant of  $\tau = 36.8 \ \mu s$ .

**Method** The observed rate is the reciprocal of the time constant, so  $1/\tau = k_f([H^+]_e + [OH^-]_e) + k_r$ . We also know  $K_e$ , so we can both calculate the equilibrium concentrations and relate  $k_f$  to  $k_r$ :  $k_f/k_r = K_e$ . With two equations and two unknowns, we should be able to solve for both  $k_f$  and  $k_r$ .

**Solution** First, notice that  $k_r = k_f/K_e$  and that  $[H^+] = [OH^-] = ([H_2O]/K_e)^{1/2}$ . Consequently,  $1/\tau = 1/(36.8 \times 10^{-6} \text{ s}) = k_f \{2([H_2O]/K_e)^{1/2} + (1/K_e)\}; k_f = 1/\{2[(1000 \text{ g/L})/(18 \text{ g/mol})(0.51 \times 10^{16} \text{ M}^{-1}]^{1/2} + 1/(0.51 \times 10^{16} \text{ M}^{-1})\}\{36.8 \times 10^{-6} \mu\text{s}\} = 1.30 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}.$ Thus  $k_r = k_f/K_e = (1.30 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1})/(0.51 \times 10^{16} \text{ M}^{-1}) = 2.55 \times 10^{-5} \text{ s}^{-1}.$ 

#### 5.4.2 Ultrafast Laser Techniques

Even the relaxation techniques described above are not fast enough to measure some reaction rates in solution. A more recently developed method for measuring fast processes relies on the extremely short pulse durations available from modern lasers. Although this field is still developing rapidly, the current record for short pulse generation is a few femtoseconds ( $1 \text{ fs} = 10^{-15} \text{ s}$ ), substantially shorter than the time it takes molecules to vibrate. On such time scales, the reactants and solvent molecules stand still. Thus, even the fastest solution reactions occur on somewhat longer time scales, those compatible with laser pulses in the picoseconds ( $1 \text{ ps} = 10^{-12} \text{ s}$ ) and nanosecond region. Such pulses can be used to clock the concentration changes through a method generally known as the pump and probe technique (for more detail on this technique, see Section 7.5.1).

**Figure 5.8** shows a schematic diagram for a typical pump-probe apparatus. A short pulse laser generates bursts of radiation. The light beam from this laser is then divided into two beams of different intensity using a partially transmitting



#### Figure 5.8

Schematic diagram of the pump-probe technique using fast laser pulses to probe reaction rates in solution.

#### Chapter 5 Reactions in Liquid Solutions

mirror (PTM), and each light beam is then converted to the desired wavelength by the use of nonlinear optical processes (NL). Because light travels roughly 0.3 mm in 1 ps, the pathlengths for the two beams can be adjusted so that the pulse of low intensity reaches the sample (S) after the pulse of high intensity. The delay time is scanned by translating the retroreflector (R). The pump pulse is used to initiate the reaction of interest, and the absorption of the probe pulse, proportional to the concentration of a reactant or product, is monitored as a function of the position of the reflector (R). By such a technique one can measure the reaction rate on a picosecond or even femtosecond timescale (see Section 7.5.6).

For example, the pump-probe technique has been used to investigate the isomerization of 1-1'-binaphthyl, shown in **Figure 5.9**. The angle between the two naphthyl groups is changed by about 40° upon excitation from the ground to the first excited singlet state of this molecule. Since the molecule absorbs at a different wavelength in its excited state geometry, the reaction can be followed by exciting the first singlet state with one short laser pulse and observing as a function of time delay the increase in absorption of a second pulse tuned to probe the product. As one might expect, the time it takes to increase the dihedral angle between the two naphthyl groups depends on the surrounding solvent, which must be pushed out of the way as the geometry changes. Because the forces of friction dominate, the time for reaction varies with the viscosity of the solvent. **Table 5.2** shows some typical experimental results and compares these to a theoretical result based on the frictional forces. Experiments such as this allow one to directly evaluate the role of friction in chemical reactions that we considered in Section 5.2.2.



#### **Experimental and Theoretical Reaction Times for the Isomerization of** 1-1'-binapthyl in Solvents of Varying Viscosity

Solvent	Viscosity (cP)*	Experimental Rise Time (ps)	Theoretical Prediction (ps)
Ethanol	1.08	$12.2 \pm 1.0$	12.2
n-Propanol	2.23	$13.7 \pm 1.0$	13.9
n-Butanol	2.95	$15.0 \pm 1.0$	15.2
<i>n</i> -Pentanol	4.33	$17.6 \pm 1.0$	17.7
n-Hexanol	5.27	$19.2 \pm 1.0$	19.5
<i>n</i> -Heptanol	6.90	$24.0 \pm 2.0$	22.9
n-Octanol	8.95	$27.0 \pm 2.0$	27.4

From D. P. Millar and K. B. Eisenthal, J. Chem. Phys. 83, 5076 (1985).

\*1 poise =  $0.1 \text{ N m}^{-2} \text{ s}$ 

and the second second



Solvation coordinate

#### Figure 5.10

The change in electric dipole on excitation induces a change in the solvation. Emission from  $S_1$  back to  $S_0$  can then be used to study the dynamics of the solvation.

From R. M. Stratt and M. Maroncelli, J. Phys. Chem. 100, 12981–12996 (1996). Reprinted with permission from The Journal of Physical Chemistry. Copyright 1996 American Chemical Society.

Another use of ultrafast lasers is to measure the solvation dynamics associated with the electron transfer reactions we considered in Section 5.3.2. Figure 5.10 shows the principle. Suppose optical excitation from the ground singlet  $S_0$  to the first excited singlet  $S_1$  results in a substantial change in the dipole moment of the molecule. The solvent cannot adjust to the change in dipole on the time scale of the excitation, nor is the geometrical arrangement of the solvent likely to be of the lowest energy configuration for the new electronic configuration. With increasing time, however, the solvent molecules will rearrange their orientation so as to stabilize the new dipole moment and lower the energy.

Imagine now that one could resolve in time the emission from  $S_1$  back to  $S_0$ . Immediately after the excitation, emission would be at roughly the wavelength of the excitation, but as time progresses, the emission will occur to longer wavelengths as the energy on the upper potential surface approaches a minimum. **Figure 5.11** shows how the emission spectrum shifts to the red as time progresses from 0 to 50 ps. The authors used a fluorescence up-conversion technique to obtain the subpicosecond time resolution. The fluorescence at a particular time delay and wavelength was combined with a probe laser pulse to produce a signal at the sum of the frequencies of the probe laser and the fluorescence. For a fixed delay between the probe laser pulse and the initial excitation pulse, the up-converted signal was then scanned in wavelength to generate a curve in the figure. The time delay between the probe pulse and the excitation pulse was then changed and the wavelength scan repeated to obtain the series of curves shown in the figure. Not surprisingly, different solvent molecules respond more or less rapidly depending on their dielectric constant.



#### Figure 5.11

The shift in the fluorescence spectrum of Coumarin 153 in formamide as a function of time following excitation. The times are 0, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, and 50 ps, in order of decreasing peak intensity.

From R. M. Stratt and M. Maroncelli, J. Phys. Chem. 100, 12981–12996 (1996). Reprinted with permission from *The Journal of Physical Chemistry*. Copyright 1996 American Chemical Society.

#### 5.5 SUMMARY

Reactions in solution are found to differ little from their gas phase counterparts when the solvent does not participate as a reactant. The principal difference is that the solvent molecules both prevent the initial approach of reactants and also form a cage around them when they finally encounter one another. The forces responsible for the cage effect are related to the friction coefficient,  $\zeta$ , in the Langevin equation. Using Langevin's model, the diffusion coefficient *D* in the fluid can be related to the friction coefficient:

$$D = \frac{kT}{\zeta}.$$
 (5.7)

If the reaction between reactants is facile when they are caged, then the reaction rate is often controlled by the rate at which the reactants can diffuse toward one another; the reaction is *diffusion controlled*. For such reactions, we found that the rate constant was given by

$$k = 4\pi (D_{\rm A} + D_{\rm B})\beta, \qquad (5.27)$$

where, for nonionic species,  $\beta$  is simply equal to *R*, the average diameter of the reactants. For ionic species,

ŀ

$$3 = \frac{-z_{\rm A} z_{\rm B} r_0}{1 - \exp(z_{\rm A} z_{\rm B} r_0/R)},$$
(5.29)

where  $r_0 = e^2/\epsilon kT$ , with *e* here signifying the charge on an electron and  $\epsilon$  here signifying the dielectric constant of the medium.

When a reaction involves charged species in solution, the solvent can influence the reaction by stabilizing differently the reactants, activated complexes, and products. The influence on the reaction rate of the ionic strength of the solution can be understood by considering how the activity coefficients deviate from unity. When these deviations can be approximated by the Debye-Hückel limiting law, then we obtain the following relationship between the rate constant and the ionic strength:

$$\log_{10}k_0 = \log_{10}k_0 + 2Az_A z_B I_c^{1/2},$$
(5.35)

where  $I_c$  is the ionic strength and A is a constant equal to 0.50 (L/mol)<sup>1/2</sup> for water at 25°C. When unlike ions form an activated complex, the complex is less charged than the reactants and is thus less stabilized by increasing ionic strength than the reactants; the apparent activation energy increases so that the rate constant decreases. When like ions form an activated complex, on the other hand, the complex has a higher charge than the reactants and is more stabilized by increasing ionic strength; the apparent activation energy decreases and the rate constant increases.

A second situation where the solvent can affect the reaction rate constant is during electron transfer. Marcus has addressed the problem of how the activation energy for the reaction depends on  $\Delta G^0$ , the free energy of the reaction. By using an approximate derivation of his theory, we determined that the rate constant for the electron transfer reaction is given by

$$k_{\rm ET}(T) = \frac{kT}{h} \exp\left(-\frac{(E_{\rm m} + \Delta G^0)^2}{4E_{\rm m}kT}\right),$$
 (5.38)

where  $E_{\rm m}$ , called the reorganization energy, is the energy the donor would have in excess of the acceptor if it and its surrounding solvent were placed at the minimum energy configuration of the acceptor. This equation predicts that the rate constant for electron transfer will first increase with  $-\Delta G^0$ , that is as the products become more stable with respect to the reactants, but that it will then decrease as  $-\Delta G^0$  increases further. This latter region is called the Marcus inverted region.

In the above examples, the solvent influences the stability of reactants, activated complexes and products, but it does not itself react. When the solvent does participate as a reactant, the reaction rates in solution are often large enough to require special experimental techniques for determination of the rate constant. Relaxation and ultrafast laser techniques were briefly described as ways to measure rapid rate constants.

## appendix 5.1

#### The Langevin Equation and the Mean Squared Displacement

In this appendix we solve the Langevin equation, equation 5.1, for the root-meansquared distance traveled by a Brownian particle. Noting that v = dx/dt, we multiply both sides of equation 5.1 by x and rewrite it as

$$mx\frac{\mathrm{d}}{\mathrm{d}t}\frac{\mathrm{d}x}{\mathrm{d}t} = -\zeta x\frac{\mathrm{d}x}{\mathrm{d}t} + xf(t). \tag{5.39}$$

Since  $d/dt (x dx/dt) = (dx/dt)^2 + x (d/dt) (dx/dt)$ , we rewrite the first term:

$$m\frac{\mathrm{d}}{\mathrm{d}t}\left(x\frac{\mathrm{d}x}{\mathrm{d}t}\right) - m\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)^2 = -\zeta x\frac{\mathrm{d}x}{\mathrm{d}t} + xf(t). \tag{5.40}$$

#### Chapter 5 Reactions in Liquid Solutions

We now take the ensemble average of both sides of the above equation. On the right-hand side,  $\langle xf(t) \rangle = \langle x \rangle \langle f(t) \rangle$  since we assume that the fluctuating forces are random and independent of position; note that  $\langle f(t) \rangle = 0$ , as stated in equation 5.2. Thus,

$$m\left\langle \frac{\mathrm{d}}{\mathrm{d}t} \left( x \frac{\mathrm{d}x}{\mathrm{d}t} \right) \right\rangle = -\zeta \left\langle x \frac{\mathrm{d}x}{\mathrm{d}t} \right\rangle + m\left\langle \left( \frac{\mathrm{d}x}{\mathrm{d}t} \right)^2 \right\rangle.$$
(5.41)

The last term is just  $m < v^2 >$ , which is equal to kT for a particle with one degree of freedom (in the x direction, as assumed here). The solution to the resulting differential equation is then simply

$$m\frac{\mathrm{d}}{\mathrm{d}t}\left\langle x\frac{\mathrm{d}x}{\mathrm{d}t}\right\rangle = -\zeta\left\langle x\frac{\mathrm{d}x}{\mathrm{d}t}\right\rangle + kT$$

$$\left\langle x\frac{\mathrm{d}x}{\mathrm{d}t}\right\rangle = Ae^{-\zeta t/m} + \frac{kT}{\zeta},$$
(5.42)

where the validity of the second step can be verified by differentiation. The constant A must be determined from the initial condition, which we take to be x = 0 when t = 0 so that  $A = -(kT/\zeta)$ . We now write x(dx/dt) as  $\frac{1}{2}(d/dt)(x^2)$  and obtain the equation

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle = \frac{kT}{\zeta}(1-e^{-\zeta t/m}).$$
(5.43)

Integrating both sides of this equation gives the final expression for the mean squared displacement

$$\langle x^2 \rangle = \frac{2kT}{\zeta} \bigg[ t - \frac{m}{\zeta} (1 - e^{-\zeta t/m}) \bigg].$$
(5.44)

Let us now investigate two limiting cases for this formula. When t is short enough so that  $t/m \ll 1$ , then we can approximate the exponential by its first few terms:  $\exp(-\zeta t/m) \approx 1 - (\zeta t/m) + \frac{1}{2} (\zeta t/m)^2$ , so that

$$\langle x^2 \rangle = \frac{kT}{m} t^2. \tag{5.45}$$

This formula just tells us that on such short time scales, the rms displacement goes as  $(kT/m)^{1/2}t$ , or that the particle just moves freely with its one-dimensional rms speed,  $(kT/m)^{1/2}$ . On this time scale, when  $t \ll m/\zeta$ , the particle does not encounter the friction of the medium (note that the friction coefficient does not appear in equation 5.45). For a particle of water's density and a radius 100 nm moving in a fluid such as water, the time  $m/\zeta$  is about  $10^{-9}$  s.

Now consider the case when  $t >> m/\zeta$ . Under this condition, equation 5.44, reduces to

$$\langle x^2 \rangle = \frac{2kT}{\zeta}t.$$
 (5.46)

This last equation is the long-time mean squared displacement. Note that the mean squared displacement is inversely proportional to the friction coefficient  $\zeta$ .

#### **Diffusion with an Electrostatic Potential**

For neutral species, motion is controlled by the response to a concentration gradient, but for ionic species, motion is also affected by the electrostatic potential between the ions. Before proceeding to calculate the diffusion controlled rate constant, we digress briefly to consider how the diffusion equation,  $J_z = -D(\partial c/\partial z)$ , would need to be modified if species responded not only to a concentration gradient but also to an electric field.

An ion which is moving in a potential gradient  $\nabla \Phi$  caused has a *mobility*  $\mu = v/(\nabla \Phi)$ . Thus, the mobility is simply the proportionality constant between the velocity v and the potential gradient; the bigger the gradient, the faster the ion will move. If A and B, for example, are oppositely charged, the potential gradient between them will cause them to move toward one another, so that the flux toward one another will be increased. Since v is the velocity toward one another, the flux toward one another is increased by  $cv = c\mu\nabla\Phi$ , where c is the concentration. The general diffusion equation  $J_z = -D(\partial c/\partial z)$  would then need to be modified to give

$$J_{z} = -\left(D\frac{\partial c}{\partial z} + \frac{z}{|z|}\mu c\frac{\partial \Phi}{\partial z}\right),$$
(5.47)

where z is the charge on the ion and the factor z/|z| is used to take care of the sign of the charge. The first term is the contribution to the flux due to diffusion, whereas the second term is the contribution due to the gradient of the electric field.

At equilibrium in a solution, the overall flux at any point must be zero, so that

$$J_{z} = 0 = -\left(D\frac{\partial c}{\partial z} + \frac{z}{|z|}\mu c\frac{\partial \Phi}{\partial z}\right).$$
(5.48)

Solution of this equation is relatively straightforward:

$$\frac{\mathrm{d}c}{c} = -\frac{z}{|z|} \frac{\mu}{D} \,\mathrm{d}\Phi,\tag{5.49}$$

or

$$\ln\frac{c}{c^0} = -\frac{z}{|z|}\frac{\mu}{D}\Phi,$$
(5.50)

where  $c^0$  is the concentration when the electric field is zero. We now assume that at equilibrium the concentration must obey the Boltzmann law:

$$c = c^0 \exp\left(-\frac{U}{kT}\right),\tag{5.51}$$

where the potential energy U of the ions in the field is given by  $U = ze\Phi$ .

Substitution of equation 5.51 into equation 5.50 and use of  $U = ze\Phi$  gives an equation that relates the mobility and the diffusion coefficient:

$$\frac{\mu}{D} = \frac{|z|e}{kT}.$$
(5.52)

Finally, substitution of equation 5.52 and  $U = ze\Phi$  into equation 5.47 gives

$$J_z = -D\left(\frac{\partial c}{\partial z} + \frac{c}{kT}\frac{\partial U}{\partial z}\right).$$
(5.53)

#### Chapter 5 Reactions in Liquid Solutions

More generally, we recognize that the flux can have components in each of the three spatial dimensions, so that

$$\boldsymbol{J} = -D\bigg(\nabla c + \frac{c}{kT}\nabla U\bigg). \tag{5.54}$$

We now return to the development of Section 5.2.4 and generalize equation 5.21 for the case of diffusion in an electrostatic field to obtain:

$$k_{\rm r}[{\rm A}]B(R) = [{\rm A}]4\pi r^2 (D_{\rm A} + D_{\rm B}) \left[\frac{{\rm d}B(r)}{{\rm d}r} + \frac{B(r)}{kT}\frac{{\rm d}U(r)}{{\rm d}r}\right].$$
 (5.55)

In this equation [A] is again constant, B(R) is constant (to be determined), and B(r) denotes how the microscopic concentration of B varies with distance.

We now rewrite the right-hand side of the last equation as

$$k_{\rm r}[{\rm A}]B(R) = [{\rm A}]4\pi r^2 (D_{\rm A} + D_{\rm B})e^{-U(r)/kT} \frac{{\rm d}}{{\rm d}r} [B(r)e^{U(r)/kT}].$$
(5.56)

Division of both sides of the equation by  $[A]r^2 \exp[-U(r)/kT]$  and multiplication by dr yields

$$k_{\rm r}B(R)\frac{e^{U(r)/kT}{\rm d}r}{r^2} = 4\pi(D_{\rm A}+D_{\rm B})\,{\rm d}B(r). \tag{5.57}$$

Finally, if we define

$$\beta^{-1} = \int_{R}^{\infty} \frac{e^{U(r)/kT} \,\mathrm{d}r}{r^2},$$
(5.58)

then integration of both sides of equation 5.62 over dr from r = R to  $r = \infty$  gives

$$k_{\rm r}B(R)\int_{R}^{\infty} \frac{e^{U(r)/kT}}{r^2} \,\mathrm{d}r = 4\pi (D_{\rm A} + D_{\rm B})\int_{R}^{\infty} \mathrm{d}[B(r)e^{U(r)/kT}],$$
$$\frac{k_{\rm r}B(R)}{\beta} = 4\pi (D_{\rm A} + D_{\rm B})[B(r = \infty)e^{U(r=\infty)/kT} - B(r = R)e^{U(r=R)/kT}]$$

or

$$B(R)\left[\frac{k_{\rm r}}{\beta} + 4\pi(D_{\rm A} + D_{\rm B})e^{U(R)/kT}\right] = 4\pi(D_{\rm A} + D_{\rm B})[{\rm B}]$$

$$B(R) = \frac{[{\rm B}]}{e^{U(R)/kT} + \frac{k_{\rm r}}{4\pi(D_{\rm A} + D_{\rm B})\beta}},$$
(5.59)

where  $U(r = \infty)$  has been assumed to be zero. Note that U(R) is very small, since the two ions are in contact, so that  $\exp[U(R)/kT] \approx 1$ . Substitution of this solution for B(R) into equation 5.20 gives

$$\frac{\mathbf{d}[\mathbf{P}]}{\mathbf{d}t} \approx \frac{k_{\mathrm{r}}}{1 + \frac{k_{\mathrm{r}}}{4\pi (D_{\mathrm{A}} + D_{\mathrm{B}})\beta}} [\mathrm{A}][\mathrm{B}].$$
(5.60)

Thus, when  $k_r >> 4\pi (D_A + D_B)\beta$ , the overall rate constant for the reaction is given by

$$k = 4\pi (D_{\rm A} + D_{\rm B})\beta. \tag{5.61}$$

This is the equation given as equation 5.27.

## suggested readings

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# problems

- 5.1 For a diffusion-controlled reaction the rate constant depends on the size of the reactants both through R and through the diffusion coefficients. In solution the diffusion coefficient can be approximated by the Stokes-Einstein relationship,  $D = kT/6\pi\eta r$ ; where  $\eta$  is the viscosity coefficient of the solvent and r is the radius of the diffusing species. For reactants of the same size, will the diffusion-controlled rate constant depend on the size?
- 5.2 The reaction rate between species of charge +1 and one of charge -2 will (a) increase, (b) decrease, or (c) remain constant with increasing ionic strength?
- 5.3 For the mechanism

$$A + B \rightleftharpoons_{k_r}^{k_f} C$$

show that in the limit of small perturbations the concentration of A relaxes to its new equilibrium value  $A_e$  according to the equation  $A(t) = A_e + x_e \exp \{-[k_f(A_e + B_e) + k_r]t\}$ , where  $x_e$  is the initial concentration change between [A] and its equilibrium value;  $x_e = A(t = 0) - A_e = B(t = 0) - B_e = C_e - C(t = 0)$ .

5.4 The reaction between hydrogen peroxide and iodide has been investigated by F. Bell, R. Gill, D. Holden, and W. F. K. Wynne-Jones in J. Phys. Chem. 55, 874 (1951):  $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$ . The reaction proceeds by two parallel mechanisms and leads to rate law

$$\frac{-d[H_2O_2]}{dt} = \frac{d[I_2]}{dt} = k_1[H_2O_2][I^-] + k_2[H_2O_2][I^-][H^+].$$

The rate constants  $k_1$  and  $k_2$  are observed to vary with ionic strength in the fashion shown in the table. Are these data qualitatively and quantitatively consistent with the primary salt effect in **equation 5.35**?

•	<i>I</i>	$k_1(M^{-1} s^{-1})$	$\underline{k_2(M^{-2} s^{-1})}$
	0.000	0.658	19.0
	0.0207	.0.663	15.0
	0.0525	0.670	12.2
	0.0925	0.679	11.3
	0.1575	0.694	9.7
	0.2025	0.705	9.2

- 5.5 Suppose that the critical distance for reaction of iodine with  $CCl_4$  is  $2 \times 10^{-10}$  m and that the diffusion coefficient of iodine atoms in  $CCl_4$  is  $3.0 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup> at 25°C. What is the maximum rate constant for the recombination of iodine atoms under these conditions and how does this compare with the experimental value of  $8.2 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> measured by R. M. Noyes in J. Am. Chem. Soc. **86**, 4529 (1964)?
- 5.6 Suppose that three ions, A with charge  $z_A$ , B with charge  $z_B$ , and C with charge  $z_C$  react in a termolecular process. Derive an equation similar to equation 5.35 to describe the primary salt effect on this reaction.

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# 6

# Reactions at Solid Surfaces

#### **Chapter Outline**

- 6.1 Introduction
- 6.2 Adsorption and Desorption
- 6.3 Reactions at Surfaces: Catalysis
- 6.4 Surface Diffusion
- 6.5 Advanced Topics in Surface Reactions
- 6.6 Summary

Appendix 6.1 Integral Transforms

#### 6.1 INTRODUCTION

Systems of high surface-to-volume ratio play extremely important roles in life processes, industrial manufacture, and even geological change. The exchange of oxygen and carbon dioxide in our lungs or in green plants, the conversion of straight-chain hydrocarbons to aromatic compounds on a platinum catalyst, the formation of ClONO<sub>2</sub> on ice crystals responsible for the "ozone hole," and the reactions responsible both for the formation of soil and for the use of its mineral content by living organisms are all due to chemical reactions that occur at the surface of a substance.

In this chapter we examine the special kinetic behavior of systems reacting at surfaces. Our goal is to see how the kinetic principles we have developed can be used to understand the kinetics at surfaces. While we will focus on the solid-gas interface, much of what we will discuss is applicable as well at other important interfaces. We will start by considering the nature of the surface separating two heterogeneous phases. Processes that occur at this interface are characterized by several steps: adsorption and desorption onto/from the surface, reaction at the surface, and diffusion along the surface. After considering a model of adsorption due to Langmuir, we will then investigate unimolecular and bimolecular reactions at surfaces. As we will see, there are many parallels between the catalytic action of surfaces and the catalytic action of enzymes, already studied in Chapter 2. We will next comment briefly on the nature of catalytic sites on surfaces and then discuss

#### Chapter 6 Reactions at Solid Surfaces

surface diffusion in some detail. We end the chapter with a description of two important techniques for surface study: temperature programmed desorption and modulated molecular beam methods.

Of course, the special feature of the gas-solid interface, or indeed of any surface, is that molecules can be exchanged there between two heterogeneous phases. A naive view of the surface dividing two phases is simply a flat layer of atoms, but detailed experiments have demonstrated that surfaces themselves have structure. **Figure 6.1** shows a schematic model of a solid surface. Most of the atoms (or molecules) on the surface are arranged in layers called *terraces*, but the terraces often have either *adatoms* or *vacancies*. Between the terraces are *steps*, often, but not always, of 1 atom. The steps themselves are not straight, but rather have *kinks* and *step-adatoms*. An image of an actual surface, taken by a technique called scanningtunneling microscopy, is shown in **Figure 6.2**. This structure of surfaces is extremely important to kinetics, since the rate of a surface chemical reaction may vary by several orders of magnitude, depending on the number of steps or on the detailed arrangement of the atoms in the terraces.

The arrangement of atoms on the terraces is, of course, related to the arrangement of atoms in the bulk. While it is beyond our current interest to investigate in detail the crystallographic designations for atomic arrangements in the terraces, it is important to note that different arrangements are possible and that the chemistry that occurs may be dramatically influenced by the structure of the surface. **Figure 6.3** shows a few commonly observed structures.

This chapter will be concerned principally with the characterization of the kinetics of reactions at the gas-solid interface. Such reactions typically involve five main processes: flux of reactants to the surface, adsorption onto the surface, diffusion to reactive sites, reaction, and desorption of the products into the gas phase.

The first process, the flux of reactants to the surface, has already been discussed in Section 4.3.2, where we saw that the flux of molecules through a plane was given by **equation 4.6:**  $J_z = \frac{1}{4} n^* \langle v \rangle$ , where  $n^*$  is the concentration of the reactant and  $\langle v \rangle$  is its average velocity. This flux times the surface area gives the number of reactants that strike the surface per unit time; it is an upper limit on the rate of the reaction. **Example 6.1** shows that during an exposure of 1 langmuir (1  $L = 10^{-6}$  torr-s) about as many molecules hit the surface per unit area as there are atoms on the surface.



#### Figure 6.1

Model of a solid surface depicting different surface sites.

From G. A. Somorjai, *Chemistry in Two Dimensions: Surface* (Cornell University Press, Ithaca, NY, 1981). Reprinted with permission of Dr. G. A. Somorjai.



A scanning-tunneling microscope image of an Si(001) miscut 0.5° toward [100]. The surface steps down from left to right.

Courtesy of M. G. Lagally; for a description of a similar figure see B. S. Swartzentuber, Y.-W. Mo, R. Kariotis, M. G. Lagally, and M. B. Webb, *Phys. Rev. Lett.* 65, 1913 (1990).



#### Figure 6.3

The surfaces of single-crystal metals correspond to planes drawn through the solid. A few simple planes for body-centered cubic crystals are given in this figure.

From R. Gomer, "Surface Diffusion," Scientific American, August, 1982. Reprinted by permission of Jerome Kuhl.

# example 6.1

#### The Number of Molecules Striking the Surface during a 1-Langmuir Exposure Compared to the Number of Surface Sites

Objective	A 1-langmuir (1-L) exposure is defined as an exposure of $10^{-6}$
	torr-s. Assuming that the surface of interest is a square array of
	atoms separated by 4 Å and that every atom provides an adsorption
	site, calculate the fractional coverage of the surface after an expo-
	sure to 1 L of a gas that adsorbs on the surface at each collision.

**Method** The flux of the adsorbate to the surface is given by  $J = \frac{1}{4} < v > n^*$ . We need to calculate how many adsorbates hit the surface given a 1-L exposure and to compare this to the number of adsorption sites. The latter number can be calculated from the number of atoms on the surface given the geometry of the surface layer and the spacing.

**Solution** We are given that the exposure is  $1 L = 10^{-6} \text{ torr-s} = n^* \Delta t$ , where  $\Delta t$  is the duration of the exposure; thus  $n^* = (10^{-6} \text{ torr-s})/\Delta t$  and  $J\Delta t = \frac{1}{4} < v > (10^{-6} \text{ torr-s})$ . Supposing < v > to be around 500 m/s gives the number of molecules striking the surface during this exposure:  $J\Delta t = (0.25)(500 \text{ m/s})(10^2 \text{ cm/m})(10^{-6} \text{ torr-s})(3.22 \times 10^{16} \text{ molec cm}^{-3} \text{ torr}^{-1}) = 4.0 \times 10^{14} \text{ molec cm}^{-2}$ , where the last number in parentheses is the conversion factor from torr (1/760 atm) to molecules cm<sup>-3</sup> at 300 K. Now we need to see how many surface sites per cm<sup>2</sup> are on the surface. The spacing between atoms is 4 Å, so there are  $1/(4 \times 10^{-8})^2 = 6.25 \times 10^{14}$  sites cm<sup>-2</sup>. Thus the coverage is roughly  $(4 \times 10^{14})/(6.25 \times 10^{14}) = 0.64$ . For order-of-magnitude calculations, one often assumes that an exposure of 1 L gives unity coverage.

The remaining processes have not been considered previously. Molecules in the gas phase must become adsorbed on the surface. They then typically migrate by diffusion to sites where they can react or where they can encounter another reactant. Following reaction, the products desorb from the surface into the gas phase. We will examine each of these processes in detail in the subsequent sections and end this chapter with a discussion of a few advanced topics for the study of surface reactions.

#### 6.2 ADSORPTION AND DESORPTION

An early and important discovery in the history of surface catalysis was the observation by Faraday that molecules must first become attached to, or *adsorb* on, a surface before they can react.<sup>a</sup> The mutual attraction between an approaching molecule and a surface can be attributed to two types of interactions. In the first, called

<sup>&</sup>lt;sup>a</sup>M. Faraday, Philos. Trans. 124, 55 (1834).

*physisorption*, the attraction is due to the weak *van der Waals* or dispersion forces. Although, in the general case neither the molecule nor the surface atom will have an average dipole moment, the instantaneous positions of the nuclei and electrons will give rise at any time to dipole moments on the molecule and on the surface atom. The attraction between these instantaneous dipole moments leads to the force responsible for physisorption. The strength of the physisorption bond is typically less than 20 kJ mole<sup>-1</sup>.

In the second type of adsorption, called *chemisorption*, the molecule is attracted to the surface by the same forces that are present in a normal chemical bond, with strengths of  $300-500 \text{ kJ mole}^{-1}$ . Just as in a normal chemical reaction, a barrier to chemisorption is frequently observed.

Figure 6.4 shows a simplified view based on the ideas of Lennard-Jones<sup>b</sup> of the potential energy V(R) between an approaching molecule and a surface atom as a function of the molecule-surface distance R. Curves are shown for both the physisorption and chemisorption bonds. At infinite separation, the physisorbed molecule is free of the influence of the surface; it is customary to define this state as the zero of potential energy. Note that the physisorption bond is rather weak and that its minimum occurs at larger separation compared to the chemisorption bond. Note also that the chemisorption curve is shown as having its energy at infinite separation somewhat higher than the zero of potential energy. This is because chemisorption



#### Figure 6.4

Potential energy curves for chemisorption and physisorption. In (A) the transition from chemisorption to physisorption occurs over a barrier which lies below the energy of infinite separation, while in (B) the barrier lies above this energy. Chemisorption in case (B) is said to be *activated*. The depth of the physisorbed well is exaggerated in the figure compared to the depth of the chemisorbed well.

<sup>&</sup>lt;sup>b</sup>J. E. Lennard-Jones, Trans. Farad. Soc. 28, 333 (1932).

#### Chapter 6 Reactions at Solid Surfaces

typically involves a rearrangement of the structure of the adsorbed molecule. If the adsorbed molecule is pulled away from the surface but frozen in structure, its potential energy will generally be higher than that of the free molecule.

It is typical that to pass from the physisorbed state to the chemisorbed state, the system must overcome a potential barrier. As shown in the figure, this barrier corresponds to the crossing between the physisorption and chemisorption potential energy curves. If the barrier is above the energy corresponding to infinite separation (taken as the zero of energy in the figure), then the chemisorption is said to be *activated*; energy must supplied for the chemisorption reaction to take place. If the barrier is below the energy corresponding to infinite separation, the reaction can proceed even if the molecule approaches the surface with nearly zero kinetic energy. Of course, this one-dimensional picture is highly simplified, since the potential of interaction will depend not only on R but also on the orientation of the molecule and on the specific site on the surface which it approaches.

#### 6.2.1 The Langmuir Isotherm

It was Irving Langmuir who first studied the adsorption process quantitatively.<sup>c</sup> In the simplest model, we suppose that molecules can adsorb only at specific sites on the surface, and that once a site is occupied by one molecule, it cannot adsorb a second molecule. The adsorption process can then be represented as

$$A + S \rightarrow A - S$$
,

where A is the adsorbing molecule, S is the surface site, and A–S represents an A molecule bound to the surface site. In a similar way, the reverse desorption process can be represented as

$$A-S \rightarrow A + S.$$

If [A] is the concentration of molecules and if  $\theta$  is the fraction of the surface sites covered by A, then in the Langmuir model the rate of adsorption is proportional to  $k_a[A](1-\theta)$ , while the rate of desorption is proportional to  $k_d\theta$ , where  $k_a$  and  $k_d$  are the rate constants for the two processes. At equilibrium we know that the rates of the two processes are equal, so that

 $k_{\rm a}[{\rm A}](1-\theta) = k_{\rm d}\theta,$ 

or

$$\frac{\theta}{1-\theta} = \frac{\kappa_a}{k_d} [A].$$
(6.1)

Denoting  $K = k_a/k_d$  and solving for the fraction of occupied sites, we obtain the Langmuir adsorption isotherm:

$$\theta = \frac{K[A]}{1 + K[A]}.$$
(6.2)

Note that equation 6.2 predicts that the fraction of occupied sites should increase linearly with [A] when [A] is low enough so that K[A] << 1, while it should approach unity when [A] is large enough so that K[A] >> 1. This behavior is demonstrated in the plot of  $\theta$  versus [A] shown in Figure 6.5.

<sup>&</sup>lt;sup>c</sup>I. Langmuir, J. Am. Chem. Soc. 38, 221 (1916); 40, 1361 (1918). Langmuir won the Nobel Prize in Chemistry in 1932 for this work.



The surface coverage as a function of adsorbate concentration for the simple Langmuir model.

A somewhat different situation occurs if, as is often observed, the adsorbing molecule dissociates when it chemisorbs. In this case, each dissociated molecule occupies two sites rather than one. A detailed consideration of this situation is outlined in Problem 6.6.

#### 6.2.2 Competitive Adsorption

When two or more species can occupy the same sites on a surface the situation becomes more interesting. Let one species A have fractional surface coverage  $\theta_A$  and let a second species B have coverage  $\theta_B$ . Then the rates for adsorption of species A and B are  $k_a^A(1 - \theta_A - \theta_B)[A]$  and  $k_a^B(1 - \theta_A - \theta_B)[B]$ , respectively, since in each case the rate of adsorption is proportional to the fraction of free sites  $(1 - \theta_A - \theta_B)$ . Similarly, the rate of desorption in each case is proportional to the number of sites occupied by each species. For A and B these rates are  $k_d^A \theta_A$  and  $k_d^B \theta_B$ , respectively. At equilibrium the rates of adsorption and desorption for each species must be the same, so that, denoting  $K_A \equiv k_a^A/k_d^A$  and  $K_B \equiv k_a^B/k_d^B$ , we find

$$\frac{\theta_{\rm A}}{1-\theta_{\rm A}-\theta_{\rm B}}=K_{\rm A}[{\rm A}], \qquad (6.3)$$

and

$$\frac{\theta_{\rm B}}{1-\theta_{\rm A}-\theta_{\rm B}}=K_{\rm B}[{\rm B}]. \tag{6.4}$$

**Equations 6.3** and **6.4** are two simultaneous equations in the variables  $\theta_A$  and  $\theta_B$  that we would like to know. After a little algebra, we find that

$$\theta_{\rm A} = \frac{K_{\rm A}[{\rm A}]}{1 + K_{\rm A}[{\rm A}] + K_{\rm B}[{\rm B}]}$$
(6.5)

#### Chapter 6 Reactions at Solid Surfaces

and that

$$\theta_{\rm B} = \frac{K_{\rm B}[{\rm B}]}{1 + K_{\rm A}[{\rm A}] + K_{\rm B}[{\rm B}]}.$$
(6.6)

Note that if the product of K and the concentration for one of the species, say A, is much higher than for the other, then the surface coverage of the other, B in this case, will be reduced. This is because both species are competing for the same sites on the surface. In the extreme limit when  $K_A[A] >> K_B[B]$ , B will be almost totally excluded from the surface, while the surface coverage of A will approach the value it would have in the absence of B; in this limit equation 6.5 reduces to equation 6.2. The situation is analogous to the competitive inhibition in enzyme catalysis that we encountered in Section 2.5.2.

#### 6.2.3 Heats of Adsorption

It is instructive to consider the equilibrium between adsorption and desorption in light of thermodynamics. From the Clausius-Clapeyron equation we know that the quantity  $[d \ln(P_A/P_A^0)/d(1/T)]_{\theta=\text{const}}$  gives a measure of the heat of adsorption:

$$\frac{\mathrm{d}\ln(P_{\mathrm{A}}/P_{\mathrm{A}}^{0})}{\mathrm{d}(1/T)}\Big|_{\theta=\mathrm{const}} = -\frac{\Delta H_{\mathrm{ad}}}{R},$$
(6.7)

where  $P_A^0$  is a reference pressure (normally one atmosphere) and  $\Delta H_{ad}$  is the molar heat of adsorption. Because  $\Delta H_{ad} = \Delta (E + pV)_{ad}$ , we find  $\Delta E_{ad} = \Delta H_{ad} - \Delta (pV)_{ad}$ . For an ideal gas,  $\Delta (pV)_{ad} = \Delta nRT = -RT$ , so  $\Delta E_{ad} = \Delta H_{ad} + RT$ . **Figure 6.6** shows the heat of adsorption in kcal/mole for CO on various poly-

crystalline transition-metal surfaces.



#### Figure 6.6

Heats of adsorption of CO on polycrystalline transition-metal surfaces. From G. A. Somorjai, Chemistry in Two Dimensions: Surfaces (Cornell University Press, Ithaca, NY, 1981). Reprinted with permission of Dr. G. A. Somorjai.

#### 6.3 REACTIONS AT SURFACES: CATALYSIS

Having considered in detail the processes of adsorption and desorption, we now turn to overall reaction mechanisms for surface reactions. In what follows, we assume that the overall mechanism consists of adsorption and desorption of the reactant(s) followed by reaction on the surface. We will assume for the moment that diffusion on the surface and desorption of the products are rapid enough not to be rate limiting. Diffusion on the surface will be treated in more detail in Section 6.4.

Overall reactions at surfaces, like those in the gas phase, can be categorized by the order of the reaction, and, as in the gas phase, the order for an elementary step is equal to the molecularity.

#### 6.3.1 Unimolecular Surface Reactions

A unimolecular elementary step in a reaction at a surface is one whose rate is first order in the surface coverage of the reactant,  $\theta$ :

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k\theta = \frac{kK[\mathrm{A}]}{1+K[\mathrm{A}]},$$
(6.8)

where P is the product of the surface reaction and the last equality follows from **equation 6.2.** Note that the order of the overall reaction depends on the conditions. Thus, for low values of K[A], the reaction rate increases linearly with [A] because adsorption is the rate limiting step; the reaction is first order in [A]. However, at high values of K[A] where the surface is saturated with A, the rate of the reaction becomes zero order in [A] and depends only on the rate constant k. This situation is analogous to the enzyme catalyzed reaction studied in Section 2.5.2.

An example of a unimolecular surface reaction is the decomposition of ammonia on platinum to give nitrogen and hydrogen at temperatures where both products desorb rapidly. (Under conditions where  $N_2$  desorbs rapidly but  $H_2$  does not, the reaction rate is still first order in NH<sub>3</sub> but is inversely proportional to [H<sub>2</sub>]; see Problem 6.7.) **Example 6.2** shows that dehydrogenation of alcohols at surfaces is also a unimolecular reaction.

#### **Dehydrogenation of Alcohols**

Objective	The dehydrogenation of gaseous alcohols, $RCH_2CH_2OH$ , to give an olefin, $RCH_2 = CH_2$ , plus water on many metal oxides pro- ceeds rapidly at 300°C. If the rate of olefin production is $10^{13}$ molec s <sup>-1</sup> cm <sup>-2</sup> of surface area at an alcohol pressure of 1 torr, and the rate constant for the reaction is $k = 10^{14}$ molec s <sup>-1</sup> cm <sup>-2</sup> , what would the rate of the reaction be for an alcohol pressure of 2 torr?
Method	From <b>equation 6.8</b> , we see that $d[P]/dt = k\theta = k\{K[A]/(1 + K[A])\}$ , where [A] represents the concentration of alcohol. We are given $d[P]/dt$ as $10^{13}$ molec s <sup>-1</sup> cm <sup>-2</sup> and k as $10^{14}$ molec s <sup>-1</sup> cm <sup>-2</sup> , so we need to see how $\{K[A]/(1 + K[A])\}$ changes as [A] goes from 1 to 2 torr.

example 6.2

**Solution** At 1 torr {K[A]/(1 + K[A])} must be 0.1 from the fact that d[P]/dt is 10 times smaller than k, so K[A] = 0.1(1 + K[A]), or 0.9K[A] =0.1, or  $K[A] = \frac{1}{9}$  for [A] = 1 torr. If we double [A] to 2 torr, then  $K[A] = \frac{2}{9}$ , or {K[A]/(1 + K[A])} =  $\frac{2}{9}/(1 + \frac{2}{9}) = 0.182$ , whereas for 1 torr this value was 0.1. Thus the rate increases by a factor of 1.82 to  $1.82 \times 10^{14}$  molec s<sup>-1</sup> cm<sup>-2</sup>.

#### 6.3.2 **Bimolecular Surface Reactions**

For most bimolecular surface reactions, the reaction rate is proportional to the product of the surface coverages of the two reactants:<sup>d</sup>

$$\frac{\mathrm{d}[\mathbf{P}]}{\mathrm{d}t} = k\theta_{\mathrm{A}}\theta_{\mathrm{B}}$$

$$= \frac{kK_{\mathrm{A}}K_{\mathrm{B}}[\mathrm{A}][\mathrm{B}]}{(1 + K_{\mathrm{A}}[\mathrm{A}] + K_{\mathrm{B}}[\mathrm{B}])^{2}},$$
(6.9)

where the last equality follows from equations 6.5 and 6.6. For a constant gasphase concentration of [B], the rate of the reaction will at first increase linearly with [A]. In this region, the adsorption of A is the rate-limiting step in the reaction. As [A] is increased further, the reaction rate will reach a maximum and then finally decrease as 1/[A]. In this last region, the rapid adsorption of A prevents B from reaching the surface. Figure 6.7 contrasts the overall rate of the reaction as a function of [A] for a unimolecular and bimolecular reaction process.

An example of a bimolecular surface reaction is the addition of hydrogen to conjugated hydrocarbons, such as ethylene. Another example is the exchange between  $D_2$  and  $NH_3$ , as described in **Example 6.3**.

# example 6.3

#### H/D Isotope Exchange in Ammonia

**Objective** The exchange between  $D_2$  and  $NH_3$  on an iron catalyst at 150°C has been found to exhibit a peak in the rate of  $NH_2D$  production as the concentration of  $NH_3$  is increased. Suggest why. Ammonia is known to bind to iron more strongly than deuterium, and deuterium is adsorbed as atomic D.

Method Consider Figure 6.7 and equation 6.9 in the limits of low and high [NH<sub>3</sub>].

<sup>&</sup>lt;sup>d</sup>The situation described in the text is called the Langmuir-Hinshelwood model for a bimolecular reaction, for which both species must be adsorbed on the surface before they can react with one another. An alternative bimolecular model known as the Eley-Rideal mechanism involves the direct reaction of a gas-phase molecule with an adsorbed one, for which  $d[P]/dt = k\theta_A[B]$ . Only a very few reactions are thought to proceed by the Eley-Rideal mechanism (see Problem 6.12). In reality, the Langmuir-Hinshelwood and Eley-Rideal models are two limiting cases; most reactions will have a mechanism somewhere between these two extremes.

**Solution** If  $K_{\text{NH}_3}[\text{NH}_3]$  is larger than  $K_D[D]$ , then the numerator of the righthand side of equation 6.9 will be proportional to  $[\text{NH}_3]$ , whereas the denominator will be proportional to  $\{1 + K_{\text{NH}_3}\{[\text{NH}_3]\}^2$ . Thus,  $d[\text{NH}_2D]/dt \propto [\text{NH}_3]/\{1 + K_{\text{NH}_3}\{[\text{NH}_3]\}^2$ . This function is proportional to  $[\text{NH}_3]$  at low concentrations (where  $K_{\text{NH}_3}[\text{NH}_3] \ll 1$ ), but inversely proportional to  $[\text{NH}_3]$  at high concentrations, so the function must have a maximum at some intermediate ammonia concentration.

#### 6.3.3 Activated Complex Theory of Surface Reactions

Activated complex theory, discussed in Chapter 3 in connection with gas-phase reactions, is equally applicable to surface reactions. The only reinterpretation necessary is that the partition functions for species on the surface are now partition functions per unit surface area rather than per unit volume. Thus, following equation 3.17, the rate constant for adsorption of a gas-phase molecule on a surface,  $G + S \rightleftharpoons [G-S]^{\ddagger} \rightarrow G-S$ , is

$$k = \frac{kT}{h} \frac{q^{\dagger \prime}}{q_{\rm g} q_{\rm s}} \, \exp\left(-\frac{\epsilon^*}{kT}\right),\tag{6.10}$$

where  $q_g$  is the partition function (per unit volume) of the free gas,  $q_s$  is the partition function (per unit area) of the unoccupied surface site, and  $q^{\ddagger'}$  is the partition



#### Figure 6.7

Overall rate of (A) first-order and (B) second-order surface reactions as a function of the gasphase concentration of one of the reactants. In (B) the second reactant has been held at fixed concentration.

#### Chapter 6 Reactions at Solid Surfaces

function (per unit area) of the activated complex, omitting the degree of freedom along the reaction coordinate. It is usually assumed that the partition function for the unoccupied surface site (involving only internal motions of the solid surface) is unchanged by the adsorption, so that the ratio of  $q^{\ddagger'}$  to  $q_s$  depends only on the internal degrees of freedom of the activated complex. Problem 6.9 shows that **equation 6.10** reduces to  $k = \frac{1}{4} < v >$  under certain limiting assumptions about the activated complex, confirming that the rate of collisions of molecules with the surface,  $kn^* = \frac{1}{4}n^* < v >$ , is an upper limit on the rate of adsorption.

In a similar manner, activated complex theory gives the rate constant for a unimolecular elementary step in a surface reaction,  $A \Longrightarrow A^{\ddagger} \rightarrow$  with A and  $A^{\ddagger}$  as both adsorbed species:

$$k = \frac{kT}{h} \frac{q^{\dagger\prime}}{q_{\rm A}} \exp\left(-\frac{\epsilon^*}{kT}\right),\tag{6.11}$$

where  $q_A$  is the partition function per unit area of the adsorbate A and  $q^{\ddagger'}$  is the partition function per unit area of the activated complex, omitting the degree of freedom along the reaction coordinate.

For a bimolecular elementary step between two adsorbed species in a surface process we likewise obtain

$$k = \frac{kT}{h} \frac{q^{\dagger \prime}}{q_{\rm A} q_{\rm B}} \exp\left(-\frac{\epsilon^*}{kT}\right),\tag{6.12}$$

with similar interpretations for the partition functions.

#### 6.3.4 The Nature of Surface Catalytic Sites

It has long been assumed that the catalytic nature of solid surfaces is due to "active sites" where reaction proceeds preferentially due to a structural feature that can help in some way to lower the barrier between reactants and products. H. S. Taylor<sup>e</sup> was the first to propose that defect sites (steps, kinks, adatoms, etc.), where low-coordinated surface atoms have unsaturated valencies, are most effective in the catalytic process. However, it is only recently that direct evidence for this thesis has been obtained. Zambelli et al.<sup>f</sup> examined the dissociation of nitric oxide on a ruthenium(0001) surface using scanning-tunneling microscopy and found from the distribution of nitrogen atoms after the reaction that the steps between terraces were responsible for the catalysis. Figure 6.8 shows an image of the Ru(0001) surface with two terraces separated by a step. The left terrace is the upper terrace, and the step is along the dark line in the center of the diagram. The gray spots are nitrogen atoms, and it is noticeable in the image that the density of these atoms decreases with increasing distance from the step. This density distribution is exactly what would be expected if reaction occurs at the step edge. More detailed analysis of this and other images showed that the Ru atoms on the upper level of the step were responsible for the dissociation.

Not all surface reactions occur at steps, but there is usually some feature of the surface that is most responsible for the catalysis. Since the "active sites" are not likely to be at the location where a molecule first adsorbs, it is clear that diffusion to and from the active sites must play an important role. We thus examine surface diffusion next.

eH. S. Taylor, Proc. R. Soc. London Ser. A 108, 105 (1925).

<sup>&</sup>lt;sup>f</sup>T. Zambelli, J. Wintterlin, J. Trost, and G. Ertl, Science 273, 1688–1690 (1996).



A scanning-tunneling microscopy image of a Ru(0001) surface after the dissociative adsorption of 0.3 langmuirs of NO at 315 K. The dark line in the center of the image is a step separating two terraces, with the upper one on the left. The gray dots are nitrogen atoms, while the darker and broader spots are islands of oxygen atoms. Note that the density of nitrogen atoms decreases with distance from the step.

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#### 6.4 SURFACE DIFFUSION

Most surface reactions involve diffusion following adsorption. In the case of unimolecular reactions, the surface adsorbate might need to diffuse to an active site a kink or step, for example. In the case of a bimolecular reaction, the two adsorbates must diffuse to a common location where they can react to give products.

From the macroscopic point of view, a minor reinterpretation of **equation 4.40** (see Section 4.7) gives us the connection between the diffusion coefficient, *D*, and the change in concentration with time and space:

$$\frac{\partial n^*(x,t)}{\partial t} = D \frac{\partial^2}{\partial x^2} n^*(x,t), \qquad (6.13)$$

where  $n^*(x,t)$  is now the number of adsorbates per unit area as a function of position and time, and *D* is the diffusion coefficient in units of area per time. Thus, if one can measure the surface concentration in the presence of a gradient as a function of position and time, one can deduce the diffusion coefficient. In the absence of a gradient, molecules on a surface execute a random walk, so that the diffusion coefficient can be determined by the root-mean-squared distance the adsorbate travels in a given time. Following **equation 4.43**, this distance is given as

$$x_{\rm rms} = (2Dt)^{1/2}$$
. (6.14)

Several techniques have been developed for determining the rates of surface diffusion. Perhaps the most dramatic is the field emission microscope, developed in

#### Chapter 6 Reactions at Solid Surfaces











#### Figure 6.9

Field ion images showing the diffusion of an Ir adatom on an Ir surface. The dot near the center of each photograph is the image of the Ir adatom.

Reprinted with permission from T. T. Tsong, *Physics Today*, **46**, 24 (1993). Copyright American Institute of Physics, 1993.

the 1930s by E. W. Müller.<sup>g</sup> In this technique, a highly magnified image of a pointed metallic sample is formed on a fluorescence screen by field ionization of (typically) helium atoms. The ionization is most efficient at regions of high curvature on the tip surface, which, like lightning rods, have the highest field when the tip is held at a negative potential with respect to the fluorescence screen. Since atoms adsorbed onto the tip provide a highly curved surface, ions are very effectively produced at these locations; the adatoms show up as an intense spot on the screen.

Motion of the adatoms can be followed by examination of images taken at different times. For example, **Figure 6.9** shows several images of an Ir adatom on an Ir surface. By measuring the root-mean-squared displacement of the adatom as a function of time, it is then possible to determine the diffusion coefficient through **equation 6.14.** Diffusion coefficients measured in such studies of single atoms on metal surfaces range from about  $1 \times 10^{-8}$  to  $3 \times 10^{-5}$  in units of m<sup>2</sup> s<sup>-1</sup>.

It is interesting to compare the magnitude of diffusion coefficients on a surface to those of molecules in the gas phase. From **Table 4.4** we see that coefficients for gas-phase molecules have magnitudes of  $1 \times 10^{-5}$  to  $2 \times 10^{-4}$  m<sup>2</sup> s<sup>-1</sup>. Thus, diffusion is much slower on a surface than in the gas phase. A key to why this is true comes from the temperature dependence. Whereas diffusion in gases has a very weak temperature dependence, diffusion on surfaces increases dramatically with temperature. From the microscopic point of view, the reason for this behavior lies in a potential energy barrier between adjacent preferred adsorption sites, as shown in **Figure 6.10**. Experimentally it is found that the temperature-dependent diffusion coefficient is given by  $D(T) = D_0 \exp(-\Delta E_m/kT)$ , where  $\Delta E_m$  is the barrier to diffusion and  $D_0$  is a constant. Typically,  $\Delta E_m$  is found to be about one quarter of the energy required for desorption. From a microscopic point of view,  $D_0$  may be interpreted from a rearrangement of **equation 6.14**:  $D = \frac{1}{2}x_{rms}^2/t$ . Thus, the diffusion constant is given as  $\frac{1}{2}$  times the product of the rate of hopping attempts, 1/t, times the square of the average distance per hop,  $x_{rms}^2$ .

#### Figure 6.10

Potential energy V(x) as a function of lateral surface displacement x for a molecule diffusing on a surface. The barrier to migration due to diffusion,  $\Delta E_{\rm m}$ , is typically one quarter of the barrier to desorption,  $\Delta E_{\rm a}$ .



<sup>&</sup>lt;sup>8</sup>E. W. Müller, *Ergeb. Exakten Naturwiss.* 27, 290 (1953); R. H. Good, Jr., and E. W. Müller, *Handbuch der Physik*, S. Flügge, ed., 21, 176 (1956).

## *example 6.4*

#### Estimating the Surface Diffusion Coefficient of CO on Iron

Objective	Estimate the diffusion coefficient for CO on iron at 300 K given the heat of adsorption from <b>Figure 6.6</b> and the knowledge that adjacent sites are separated by 1.0 nm.
Method	The diffusion coefficient should be one half the product of a hopping attempt frequency times the square of the hop length times a Boltzmann factor accounting for $\Delta E_{\rm m}$ . As an estimate, we may take $\Delta E_{\rm m}$ to be about $0.25\Delta E_{\rm a}$ , which, from the figure is about $(0.25)(50 \text{ kcal/mol})$ . The hopping attempt frequency may be approximated by a low vibrational frequency, about $1.5 \times 10^{12} \text{ s}^{-1}$ .
Solution	The diffusion coefficient is then given by $D \approx (0.5)(1.5 \times 10^{12} \text{ s}^{-1})(1.0 \times 10^{-9} \text{ m})^2 \exp\{-[(0.25)(50 \times 10^3 \text{ cal/mol})(4.184 \text{ J/cal})/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})]\} = 0.7 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}.$

So far we have considered molecular diffusion on a bare surface, i.e., in the limit of zero coverage. When molecules of either the same or another type partially cover the surface, the diffusion coefficient will be different than that on a bare surface. First of all, fewer sites are available to which the molecules can jump. Second, the lateral interactions between molecules at adjacent sites may affect the rate at which the migration takes place. Measurement of diffusion coefficients as a function of coverage is a field that is currently under investigation by a variety of new techniques. One of these is described in Problem 6.10.

#### 6.5 ADVANCED TOPICS IN SURFACE REACTIONS

#### 6.5.1 Temperature-Programmed Desorption

We consider in this section a method, called temperature-programmed desorption (TPD), that makes it possible to estimate the energy of desorption or reaction as well as the Arrhenius preexponential factor.<sup>h</sup> Consider molecules that are irreversibly adsorbed on the surface indicated in **Figure 6.11** at some low temperature  $T_0$ . The leak valve is then closed, the valve to the pump is opened, and the density of product molecules is monitored with a mass spectrometer as the crystal is heated in time at a rate  $\beta$  degrees per second (typically  $\beta \approx 10$  K s<sup>-1</sup>). The crystal temperature is thus  $T = T_0 + \beta t$ .

The density of desorbed molecules measured by the mass spectrometer will be given by a balance between the rate of desorption and the pumping speed. When the pumping speed is high enough so that no readsorption takes place, the density of desorbed molecules will be directly proportional to the rate of desorption. Of

<sup>&</sup>lt;sup>h</sup>G. Ehrlich, J. Appl. Phys. **32**, 4 (1961); Adv. Catal. Relat. Subj. **14**, 271 (1963); P. A. Redhead, Vacuum **12**, 203 (1962).

programmed desorption apparatus.



course, the rate of desorption depends strongly on temperature, so that when the temperature of the crystal reaches a high enough value so that the rate of desorption is appreciable, the mass spectrometer will begin to record a rise in density. At higher crystal temperatures, the surface will eventually become depleted of desorbing molecules, so that the mass spectrometer signal will decrease. The shape and position of the peak in the mass spectrometer signal can be used to learn about the activation energy for desorption and the Arrhenius preexponential factor.

Consider a first-order desorption process:  $A-S \rightarrow S + A$  with a rate constant  $k_{\rm d} = A \exp(-\Delta E_a/RT)$ . If  $\Gamma$  represents the number of surface adsorbates per unit area,<sup>i</sup> the rate of desorption will be given by

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = k_{\mathrm{d}}\Gamma$$

$$= \Gamma A \exp\left(-\frac{\Delta E_{\mathrm{a}}}{RT}\right).$$
(6.15)

However, since the heating rate is  $dT/dt = \beta$ , we see that

$$\frac{1}{dt} = \frac{\beta}{dT}.$$
(6.16)

Multiplying by  $-d\Gamma$  gives

$$-\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = -\beta \frac{\mathrm{d}\Gamma}{\mathrm{d}T},\tag{6.17}$$

and combination of this last equation for  $-d\Gamma/dt$  with equation 6.15 gives

$$-\frac{\mathrm{d}\Gamma}{\mathrm{d}T} = \frac{\Gamma A}{\beta} \exp\left(-\frac{\Delta E_{\mathrm{a}}}{RT}\right). \tag{6.18}$$

Note that  $\Gamma$  and  $\theta$  are related.  $\Gamma$  is the number of adsorbates per area, whereas  $\theta$  is the number of adsorbates per number of sites. Thus  $\Gamma$  times the number of sites per area gives  $\theta$ .

At the peak of the mass spectrometer signal, the increase in the desorption rate is matched by the decrease in surface concentration per unit area so that the change in  $d\Gamma/dT$  with temperature is zero:

$$\left. \frac{\mathrm{d}}{\mathrm{d}T} \frac{\mathrm{d}\Gamma}{\mathrm{d}T} \right|_{T=T_{\mathrm{M}}} = 0, \tag{6.19}$$

$$\frac{\mathrm{d}}{\mathrm{d}T} \left[ \frac{\Gamma A}{\beta} \exp\left( -\frac{\Delta E_{\mathrm{a}}}{RT} \right) \right] = 0,$$

$$\left[ \frac{\mathrm{d}\Gamma}{\mathrm{d}T} + \frac{\Delta E_{\mathrm{a}}}{RT_{\mathrm{M}}^{2}} \Gamma \right] \frac{\mathrm{A}}{\beta} \exp\left( -\frac{\Delta E_{\mathrm{a}}}{RT_{\mathrm{M}}} \right) = 0,$$

$$\frac{\Delta E_{\mathrm{a}}}{RT_{\mathrm{M}}^{2}} = -\frac{1}{\Gamma} \frac{\mathrm{d}\Gamma}{\mathrm{d}T}.$$
(6.20)

Finally, substitution of equation 6.18 into this last equation yields

$$\frac{\Delta E_{\rm a}}{RT_{\rm M}^2} = \frac{A}{\beta} \exp\left(-\frac{\Delta E_{\rm a}}{RT_{\rm M}}\right),\tag{6.21}$$

or

$$2 \ln T_{\rm M} - \ln \beta = \frac{\Delta E_{\rm a}}{RT_{\rm M}} + \ln \frac{\Delta E_{\rm a}}{RA}.$$
 (6.22)

If different heating rates  $\beta$  are used and the left-hand side of this last equation is plotted as a function of  $1/T_{\rm M}$ , we see that a straight line should be obtained whose slope is  $\Delta E_{\rm a}/R$  and whose intercept is  $\ln(\Delta E_{\rm a}/RA)$ . Note also that the value of  $T_{\rm M}$  does not depend on the initial coverage.

The situation is a bit more complicated for a second-order desorption process such as  $2 A-S \rightarrow A_2 + 2 S$ . Problem 6.11 shows that the resulting equation for  $T_M$  is

$$2\ln T_{\rm M} - \ln \beta = \frac{\Delta E_{\rm a}}{RT_{\rm M}} + \ln \frac{\Delta E_{\rm a}}{AR\Gamma_0},$$
(6.23)

where  $\Gamma_0$  is the initial surface coverage. Again, a plot of the left-hand side of the equation against  $1/T_{\rm M}$  provides information about  $\Delta E_{\rm a}$  and  $A_{\rm d}$ . Note, however, that the temperature of the peak will change with initial surface coverage. This variation is the hallmark of a second-order desorption. For example, note how the D<sub>2</sub> desorption peak at 380 K in **Figure 6.12** shifts to lower temperature with increasing coverage.

It frequently occurs that molecules decompose before they desorb. For example, formic acid decomposes on a nickel surface to  $H_2$ , CO, and CO<sub>2</sub> at a temperature of about 388 K. Figure 6.13 shows the temperature-programmed desorption spectrum of this molecule (the lower-temperature desorption of water is not shown in the figure). If adsorbed separately on this surface,  $H_2$  and CO would desorb at 353 and 438 K, respectively. The fact that the principal peaks for  $H_2$  and CO occur at 388 K indicates that these species are initially produced by decomposition of the acid. Some of the CO escapes from the surface due to the exothermicity of the reaction, while some is readsorbed and then desorbs later at 438 K.

#### 6.5.2 Modulated Molecular Beam Methods

We consider in this section the application of molecular beam methods to surface reactions. These methods provide insight into the kinetics of surface processes as

or



Thermal desorption spectra of  $D_2$ from Rh(100) for different exposures in langmuirs (1 langmuir =  $10^{-6}$  torrs). Note how the peak shifts to lower temperature with increasing coverage. From Y. Kim, H. C. Peebles, and J. M. White, *Surface Science* **114**, 363 (1982). Reprinted from *Surface Science*, copyright 1982, with permission from Elsevier Science.





TPD of formic acid adsorbed at 325 on a nickel surface.

From M. Boudart and G. Djéga-Mariadassou, *Kinetics of Heterogeneous Catalytic Reactions* (Princeton University Press, Princeton, NJ, 1984) based on original data of J. McCarthy, J. Falconer, and R. Madix, *J. Catal.* **30**, 235 (1973). Copyright © 1984 by Princeton University Press. Reprinted by permission of Princeton University Press.



Schematic diagram of the molecular beam-surface scattering technique. From G. A. Somorjai, *Chemistry in Two Dimensions: Surfaces* (Cornell University Press, Ithaca, NY, 1981). Reprinted with permission of Dr. G. A. Somorjai.

well as detail concerning the dynamics of the gas-surface interaction. Molecular beam methods are also important to our understanding of gas-phase reactions and dynamics, but we will postpone our examination of this field until Chapter 8.

**Figure 6.14** shows a typical molecular beam apparatus for studies of surface processes. A molecular beam of reactants is formed using methods to be described in Chapter 8. The beam is chopped by a rotating, slotted disk before it impinges on a solid surface. Unreacted reactants and newly formed products are detected by a rotatable mass spectrometer as a function of time. Two important quantities can be determined using this technique: the time dependence of the product flux and the angular distribution of the scattered species. We consider the angular distribution first.

#### 6.5.2.1 Angular Distributions

The angular distribution of the scattered molecules provides information on the exchange (or "accommodation") of momentum during the surface collision. Consider two possible limits. In one, the molecule colliding with the surface "sticks" to the surface long enough to lose all memory of its incoming direction and momentum. After such a strong energy exchange, we can regard the surface and gas to be at equilibrium at some specific temperature. If the molecule subsequently escapes from the surface attractive potential, we might wonder what angular distribution its velocity would have with respect to a line normal to the surface. The answer is shown for CO scattering from Pt(111) in Figure 6.15, where the distance of a point from the origin in the plot is proportional to the probability of finding the product velocity at the given angle with respect to the surface normal. For the highest coverage of preadsorbed CO on the surface the scattering is given approximately by  $\cos \theta$ . In fact, we already know that the  $\cos \theta$  distribution, given by the dashed circle in the plot, should be the answer to the equilibrium problem! Consider the velocity distribution function for molecules leaving an area A of the surface. If the surface and gas temperatures are the same, i.e., if there is equilibrium, this distribution will be the same as the velocity distribution for molecules which strike that area of the surface, except that the velocity vectors will be reversed in sign. We have already seen in Section 4.3.2 (see Figure 4.2 and equation 4.3) that the velocity



The angular distribution of CO scattered from Pt(111) at 310 K and for three different coverages. The CO beam was incident at 55°, as shown by the arrow. The dashed circles indicate the distribution expected for purely cosine scattering.

From C. T. Campbell, G. Ertl, H. Kuipers, and J. Segner, *Surface Science* **107**, 207 (1981). Reprinted from *Surface Science*, copyright 1981, with permission from Elsevier Science.

distribution for molecules striking the surface starting from the three-dimensional "volume" element  $v^2 \sin \theta \, d\theta \, d\phi \, dv$  is proportional to  $\cos \theta$ . Thus, the angular distribution for molecules leaving the surface in equilibrium with the surface temperature will also be proportional to  $\cos \theta$ , an observation known as the Knudsen cosine law.

Now consider another limit for the angular distribution, one in which the molecules simply bounce off an unmoving surface in the same way light might be reflected from a mirror. In this case the outgoing angle of deflection with respect to the surface normal will simply be the negative of the incoming angle of incidence. Such scattering is termed *specular scattering* or *elastic scattering*. Figure 6.15 shows that CO scatters nearly specularly when the surface is bare ( $\Theta_{CO} = 0$ ), but that as the coverage increases the scattering follows more and more the cosine law. At the highest coverage there is still a remnant of the specular scattering, but the distribution nearly follows the Knudsen law.

Most angular scattering distributions lie somewhere in between these two limits, as shown in the CO/Pt(111) case for intermediate coverages of CO. Furthermore, even in the specular limit, the peak of the scattering distribution is often shifted from the exact specular direction. **Figure 6.16** shows such a shift for the scattering of Ar from Pt. The reason for the shift is that the collision with the surface is rarely elastic. Movement of the surface atoms either imparts energy to or takes energy from the component of velocity perpendicular to the surface. In this case, Ar atoms on average gain perpendicular momentum by collision with the energetic surface atoms.

Occasionally one finds a dramatic departure from either the specular or cosine scattering. Figure 6.17 shows the angular distribution of  $H_2$  found after passing  $H_2$  through a thin iron membrane. The  $H_2$  dissociates as it passes through the membrane





Polar plot of the angular distribution of Ar scattered from Pt with a surface temperature of 1173 K and an incident angle of  $55^{\circ}$ .

From F. O. Goodman and H. Y. Wachman, *Dynamics of Gas-Surface Scattering* (Academic Press, New York, 1976) based on data from A. R. Rudnicki and H. Y. Wachman, *Surf. Sci.* **34**, 679 (1973). Reprinted from *Surface Science*, Copyright 1973, with permission from Elsevier Science.



**Figure 6.17** 

Angular distribution of H<sub>2</sub> desorbed from polycrystalline iron at 1140 K. From T. L. Bradley and R. E. Stickney, *Surf. Sci.* **38**, 313 (1973). Reprinted from *Surface Science*, copyright 1973, with permission from Elsevier Science.

#### Chapter 6 Reactions at Solid Surfaces

and then the hydrogen atoms recombine on the front surface. The recombination releases substantial energy, forcing the  $H_2$  off the surface in a peak centered on the surface normal.

#### 6.5.2.2 Kinetic Parameters

Modulated molecular beam methods also allow the determination of rate constants. To gain an intuitive understanding of how such an experiment might work, consider the analogy of the sun heating the Earth during a yearly cycle. The average amount of sunlight varies nearly sinusoidally throughout the year, so that if the heating were instantaneous, the peak in the Earth's average monthly temperature should follow the peak in the exposure to sunlight; the warmest month would be June, while the coldest month would be December. However, the rate of heating of the Earth's surface and atmosphere depend on the heat capacity. The result is that the temperature varies sinusoidally, but there is a phase lag of about 1 month. Turning this around, the observation of a 1-month phase lag between exposure and response can be used to calculate the rate of heating, or the heat capacity in this case. Another observation concerns the depth of modulation. The average monthly temperatures over the ocean vary less with season than those over land, because the heat capacity of salt water is higher than that of land. By analogy, measurement of the phase lag and depth of modulation of reactant products following periodic exposure of a surface to reactants provides information on the rate constant for the reaction.

Now let's put these concepts on a firmer mathematical foundation. Consider the simple mechanism outlined below in which a modulated beam of intensity I(t) interacts with the surface:

$$A + S \xrightarrow{s_0 I(r)} A - S,$$

$$A - S \xrightarrow{k} A + P,$$
(6.24)

where  $s_0$  is the sticking coefficient of A on the surface and k represents the rate constant for reaction of the surface-bound species to products. The differential equations for the intermediate and the products are given by

$$\frac{\mathrm{d}C(t)}{\mathrm{d}t} = s_0 I(t) - kC(t),$$

$$\frac{\mathrm{d}P(t)}{\mathrm{d}t} = kC(t),$$
(6.25)

where C(t) and P(t) represent the time-dependent concentrations [A–S] and [P], respectively. In the experiment, the concentration of products in the gas phase is measured by a mass spectrometer as a function of time for different incident fluxes I(t). The concentration of products in the gas phase is determined both by their production rate, dP(t)/dt, and by the rate at which they are pumped away. Under normal experimental conditions the mass spectrometer signal, S(t), is directly proportional to dP(t)/dt. Thus, (taking the proportionality constant to be unity for simplicity) we have S(t) = dP(t)/dt = kC(t).

In the general case, I(t) may vary on a time scale comparable to the reaction, so that it would be inappropriate to use the steady-state principle to solve this problem. Instead, we use the Laplace transformation method of solution outlined in

Appendix 6.1. Consider the transform of the equation for dC(t)/dt, where the transformation variable is the pure complex variable  $i\omega$ . Using **Table 6.1** in the appendix with  $s = i\omega$ , we find that the transformed equation is

$$i\omega c(\omega) = s_0 I(\omega) - kc(\omega),$$
  

$$c(\omega) = \frac{s_0 I(\omega)}{k + i\omega}.$$
(6.26)

From the equation S(t) = kC(t), we obtain  $S(\omega) = kC(\omega)$ , so

$$t(\omega) \equiv \frac{s(\omega)}{I(\omega)} = \frac{ks_0}{k + i\omega},$$
  
$$= \frac{ks_0}{(k + i\omega)} \frac{(k - i\omega)}{(k - i\omega)},$$
  
$$= \frac{s_0(k^2 - ik\omega)}{k^2 + \omega^2},$$
  
(6.27)

where  $t(\omega)$  is called the *transfer function*. This function indicates how the amplitude and phase of the mass spectrometer signal will depend on the frequency of the input signal. Specifically, writing  $t(\omega)$  in vector notation in a complex plane, as shown in **Figure 6.18**, we obtain

$$t(\omega) = a(\omega) \exp[-i\phi(\omega)], \qquad (6.28)$$

where the real part,  $a(\omega)$ , indicates how the amplitude of the signal changes with frequency, while the phase indicates how the output waveform is shifted from the input one. Comparison of equation 6.28 with equation 6.27 yields

$$a(\omega) = \frac{s_0}{\sqrt{1 + (\omega/k)^2}},$$
  

$$\tan \phi(\omega) = \frac{\omega}{k}.$$
(6.29)



#### Figure 6.18

The transfer function can be expressed in terms of amplitude  $a(\omega)$  and phase  $\phi(\omega)$  in the complex plane.



The modulated molecular beam (here assumed to be sinusoidal) and the mass spectrometer signal for the kinetic scheme of the text and for different values of the rate constant k in compared to the frequency of modulation  $\omega$ .

**Figure 6.19** shows an input waveform (assumed to be a sine wave rather than a square wave) and the signal waveforms for various cases of k compared to  $\omega$ . Note that the signal  $s(\omega) = t(\omega)I(\omega) = a(\omega)\exp[-i\phi(\omega)]I(\omega)$ . When the modulation of the input signal is slow on the time scale of the reaction kinetics, the output waveform is just like the input waveform, but when the modulation is fast on the time scale of the kinetics, the output waveform is reduced in amplitude and shifted in phase. A measurement of the phase shift as a function of modulation frequency can be used to determine the rate constant. For example, if the rate constant were equal to the modulation frequency, then the phase shift would be 45° and the amplitude would be the original amplitude divided by the square root of 2.

In practice, the input waveform is often a square wave rather than a sine wave. Since a square wave contains frequency components at odd multiples of the fundamental, the transfer function actually can provide information on several frequencies simultaneously. Problem 6.13 outlines a method for recovering the information.

#### 6.6 SUMMARY

Our study of reactions at solid surfaces has taken us from the structure of the surfaces, involving terraces, steps, kinks, and adatoms, to the kinetics of surface processes, involving adsorption, desorption, diffusion, and reaction. The flux of atoms or molecules to the surface is given by

$$J_z = \frac{1}{4}n^* < v >.$$
 (4.6)

The adsorption of molecules striking the surface can occur through both *physisorption* and *chemisorption*, and the latter process will be activated if the barrier between the physisorption well and the chemisorption well lies above the energy corresponding to infinite separation of the molecule from the surface.

The Langmuir model for adsorption assumes that molecules can adsorb only at specific sites on the surface and that once a site is occupied by one molecule it cannot adsorb a second molecule. The model leads to the following equation for the surface coverage:

$$\theta = \frac{K[\mathbf{A}]}{1 + K[\mathbf{A}]},\tag{6.2}$$

where K is the equilibrium constant for adsorption:  $K = k_a/k_d$ . When two molecules of different types compete for the same adsorption sites, the coverage of one is given by

$$\theta_{\rm A} = \frac{K_{\rm A}[{\rm A}]}{1 + K_{\rm A}[{\rm A}] + K_{\rm B}[{\rm B}]},$$
(6.5)

with a similar equation for  $\theta_{\rm B}$ .

From application of the Clausius-Clapeyron equation we find that

$$\frac{\mathrm{d}\ln(P_{\mathrm{A}}/P_{\mathrm{A}}^{0})}{\mathrm{d}(1/T)}\Big|_{\theta=\mathrm{const}} = -\frac{\Delta H_{\mathrm{ad}}}{R}.$$
(6.7)

Reactions at surfaces are unimolecular, bimolecular, etc. just as in the gas phase or in solution. For unimolecular processes we found that

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k\theta = \frac{kK[\mathrm{A}]}{1+K[\mathrm{A}]},$$
(6.8)

where P is the product of the reaction. For a bimolecular process

$$\frac{\mathbf{d}[\mathbf{P}]}{\mathbf{d}t} = k\theta_{\mathrm{A}}\theta_{\mathrm{B}}$$

$$= \frac{kK_{\mathrm{A}}K_{\mathrm{B}}[\mathbf{A}][\mathbf{B}]}{(1 + K_{\mathrm{A}}[\mathbf{A}] + K_{\mathrm{B}}[\mathbf{B}])^{2}}.$$
(6.9)

The two processes have remarkable differences in their pressure dependence, since in the latter case one of the reactants can "poison" the surface toward adsorption of the second. Activated complex theory can be applied to surface reactions to yield estimates of rate constants.

Surface diffusion plays an important role in surface reactions. The barrier to diffusion on the surface is less than the barrier to desorption, and diffusion constant on a surface can be obtained by measuring how far a molecule moves in a given time:

$$\frac{\partial n^*(x,t)}{\partial t} = D \frac{\partial^2}{\partial x^2} n^*(x,t).$$
(6.13)

A convenient method for estimating the energy of desorption or reaction is by temperature programmed desorption. For a first-order process the temperature  $T_M$  at which the signal has a maximum is related to the activation energy by the equation

$$2 \ln T_{\rm M} - \ln \beta = \frac{\Delta E_{\rm a}}{RT_{\rm M}} + \ln \frac{\Delta E_{\rm a}}{RA}.$$
 (6.22)

#### Chapter 6 Reactions at Solid Surfaces

For a second-order process the temperature at which the signal is a maximum also depends on the surface coverage:

$$2 \ln T_{\rm M} - \ln \beta = \frac{\Delta E_{\rm a}}{RT_{\rm M}} + \ln \frac{\Delta E_{\rm a}}{AR\Gamma_0}.$$
 (6.23)

Modulated molecular beam methods allow one to measure both the angular distribution and the reaction rate constant. Under conditions of equilibrium adsorption and desorption, the angular distribution varies as  $\cos \theta$  (where  $\theta$  is the angle measured from the surface normal). Under nonequilibrium conditions, the scattering is often more strongly directed—toward the specular angle in the case of a repulsive interaction at the surface and toward the surface normal if a reaction takes place releasing a large amount of energy.

The rate constant is related to the phase of the modulated product signal and the frequency of modulation:

$$\tan \phi(\omega) = \frac{\omega}{k}.$$
 (6.29)

appendix 6.1

#### **Integral Transforms**

The Laplace transform provides a convenient method for solution of differential equations. Consider the function F(t). Let the Laplace transform of F(t) be defined as

$$f(s) = \mathscr{L}[F(t)] = \int_0^\infty e^{-st} F(t) dt, \qquad (6.30)$$

where t is a real variable, F(t) is a real function of t whose value when t < 0 is zero, f(s) is a function of s, and s is a complex variable. The function f(s) is called the Laplace transform of F(t), while F(t) is called the inverse Laplace transform of f(s).

The usefulness of the Laplace transform for differential equations comes from the observation that the Laplace transformation of derivatives like dF(t)/dt converts them to simple algebraic expressions of *s*.

Consider the Laplace transform of dF(t)/dt:

$$\mathcal{L}[dF(t)/dt] = \int_0^\infty \frac{dF(t)}{dt} e^{-st} dt,$$
  
=  $F(t)e^{-st}|_0^\infty - \int_0^\infty F(t) d(e^{-st}),$   
=  $-F(t=0) + s \int_0^\infty F(t)e^{-st} dt,$   
=  $-F(t=0) + sf(s),$   
(6.31)

where we have used integration by parts in going from the first line to the second.

In a similar way, it is possible to build up a table of Laplace transforms of particular functions. **Table 6.1** provides the transforms of some of the more common functions.
TABLE 6.1	Table of Lapla	ce Transforms
	F(t)	f(s)
	F(t)	$\int_0^\infty e^{-st} F(t) \mathrm{d}t$
	$\frac{\mathrm{d}F(t)}{\mathrm{d}t}$	sf(s) - F(t=0)
	1	$\frac{1}{s}$
	$e^{at}$	$\frac{1}{s-a}$
	te <sup>at</sup>	$\frac{1}{(s-a)^2}$
	t	$\frac{1}{s^2}$
	sin <i>bt</i>	$\frac{b}{s^2+b^2}$
	cos bt	$\frac{s}{s^2+b^2}$
	$\frac{1}{(a-b)}\left(e^{at}-e^{bt}\right)$	$\frac{1}{(s-a)(s-b)}$

As an example of the usefulness of Laplace transforms, consider the differential equation we encountered (Section 2.4.3, Consecutive Reactions) in **equation 2.63**:

$$\frac{d[B]}{dt} = k_1 A(0) e^{-k_1 t} - k_2 [B].$$
(6.32)

The solution can be obtained by taking the Laplace transform of both sides, solving the resulting algebraic equation, and then taking the inverse Laplace transform. First we take the Laplace transform:

$$sb(s) - B(t = 0) = \frac{k_1 A(0)}{s + k_1} - k_2 b(s).$$
 (6.33)

Next, note that B(t = 0) = 0 from the initial condition that all population in the  $A \rightarrow B \rightarrow C$  reaction is initially in A. Solution of the algebraic equation gives

$$sb(s) + k_2b(s) = \frac{k_1A(0)}{s+k_1},$$
  

$$b(s) = k_1A(0)\frac{1}{s+k_2}\frac{1}{s+k_1}.$$
(6.34)

If we now take the inverse Laplace transform of both sides of the last equation we obtain

$$[\mathbf{B}] = \frac{k_1}{k_2 - k_1} \mathbf{A}(0) (e^{-k_1 t} - e^{-k_2 t}).$$
(6.35)

This last equation is just equation 2.64.

It should be noted that the Laplace transform method is appropriate only for *linear* differential equations; that is, ones that involve in every term only one variable concentration rather than the product of two or more. Transformation then gives a set of linear algebraic equations. The solutions can then be inverse transformed to obtained the concentrations as a function of time.

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### problems

- 6.1 The analysis of adsorption by Langmuir predicts that with increasing exposure the coverage of a species on a surface (a) increases monotonically, (b) decreases monotonically, (c) increases then decreases, or (d) decreases then increases.
- 6.2 Under Langmuir's assumptions, if two species can adsorb on a surface, then the equilibrium coverage of one of them will (a) increase, (b) decrease, or (c) remain constant as the exposure of the surface to the other species increases.
- 6.3 The barrier to diffusion is typically (a) a bit larger than, (b) a bit smaller than, (c) a lot larger than, or (d) a lot smaller than the barrier to desorption.

- 6.4 For a first-order desorption process, the temperature at which a peak might be expected in the temperature-programmed desorption spectrum depends on which of the following: (a) the Arrhenius *A* parameter, (b) the Arrhenius activation energy, (c) the rate of surface heating, (d) the coverage, (e) the heat of adsorption, or (f) the diffusion coefficient?
- 6.5 Suppose a molecule is completely accommodated on the surface before desorbing. To detect the desorbed species most sensitively, we would place a detector so that it accepted molecules (a) moving perpendicular to the surface normal, (b) moving at the specular angle, or (c) moving along the surface normal. (Specify which.)
- 6.6 Consider adsorption with dissociation:  $A_2 + S + S \rightarrow A-S + A-S$ . Show from an analysis of the equilibrium between adsorption and desorption that the surface coverage  $\theta$  is given as a function of  $[A_2]$  by

$$\theta = \frac{K^{1/2} [A_2]^{1/2}}{1 + K^{1/2} [A_2]^{1/2}}.$$

- 6.7 As might be expected, the decomposition of ammonia on platinum is first order in the gas-phase concentration of ammonia. However, at certain temperatures, where the  $N_2$  coverage is nearly zero but the  $H_2$  coverage is not, the reaction is inversely proportional to the  $H_2$  pressure. Suggest a mechanism for this observation, evaluate the rate expression for the mechanism, and show under what limit the mechanism gives the observed result.
- 6.8 A second-order surface reaction involves two gas-phase species A and B, which are adsorbing and desorbing from the surface. For a fixed concentration of B denoted as  $[B]_0$  in the gas phase, it is observed that the overall rate of the reaction has a maximum at a particular concentration of A denoted as  $[A]_{max}$ . What is the relationship between  $[A]_{max}$  and  $[B]_0$ ?
- 6.9 Show that (6.10) reduces to  $k = \frac{1}{4} < v >$  for atomic adsorption under the limiting assumption where the activated complex is mobile in two dimensions and there is no activation energy.
- 6.10 One method for measuring the surface diffusion coefficient at arbitrary initial coverages is to thermally desorb molecules from the surface using two pulsed laser beams coincident in time and crossed at a slight angle. The interference between the light waves from the two beams creates a concentration grating of adsorbed molecules on the surface. As diffusion takes place, the concentration grating decreases in time. A convenient method for measuring the decay of the grating is to use it to scatter light from a third laser pulse, delayed in time from the first two. For reasonable intensities of the probe beam, second-harmonic generation can be obtained at each of the diffraction peaks. The method, which was developed by Shen and his coworkers,<sup>j</sup> has recently been used by Rosenzweig, Farbman, and Asscher [*J. Chem. Phys.* 98, 8277 (1993)] to study the diffusion of ammonia on Re. A theoretical analysis shows that the second-harmonic intensity for the *n*th order diffraction peak should decay as

<sup>&</sup>lt;sup>j</sup>X.-D. Xiao, D. D. Zhu, W. Daum, and Y. R. Shen, *Phys. Rev.* **B46**, 9732 (1992); *Surf. Sci.* **271**, 295 (1992); X. D. Zhu, Th. Rasing, and Y. R. Shen, *Phys. Rev. Lett.* **61**, 2883 (1988).

Chapter 6 Reactions at Solid Surfaces

$$I_n^{2\omega}(t) = I_n^{2\omega}(0) \exp\left(-\frac{8\pi^2 n^2 D t}{s^2}\right),$$

where s is the spacing of the grating and D is the diffusion coefficient. If the second-harmonic signal at the first-order diffraction peak falls to 1/e of its original value in 200 s and the grating spacing is  $s = 8.0 \ \mu m$ , what is the diffusion coefficient for NH<sub>3</sub> on Re at the temperature and coverage of the experiment (110 K and  $\theta = 0.25$ )?

- 6.11 Show that for a second-order desorption process the temperature at the peak maximum in the temperature programmed desorption experiment is given by **equation 6.23.** (*Hint*: The surface coverage at the temperature corresponding to the peak has been shown by Redhead to be  $\Gamma_0/2$ .)
- 6.12 A few reactions are thought to proceed by the Eley-Rideal mechanism. For example, the reaction  $D_{(g)} + H_{(ad)} \rightarrow HD_{(g)}$  is thought not to require adsorption of the H atom before reaction; that is, the attacking D picks up the H on a single bounce. Evidence that this is the case is shown in **Figure 6.20**, which plots the HD product angular distribution for an incidence D-atom angle of  $-60^{\circ}$  [from C. T. Rettner, *Phys. Rev. Lett.* **69**, 383 (1992)]. The solid circles are for an incident energy of 0.06 eV, whereas the open squares are for an incident energy of 0.33 eV.
  - a. Point out two features of this data that support the hypothesis that the reaction proceeds by the Eley-Rideal mechanism.
  - b. Suggest another possible experiment that might test this hypothesis.
- 6.13 We saw in Section 6.5.2.2 that modulated molecular beam techniques could be used to determine kinetic parameters. Normally, the molecular beam is modulated in a square-wave fashion rather than in a sine-wave fashion. The





Plot of the HD product angular distribution for an incidence D-atom angle of  $-60^{\circ}$ . From C. T. Rettner, *Phys. Rev. Lett.* **69**, 383 (1992). Copyright 1992 by the American Physical Society.

Laplace transform of a square wave contains amplitude at all odd multiples of the fundamental frequency (though with decreasing amplitude as the frequency increases), so that the transfer function, given in **equation 6.28**, also has such frequency components. If the amplitude and phase of the transfer function are plotted in polar coordinates, the resulting figure can be used to determine many aspects of the mechanism of the surface reaction. For example, consider the kinetic scheme

$$+ S \xrightarrow{ps_0I(i)} C_1,$$

$$(1-p)s_0I(i) \longrightarrow C_2,$$

$$C_1 \xrightarrow{k_1} A + F$$

$$C_2 \xrightarrow{k_2} A + F$$

Α

where p and (1 - p) are the fraction adsorbing to the two different species  $C_1$  and  $C_2$ , respectively, and both species can react to give the product P. Determine the transfer function for this system of parallel reactions when p = 0.5 and plot the transfer function in polar coordinates for the following three values of  $k_1/k_2$ : 1, 10, 100.

6.14 Molecular beam techniques can also be used to study processes at the gasliquid interface. Figure 6.21 shows the schematic of an apparatus used by Saecker and Nathanson for investigation of the energy exchange between a



#### Figure 6.21

Schematic diagram of an apparatus for studying gas-liquid interactions. A rotating wheel and a scraper provide a fresh surface for interaction with the molecular beam. The speed of the scattered beam is measured by a time-of-flight method using a rotating chopper.

From M. E. Saecker and G. M. Nathanson, J. Chem. Phys. 99, 7056 (1993). Reprinted with permission from the Journal of Chemical Physics. Copyright, American Institute of Physics, 1993.

#### Chapter 6 Reactions at Solid Surfaces

variety of atoms and molecules with glycerol [HO– $CH_2$ –CH(OH)– $CH_2$ –OH]. The speed distribution of the scattered species was determined by timing the flight between the slotted chopper wheel and the ionization region of a quadrupole mass spectrometer.

**Figure 6.22** displays the resulting time-of-flight distributions for Ne,  $CH_4$ ,  $NH_3$ , and  $D_2O$ . The distributions are characterized by two components, an inelastic component at short times and a trapping-desorption component at longer times. The "inelastic" component corresponds to molecules that collide once with the surface of the liquid and, while losing some energy, scatter impulsively from the surface (see Section 8.4.4 for more discussion of inelastic processes). The trapping-desorption component corresponds to molecules that lose enough energy to bind momentarily to the surface or dissolve in the liquid. These molecules have sufficient contact with the surface to then desorb with a speed characteristic of the surface temperature. Explain why the ratio of the trapping-desorption component to the inelastic component might increase dramatically as shown.



#### Figure 6.22

Time-of-flight distributions for collisions of various gases with glycerol. From M. E. Saecker and G. M. Nathanson, *J. Chem. Phys.* **99**, 7056 (1993). Reprinted with permission from the *Journal of Chemical Physics*. Copyright, American Institute of Physics, 1993.

# Photochemistry

#### **Chapter Outline**

- 7.1 Introduction
- 7.2 Absorption and Emission of Light
- 7.3 Photophysical Processes
- 7.4 Atmospheric Chemistry
- 7.5 Photodissociation Dynamics
- 7.6 Summary

#### 7.1 INTRODUCTION

The field of photochemistry combines our knowledge of the quantum mechanical interaction of light and matter with the kinetics of chemical processes. It is a field important for both the fundamental information it yields about molecular structure and dynamics and the practical understanding it provides for processes ranging from the chemistry of the atmosphere to the mechanism of vision. In this chapter we explore several aspects of molecular photochemistry. We will concentrate largely on examples in isolated or gas-phase molecules, because it is in these systems that experiments have led to new theoretical concepts. After reviewing fundamental issues concerning the absorption and emission of light, we illustrate some of the fates of photoexcited molecules, including fluorescence, quenching, intramolecular vibrational energy redistribution, internal conversion, intersystem crossing, phosphorescence, and photodissociation. As a practical application of photochemistry and kinetics, we turn to processes affecting the concentration of stratospheric ozone, touching briefly on the origin of the Antarctic "ozone hole" and outlining both the basic Chapman mechanism for ozone production and destruction as well as the catalytic cycles which modify this simple mechanism. A major section of this chapter deals with the dynamics of photochemical processes. It is here that we see how measurement of the dynamics can provide fundamental information about how molecules interact, how they are held together, and what happens when they fall apart. The section begins with a description of the "pumpprobe" technique for measuring dynamics and moves quickly to a description of two important probe methods, laser-induced fluorescence and multiphoton ionization. It then turns to a consideration of the rates for unimolecular processes and introduces the principles of the RRKM theory (see Section 7.5.4). It closes with discussions of photochemical angular distributions, photochemistry on very short time scales, and the relationship between photodissociation dynamics, potential energy surfaces, and absorption spectra. A summary section emphasizes the major points of the chapter.

#### 7.2 ABSORPTION AND EMISSION OF LIGHT

Because any photochemical reaction involves the absorption of light, we begin by reviewing the fundamentals of the interaction of light with matter. The intensity of absorption is characterized by the fraction of light that is absorbed when it traverses a thickness  $\ell$  of sample of concentration *c* or pressure *p*. This fraction is  $(I_0 - I)/I_0$ , where  $I/I_0$ , the fraction transmitted, is given by the Beer-Lambert law,

$$\frac{I}{I_0} = \exp(-\alpha \ell p), \tag{7.1}$$

where  $\alpha$  is called the absorption coefficient. This exponential form of the Beer-Lambert law is usually used for gases, in which case  $\alpha$  has the units of torr<sup>-1</sup> cm<sup>-1</sup>, and p and  $\ell$  are expressed in torr and cm, respectively. In solutions an equivalent form of the law is more often used,

$$\frac{I}{I_0} = 10^{-\epsilon \ell c},\tag{7.2}$$

where  $\epsilon$  has the units of liters mole<sup>-1</sup> cm<sup>-1</sup>, and *c* and  $\ell$  are expressed in moles/liter and cm, respectively. Another form of the law expresses the transmission in terms of a frequency-dependent cross section,  $\sigma(\nu)$ , for absorption:

$$\frac{I}{I_0} = \exp[-\sigma(\nu)\ell\rho], \qquad (7.3)$$

where the absorption cross section might be given in cm<sup>2</sup>, with  $\ell$  in cm and the density  $\rho$  in molecules cm<sup>-3</sup>.

The absorption coefficients and cross section are related to three more fundamental quantities, the Einstein coefficients:  $A_{21}$  for spontaneous emission from state 2 to 1,  $B_{21}$  for stimulated emission from state 2 to 1, and  $B_{12}$  for absorption from state 1 to 2. For this two-level system, illustrated in **Figure 7.1**, if  $\rho(\nu)$  is the energy density per unit frequency of light at frequency  $\nu$ , then the change in  $N_1$ , the population of level 1, is given as

$$\frac{\mathrm{d}N_1}{\mathrm{d}t} = -N_1 B_{12} \rho(\nu) + N_2 [B_{21} \rho(\nu) + A_{21}].$$
(7.4)



#### Figure 7.1

Einstein absorption  $(B_{12})$ , stimulated emission  $(B_{21})$ , and spontaneous emission  $(A_{21})$  coefficients for a two-level system. The absorption and stimulated emission rates are proportional to the density of radiation at the resonant frequency. The first term in this expression is the loss of  $N_1$  due to absorption to level 2, while the second term accounts for the production of  $N_1$  due to stimulated and spontaneous emission from level 2. In these equations,  $\rho(\nu)$  has units of energy length<sup>-3</sup> (time<sup>-1</sup>)<sup>-1</sup> (energy density per unit frequency), and  $B_{12}$  and  $B_{21}$  have units of energy<sup>-1</sup> length<sup>3</sup> time<sup>-2</sup>. At equilibrium for this two level system we have  $dN_1/dt = 0$ , or

$$\frac{N_2}{N_1} = \frac{B_{12}\rho(\nu)}{B_{21}\rho(\nu) + A_{21}}.$$
(7.5)

Comparison of this last equation with the Boltzmann distribution and use of  $\rho(\nu)$  for a blackbody distribution provides relationships between the three coefficients (see Problem 7.13):

$$B_{12} = B_{21} \frac{g_2}{g_1},$$

$$A_{21} = \frac{8\pi h\nu^3}{c^3} B_{21}.$$
(7.6)

Here,  $g_1$  and  $g_2$  are the degeneracies of levels 1 and 2, respectively.

An important consequence of the Einstein analysis of absorption and emission is the prediction of *laser* action (light amplification by stimulated emission of radiation). **Equation 7.4** shows that emission of light will dominate if

$$N_2[B_{21}\rho(\nu) + A_{21}] > N_1 B_{12}\rho(\nu).$$
(7.7)

Thus, provided that the density of radiation is high enough so that  $B_{21}\rho(\nu) >> A_{21}$ , stimulated emission will occur when

$$\frac{N_2}{N_1} > \frac{B_{12}}{B_{21}} = \frac{g_2}{g_1},\tag{7.8}$$

where the last equality follows from equation 7.6. We will see in Section 8.2 that chemical reactions sometimes produce products with  $N_2 > N_1$ , an "inverted" population.

A relationship between  $B_{12}$  and the absorption cross section  $\sigma(\nu)$  can be developed by comparing the differential form of equation 7.3,

$$-dI(\nu) = I(\nu)\sigma(\nu)N_1d\ell, \qquad (7.9)$$

and the total decrease in population of  $N_1$  given by the negative of equation 7.4:

$$-dN_1 = N_1 B_{12} \rho(\nu) dt - N_2 [B_{21} \rho(\nu) + A_{21}] dt.$$
(7.10)

In the first of these equations we use  $I(\nu)$  to signify the intensity per unit frequency [so that its units are energy length<sup>-2</sup> time<sup>-1</sup> (time<sup>-1</sup>)<sup>-1</sup>). Thus,  $I(\nu) d\nu$  is the intensity (in energy length<sup>-2</sup> time<sup>-1</sup>) of radiation in the region from  $\nu$  to  $\nu + d\nu$ . The density of light times its speed, c, is the intensity:  $\rho(\nu)c = I(\nu)$ . Thus, division of the intensity decrease  $-I(\nu) d\nu$ , by the energy of the photon,  $h\nu$ , and by the speed of light gives the decrease in the number density of photons,  $-dI(\nu) d\nu/(ch\nu)$ . Assuming that the transition is of sufficient energy that the population of level 2 is negligible (i.e., that  $N_2 << N_1$ ), the number density of photons absorbed must be equal to the number density of molecules excited from level 1; i.e.,  $-dI(\nu) d\nu/(ch\nu) = -dN_1$ . Combining this last equation with **equation 7.10** gives

$$\frac{I(\nu) \,\mathrm{d}\nu \sigma(\nu) N_1 \,\mathrm{d}\ell}{ch\nu} = N_1 B_{12} \rho(\nu) \,\mathrm{d}t,$$

$$\frac{\sigma(\nu)\,\mathrm{d}\nu}{h\nu}\frac{\mathrm{d}\ell}{\mathrm{d}t} = B_{12}\frac{c\rho(\nu)}{I(\nu)}.$$
(7.11)

On the left-hand side of this equation,  $d\ell/dt$  can be replaced by the speed of light, c, while on the right-hand side  $c\rho(\nu)$  is equal to  $I(\nu)$ . Consequently,

$$B_{12} = \frac{c\sigma(\nu)\,\mathrm{d}\nu}{h\nu}.\tag{7.12}$$

This equation can be used in either of two ways. If we integrate over frequency, we obtain the Einstein coefficient for the entire absorption band. If we multiply the frequency-dependent cross section by the bandwidth of a narrow light source, we obtain the Einstein coefficient for absorption at that particular frequency.

The Einstein coefficients are also related to the transition dipole moment for the transition:

$$A_{21} = \frac{64\pi^2 \nu^3}{3hc^3} |\mu_{21}|^2, \qquad (7.13)$$

where

$$\mu_{21} = -e \int \psi_{\mathbf{e}_{2}\mathbf{v}_{2}}(\mathbf{r},\mathbf{R}) \mathbf{r} \psi_{\mathbf{e}_{1}\mathbf{v}_{1}}(\mathbf{r},\mathbf{R}) \,\mathrm{d}\tau_{\mathrm{el}} \,\mathrm{d}\tau_{\mathrm{nuc}}. \tag{7.14}$$

Under the Born-Oppenheimer approximation, the electronic-vibrational wave functions,  $\psi_{ev}(\mathbf{r},\mathbf{R})$  can be expressed as products,  $\psi_{e}(\mathbf{r})\psi_{v}(\mathbf{R})$ , so that

$$\mu_{21} = -e \int \psi_{e_2}(\mathbf{r}) \mathbf{r} \psi_{e_1}(\mathbf{r}) d\tau_{ei} \int \psi_{v_2} \psi_{v_1} d\tau_{nuc}. \qquad (7.15)$$

Since the second of these integrals is the overlap between the vibrational wave functions in the upper and lower levels, the absorption or emission of light will occur preferentially to states for which this overlap is greatest.

Since the electrons move much faster than the nuclei, absorption or emission is not accompanied by a change in the nuclear coordinates; the transition is *vertical* in a diagram such as **Figure 7.2**, plotting potential energy as a function of nuclear coordinates. Note in this figure that the transition is drawn as a vertical arrow and that the preferentially populated upper vibrational level, here shown as v = 3, is the



#### Figure 7.2

According to the Franck-Condon principle, absorption occurs preferentially to the state whose wave function has the maximum overlap with the initial wave function. 207

one whose vibrational wave function has the maximum overlap with the wave function of the lower level, here taken as v = 0. This important consequence of equation 7.15 is known as the *Franck-Condon principle*.

While the absorption depicted in **Figure 7.2** often results in a line spectrum, where each line corresponds to a transition between not only individual vibrational but also individual rotational levels of the upper and lower electronic states, the lines are never infinitely sharp. The widths of the lines are caused by *Doppler broadening*, where the motion of the molecule relative to the observer or source of light causes emission or absorption of light at different frequencies, and by *lifetime broadening*, where the finite lifetime of the molecule due to emission, dissociation, or other processes gives rise to a width in accordance with the uncertainty principle,  $\Delta E \Delta t \approx \hbar$ . For molecules with a Maxwell-Boltzmann distribution of velocities, the Doppler-broadened line shape is given by the formula

$$\sigma(\nu) = \sigma_0 \exp\left[-\frac{mc^2}{2kT} \frac{(\nu - \nu_0)^2}{\nu_0^2}\right],$$
(7.16)

where  $\nu_0$  is the frequency at line center. The constant  $\sigma_0$  is a normalization factor

$$\sigma_0 = \frac{c}{\nu_0} \sqrt{\frac{m}{2\pi kT}},\tag{7.17}$$

and the Doppler width (full width at half maximum) is given by

$$\Delta \nu = 2 \frac{\nu_0}{c} \sqrt{\frac{2kT \ln 2}{m}}.$$
(7.18)

A Doppler profile is shown as the solid line of Figure 7.3.

For molecules whose lifetime is given by  $\tau$ , the Lorentz-broadened line shape is given by

$$\sigma(\nu) = \frac{\Delta\nu}{2\pi} \frac{1}{(\nu - \nu_0)^2 + (\Delta\nu/2)^2},$$
(7.19)



Figure 7.3

Doppler- and Lorentz-broadened line shapes.

where  $\nu_0$  is the frequency at line center and  $\Delta \nu = 1/(\pi \tau)$  is the full width at half maximum. A Lorentz-broadened profile is shown as the dashed line of Figure 7.3.

We can define a *quantum yield* for a photochemical process as simply the number of events of interest divided by the number of photons of light absorbed by the system. For example, if the process of interest were the production of a photochemical product *P*, then the "quantum yield of *P*" would be given by the number of product molecules produced during a given time,  $N_P$ , divided by the number of photons absorbed by the system during that same time,  $N_{h\nu}$ :  $\Phi_P = N_P/N_{h\nu}$ . Alternatively, the quantum yield could be expressed as the ratio of the rate of production of *P* divided by the rate of absorption of light.

In determining the quantum yield, it will not always be the case that the process of interest is production of a product molecule. We next examine the possible fates of molecules excited by radiation.

#### 7.3 PHOTOPHYSICAL PROCESSES

Absorption of light at visible or shorter wavelengths typically results in a combination of vibrational, rotational, and electronic excitation. We examine in this section the fate of the energy deposited in the molecule. In many cases, the energy is lost by a radiative process, either fluorescence—radiation to a lower electronic state of similar multiplicity as the upper one—or phosphorescence—radiation to a state of different multiplicity. But many nonradiative processes can occur as well, either as the result of collision or, particularly for larger molecules, as collisionless, intramolecular processes. These include intramolecular vibrational energy redistribution, internal conversion, and intersystem crossing. Of more interest from the chemical point of view, the energy can also be used to break a bond in the molecule. Such dissociation can be caused by a direct process, such as absorption to a level which, while bound at the level of the Born-Oppenheimer approximation, is coupled to the continuum of dissociative states by higher-order terms in the Hamiltonian.

#### 7.3.1 Fluorescence and Quenching

Perhaps the simplest photochemical processes are absorption and re-emission of light. According to the Franck-Condon principle, in the absence of collisions that change the initially excited vibrational level, light will be emitted preferentially at two frequencies. One frequency is the same as the frequency that caused the excitation, since at this frequency the overlap between the ground and excited vibrational wave functions is strong. Another frequency, where strong emission will occur corresponds to a downward vertical transition from a location near the outer turning point of vibrational motion on the upper surface, since at this location the wave function also has maximum amplitude.

We now consider the situation when collisions with other molecules cause vibrational relaxation in the upper electronic state. The situation is shown schematically in **Figure 7.4.** If vibrational relaxation were to take place rapidly enough, nearly all the subsequent fluorescence would occur from v = 0, as shown in the figure. In reality, of course, the rate of vibrational relaxation is not infinitely fast compared to the rate of fluorescence, particularly when the pressure of the collision partner is low, so that emission from intermediate levels will occur.



Figure 7.4

Vibrational relaxation in the upper electronic state prior to fluorescence back to the ground electronic state.

**Figure 7.5** displays the fluorescence spectrum of I<sub>2</sub> following excitation of the v = 25, J = 34 level of the  $B \,{}^{3}\Pi_{0u}$  electronic state with a filtered mercury lamp. The fluorescence is resolved by a monochromator in the absence and presence of a quenching gas, He. In the upper panel, resonance fluorescence is observed only from the initially excited level; two lines are observed corresponding to  $\Delta J = \pm 1$  transitions. In the lower panel, emission occurs from other vibrational and rotational levels produced in collision with He.

The way in which the intensity of emission from the initial and intermediate levels varies as a function of pressure can be used to provide a measure of the relaxation. Suppose a molecule M is excited by radiation at an intensity that is constant in time (sometimes called *cw* [continuous wave] radiation). The excited species,  $M^*$ , can then emit radiation or suffer a quenching collision that takes it to a state,  $M^{\dagger}$ , that does not emit at the frequency being detected. The state  $M^{\dagger}$  might be another vibrational level of the excited electronic state, as in **Figure 7.4**, or it might be another electronic state, as will be discussed in later sections. In either case, the kinetic scheme is

$$M + h\nu_{a} \xrightarrow{l_{a}\sigma} M^{*},$$

$$M^{*} + Q \xrightarrow{k_{q}} M^{\dagger},$$

$$M^{*} \xrightarrow{k_{f}} M + h\nu_{f}.$$
(7.20)

The rate for excitation of M to M<sup>\*</sup> is equal to the intensity of radiation at the excitation frequency,  $I_a$ , times the cross section for absorption,  $\sigma$ , whereas the intensity of fluorescence,  $I_f$ , is proportional to  $k_f[M^*]$ . Now assume that the initial concentration of M, M<sub>0</sub>, is not appreciably perturbed by the excitation and that the assumptions implicit in the steady-state approximation are valid. Solution of the steadystate equations leads (Problem 7.6) to the equation

$$\frac{1}{I_{\rm f}} = \frac{1}{I_{\rm a}\sigma M_0} \left( \frac{k_{\rm q}}{k_{\rm f}} [Q] + 1 \right).$$
(7.21)



Figure 7.5

Fluorescence spectrum of  $I_2$  without (*upper panel*) and with (*lower panel*) added helium. From J. I. Steinfeld and W. Klemperer, J. Chem. Phys. 42, 3475 (1965). Reprinted with permission from the *Journal of Chemical Physics*. Copyright, American Institute of Physics, 1965.

Thus, a plot of  $1/I_f$  versus [Q] should yield a straight line whose slope is proportional to the ratio between the quenching and fluorescence rate constants. This equation is known as the *Stern-Volmer* equation, and systems obeying the relationship are said to follow Stern-Volmer kinetics. Problem 7.14 provides an example.

An alternative experimental procedure, which yields somewhat more information, is to excite the molecule M with pulsed radiation rather than with radiation of constant intensity and to detect the decay time of the fluorescence as a function of quencher concentration rather than the fluorescence intensity. Let the pulse of radiation be short compared to the time scale for fluorescence or quenching, and let the initial excited-state concentration it creates be  $M_0^*$ . The solution for  $M^*(t)$  follows immediately since there are two parallel decay channels (see Section 2.4.2):

$$M^{*}(t) = M_{0}^{*} \exp[-(k_{a}[Q] + k_{f})t].$$
(7.22)

Thus, M<sup>\*</sup> decays with a time constant  $\tau$  given by the relationship

$$\frac{1}{\tau} = (k_{\rm q}[Q] + k_{\rm f}). \tag{7.23}$$

A plot of  $\tau^{-1}$  as a function of [Q] thus gives  $k_q$  as the slope and  $k_f$  as the intercept. Example 2.3 illustrated the use of lifetime measurements to determine the quenching of I<sup>\*</sup> fluorescence by collisions with NO.

#### 7.3.2 Intramolecular Vibrational Energy Redistribution

While intermolecular collisions are required to effect vibrational energy redistribution in diatomic molecules, in larger systems, due to the coupling of different vibrational modes by small perturbations usually neglected in the Hamiltonian (e.g., anharmonicity, vibration-rotation coupling), energy can become redistributed in a collisionless process known as intramolecular vibrational energy redistribution (IVR). Indeed, as we will see in Section 7.5.4, rapid, collisionless exchange of energy between vibrational modes at high levels of excitation is one of the assumptions of the RRKM theory of unimolecular dissociation.

The observation that intramolecular vibrational energy redistribution takes place only at high levels of excitation provides a key to understanding the basic chemistry of this phenomenon. First, consider some data. Figure 7.6 shows the fluorescence spectrum of anthracene excited in a jet-cooled molecular beam.<sup>a</sup> When this molecule is excited to a vibrational level only 766 cm<sup>-1</sup> above the ground vibrational level of the first excited singlet state  $(S_1)$ , the fluorescence shows the expected line spectrum. Each line corresponds to fluorescence from the selected excited level to a different vibrational level of the ground electronic state  $(S_0)$ , and the intensity distribution is governed by the Franck-Condon principle. The fluorescence lifetime of the spectral feature marked with an asterisk is shown in the uppermost trace of the left-hand panel; a single exponential decay is observed with a lifetime of about 18 ns. At 1420 cm<sup>-1</sup> of vibrational energy, the fluorescence spectrum still shows some distinct lines, but it has become much more congested. It appears that fluorescence from  $S_1$ is occurring from many vibrational levels besides the one that was initially excited. In addition, the time-resolved fluorescence from the corresponding spectral feature now shows oscillations (called quantum beats) superimposed on an exponential decay. At 1792 cm<sup>-1</sup> of vibrational energy, the fluorescence spectrum is nearly continuous and the time-resolved fluorescence shows a very complicated behavior, with most of the fluorescence disappearing in 75 ps. The experiment suggests an interesting phenomenon. It appears from the spectra that the initially excited state redistributes its vibrational energy to other vibrational levels and that the amount of redistribution increases with increasing vibrational excitation.

A detailed theoretical treatment<sup>b</sup> of this phenomenon was provided nearly 20 years before the experimental observation of **Figure 7.6**. Vibrations approximated as harmonic normal modes at low levels of vibrational excitation are actually coupled

<sup>&</sup>lt;sup>a</sup>A brief description of the supersonic expansion technique needed for such cooling is given in Section 8.4.1.

<sup>&</sup>lt;sup>b</sup>M. Bixon and J. Jortner, J. Chem. Phys. 48, 715 (1968); 50, 3284 (1969); 50, 4061 (1969).



Figure 7.6

Fluorescence spectrum of anthracene at various levels of vibrational excitation. (*left*) Timeresolved fluorescence from corresponding levels of excitation.

From P. M. Felker and A. H. Zewail, Adv. Chem. Phys. 70, 265 (1998). Copyright © 1988 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

to one another by weak anharmonic, Coriolis, or other forces at higher levels of excitation, but we normally leave out these terms in a zeroth-order approximation to the Hamiltonian. Let the coupling be described by an interaction potential V. When this interaction is evaluated between two zero-order states la> and lb>,<sup>c</sup> the resulting matrix element,  $V_{ab} = \langle b|V|a \rangle$ , tells us, roughly speaking, how close in energy two states would have to be before the coupling between them would cause perturbation of the energy levels. Because the density of vibrational levels increases dramatically with energy for large polyatomic molecules, at some level of excitation the spacing between vibrational levels will become smaller than the value of the coupling matrix element. Above this level of energy, the coupling will be observed as an apparent vibrational energy redistribution. Excitation of one "normal mode" will produce fluorescence from another.

To see the effect of the redistribution on the time-resolved fluorescence signal, consider the intramolecular transfer of energy between just two zero-order modes,  $|a\rangle$  and  $|b\rangle$ , shown schematically in **Figure 7.7.** Because of the coupling element  $V_{ab}$ , the modes  $|a\rangle$  and  $|b\rangle$  are not eigenstates of the true Hamiltonian. In the limit where the true Hamiltonian couples only these two modes, the actual eigenstates,

<sup>°</sup>We use the notation ln here as a shorthand for  $\Phi_n(q)$ , the vibrational wave function. This is the socalled "bra-ket" notation in which  $\leq ml$  denotes the complex conjugate of  $\Phi_m(q)$  and  $\leq mlVln >$  is an integral,  $\int \Phi_m(q) * V \Phi_n(q) dq$ .



#### Figure 7.7

Schematic level structure diagram. The two states  $|a\rangle$  and  $|b\rangle$  are coupled by the interaction potential  $V_{ab}$ .

From P. M. Felker and A. H. Zewail, *Chem. Phys. Lett.* **102**, 113 (1983). Reprinted from *Chemical Physical Letters*, copyright 1983, with permission from Elsevier Science.

 $|e_1\rangle$  and  $|e_2\rangle$ , will be linear combinations of  $|a\rangle$  and  $|b\rangle$ :  $|e_1\rangle = \alpha |a\rangle + \beta |b\rangle$ and  $|e_2\rangle = \beta |a\rangle + \alpha |b\rangle$ , where  $\alpha^2 + \beta^2 = 1$ . It is often the case that the mixing is weak, so that we can think, for example, of  $|e_1\rangle$  as being mostly  $|a\rangle$  with a little bit of  $|b\rangle$  and of  $|e_2\rangle$  as being mostly  $|b\rangle$  with a little bit of  $|a\rangle$ . For this example  $\alpha^2 > \beta^2$ , but the specific values of  $\alpha$  and  $\beta$  will depend on both  $V_{ab}$  and the energy separation between the levels. Because this separation is usually quite small, most excitation mechanisms will excite states  $|e_1\rangle$  and  $|e_2\rangle$  coherently (simultaneously and in phase). However, it often occurs that only one of these states has appreciable transition strength from the ground level. In **Figure 7.7** this state is shown as the one composed mostly of the zero-order mode  $|a\rangle$ .

An analogy can be made to the excitation of two pendulums of nearly the same frequency, coupled by a weak spring. The excitation makes both pendulums swing, but one has a large amplitude of motion and the other a small one. As time progresses, the coupling causes the amplitude of one pendulum to decrease while that of the other pendulum increases. Vibrational amplitude flows from one pendulum to the other and back again at a rate that depends on the difference in frequencies.

Returning to the radiation problem, when the coupled system fluoresces back to different levels of the ground state, a modulation on the fluorescence will be observed corresponding to the oscillatory flow of amplitude between the two coupled levels.

**Figure 7.8** shows the fluorescence from two levels of anthracene. The upper trace gives the signal from the level composed mostly of the mode,  $|a\rangle$ , which is optically coupled to the ground level, while the lower trace gives the signal from the level composed mostly of mode  $|b\rangle$ . Note that the oscillations have exactly the same period but they are 180° out of phase, just as we would expect from the pendulum analogy.

Now suppose that not just two vibrational levels are coupled by the interaction, but rather that the density of vibrational levels,  $\rho_v$  is so high that  $V\rho_v >> 1$  (the so-called statistical limit). Now the optically connected level, consisting mostly of la>, will be coupled to a very large number of other levels, so that the probability that the energy will return to that level will be small. The fluorescence from the





Experimental fluorescence decay curves showing quantum beats. From P. M. Felker and A. H. Zewail, *Chem. Phys. Lett.* **102**, 113 (1983). Reprinted from *Chemical Physical Letters*, copyright 1983, with permission from Elsevier Science.

optically coupled level will be observed for only a short time, a time characterizing the redistribution of energy to the manifold of other vibrational levels. In the lower left-hand panel of **Figure 7.6**, this time for anthracene with 1792 cm<sup>-1</sup> of vibrational energy is seen to be about 75 ps.

Intramolecular vibrational energy redistribution is critical to a wide range of chemical problems. It is particularly important to our understanding of unimolecular reactions, to be discussed in more detail in Section 7.5.4.

#### 7.3.3 Internal Conversion, Intersystem Crossing, and Phosphorescence

The intramolecular vibrational energy redistribution we have just examined takes place between the excited level and other densely spaced vibrational levels of the same electronic state. Energy redistribution may also occur from vibrational levels of one electronic state to those of another, a process generally called a *radiation-less transition*. When the final electronic state is of the same spin multiplicity as the initial state, this transition is called *internal conversion*, whereas when it is of a different multiplicity the transition is called *intersystem crossing*. Internal conversion and intersystem crossing either can take place as a collisionless, intramolecular processes or can be induced by collisions. The chemistry of these processes is not, in principle, very different from that of intramolecular vibrational energy redistribution; it again involves coupling between the excited state and the dense manifold of highly excited vibrational levels of the lower electronic state. The difference is that the interaction potential involves not only vibrational coupling but also an electronic coupling. Interactions that couple different zeroth-order electronic states are

those neglected in making the Born-Oppenheimer approximation; i.e., terms involving the coupling of electronic and nuclear motions. In addition, for intersystem crossing, the coupling involves the spin-orbit interaction.

**Figure 7.9** illustrates the process of internal conversion from an initially excited vibrational level of  $S_1$  to high vibrational levels of  $S_0$ . It is important to remember that, in most cases, there will be several modes of vibration, so that the potential energy surfaces for  $S_1$  and  $S_0$  will depend on many internuclear coordinates rather than just the one plotted as the abscissa in **Figure 7.9**.

Figure 7.10 illustrates the process of intersystem crossing from an initially excited vibrational level of  $S_1$  to high vibrational levels of the lowest triplet state,  $T_1$ . In the presence of collisions, intersystem crossing will typically be followed by vibrational relaxation and phosphorescence back to the ground singlet state.

If the internal conversion or intersystem crossing is caused by collisions, the process can be studied experimentally by observing the loss of fluorescence from the initially excited level of  $S_1$  as the pressure of the collision partner is increased. The intensity of this fluorescence, or in a time-resolved experiment, the lifetime of the fluorescence, will decrease with increasing pressure, following the Stern-Volmer kinetics already discussed in Section 7.3.1.

If the internal conversion or intersystem crossing takes place as an intramolecular process, it is experimentally more difficult to observe. One way to tell that the conversion or crossing has occurred is to compare the lifetime of the fluorescence with the integrated absorption cross section. **Equations 7.12** and **7.6** show, respectively, that the integrated absorption cross section is related to the Einstein  $B_{12}$  coefficient and that the Einstein  $B_{12}$  coefficient is related to the A<sub>12</sub> coefficient, the reciprocal of the radiative lifetime. Thus, if the observed lifetime is due solely to radiative processes, it will be equal to the lifetime calculated from the integrated absorption cross section using **equations 7.12** and **7.6**. On the other hand, if internal



Internuclear separation

#### Figure 7.9

Internal conversion from low vibrational levels of the first excited singlet state ( $S_1$ ) to high vibrational levels of the ground singlet state ( $S_0$ ).



#### Figure 7.10

Intersystem crossing from  $S_1$  to  $T_1$ . Following vibrational relaxation on  $T_1$ , phosphorescence occurs to  $S_0$ .

conversion or intersystem crossing compete with fluorescence as decay channels for the initially excited state, the observed fluorescence lifetime will typically be shorter than that calculated from the integrated absorption cross section.

A second method for learning that intramolecular internal conversion or intersystem crossing has taken place is to observe the low-pressure fluorescence intensity or fluorescence lifetime as a function of vibrational excitation in the  $S_1$  manifold of states. If fluorescence is the only decay channel, its intensity or lifetime will vary irregularly and only slowly with increasing excitation energy, reflecting primarily the change in Franck-Condon factors for fluorescence as different initial levels are selected. On the other hand, because intersystem crossing and internal conversion depend on the density of vibrational levels in the final electronic state, and because this density increases dramatically with energy, the fluorescence intensity and lifetime will decrease dramatically with increasing excitation energy if either of these intramolecular processes is occurring.

An example of how the fluorescence lifetime varies with excitation energy in a system undergoing internal conversion or intersystem crossing is provided by the benzene molecule. Figure 7.11 shows the lifetime of benzene fluorescence under collisionless conditions as a function of the vibrational energy above the origin of the first singlet state ( ${}^{1}B_{2u}$ ). The experimental points are labeled with their vibrational mode assignment in the excited state; for example,  $6{}^{1}1{}^{1}$  means one quantum of  $\nu_{6}$  (a carbon–carbon bending mode) and one quantum of  $\nu_{1}$  (the symmetric stretching mode) with zero quanta in all other modes. The important point to notice from the figure is that the lifetime decreases rapidly with increasing vibrational energy. Some more subtle points of the data are worth remarking on as well. Note that the lifetime decreases dramatically with the number of quanta of  $\nu_{16}$ , an out of plane bending mode. This mode is a so-called "promoting mode" for the radiationless



#### Figure 7.11

The lifetime of fluorescence from benzene vapor as a function of energy above the origin of the first singlet state.

From K. G. Spears and S. A. Rice, J. Chem. Phys. 55, 5561 (1971). Reprinted with permission from the Journal of Chemical Physics. Copyright, American Institute of Physics, 1971. transition since it is particularly effective in causing an interaction between the excited and ground states of the molecule, states that would not mix if the Born-Oppenheimer approximation were rigorously obeyed. The behavior illustrated for benzene is typical of molecules undergoing internal conversion.

# example 7.1

Radiative and Nonradiative Lifetimes		
Objective	Integrated absorption data shows that the quantum yield for fluo- rescence from the $0^0$ level of benzene is 0.25. What would be the fluorescence lifetime of benzene excited to this state if there were no internal conversion?	
Method	In the absence of collisions the total rate of decay of the 0 <sup>0</sup> level is given by the sum of the radiative and nonradiative contribu- tions: $k_{\text{tot}} = k_{\text{r}} + k_{\text{nr}}$ , where $k_{\text{tot}} = 1/\tau_{\text{obs}}$ . In addition, the quantum yield of fluorescence is given by $\Phi_{\text{f}} = k_{\text{r}}/(k_{\text{r}} + k_{\text{nr}})$ . Thus, the value of $\Phi_{\text{f}} = 0.25$ and $\tau_{\text{obs}} \approx 128$ ns (from Figure 7.11), can be used to calculate $k_{\text{r}}$ , which is simply $1/\tau_{\text{r}}$ , the reciprocal of the fluorescence lifetime in the absence of internal conversion.	
Solution	Taking the reciprocal of both sides of the equation $\Phi_f = 0.25$ gives $1 + (k_{nr}/k_r) = 4.0$ , or $k_{nr} = 3.0 k_r$ . We know that $k_{obs} = k_r + k_{nr} = (1 + 3.0)k_r = 1/\tau_{obs} = 1/(128 \text{ ns})$ , so that $4.0k_r = 1/(128 \text{ ns})$ . Since $k_r = 1/\tau_r$ , we find that $\tau_r = (4.0)(128 \text{ ns}) = 512 \text{ ns}$ .	
Comment	Note that $k_r$ is called the <i>radiative</i> decay rate, while $k_{nr}$ is called the <i>nonradiative</i> decay rate.	

#### 7.3.4 Photodissociation

Excitation of some molecules results in dissociation into two or more fragments. With the aid of **Figure 7.12** we can distinguish between two types of such photodissociation processes, direct and indirect. In all panels of this figure, the total energy of the molecule following absorption of the photon is fixed and given by the level of the vertical arrow. As time progresses, potential energy is converted into kinetic energy, and the internuclear separation between the fragments increases. In a direct process, all motion takes place on a single excited potential energy surface and the dissociation is complete on the time scale of a single vibration. In an indirect process, a crossing takes place between two surfaces which, at the level of the Born-Oppenheimer approximation, can be classified as bound and unbound. Because the process depends on the coupling, the dissociation might take considerably longer than a vibrational period. Panels (A) and (B) show direct dissociation processes caused either by the excitation of a region of the excited potential energy surface above the dissociation limit or by excitation of a purely repulsive surface, respectively. Panel (C) shows an example of an indirect process. In this case, excitation is to a level that would be bound if it were not for an avoided crossing with a dissociative state. Along the adiabatic curves that result from the interaction, the molecule dissociates. This indirect process is also known as *predissociation*.



As we will see in the next sections, photodissociation has profound practical consequences. The energy for nearly all chemical reactions in the Earth's atmosphere and on its surface comes from sunlight, so that an understanding of the lightinduced processes, particularly dissociation, is extremely important.

A simple example of the direct dissociation process of panel (A) and the indirect dissociation process of panel (C) in Figure 7.12 is provided by the O2, whose absorption spectrum is shown in Figure 7.13. There is virtually no absorption in the visible region of the spectrum, but the cross section for absorption increases strongly

The ultraviolet absorption cross

Figure from "Photochemical Processes and Elementary Reactions" in CHEMISTRY OF THE NATURAL ATMOSPHERE by Peter Warneck, copyright © 1988 by Academic Press, reproduced by permission of the publisher. All rights or reproduction in any form reserved.

through the ultraviolet and vacuum ultraviolet regions. It is largely this absorption that prevents vacuum ultraviolet radiation from reaching the surface of the Earth.

**Figure 7.14** shows some of the potential energy curves for O<sub>2</sub> (recall that the ground state of O<sub>2</sub> is a triplet:  ${}^{3}\Sigma_{g}^{-}$ .) While there is an enormous number of states for even such a simple diatomic molecule, let us concentrate our interest on the lowest five curves. The absorption regions of **Figure 7.13** labeled "Schumann continuum" and "Schumann-Runge bands" correspond to absorption from the  ${}^{3}\Sigma_{g}^{-}$  ground state to the continuum and bound regions of the  ${}^{3}\Sigma_{u}^{-}$  potential curve. Absorption to the continuum region leads to dissociation of O<sub>2</sub> into O( ${}^{3}P$ ) + O( ${}^{1}D$ ), which is the process illustrated in panel (A) of **Figure 7.12**. Absorption to the bound region leads to predissociation via the  ${}^{3}\Pi_{u}$  repulsive curve and produces 2 O( ${}^{3}P$ ) atoms, illustrating the process in panel (C) of **Figure 7.12**.

Note from **Figure 7.13** that the absorption by  $O_2$  at wavelengths longer than 200 nm is quite weak, so that  $O_2$  does not very effectively block sunlight in the region, say, near 250 nm, where the principal component of life, DNA, absorbs strongly. However, as we will examine in detail in the next section, the oxygen atoms produced via absorption on the Schumann continuum and on the Schumann-Runge bands can recombine with  $O_2$  to form  $O_3$ . Ozone does absorb light in the 200-to 300-nm region, and it is this absorption that protects life on Earth from ultraviolet radiation–induced mutations, as discussed in detail in the next section.



Figure 7.14

Calculated potential curves for the triplet valence states of O<sub>2</sub>. Note the crossing of the  ${}^{3}\Sigma_{u}^{-}$  state by the repulsive  ${}^{3}\Pi_{u}$  state.

Based on curves published by F. R. Gilmore, J. Quant. Spectrosc. Radiat. Transfer 5, 369 (1965). Reprinted from Journal of Quantitative Spectroscopy and Radiative Transfer, copyright 1965, with permission from Elsevier Science.

#### 7.4 ATMOSPHERIC CHEMISTRY

The composition of the atmosphere provides an interesting and important application of photochemistry. We start by categorizing the different regions of the atmosphere, using **Figure 7.15** as a reference. As a function of the height above sea level, the solid line in this figure shows the average temperature and the bars give its range of variation. Note that the temperature decreases as the height increases to about 10 km, and then the temperature increases to a height of roughly 50 km. The extremes in temperature are used to define the different regions of the atmosphere, as identified in the figure.

The *troposphere* is the region nearest the surface of the Earth, and the photochemistry in this region is extremely complex because of the large variety of atmospheric components. The light reaching this region is limited primarily to the visible and infrared parts of the spectrum. It is in the troposphere that human activity has had the most effect on the atmosphere. Acid rain, photochemical smog, and global warming, for example, are largely issues of the troposphere.

The *stratosphere* is the region in which the temperature increases with increasing height. The photochemistry of this region is dominated by the dissociation of ozone and, in the upper regions, oxygen. It is here that the issues of ozone depletion by nitric oxide and chlorofluorocarbons are most important. The light reaching this area of the atmosphere is primarily at wavelengths above about 200 nm; light below this wavelength is absorbed by oxygen.



#### Figure 7.15

The temperature of the atmosphere as a function of height above sea level.

Figure from "Bulk Composition, Structure, and Dynamics of the Atmosphere" in CHEMISTRY OF THE NATURAL ATMOSPHERE by Peter Warneck, copyright © 1988 by Academic Press, reproduced by permission of the publisher. All rights or reproduction in any form reserved.

The *mesosphere* is a region of the upper atmosphere dominated by the photochemistry of small diatomic molecules and the reactions of atoms and ions. The *thermosphere* is the outer limit of the atmosphere, above about 90 km.

The stratosphere provides a good example of how our understanding of photochemistry can lead to an improved understanding of the atmosphere. The major chemical constituents of this region of the atmosphere are N<sub>2</sub> (with a mole fraction of 0.79), O<sub>2</sub> (of mole fraction 0.21), and O<sub>3</sub> (of mole fraction  $1.3 \times 10^{-5}$ ). Since we have already remarked that it is the ozone that prevents near ultraviolet light from reaching the surface of Earth, it is of importance to understand the photochemical processes that maintain these steady-state concentrations. A first approximation to a chemical mechanism for the stratosphere was given by Chapman in 1930.<sup>d</sup> In this simple model, the nitrogen is chemically inert, whereas the oxygen and ozone are coupled by two photochemical and two chemical reactions. The first of the photochemical processes is the dissociation of oxygen, already discussed in the preceding section:

$$O_2 + h\nu (\lambda < 200 \text{ nm}) \rightarrow 2 \text{ O}. \tag{R1}$$

The second photochemical process is the dissociation of ozone:

$$O_3 + h\nu (200 \text{ nm} < \lambda < 310 \text{ nm}) \rightarrow O_2 + O.$$
 (R2)

The absorption spectrum of ozone is shown in **Figure 7.16.** Because the mole fraction of ozone is small relative to that of oxygen and because the oxygen absorbs strongly below 200 nm, the primary region of ozone photochemistry is the so-called Hartley band between 200 and 310 nm.



Figure 7.16

The absorption cross section (in cm<sup>2</sup>) of  $O_3$ . Figure from "Photochemical Processes and Elementary Reactions" in CHEMISTRY OF THE NATURAL ATMOSPHERE by Peter Warneck, copyright © 1988 by Academic Press, reproduced by permission of the publisher. All rights or reproduction in any form reserved.

<sup>&</sup>lt;sup>d</sup>S. Chapman, J. R. Meteorol. Soc. 3, 103 (1930); Philos. Mag. 10, 345 (1930).

Two chemical reactions complete the Chapman mechanism, the recombination of O with  $O_2$ ,

$$O + O_2(+M) \rightarrow O_3(+M),$$
 (R3)

and the reaction between O and  $O_3$ ,

$$O + O_3 \rightarrow 2 O_2, \tag{R4}$$

where M is either  $O_2$  or  $N_2$  and serves to take away enough energy to stabilize the  $O_3$ . The process **reaction R4** is of minor importance compared to that in **reaction R3**.

Although the Chapman model is a reasonable first approximation, the steadystate concentration of  $O_3$  that it predicts (Problem 7.7) is three times higher than that observed. It should be noted that, given the flux of solar radiation in the stratosphere and the steady-state concentrations, ozone is photodissociated and regenerated by **reaction R2** and **reaction R3** about 30 times for every  $O_2$  molecule dissociated in **reaction R1**. Thus, even minor components of the atmosphere that interfere with the cycle of **reactions R2–R3** can have a large effect on the steadystate concentration of  $O_3$ .

Two such minor components of the natural atmosphere are  $N_2O$  (~100 parts per billion by volume, ppbv) and  $H_2O$  (~5 ppmv).  $N_2O$  undergoes photodissociation in the stratosphere, while  $H_2O$  reacts with oxygen atoms. The resulting NO and HO radicals participate in catalytic reactions that lower the steady-state concentration of ozone. The reaction mechanisms are

Net:

$$NO_2 + O \rightarrow NO + O_2$$
  

$$O_3 + O \rightarrow 2 O_2,$$

 $NO + O_3 \rightarrow NO_2 + O_2$ 

and

$$HO + O_3 \rightarrow HOO + O_2$$
$$HOO + O_3 \rightarrow HO + 2 O_2$$
$$2 O_3 \rightarrow 3 O_2.$$

Net:

Net:

Notice that the net result of each of these cycles is to destroy ozone and that in each case the initial radical is regenerated so that it continues the cycle.

In the 1970s, the airline industries proposed to develop a fleet of supersonic aircraft that would fly at a height of 20–40 km. Fortunately, enough was known about the chemistry of the stratosphere at that time so that chemists were able to prevent a potential disaster. The nitric oxides injected into the ozone layer by the exhaust from such a fleet of planes might have seriously depleted the steady-state concentration ozone by participating in the first of the catalytic cycles listed above.<sup>e</sup>

Unfortunately, chemists did not have an early enough understanding to head off another anthropogenic cause of ozone depletion. In 1974 Rowland and Molina proposed another possible catalytic cycle involving chlorine atoms<sup>f</sup>

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

$$O_3 + O \rightarrow 2O_2.$$

<sup>e</sup>For an interesting account, see H. S. Johnston, Ann. Rev. Phys. Chem. 43, 1 (1992).

<sup>&</sup>lt;sup>f</sup>M. J. Molina and F. S. Rowland, *Nature* **249**, 810 (1974). Rowland and Molina shared the 1995 Nobel Prize in Chemistry (with P. Crutzen) for their work in this area.

Net:

They warned that chlorofluorocarbons used for industrial cleaning and refrigerants might produce Cl atoms that could destroy ozone. Ironically, for reasons involving human safety, the chlorofluorocarbons used for these purposes were designed to be relatively inert. They turned out to be too inert. Whereas most chlorine-containing compounds dissolve in rain and are returned to the Earth's surface, these substances rise all the way to the upper stratosphere, where they are dissociated to produce chlorine atoms that then catalytically destroy ozone.

Over the past 50 years, stratospheric chlorine concentrations have increased from a background level of 0.5 ppbv to a level today of 3.5 ppbv. The ozone concentration is beginning to show the effects, as demonstrated by satellite measurements. Whereas the average range of ozone concentration during the period 1979–1990 was nearly 300 Dobson units (the equivalent ozone column height in units of  $10^{-5}$  m at standard temperature and pressure), the 1992 average was about 7 units lower and the 1993 average (taken until the *Nimbus-7* satellite ceased to function) was lower by another 7 units.

The effect has been even more dramatic in the region of the polar caps, particularly above Antarctica, where in 1985 an "ozone hole" has been detected just following the return of the solar radiation in the spring of that and each subsequent year.<sup>g</sup> A stream of air known as the polar vortex isolates the region of the stratosphere above the Antarctic continent. During the winter, ice and nitric acid trihydrate condense to form polar stratospheric clouds, and the crystals in these clouds provide reactive surfaces that store chlorine as CIONO<sub>2</sub>. When the sun reappears in the early spring, the crystals melt and release the both Cl atoms and ClO. The atoms destroy ozone in the catalytic cycle predicted by Molina and Rowland, while the chlorine monoxide participates in its own catalytic cycle:

$$ClO + ClO \rightarrow Cl_2O_2$$

$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO$$

$$ClOO + M \rightarrow Cl + O_3 + M$$

$$2 (Cl + O_3 \rightarrow ClO + O_2)$$

$$2 O_3 + h\nu \rightarrow 3 O_2.$$

Experiments monitoring ClO and ozone concentrations in the region of the Antarctic vortex have further established the connection between chlorine and ozone concentrations. Figure 7.17 demonstrates the close inverse correlation between the ClO concentration and the ozone concentration just following the spring thaw. As a high-altitude airplane flew its instruments through layers formed by the vortex, it recorded a dip in the ozone concentration at every location where the ClO concentration increased. Within the vortex, the ozone concentration was found to be less than half the concentration outside the vortex.

Fortunately, the end of this story may be in sight. Under the 1990 revisions of the Montreal protocol, agreed to by most nations producing chlorofluorocarbons, the rate of human injection of chlorine into the stratosphere should be cut back enough so that the chlorine concentration should peak around the year 2000 and fall after that. Models predict, however, that the Antarctic ozone hole will not disappear until 2050.

<sup>&</sup>lt;sup>g</sup>J. C. Farman, B. G. Gardiner, and J. D. Shankin, Nature 315, 207 (1985).



#### Figure 7.17

Mixing ratio in parts per trillion by volume for ClO and  $O_3$  as a function of latitude in degrees south. Note the close inverse correlation between the two concentrations. From J. G. Anderson, D. W. Toohey, and W. H. Brune, *Science* **251**, 39 (1991). Reprinted with permission from *Science*. Copyright 1991 American Association for the Advancement of Science.

While the stratospheric ozone concentration illustrates both the importance of photochemistry to the composition of the atmosphere and the importance of understanding the atmospheric implications of anthropomorphically generated chemicals, it is but one of many problems of current global concern. Global warming due to the emission of gases that absorb infrared light, acid rain due to sulfuric acid emissions, and photochemical smog generated by the interaction of sunlight and automobile exhaust are but a few of the problem areas where a knowledge of photochemistry is of practical relevance. These and other problems are discussed in detail in a few of the books listed in the Suggested Readings section.

#### 7.5 PHOTODISSOCIATION DYNAMICS

The goal of a subfield of photochemistry known as photodissociation dynamics is to understand at the molecular level the process by which light induces a dissociation. What causes the absorption? What are the forces on the fragments as they fly apart? What are the final states of the products, and how do they depend on which initial state was created by the photon? To physical chemists, the field of photodissociation dynamics emerged as a science with the development by Norrish and Porter of the flash photolysis or pump-probe technique.<sup>h</sup>

<sup>&</sup>lt;sup>h</sup>G. Porter, *Proc. R. Soc.* A200, 284 (1950). R. G. W. Norrish and G. Porter shared the 1967 Nobel Prize in Chemistry (with M. Eigen) for their work in this area.

#### 7.5.1 The Pump-Probe Technique

In the earliest versions of the pump-probe technique, photolysis of a starting material was achieved by one flash lamp while the production of photochemical fragments was monitored by their absorption of continuum light from another flash lamp. In observing spectroscopically the internal energy states of the photofragments, Norrish and Porter demonstrated the first general technique that provided information about the *dynamics* of a photochemical event. The pace of investigation increased rapidly in the 1960s due to two improvements. Tunable lasers with powers high enough to dissociate a large fraction of the parent molecule and with spectral resolution high enough to excite individual internal energy levels gradually replaced the photolysis flash lamp. In addition, fragment detection by absorption from a second flashlamp was replaced by one of three more sensitive laser detection techniques: time-resolved laser absorption, laser-induced fluorescence, or multiphoton ionization. We now briefly explore with an example how results obtained using these experimental techniques compare with theory.

A major goal of the field is to determine the forces acting on the fragments as they separate. This force is simply the negative of the gradient of the potential energy surface. For example, **Figure 7.18** shows the sections of the excited potential energy surface for the water molecule leading to dissociation into OH + H. Each curve gives the potential energy as a function of (HO)–H distance for a fixed value of the OH bond length. The different curves are for different angles of departure; the curve labeled  $V_0$  gives the angle averaged potential. Note that the energy



#### Figure 7.18

Potential energy curves for H<sub>2</sub>O as a function of R in the coordinate system shown for different values of  $\gamma$  and for r = 0.971 Å.

From R. Schinke, V. Engel, and V. Staemmler, J. Chem. Phys. 83, 4522 (1985). Reprinted with permission from the Journal of Chemical Physics. Copyright, American Institute of Physics, 1985.

decreases rapidly with increasing (HO)–H distance, so that there is a large repulsive force between the recoiling fragments. The potential was calculated using *ab initio* techniques. How well does it do in predicting the experimental results?

An experiment performed in 1987 prepared individual rotational levels of vibrationally excited water using one laser, dissociated them by excitation to the repulsive curves of **Figure 7.18** with a second laser, and then probed the OH fragment rotational distribution using laser-induced fluorescence (a technique to be described below) with a third laser. **Figure 7.19** shows the close agreement between the distributions calculated using the *ab initio* potential energy surface of **Figure 7.18** and that measured by the experiment. The combination of experiment and theory gives confidence that the dissociation dynamics of water are understood at the molecular level.



#### Figure 7.19

Experimental and theoretical OH rotational distributions. The panels give the results for dissociation of different  $J_{K_a,K_c}$  levels. From D. Häusler, P. Andresen, and R. Schinke, J. Chem. Phys. 87, 3949 (1987). Reprinted with permission from the Journal of Chemical Physics. Copyright, American Institute of Physics, 1987.

Before proceeding further, it is helpful to understand the two detection techniques of laser-induced fluorescence and multiphoton ionization.

#### 7.5.2 Laser-Induced Fluorescence

One of the most sensitive and commonly used probe techniques is called laser-induced fluorescence (LIF). **Figure 7.20** shows the basic principle of the technique, which was first recognized as a tool for studying dynamics by Schultz, Cruse, and Zare.<sup>i</sup> The physical processes are similar to those discussed in Section 7.3.1. For simplicity, the figure shows schematic-level diagrams for the vibrational and rotational levels of the lower and upper states but omits the electronic potential energy curves. A tunable laser of frequency  $\nu_{\rm L}$  excites molecules from vibrational-rotational levels of the ground electronic state to an upper electronic state that subsequently fluoresces. If the total fluorescence intensity is recorded as a function of the frequency or wavelength of the exciting laser, a line spectrum will be observed. At every frequency for which the laser is in resonance with an allowed transition from the lower to upper state, molecules will be observed if the laser is not in resonance with an allowed transition.

For example, **Figure 7.21** shows a laser-induced fluorescence spectrum of CO produced in the 193-nm photodissociation of acetone to yield CO + 2 CH<sub>3</sub>. The top panel probes a region of the CO absorption band corresponding to excitation from rotational levels of CO in v = 0 of the ground electronic state to rotational levels in v = 2 of the upper electronic state, whereas the bottom panel probes a region taking CO from v = 1 in the lower state to v = 0 in the upper state. *Q*-branch transitions (those with  $\Delta J = 0$ ) are identified in each scan, although *P*- and *R*-branch transitions ( $\Delta J = -1$  and  $\Delta J = +1$ ) are also present. It is thus qualitatively clear from the spectrum that CO is produced in both v = 0 and v = 1 and in rotational levels ranging up to at least J = 50.

A quantitative analysis of the spectrum can yield accurate relative populations for the CO levels produced. Assuming (as is nearly valid in this case) that the fluorescence intensity is unaffected by nonradiative processes, the signal is proportional to the population in the lower level (because of the high excitation energy, we assume no initial population in the upper level). The quantities involved in the proportionality constant include the Franck-Condon factor for excitation between the two



<sup>&</sup>lt;sup>i</sup>A. Schultz, H. W. Cruse, and R. N. Zare, J. Chem. Phys. 57, 1354 (1972); P. J. Dagdigian and R. N. Zare, Science 185, 739 (1974).



Figure 7.21

Laser-induced fluorescence spectrum of CO produced in the 193-nm photodissociation of acetone. From K. A. Trentelman, S. H. Kable, D. B. Moss, and P. L. Houston, *J. Chem. Phys.* **91**, 7498 (1989). Reprinted with permission from the *Journal of Chemical Physics*. Copyright, American Institute of Physics, 1989.

vibrational levels and the rotational line strengths, called Hönl-London factors. For CO, these quantities have been accurately measured. Problem 7.12 provides an example of how these are used.

Figure 7.22 shows the populations derived from the spectrum of Figure 7.21 using the known Franck-Condon and Hönl-London factors for the CO  $\widetilde{A} \leftarrow \widetilde{X}$  band (see Problem 7.12 for details). The figure also includes results based on additional data probing CO in v = 2. At room temperature, the most populated level of CO is near J = 10. Note, therefore, that very high rotational levels are produced in all vibrational levels, suggesting that the force on the CO fragment due to the departure of the two methyl fragments is unequal. A likely explanation is that the dissociation proceeds in a sequential fashion with an acetyl intermediate, as shown in Figure 7.23.

#### 7.5.3 Multiphoton Ionization

A second technique commonly used to probe the products of photodissociation is called multiphoton ionization (MPI). Although the technique was first used to detect atoms, the initial application to molecules was in the detection of  $Cs_2$  by Collins et al.<sup>j</sup> Extension to more chemically interesting species, such as benzene and NO, was subsequently made by Johnson and his coworkers.<sup>k</sup>

<sup>&</sup>lt;sup>j</sup>C. B. Collins, B. W. Johnson, and M. Y. Mirza, Phys. Rev. A 10, 813 (1974).

<sup>&</sup>lt;sup>k</sup>P. M. Johnson, M. R. Berman, and D. Zakheim, J. Chem. Phys. 62, 2500 (1975).



#### Figure 7.22

Relative populations of CO energy states produced in the photodissociation of acetone determined from spectrum of **Figure 7.21**.

From K. A. Trentelman, S. H. Kable, D. B. Moss, and P. L. Houston, J. Chem. Phys. **91**, 7498 (1989). Reprinted with permission from the *Journal of Chemical Physics*. Copyright, American Institute of Physics, 1989.



#### Figure 7.23

Probable dissociation mechanism for acetone at 193 nm.

Figure 7.24 shows the principle of the technique, which is very similar to that used in laser-induced fluorescence. A pulsed, tunable laser at frequency  $\nu_{\rm L}$  excites molecules from a specific vibrational-rotational level of the ground electronic state of AB to a level of an excited electronic state, AB<sup>\*</sup>. The number of AB<sup>\*</sup> molecules thus produced is again given by the same equation that governs the laser-induced fluorescence signal (see Problem 7.12). If the intensity of the laser is strong enough, a second photon from the same laser pulse can cause further excitation of AB<sup>\*</sup> to the ionization continuum, producing AB<sup>+</sup> + e<sup>-</sup>. The ions are accelerated into a detector and counted. If, as is typical, the ionization step has a high cross section, nearly every AB<sup>\*</sup> will be ionized. Thus the number of ions is proportional to the population in the initially selected vibrational-rotational level of the ground state. Because the detection of ions is often more sensitive than the detection of

# 8

# Molecular Reaction Dynamics

#### **Chapter Outline**

- 8.1 Introduction
- 8.2 A Molecular Dynamics Example
- 8.3 Molecular Collisions—A Detailed Look
- 8.4 Molecular Scattering
- 8.5 Potential Energy Surfaces
- 8.6 Molecular Energy Transfer
- 8.7 Molecular Reaction Dynamics—Some Examples
- 8.8 Summary

#### 8.1 INTRODUCTION

The underlying goal of this book has been to understand kinetic processes at the molecular level. We started in Chapter 1 to look at the details of molecular collisions. In Chapter 2 we broke down overall reactions into their component elementary steps, and in Chapter 3 we examined how our understanding of collisions could be extended to predict and understand rate constants for reactions. In this chapter we will go one step further by breaking down elementary steps into *state-to-state* reaction rates and by seeing how these are related to the potential energy surface that controls the reaction. This field, called *reaction dynamics*, seeks to understand the dynamics of chemical systems at a molecular level.

In addition to the intellectual challenge of learning how a rate constant depends on both the initial state of the reactant and the final state of the product, there are ample practical reasons to explore the field of reaction dynamics. Many reactions take place under nonequilibrium conditions, so that if the reaction rate depends on the initial state of the reactant, the rate constant for the process might be quite different from that for reactants in Boltzmann equilibrium. Perhaps by understanding the dynamics we can direct the reaction to produce either desired, unconventional products or products with a particular final state distribution. Furthermore, if a reaction, even one starting from thermal equilibrium, selectively produces a nonequilibrium distribution of products, we might be able to use that distribution in some practical way, for example, to convert chemical energy into another useful form.

#### Chapter 8 Molecular Reaction Dynamics

In this chapter we start by considering a simple reaction system that has had both historical and practical importance in the of field reaction dynamics,  $F + D_2 \rightarrow$ DF + D. After learning how the state-resolved reaction rate constants are related to the overall thermal rate constant in Section 8.3, we look in a more detailed way at molecular scattering in Section 8.4. In Section 8.5 we examine how the angular distribution of scattering and the state-resolved rate constants are related to the potential energy surface. Not all of the processes of interest to chemists involve reactions, so we spend some effort in Section 8.6 investigating processes in which the reactants and products have the same chemical identity but in which energy has been exchanged between various degrees of freedom. We end the chapter by exploring several examples to convey some of the excitement of the field and to point to directions for future effort.

#### 8.2 A MOLECULAR DYNAMICS EXAMPLE

The goals of this chapter are illustrated with a simple example. In 1961, John Polanyi suggested that it might be possible to use a chemical reaction to produce a population inversion that could be used to power a new type of "chemical" laser.<sup>a</sup> The idea was to find a reaction that, for example, produced more product in a high vibrational level than in a lower one, so that stimulated emission might occur between the two levels to produce a laser in the infrared region of the spectrum. It was clear that one wanted preferentially to consider exothermic reactions, which could provide enough energy to populate several different internal states of the products. Several examples were found,<sup>b</sup> but we will focus our attention on the F +  $H_2$  and F +  $D_2$  systems. For some practical reasons, F +  $D_2$  has been more carefully studied.

**Figure 8.1** shows, on the left, the energetics of the reaction; the DF product can be produced in any of five vibrational levels from v = 0 to v = 4. The right-hand side of the figure gives the distribution of population among the vibrational levels as measured by three techniques: observing the chemiluminescence from the reaction, observing the behavior of a DF laser based on the reaction, and observing the velocity distribution of the DF product following a crossed molecular beam reaction. This latter technique, whose results are summarized in **Table 8.1**, will be discussed in more detail in Section 8.4. The important point to note at this stage is that the reaction produces a higher population of DF(v = 3) than DF(v = 2). Because the  $v = 3 \rightarrow v = 2$  transition is optically allowed, this population "inversion" can form the basis for a chemical laser. Indeed, one reason that this reaction was studied in so much detail is that there had been interest at one time on the part of the military in using chemical lasers as weapons.<sup>c</sup> Figure 8.2 shows a TRW-built high-energy laser that successfully targeted and shot down an operational short-range rocket in a 1996 flight test—on the first firing.

<sup>&</sup>lt;sup>a</sup>J. C. Polanyi, *J. Chem. Phys.* **34**, 347 (1961). Polanyi shared the 1986 Nobel Prize in Chemistry (with D. R. Herschbach and Y. T. Lee) for his work in this area.

<sup>&</sup>lt;sup>b</sup>The first was discovered by J. V. V. Kasper and G. C. Pimentel, Phys. Rev. Lett. 14, 352 (1965).

<sup>&</sup>lt;sup>c</sup>American Physical Society Study Group (N. Bloembergen and C. K. N. Patel, cochairmen), "Report to the American Physical Society of the Study Group on Science and Technology of Directed Energy Weapons," *Rev. Mod. Phys.* **59**(3), Part II (July 1987); P. W. Boffey, W. J. Broad, L. H. Gelb, C. Mohr, and H. B. Noble, *Claiming the Heavens* (Time Books, New York, 1988).


(*left*) Energetics for the  $F + D_2$  reaction showing possible final vibrational states. (*right*) Population of final vibrational levels relative to v = 3.

TABLE 8.1	Population of Fin Reaction F + D <sub>2</sub>	al Vibrational Levels $v$ in the $ ightarrow$ DF( $v$ ) + D
	v	$P(v)^*$
	0	0
	1	0.19
	2	0.67
	3	1.00
	4	0.41

\*Data normalized to P(v = 3) = 1.00 and taken from D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, K. Shobotake, R. K. Sparks, T. P. Schafer, and Y. T. Lee, *J. Chem. Phys.* **82**, 3067 (1985).



#### Figure 8.2

Chemical laser based on hydrogen/fluorine reaction claimed by TRW to have shot down a short-range rocket. Courtesy of TRW, Inc.

#### Chapter 8 Molecular Reaction Dynamics

Several questions arise from even a cursory examination of this system. What features of the interaction between reactants might lead to the nonequilibrium distribution of products? Since the reaction clearly populates selected final states, does the reaction depend as well on the reactant initial state? If we assign a rate constant for the reaction between a particular state *i* of the reactants and a final state *f* of the products, how are these rate constants related to the overall rate constant, k(T), measured at thermal equilibrium? Finally, what happens if we look at this reaction in even more detail by examining the angular distribution of the products or their rotational energy levels? These are the questions that motivate the field of reaction dynamics. The goal is to learn about the molecular mechanism of elementary chemical processes by probing rate processes directly at molecular level; ideally, we would like to "watch" the atoms and molecules move as they undergo reaction.

#### 8.3 MOLECULAR COLLISIONS—A DETAILED LOOK

If we wish to understand a reaction such as  $F + D_2 \rightarrow DF + D$  at a fundamental level, we must start by recognizing that there are many internal energy levels of both the reactants and products, and that the rate constant for reaction might depend both on the initial state, *i*, of the reactant and on the final state, *f*, of the products, where *i* and *f* here each symbolize a set of quantum numbers representing, for example, vibration, rotation, and electronic degrees of freedom. Moreover, this "state-to-state" reaction might itself depend on the relative velocity of the reactants, or equivalently on the collision energy. In Section 3.3 we saw that the rate constant at a particular energy  $\epsilon_r$  could be expressed as the product of the relative velocity,  $v_r$ , and the energy-dependent cross section  $\sigma(\epsilon_r)$ :  $k(\epsilon_r) = v_r \sigma(\epsilon_r)$ . Since even at a given collision energy, the rate constants from a particular initial state to a selected final state might differ, we now need to be more specific. Let  $\sigma(\epsilon_r, i, f)$  be the reaction cross section at energy  $\epsilon_r$  for going from state *i* of the reactants to state *f* of the products. The rate constant for this process is then  $k(\epsilon_r, i, f) = v_r \sigma(\epsilon_r, i, f)$ .

We now wish to address two questions. The first is how the overall rate constant at  $\epsilon_r$ ,  $k(\epsilon_r)$ , is related to  $k(\epsilon_r, i, f)$ . The second is how the final energy distribution in the DF product is related to these "state-to-state" rate constants.

We approach the first question in two steps. First we use our knowledge of parallel reactions, Section 2.4.2, to show that the total rate for reaction from a particular initial state,  $k(\epsilon_{r},i)$  is just the sum of the state-to-state reaction rates over the final states, f. Suppose for simplicity that there are only two final states of the products, f = 1 and f = 2. Then for a given initial state, we have the parallel processes

$$\begin{bmatrix} i \end{bmatrix} \stackrel{k(\epsilon_{r},i,f=1)}{\rightarrow} \begin{bmatrix} f=1 \end{bmatrix}$$

and

$$[i] \xrightarrow{k(\epsilon_{\rm r},i,f=2)} [f=2].$$

The situation is exactly analogous to the A  $\rightarrow$  B and A  $\rightarrow$  C parallel reactions of Section 2.4.2, so that the total rate of disappearance of *i* should be given by the sum of the two rate constants; that is,  $k(\epsilon_r, i) = k(\epsilon_r, i, f = 1) + k(\epsilon_r, i, f = 2)$ . If there are many final states, we can generalize this result by summing over them all:

$$k(\boldsymbol{\epsilon}_{\mathrm{r}},i) = \sum_{f=1}^{f=f_{\mathrm{max}}} k(\boldsymbol{\epsilon}_{\mathrm{r}},i,f), \qquad (8.1)$$

where  $f_{\text{max}}$  is the highest energy level of the products consistent with the relative collision energy  $\epsilon_r$ .

The second step in the answer to how  $k(\epsilon_r)$  is related to the state-to-state rate constants is taken by recognizing that  $k(\epsilon_r)$  is an average over the rate constants starting in different initial states. Of course, when taking the average we need to weight the different initial states<sup>d</sup> according to their populations, P(i). Thus,

$$k(\boldsymbol{\epsilon}_{\mathrm{r}}) = \sum_{i=1}^{\infty} P(i)k(\boldsymbol{\epsilon}_{\mathrm{r}}, i)$$
  
$$= \sum_{i=1}^{\infty} \sum_{f=1}^{f_{\mathrm{max}}} P(i)k(\boldsymbol{\epsilon}_{\mathrm{r}}, i, f).$$
(8.2)

It should be noted that P(i) will generally depend on a temperature. For example, if the reactants are at equilibrium with a heat bath at temperature T, then P(i) will simply be the Boltzmann distribution:

$$P(i) = \frac{g_i \exp(-\epsilon_i/kT)}{Q},$$
(8.3)

where  $g_i$  and  $\epsilon_i$  are the degeneracy and energy of the *i*th level and Q is the partition function at temperature T:

$$Q = \sum_{i=1}^{\infty} g_i \exp\left(-\frac{\epsilon_i}{kT}\right).$$
(8.4)

Equation 8.2 is then the answer to the first of our two questions:

The rate constant at a particular energy is the average of the state-selected rate constants over initial states and the sum over final states.

What of the second question? How are the rate constants related to the distribution of population in the products? Our understanding of parallel reactions can again come to our aid. Recall from Section 2.4.2 that the branching ratio to a particular product, or equivalently the probability of forming that product, is given by the rate constant for the desired channel divided by the sum of the rate constants for all of the possible channels. Let  $P(\epsilon_r, f)$  be the probability of forming the final state f of the product(s). Then,

$$P(\boldsymbol{\epsilon}_{\mathrm{r}}, f) = \frac{k(\boldsymbol{\epsilon}_{\mathrm{r}}, f)}{\sum_{f=1}^{f_{\mathrm{max}}} k(\boldsymbol{\epsilon}_{\mathrm{r}}, f)},$$
(8.5)

where each of the  $k(\epsilon_r, f)$  is an average over the possible initial states for reaction at relative energy  $\epsilon_r$ :

$$k(\epsilon_{\rm r},f) = \sum_{i=1}^{\infty} P(i)k(\epsilon_{\rm r},i,f).$$
(8.6)

We close this section by recalling from Section 3.3 that the rate constant at a given temperature, k(T), is obtained from  $k(\epsilon_r)$  by averaging over the thermal distribution of energies:

$$k(T) = \int_0^\infty G(\epsilon_r) k(\epsilon_r) d\epsilon_r, \qquad (8.7)$$

<sup>&</sup>lt;sup>d</sup>A similar weighting was used in equation 1.8 to determine the average grade on an examination.

where  $G(\epsilon_r)$  is the Boltzmann distribution of energy at temperature *T* (see equation 1.37). Substitution of equation 8.2 and the definition  $k(\epsilon_r, i, f) = v_r \sigma(\epsilon_r, i, f)$  leads to

$$k(T) = \int_{\epsilon=0}^{\infty} \sum_{i=1}^{\infty} \sum_{f=1}^{f_{\text{max}}} P(i) v_r G(\epsilon_r) \sigma(\epsilon_r, i, f) \, \mathrm{d}\epsilon_r.$$
(8.8)

This last equation relates the macroscopic rate constant for an elementary process to the state-to-state energy-dependent cross sections. The field of reaction dynamics seeks to measure these cross sections and to interpret them at the molecular level. The interpretation is most compactly expressed by the potential energy surface for the system, whose relationship to  $\sigma(\epsilon_r, i, f)$  is discussed in Section 8.5. Before exploring this relationship, however, we examine the cross section at a deeper level to learn about its dependence on recoil angles, as measured by scattering experiments.

## example 8.1

Calculating	$k(T)$ from $\sigma(\epsilon,i,f)$			
Objective	A reaction has two initial states. State <i>i</i> 1 is the ground state and state <i>i</i> 2 lies 100 cm <sup>-1</sup> higher. The products have four final states: $f1, f2, f3$ , and $f4$ . The cross sections as a function of energy are given by $T(i,f) = \pi d^2 [1 - \epsilon^*(i,f)/\epsilon_r]$ , where $T(i,f)$ and $\epsilon^*(i,f)$ are given in the table, and $d = 0.10$ nm (1.0 Å). If the reduced mass for the collision is 5 amu, calculate the overall rate constant for the reaction at a temperature of 300 K; i.e., $k(T)$ for $T = 300$ .			
	i,f	T(i,f)	$\epsilon^*(i,f)$ (cm <sup>-1</sup> )	
		0.05	1000	
	i1,f2	0.20	1000	
	i1,f3	0.10	1000	
	i1,f4	0.05	1000	
	i2,f1	0.1	500	
	i2,f2	0.3	500	
	<i>i</i> 2, <i>f</i> 3	0.1	500	
	i2,f4	0.1	500	
Method	Use <b>equation 8.8</b> , integration over the of this functional for	recalling that we thermal energy d rm in the equation	have already performed the istribution for a cross section ons preceding <b>equation 3.7.</b>	
Solution	Since each of the cross sections has the same functional form with respect to $\epsilon_r$ , we can perform the integral in <b>equation 8.8</b> before doing the sum. From the equations leading to <b>equation 3.7</b> we see that $\int \pi d^2 [1 - \epsilon^*(i,f)/\epsilon_r) G(\epsilon_r) d\epsilon_r = \pi d^2 v_r \exp[-\epsilon^*(i,f)/kT]$ . The sum over final states and average over initial states is then expressed as:			
	$\sum_i \sum_f P(i) T(i,f) \pi d^2 v_r \exp\left[-\frac{\epsilon^*(i,f)}{kT}\right].$			

We next calculate P(i), noting that kT at 300 K is 207 cm<sup>-1</sup>: the number of reactants in the ground state is proportional to  $\exp(-0/kT) = 1.0$ . The number in state *i*2 is proportional to  $\exp(-100 \text{ cm}^{-1}/kT) = \exp[-100/207] = 0.617$ . Thus P(i1) = 1.0/(1.0 + 0.617) = 0.618 and P(i2) = 0.617/(1.0 + 0.617) = 0.382.

Next, note that  $\pi d^2 = 3.14 \times 10^{-2} \text{ nm}^2$  (molecule<sup>-1</sup>) and that at room temperature  $v_r = [8kT/\pi\mu]^{1/2} = [8(1.38 \times 10^{-24} \text{ J molec}^{-1} \text{ K}^{-1})(6.02 \times 10^{23} \text{ molec/mol})(300 \text{ K})/\pi(5.0 \text{ g/mol})$ (1 kg/1000 g)]<sup>1/2</sup> = 1.13 km/s; thus  $\pi d^2 v_r = (3.14 \times 10^{-20} \text{ m}^2 \text{ molec}^{-1})$  (1.13 × 10<sup>3</sup> m/s) =  $3.55 \times 10^{-17} \text{ m}^3 \text{ molec}^{-1} \text{ s}^{-1} = 2.14 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ . We also evaluate exp(-1000/207) =  $7.98 \times 10^{-3}$  and exp(-500/207) =  $8.93 \times 10^{-2}$ .

Finally we perform the sum and average to obtain  $k(T = 300 \text{ K}) = (2.14 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}) \times \{[(7.98 \times 10^{-3})(0.618)(0.05 + 0.20 + 0.10 + 0.05)] + [(8.93 \times 10^{-2})(0.382)(0.1 + 0.3 + 0.1 + 0.1)]\} = 4.80 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}.$ 

#### 8.4 MOLECULAR SCATTERING<sup>®</sup>

Ever since Rutherford obtained information about the structure of the atom from measurement of the angular distribution of deflected alpha particles, scattering experiments have been used by both physicists and chemists to explore fundamental processes in their respective fields. The objective of this section is to investigate what can be learned about chemical interactions by examination of the angular distribution? As shown in **Figure 8.3**, the angle of scattering in Rutherford's case was measured relative to the velocity of the incoming alpha particles that struck a stationary metal foil. Chemists face a somewhat more complicated situation because neither of the reacting molecules is stationary in the laboratory frame. In



<sup>&</sup>lt;sup>e</sup>D. R. Herschbach and Y. T. Lee shared the 1986 Nobel Prize in Chemistry (with J. C. Polanyi) for their work using molecular beams to study the dynamics of elementary chemical processes.

#### Chapter 8 Molecular Reaction Dynamics

the ideal experiment, the observer of a chemical reaction would like to be located in advance at the position where two reactants would collide. From this center-ofmass observation point, shown in **Figure 8.4**, one could then watch both the approach of the reactants along their relative velocity vector and the departure of the products along a new line making an angle  $\theta$  with the relative velocity vector. Unfortunately, the center-of-mass point for two reacting species is always itself moving in the laboratory frame, so we first need to investigate how the laboratory velocities are related to the velocities in the center-of-mass frame.

#### 8.4.1 The Center-of-Mass Frame—Newton Diagrams

We assume that the initial velocities of two reactants of masses  $m_1$  and  $m_2$  are defined in the laboratory frame by the use of molecular beam techniques. In a typical case, the reactants might each be coexpanded in a dilute mixture with a light rare gas from a nozzle source and collimated by skimmers, as shown in **Figure 8.5**. In such expansions, the enthalpy of the gas behind the nozzle is converted to bulk translational energy, and the distribution is shifted to higher energies. A simple way



#### Figure 8.4

 $A + BC \rightarrow AB + C$  reaction as seen by an observer from the center-of-mass point.



#### Figure 8.5

In a supersonic expansion source the random thermal motions on the high pressure side of the nozzle are converted into directed motion along the beam axis.

of thinking about what happens is that the very fast molecules are slowed by collisions with those in front of them, while the slow molecules are sped up by collisions with faster molecules behind them. The result is a beam whose velocity distribution is peaked sharply compared to a Maxwell-Boltzmann distribution, as illustrated in **Figure 8.6.** One can estimate the stream velocity,  $v_0$ , of the beam for a monatomic carrier gas by setting its enthalpy, 5kT/2, equal to the kinetic energy of the molecules,  $\frac{1}{2}mv_0^2$ , so that one obtains  $v_0 = (5kT/m)^{1/2}$ . For helium, or for heavier gases seeded in helium, and for expansion from a room-temperature reservoir, this velocity is  $v_0 = 1.76 \times 10^3$  m/s.

Now let two such beams, one containing each reactant, intersect as in the apparatus of Figure 8.7. We demonstrated in Appendix 1.4 using a diagram like that in Figure 8.8 (often called a "Newton" diagram) that the total energy,



#### Figure 8.6

Comparison between velocity distributions for a Maxwell-Boltzmann distribution and the distribution obtained from a supersonic expansion. The example shown is for He at 300 K.



#### Figure 8.7

Crossed molecular beam apparatus. The products of the reaction are detected (D) as a function of the variable laboratory angle  $\Theta$ .



Newton diagram for intersecting beams.

 $E = \frac{1}{2}m_1\mathbf{v}_1^2 + \frac{1}{2}m_2\mathbf{v}_2^2$ , could also be written as  $E = \frac{1}{2}\mu\mathbf{v}_r^2 + \frac{1}{2}M\mathbf{v}_{com}^2$ , where  $M = m_1 + m_2$ ,  $\mu = m_1m2/M$ , and  $\mathbf{v}_r$  and  $\mathbf{v}_{com}$  are shown in the figure. The speed and direction of  $\mathbf{v}_{com}$ , recall, do not change during the collisions provided that the only forces act between the two particles. Specifically,  $\mathbf{v}_r = \mathbf{v}_2 - \mathbf{v}_1$ , and  $\mathbf{v}_{com}$  is a vector from the origin to the center-of-mass point on  $\mathbf{v}_r$  located a distance  $(m_2/M)\mathbf{v}_r$  from the intersection of  $\mathbf{v}_1$  and  $\mathbf{v}_r$ . Thus, if the two molecular beams of velocities  $\mathbf{v}_1$  and  $\mathbf{v}_2$  define directions in the laboratory frame, then their angle of intersection, their magnitudes, and the masses of the reactants define the direction both of the center of mass and of their relative motion.

**Figure 8.8** shows that an observer riding along the center-of-mass point would then see reactant 1 approaching from the lower right in the diagram with velocity  $\mathbf{u}_1$  and reactant 2 approaching from the upper left with velocity  $\mathbf{u}_2$ . Note that in this frame of reference, the momentum of particle 1,  $m_1\mathbf{u}_1 = -m_1(m_2/M)\mathbf{v}_r$ , is equal in magnitude and opposite in direction to the momentum of particle 2,  $m_2\mathbf{u}_2 =$  $m_2(m_1/M)\mathbf{v}_r$ . Because the center of mass of the system will keep moving in the same direction at the same speed whatever the interaction between the reactants, the amount of energy available to the collision of the particles is not their total energy, but rather just that measured in the moving center-of-mass frame:  $\mathbf{\epsilon}_r = \frac{1}{2}m_1\mathbf{u}_1^2 + \frac{1}{2}m_2\mathbf{u}_2^2 = \frac{1}{2}m_1(m_2\mathbf{v}_r/M)^2 + \frac{1}{2}m_2(m_1\mathbf{v}_r/M)^2 = \frac{1}{2}\mu\mathbf{v}_r^2$ .

After the reaction takes place, the product molecules will move away from the center of mass along a new direction, as already illustrated in **Figure 8.4.** What will their new relative velocity be, and how will it be partitioned between the new fragments? The second question is answered by applying conservation of momentum to the problem. In the center-of-mass frame, the momenta of the particles must sum to zero. If we label the product masses by  $m_3$  and  $m_4$  and their velocities with respect to the center of mass as  $\mathbf{u}_3$  and  $\mathbf{u}_4$ , then

$$m_3 \mathbf{u}_3 + m_4 \mathbf{u}_4 = 0 \tag{8.9}$$

by conservation of momentum.

Conservation of energy can help us to answer the first question. The new relative velocity will depend on the amount of energy available for translational motion. Suppose that the energy release for the specific reaction from state *i* of the reactants to state *f* of the products is  $\epsilon_{ex}(i, f)$ ; then the total energy available for

translation is that available before the reaction,  $\epsilon_r$ , plus the excergicity,  $\epsilon_{ex}(i,f)$ . In the center-of-mass frame, the products will then have an energy  $\epsilon_r + \epsilon_{ex}(i,f)$ . Then, by conservation of energy we have

$$\frac{1}{2}m_{3}\mathbf{u}_{3}^{2} + \frac{1}{2}m_{4}\mathbf{u}_{4}^{2} = \epsilon_{r} + \epsilon_{ex}(i,f) = \frac{1}{2}\mu'\mathbf{v}_{r}'^{2}.$$
 (8.10)

If  $\mathbf{v}'_r$  is the relative velocity between  $m_3$  and  $m_4$  after the collision,  $\mathbf{v}'_r = \mathbf{u}_4 - \mathbf{u}_3$ , then the solution for  $\mathbf{u}_3$  and  $\mathbf{u}_4$  that satisfies equations 8.9 and 8.10 is

$$\mathbf{u}_{3} = -\left(\frac{m_{4}}{M}\right)\mathbf{v}_{r}',$$

$$\mathbf{u}_{4} = \left(\frac{m_{3}}{M}\right)\mathbf{v}_{r}'.$$
(8.11)

By conservation of mass,  $M = m_3 + m_4$  is the same as  $M = m_1 + m_2$ .

Figure 8.9 illustrates the relationships just described. For the example drawn,  $m_3 > m_4$ .

The task remaining is to find out where the product molecules will appear in the laboratory frame of reference. Let us first concentrate on the product with mass  $m_4$ , recognizing that generalization to the other product would follow similar arguments. The conservation laws of energy and momentum limit the length of  $\mathbf{u}_4$  but not its direction, so that, as shown in Figure 8.10,  $m_4$  could in principle be found anywhere on a sphere of radius  $\mathbf{u}_4$  centered on the center-of-mass position. Of course, the product will not necessarily be isotropically distributed on this sphere; its distribution is what we would like to learn. As shown in the figure, if we set the detector at a laboratory angle of  $\Theta$  and in the plane of the two molecular beams, it will detect products that have been scattered by an angle  $\theta$  in the center-of-mass frame. By scanning  $\Theta$  and transforming from the laboratory to the center-of-mass frame, it is then possible to map out the center-of-mass angular distribution of products. This distribution is called the differential reaction cross section, because it tells us how the cross section varies with solid angle. Specifically, we will symbolize the differential cross section by  $d^3\sigma(v_r,\theta)/d^2\omega dv'_r$ . It provides the cross section for product molecules that are scattered per unit time into a solid angle  $d^2\omega$  with



#### Figure 8.9

Products separate along their new relative velocity vector  $\mathbf{v}'_r$  making an angle  $\theta$  with respect to the reactant relative velocity vector  $\mathbf{v}_r$ .





The reaction product  $m_4$  will be found on a sphere of radius  $\mathbf{u}_4$ . Products scattered by  $\theta$  in the center-of-mass frame are scattered by  $\Theta$  in the laboratory frame.



#### Figure 8.11

Newton diagram for the heavier product,  $m_3$ .

final relative velocities in the range from  $\mathbf{v}'_r$  to  $\mathbf{v}'_r + d\mathbf{v}'_r$ . We use the notation  $d^2\omega$  for the solid angle to mean sin  $\theta \, d\theta \, d\phi$ , where  $\theta$  and  $\phi$  are the spherical coordinates in the center-of-mass frame.

It is interesting to note from Figure 8.10 that to measure the complete differential cross section for  $m_4$ , the detector would have to be moved in a complete circle around the scattering center. What would the Newton diagram look like for the other product,  $m_3$ ? Figure 8.11 shows that this product is located on a much smaller sphere, corresponding to its smaller velocity. The entire scattering angle distribution from  $\theta = 0$  to  $\theta = 2\pi$  in the center-of-mass frame can be measured by rotating the detector between  $\Theta = \Theta_1$  and  $\Theta = \Theta_2$  in the laboratory frame. Note, however, that the scattering at a particular laboratory angle, say  $\Theta_3$ , measures reaction products usually corresponding to two center-of-mass angles. If the detector is equipped to measure the laboratory velocity of the products by using, for example, a velocity selector, then it would detect fast fragments due to scattering at center-of-mass angle  $\theta_3$ , and slow fragments due to scattering at center-of-mass angle  $\theta'_3$ .

Before proceeding to an example of what can be learned from measurement of the differential cross section, we note that much of the scattering to the sphere centered on the center-of-mass point is directed toward points that are outside of the plane formed by the crossed molecular beams and in which the detector is typically located. For a given center-of-mass scattering angle  $\theta$  and for randomly oriented reactants, we can deduce that the scattering should be cylindrically symmetric about the relative velocity vector  $\mathbf{v}_r$ . The reason is shown in **Figure 8.12**. The angle of scattering  $\theta$  should depend on the impact parameter *b*, defined in Section 1.7, and on the orientation of the two reactants as they collide. If the orientation is random, then  $\theta$  depends just on *b*. However, for a given magnitude of *b* between *b* and *b* + *db*, there are an equal number of trajectories passing through any part of an annulus centered on  $\mathbf{v}_r$ . Because the annulus has circular symmetry about  $\mathbf{v}_r$ , the scattering should also be symmetric about  $\mathbf{v}_r$ ; that is, the intensity may depend on  $\theta$  but it does not depend on  $\phi$ , the azimuthal angle about  $\mathbf{v}_r$ .

With this cylindrical symmetry in mind, let us note that the differential reaction cross section,  $d^2\sigma(v_r,\theta)/d^2\omega dv'_r$ , is defined in such a way that its integral over final velocities and angles gives the total reactive cross section at a particular relative energy:

$$\sigma_{\rm R}(\epsilon_{\rm R}) = 2\pi \int_{\theta=0}^{\pi} \int_{v_{\rm r}=0}^{\infty} \frac{{\rm d}^3 \sigma_{\rm R}(v_{\rm r}',\theta)}{{\rm d}^2 \omega \, {\rm d} v_{\rm r}'} \sin \theta {\rm d} \theta.$$
(8.12)

A word of caution is necessary here. Molecular beam reaction experiments sometimes report  $\sigma_{\rm R}(v_r,\theta)$ , but they more often report the "product contour diagram." The two are related. The product contour diagram plots in polar coordinates the derivative of the cross section with respect to both angles and product velocity; that is, they plot  $d^2\sigma(v_r,\theta)/d^2\omega dv'_r$ , where  $d^2\omega$  is shorthand for sin  $\theta d\theta d\phi$  and  $v'_r$ is the product relative velocity.



#### Figure 8.12

Diagram showing that scattering should be cylindrically symmetric about  $\mathbf{v}_r$  because of the cylindrical symmetry of *b* about  $\mathbf{v}_r$ .

#### Chapter 8 Molecular Reaction Dynamics

#### 8.4.2 Reactive Scattering: Differential Cross Section for $F + D_2$

We now consider measurements of the differential cross section for the  $F + D_2$  reaction. A product contour diagram, already converted to the center-of-mass frame, is shown in **Figure 8.13.** What can be learned from such a diagram? First, note the dashed circles superimposed on the diagram. These correspond to the maximum velocities consistent with the conservation laws for production of DF in various vibrational levels. For example, the circle marked "v = 1" shows the velocity expected for DF(v = 1, J = 0). Higher rotational levels of this vibrational state would have less energy available for translation and so would lie within this circle. There are clear peaks in the contours near the energetic limits for the various vibrational levels, and these must then correspond to products formed in the indicated levels with varying amounts of rotational excitation. The contour peak for the v = 3 level is the highest, so most of the DF product must be formed in this state. A careful analysis produces the relative populations already presented in **Table 8.1**.

Note also that the DF products are "backward" scattered, i.e., that with  $\theta = 0^{\circ}$  defined as the direction in which the attacking F atom moves, the DF product is scattered primarily to angles near  $\theta = 180^{\circ}$ . The picture of the reaction which emerges is that the F atom must hit the D<sub>2</sub> or H<sub>2</sub> nearly head-on, and then bounce backward taking one of the hydrogen atoms with it. We might call this a "rebound" reaction.





Product contour map for the  $F + D_2$  reaction at a collision energy of 1.86 kcal mol<sup>-1</sup>. The contours show the DF velocity distribution.

From D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, K. Shobotake, R. K. Sparks, T. P. Schafer, and Y. T. Lee, *J. Chem Phys.* 82, 3067 (1985). Reprinted with permission from the *Journal of Chemical Physics*. Copyright, American Institute of Physics, 1985.

Reactions of other sorts are also possible. Product contour maps, or the related differential cross section, are valuable precisely because they tell us what sort of reaction we are observing. For example, in reactions such as  $K + I_2 \rightarrow$ KI + I, the newly formed product, KI, is found predominantly in the forward direction, as shown in Figure 8.14. Reaction occurs at large impact parameters where an electron is transferred from the K atom (whose ionization potential is low) to the iodine molecule (whose electron affinity is high). The K<sup>+</sup> and  $I_2^-$  are then drawn toward one another by the electrostatic force, and the more energetically stable KI + I products are formed with the KI moving off in the direction of the original K atom. This type of reaction mechanism is known as the harpoon mechanism, because, in effect, the potassium has used its electron as a harpoon to pull in an iodine atom along the line of electrostatic force. The theory of such reactions will be discussed in Section 8.6.4. Harpoon reactions are examples of a more general class of reaction, called stripping reactions, in which the attacking atom or radical carries off part of the attacked molecule in the forward direction.

Figure 8.15 shows the product contour plot for a reaction involving a *collision complex*. Note that there is backward-forward symmetry in the differential cross section. The interpretation is that the O and Br<sub>2</sub> have "stuck" together for a time long compared to their mutual rotation period. To see why such complex-forming reactions might lead to forward-backward symmetry in the product contour plots, we consider the collision of two structureless particles that form a complex. Figure 8.16 shows the two particles coming together at a given impact parameter and orbiting one another in a plane. If the collision complex lives longer than a rotational period, then the reaction products are likely to be flung out radially like water spinning off a wet frisbee. Thus, if  $dN(\theta)/dt$  is the number of products created per unit



Figure 8.14

KI contour map for the reaction  $K + I_2 \rightarrow KI + I$ . Note that the KI product is scattered in the forward direction with respect to the K velocity.

From K. T. Gillen, A. M. Rulis, and R. B. Bernstein, J. Chem. Phys. 54, 2831 (1971). Reprinted with permission from the Journal of Chemical Physics. Copyright, American Institute of Physics, 1971.

#### Chapter 8 Molecular Reaction Dynamics



#### Figure 8.15

BrO contour map for  $O + Br_2 \rightarrow BrO + Br$  reaction. Note that the scattering distribution is symmetric in the forward and backward directions.

From D. D. Parish and D. R. Herschbach, J. Am. Chem. Soc. 93, 6133 (1973). Reprinted with permission from The Journal of the American Chemical Society. Copyright 1973 American Chemical Society.





Two molecules forming a complex with angular momentum L. Products are "sprayed" out with a uniform distribution of angles in the plane of rotation.

time near the angle  $\theta$ , then  $d^2N(\theta)/dt d\theta = \text{constant}$ . Although it might thus seem that the differential cross section should have equal intensity in all directions, it is important to remember that for collisions of structureless particles, and indeed for the average collisions of structured particles if they are not oriented on average with respect to one another, the scattering is cylindrically symmetric about the relative velocity vector because of the cylindrical symmetry of  $\phi$  in **Figure 8.12**. In the frisbee analogy, we need to think of rotating the already spinning frisbee about an axis in the plane of the frisbee: the water will be more dense along this relative velocity axis because many values of  $\phi$  for  $\theta$  near 0° or 180° contribute to flinging water in the same direction.

In summary, the differential cross section, obtained by analysis of molecular scattering, is useful because it gives us a detailed picture of how the reaction proceeds. Common examples are rebound reactions, where the scattering is predominantly in the backward direction, stripping reactions, where the scattering is predominantly in the forward direction, and collision complex reactions, where the scattering exhibits forward-backward symmetry corresponding to peaking in the forward and backward directions.

Our focus in this chapter has been on reactive collisions, but scattering experiments also provide important information about other kinds of collisions. We digress briefly here to discuss elastic and inelastic collisions.

#### 8.4.3 Elastic Collisions

Even for collisions that do not result in reaction, the differential cross section, obtained from scattering experiments, provides us with the most detailed information about the collision mechanism. As we will see, the distribution of scattering angles for nonreactive collisions can be used rather directly to calculate the potential of interaction between the colliding species. We consider in this section collisions for which there is neither reaction nor energy transfer; that is, collisions for which the energy of the outgoing particles is exactly the same as that of the incoming particles, only the direction of their motion has changed. Such collisions are called *elastic collisions*; collisions between billiard balls are a familiar approximation. It was essentially collisions of this type which we considered in Chapters 1 and 4 when we introduced the concept of mean free path and then used it to examine transport properties.

**Example 8.2** shows how a Newton diagram can be used to relate the laboratory and center-of-mass scattering angles for elastic processes.

## example 8.2

#### **Newton Diagrams for Elastic Collisions**

Objective	A beam of argon ( $MW = 40$ ) intersects a beam of krypton ( $MW = 84$ ) at right angles. Calculate the laboratory angle between the krypton direction and the direction of a detector placed so as to monitor krypton scattered elastically in the backward center-of-mass direction. Assume that both collision species are traveling at the same speed.
Method	Draw a Newton diagram for the collision, noting that for elastic scattering the krypton product velocity will be located on the sur- face of a sphere whose radius is the original relative velocity of the krypton.
Solution	<b>Figure 8.17</b> shows the Newton diagram. Because the original species are traveling at the same velocity, the relative velocity vector lies at an angle of $45^{\circ}$ to each of the primary beams. The center-of-mass velocity vector is located between the origin and a point $40/(40 + 84)$ of the distance from the end of the Kr velocity and the end of the Ar velocity. The elastically scattered Kr will be on a sphere of radius $(40/124)v$ , where



The bottom portion of **Figure 8.18** shows on a log scale the angular distributions for scattering between argon and krypton and argon and xenon obtained from crossed beam experiments. The scattering distributions exhibit many features common to all elastic scattering. First, the scattering is strongly peaked in the forward direction. Second, for each collision partner there is a series of oscillations in the intensity as the angle increases. These lead to a broad relative maximum centered on the so-called *rainbow angle*. Finally, the intensity falls off strongly at angles approaching 180°. Such features can be understood both qualitatively and quantitatively as the consequence of the attractive and repulsive forces between the collision partners. Let us examine the qualitative aspects first.



(*bottom*) Scattering distributions for Ar + Kr and Ar + Xe at  $E_{col} = 1 \times 10^{-20}$  J. (*top*) Potential energy functions.

From J. M. Parson, T. P. Schafer, P. E. Siska, F. P. Tully, Y. C. Wong, and Y. T. Lee, *J. Chem. Phys.* 53, 3755 (1970). Reprinted with permission from the *Journal of Chemical Physics*. Copyright, American Institute of Physics, 1970.

The top portion of **Figure 8.18** shows a good approximation to the interatomic potential between the two closed-shell species, either argon and krypton or argon and xenon in this example. Note that the potential energy is negative (attractive) for large distances and repulsive (this part of the potential is not drawn) for small distances. It is these forces that ultimately cause the breakdown of the ideal gas approximation. By knowing these forces, it is possible to calculate the coefficients in the virial expansion for a real gas.

The consequences of the potential functions shown in **Figure 8.18** are depicted in **Figure 8.19**, where the deflection angle  $\chi$  is plotted for various reduced impact parameters,  $b^* = b/R_e$ , where  $R_e$  is the distance at which the potential energy is a minimum. For collisions involving large impact parameters, there is a slight attraction between the two species which leads to slightly negative value of  $\chi$ . As  $b^*$ decreases, this negative deflection increases until reaching a maximum when b is equal to  $b_r$ , the impact parameter where there is the maximum negative deflection,  $\chi_r$ . This impact parameter is called the *rainbow impact parameter* for reasons that will be described below. Further reduction in  $b^*$  leads to increasing (less negative) deflection. At a particular impact parameter  $b_g$  called the *glory impact parameter*, the deflection is zero. For smaller impact parameters the deflection increases rapidly until for  $b^* = 0$  there is backward scattering,  $\chi = 180^\circ$ .



Trajectories giving the deflection angle for different reduced impact parameters.

A qualitative plot of the deflection angle  $\chi$  as a function of impact parameter is given in **Figure 8.20.** Of course, a scattering experiment cannot tell whether a given center-of-mass scattering angle  $\theta$  resulted from a positive or negative deflection  $\chi$ ; what is measured is  $\theta = |\chi|$ , as shown in the dashed line.

There are several interesting features of this plot. First, note that a very large number of (large) impact parameters lead to small deflection. Qualitatively, this means that the scattering should be strongly peaked in the forward (zero deflection) direction, as observed in **Figure 8.18.** Quantitatively, note that  $d\theta/db \rightarrow 0$  as  $b \rightarrow \infty$ .

Second, note that at the so-called *rainbow angle*,  $\theta = \theta_r$ , a range of impact parameters lead to scattering at the same laboratory angle. Qualitatively, we might expect a relative maximum at this angle, as, indeed, is observed in **Figure 8.18**. Quantitatively, we note that near the rainbow angle we again have  $d\theta/db = 0$ . The same phenomenon causes rainbows of the celestial sort, where light of a given color entering raindrops at different locations is scattered to the same angle.

Third, note that there are three impact parameters that contribute to the scattering at every angle  $\theta$  smaller than the rainbow angle. From quantum mechanics we know that having more than one trajectory leading to the same final state always results in *interference*, so we might expect the differential cross section to exhibit oscillations for  $\theta < \theta_r$ , as indeed are observed. Finally, we see that only the very smallest impact parameters lead to large deflections near 180°, so that we expect there will not be very many scattering events that produce this deflection. This is the reason that the differential cross section in **Figure 8.18** falls dramatically as  $\theta \rightarrow 180^{\circ}$ .

A more quantitative analysis can be performed with the aid of **Figure 8.12.** Note that the contribution to scattering between angles  $\theta$  and  $\theta + d\theta$  comes from collisions occurring within an annulus between impact parameters b and b + db. Thus,  $d\sigma = I(\theta)\sin\theta \,d\theta \,d\phi = 2\pi b \,db$ , or, after integrating over  $d\phi$ ,



Deflection angle as a function of reduced impact parameter. Note that  $\theta = |\chi|$  is the angle observed.

$$I(\theta) = \frac{b}{\sin \theta |d\theta/db|},$$
 (8.13)

where the absolute value has been introduced in recognition that the intensity is always positive. **Equation 8.13** shows that, at least according to classical mechanics, the scattering intensity  $I(\theta)$  should be infinite when  $d\theta/db$  goes to zero. **Figure 8.21** shows the expected results. The top panel reproduces the curve of  $\theta$  as a function of  $b^*$  (**Figure 8.20**) but turned on its side so that  $\theta$  is the abscissa. The bottom panel plots the logarithm of the derivative  $d\theta/db$ . We have already noted that  $d\theta/db$ is zero at  $\theta = 0$  and at  $\theta = \theta_r$ . Experiments are necessarily performed with finite resolution, and quantum mechanics makes it impossible to specify  $\theta$  closely enough for  $I(\theta) \rightarrow \infty$ . These considerations avoid the infinities, but there are still peaks in  $I(\theta)$  at these locations. In particular, the rainbow peak in the scattering distribution is clearly evident at the angle marked by the dashed line. Note also the oscillations in  $I(\theta)$  for  $\theta < \theta_r$  corresponding to multiple impact parameter collisions contributing intensity at the same angle.

Because the scattering function  $I(\theta)$  depends on the deflection function  $\chi(b)$ , and because  $\chi(b)$  depends on the potential V(r), it should be clear that a measurement of  $I(\theta)$  can be used to determine V(r). In practice, however, the "inversion" from  $I(\theta)$  to V(r) is far from straightforward. While new techniques are still under development, the potential is usually determined iteratively by a "forward convolution" technique. A functional form is assumed, classical or quantum mechanical scattering calculations are then performed, and the results are convoluted with experimental parameters and compared to the experimental results. The functional form of the potential is then adjusted, and the cycle is repeated. For example, the solid line fits to the  $I(\theta)$  curves in **Figure 8.18** come from forward convolution of



(*top*) Relationship between scattering angle and impact parameter. (*bottom*)  $I(\theta)$  from equation 8.13.

the potentials shown at the top of the figure. Much of our knowledge concerning the potential of interaction between closed shell species comes from scattering experiments such as those just described.

#### 8.4.4 Inelastic Collisions

Although we will consider inelastic collisions in more detail in Section 8.6, it is important to note that scattering techniques provide important information about energy transfer. The Newton diagram for inelastic scattering is simpler than that for reactive scattering because the masses of the products are the same as the masses of the reactants. On the other hand, unlike the diagram for elastic scattering, the final relative velocity will be different from the initial one, because, in general, the inelastic collision will transfer energy between translational and internal degrees of freedom.

Consider, for example, the rotational excitation of NO by collision with argon. **Figure 8.22** shows a Newton diagram for the collision. In this diagram, the argon beam is traveling from top to bottom and the NO beam from right to left. Ionization of components in the two beams and projection of the ions onto a screen gives a picture of the beams and a measurement of the velocities. The circle shows the range of NO velocities expected if the scattering were elastic. For processes such as  $Ar + NO(J_i) \rightarrow Ar + NO(J_f)$  with the final rotational quantum number larger than the initial one,  $J_f > J_i$ , energy will be transferred from the translational to rotational



Image of molecular beams and the superimposed Newton diagram for Ar + NO. Reprinted with permission from L. S. Bontuyan, A. G. Suits, P. L. Houston, and B. J. Whitaker, *Journal of Physical Chemistry*, **97**, 6342, 1993. Copyright © American Chemical Society.

degree of freedom, so that the final relative velocity should be less than the initial one. We would thus expect that final NO velocity vectors should lie inside of the indicated circle.

Figure 8.23 provides images of the final velocity vector distribution obtained by a technique in which the product NO molecules are state-selectively ionized and projected onto a screen. The image is such that the observer is looking down on the Newton sphere of Figure 8.22. The circles in the three panels are the same diameter, and represent the size of the scattering sphere that would be expected if all collisions were elastic (see Example 8.3). In these experiments the initial state is  $NO(J_i = 0.5)$ , while the final state is indicated in the caption.<sup>f</sup> There are three important points to note. First, as  $J_f$  increases, the size of the scattering decreases; in the top panel the scattering is nearly at the elastic limit, whereas in the bottom panel it is substantially more confined. This observation is a simple consequence of conservation of energy (see **Example 8.3**). Second, as  $J_f$  increases the distribution of scattering moves from the forward part of the scattering sphere to the backward part. A little thought shows why this should be so. Collisions at large impact parameter produce very little change in either the direction of the NO or its rotational state. Thus, low rotational levels with  $J_f$  just a little above  $J_i$  should be forward scattered. To appreciably change the rotation of the NO, the argon must hit nearly head-on, after which it will rebound nearly along its initial direction. Thus, high  $J_f$  products are

<sup>&</sup>lt;sup>f</sup>Here *J* denotes the total angular momentum, which is half-integral because it is composed of both the angular momentum due to nuclear spin and the angular momentum of the unpaired electron.



Differential cross section for Ar + NO. (top)  $J_f = 7.5$ ; (middle)  $J_f = 18.5$ ; (bottom)  $J_f = 24.5$ . Reprinted with permission from L. S. Bontuyan, A. G. Suits, P. L. Houston, and B. J. Whitaker, Journal of *Physical Chemistry*, **97**, 6342, 1993. Copyright © American Chemical Society.

associated with backward scattering. Third, the scattering is concentrated at specific locations, called *rotational rainbows*. Their origin is similar to the origin of the rainbows in elastic scattering. At the rainbow angles, many trajectories contribute to production of NO in the specified state with the same final scattering angle.

The way in which the rainbow angle moves from the forward to the backward part of the scattering sphere as the final rotational state increases can be used to obtain detailed information about the shape of the NO molecule. Specifically, at the high collision energies of these experiments, the collision samples the repulsive part of the potential between NO and Ar, and this potential looks nearly like an ellipse centered on the NO and having a difference between the major and minor axes of about 0.031 nm.

#### **Newton Spheres for Inelastic Collisions**

Objective	Calculate the velocity corresponding to the radius of the Newton sphere for NO( $v = 0, J = 0.5$ ) in an elastic collision with argon if the center-of-mass collision energy is 0.25 eV. What would be the radius if an inelastic collision produced NO( $v = 0, J = 10.5$ ) given that the NO rotational constant is 1.7 cm <sup>-1</sup> ?
Mathad	For the electic case, we can calculate the center of mass relative

**Method** For the elastic case, we can calculate the center-of-mass relative velocity from the energy and the reduced mass. The NO velocity will then be given by conservation of momentum. For the inelastic case, the final energy will be just the collision energy minus the energy needed to rotationally excite the NO. The NO velocity is then calculated in the same manner as for the elastic collision.

**Solution**  $\frac{1}{2}\mu_{\text{NO-Ar}}v_{r}^{2} = (0.25 \text{ eV})(8066 \text{ cm}^{-1} \text{ eV}^{-1})(hc \text{ J cm}) = 0.40 \times 10^{-19} \text{ J}. \text{ Thus, } v_{r} = [2(0.401 \times 10^{-19} \text{ J})(6.02 \times 10^{23})(1000 \text{ kg/g})/(30 * 40/70 \text{ g})]^{1/2} = 1678 \text{ m/s}. \text{ The NO speed is thus } (40/70) * 1678 \text{ m/s} = 959 \text{ m/s}. \text{ For the inelastic case, the final available energy is } [(0.25 \text{ eV})(8066 \text{ cm}^{-1} \text{ eV}^{-1}) - (10)(11)(1.7 \text{ cm}^{-1})] * (hc \text{ J cm}) = 0.362 \times 10^{-19} \text{ J}. \text{ Thus, the new NO speed is } [(0.362)/(0.401)](959 \text{ m/s}) = 866 \text{ m/s}.$ 

#### 8.5 POTENTIAL ENERGY SURFACES

Having explored how molecular scattering can reveal the details of reactive, elastic, and inelastic collisions, we now return to a main theme, the connection between the potential energy surface and the measured product state distributions. We have already seen in **Figure 8.18** how the potential energy function for elastic collisions is related to the angular distribution of products. Of course, because more atoms are involved, the potential function is more complicated for reactive collisions, but it still controls both the angular and product state distributions. The potential energy surface for a system of atoms can often be determined spectroscopically for some regions of coordinate space (see, for example, Section 8.7.3), but most often these

## example 8.3

#### Chapter 8 Molecular Reaction Dynamics

measurements have to be supplemented with calculations. In this section we consider briefly how a potential energy surface is constructed and how to use it to calculate the outcome of collisional events.

Potential energy functions are calculated from the Schrödinger equation using the Born-Oppenheimer approximation. Because the motion of the electrons is much faster than that of the nuclei, it is a reasonable approximation to assume that the electrons adjust rapidly to any change in nuclear configuration. Thus, the electronic energy will be nearly independent of the nuclear motion and can be calculated for each desired geometry of the atoms. The electronic calculation typically employs a self-consistent field approach in which the energy of each electronic orbital is optimized assuming an average field of the remaining electrons. As the electrons are each considered in turn, the average field is improved. Such calculations of the electronic energy are performed for several geometries of the atoms involved in the reaction, and the resulting points on the energy surface are interpolated by a smooth fitting function.

**Figure 8.24** gives some early results obtained for the  $F + H_2$  reaction in the collinear configuration of lowest energy. The valley at the lower right corresponds to the reactants  $F + H_2$ , while that at the upper left corresponds to the products H + HF. The zero of energy has been taken as the energy of  $F + H_2$ , and the contours are labeled in units of kcal/mole. A typical reaction would proceed from the valley on the lower right to the one on the upper left over a slight barrier. Note that the barrier to the reaction is located near the entrance channel to the reaction, so that much of the exothermicity of the reaction is released before the H–H bond has stretched very far and before the HF bond has fully formed. The effect of this energy release is to accelerate the products toward short HF distances before the H–H bond has stretched, resulting in vibrational excitation of the HF product. We defer a more detailed explanation of this effect until the next section.



#### Figure 8.24

Potential energy surface for the  $F + H_2$  reaction.

From C. F. Bender, S. V. O'Neil, P. K. Pearson, and H. F. Schaefer III, *Science* **176**, 1412 (1972). Reprinted with permission from *Science*. Copyright 1972 American Association for the Advancement of Science.

In the Born-Oppenheimer approximation the electrons sense only the charges of the nuclei and not their masses. Thus, the potential energy surface for  $F + D_2$  is exactly the same as that for  $F + H_2$ ; it is only the zero-point energies and vibrational level spacings that change with the differing reduced masses. Thus, we would also expect the product acceleration to excite DF vibrationally. It is precisely this feature of the potential energy surface that leads to the vibrational inversion in the DF product that we have already observed in **Figure 8.1** and **Figure 8.13**.

Before generalizing this result, we see how a semiclassical approach to the dynamics can provide us with greater insight into the dynamics.

#### 8.5.1 Trajectory Calculations by Classical Mechanics

If particles behaved classically according to Newton's laws of motion, then the relationship between the potential energy surface and the dynamics of a reaction would be perfectly straightforward. One would simply specify the initial conditions for the reaction, for example the collision energy, the impact parameter, the angle of approach and so on, and then integrate Newton's laws to find the "trajectory" for the collision, i.e., the coordinates as a function of time. We know from the development of quantum mechanics that such an approach is deficient. Particles penetrate into regions of the potential energy that are classically forbidden, and their vibrational and rotational energies can have only quantized values rather than the continuous ones allowed in classical mechanics. Nonetheless, classical mechanics can give us a conceptual picture of the dynamics, and it often indicates the correct trends, for example, how the product state distribution might depend on the relative reactant velocity. We thus briefly explore here how this classical approach might help us to understand molecular dynamics.

The equations that we need to describe the system are basically simple, but the notation is somewhat cumbersome. Let k = 1, 2, ..., N index the atoms in the system, and let  $q_i^k$  with i = 1, 2, 3 index the three Cartesian coordinates x, y, and z for atom k. The potential energy is a function of the 3N coordinates:  $V = V(q_i^k; i = 1-3, k = 1-N)$ . Consider starting at some location on the potential energy surface. The force along any coordinate is simply the negative of the change in potential along that coordinate:  $F_i^k = -(\partial V/\partial q_i^k)$ . However, by Newton's law  $F_i^k = m_k a_i^k = d(p_i^k)/dt$ . Thus,

$$\frac{\mathrm{d}}{\mathrm{d}t}(p_i^k) = -\frac{\partial V}{\partial q_i^k}.$$
(8.14)

The kinetic energy of the system is simply given by the sum of the kinetic energies in all of the coordinates:

$$T = \sum_{i=1}^{3} \sum_{k=1}^{N} \frac{1}{2m_k} (p_i^k)^2.$$
 (8.15)

By taking the partial derivative of both sides of this equation with respect to  $p_i^k$ , we find that

$$\frac{\partial T}{\partial p_i^k} = \frac{1}{m_k} p_i^k = \frac{\mathrm{d}}{\mathrm{d}t} (q_i^k), \qquad (8.16)$$

or

$$\frac{\mathrm{d}}{\mathrm{d}t}(q_i^k) = \frac{\partial T}{\partial p_i^k} = \frac{p_i^k}{m_k}.$$
(8.17)

#### Chapter 8 Molecular Reaction Dynamics

Suppose we start the system in a particular configuration of positions and velocities corresponding to a particular kinetic and potential energy; the initial values of V, T,  $p_i^k$ , and  $q_i^k$  are thus known. Equations 8.14 and 8.17 then enable us to calculate the change in momentum and position along each coordinate. By taking small time steps and integrating these equations numerically, we can then develop the trajectory of the system. A check on the numerical accuracy of the method can be made by comparing the total energy, E = (T + V), at any time with the initial total energy. Although this method is numerically straightforward, there are several features that must be considered.

The first feature of the classical mechanics approach to notice is that it requires us to specify some parameters over which a typical experiment might have no control. For example, even collision experiments that measure cross sections from a given state of the reactants to a specified state of the products still provide no control over such parameters as the initial impact parameter, the orientation of the reactants, the phase of the reactant vibration(s) with respect to the time of collision, and so on. If classical calculations are to provide guidance in understanding our experiments they must average appropriately over these uncontrolled parameters of the collision. A typical method for such averaging is the *Monte Carlo* technique. Initial conditions are chosen at random from the appropriate distribution. For example, the initial phase of reactant vibration might be chosen by picking a number at random between 0 and  $2\pi$ .

A second feature to note is that, although we will be interested in such quantum mechanical features as the vibrational or rotational product state distribution, classical mechanics does not recognize that the products have quantum states. A given integration of Newton's equations will likely produce a product with vibrational energy different from that allowed in quantum mechanics. Of course, if many states of the products are produced we might expect the overall classical distribution of energy in a particular degree of freedom to be similar to the quantum distribution, but in order to obtain a correspondence we must use a *binning* process to assign quantum states to a particular classical outcome. For example, if the allowed quantum mechanical vibrational energies are given by  $(v + \frac{1}{2})hv$ , we might assign energies  $0 \le \epsilon < hv$  to v = 0, energies  $hv \le \epsilon 2hv$  to v = 1, and so on.

Once we recognize the need for averaging over initial conditions and for binning the final results, it is quite simple to perform a number of trajectories to see how particular features of the potential energy surface influence the dynamics of a reaction. The force a mass feels along any direction r is simply the negative derivative of the potential, F = -dV/dr, and the acceleration that the mass experiences in this direction is simply given by Newton's law, F = ma. Given the initial values for the positions and velocities, final values can be obtained by calculating the changes in positions and velocities during each of a large number of small time increments.

**Figure 8.25** shows typical results for distance as a function of time in the abstraction of an H atom from  $H_2(v = 0, J = 1)$  by O(<sup>1</sup>D). In this figure the curves labeled  $R_{OA}$  and  $R_{OB}$  give the distances between the oxygen atom and the two hydrogen atoms, denoted by A and B, while the curve labeled  $R_{AB}$  gives the H–H distance. The rapid oscillations on all three curves correspond to the  $H_2$  zero-point vibrational motion, while the slower oscillations on  $R_{OA}$  and  $R_{OB}$  correspond to  $H_2$  rotational motion. At  $t \approx 30 \times 10^{-14}$  s, the collision results in a reaction between the oxygen and the hydrogen labeled A to produce OH, so that  $R_{OA}$  now oscillates with the v = 2 vibrational motion of OH, while  $R_{OB}$  and  $R_{AB}$  increase as hydrogen B moves away from the OH product.



A trajectory for the  $O(^{1}D) + H_{2}$  abstraction reaction.

From P. A. Whitlock, J. T. Muckerman, and E. R. Fisher, J. Chem. Phys. 76, 4468 (1982). Reprinted with permission from the Journal of Chemical Physics. Copyright, American Institute of Physics, 1982.

For a reaction involving N = 3 atoms there are 3N - 6 = 3 coordinates necessary to specify all the relative atomic positions. For example, in the O(<sup>1</sup>D) + H<sub>2</sub> abstraction of **Figure 8.25** the three chosen coordinates were  $R_{OA}$ ,  $R_{OB}$ , and  $R_{AB}$ . Although all the coordinates can be described in a plot like that of **Figure 8.25**, it is often more instructive to fix all but two of the 3N - 6 coordinates and to plot the trajectory as a point moving along the potential energy surface expressed as a function of the two chosen coordinates. For example, if we constrain the atoms to be in a collinear geometry, then we could plot the trajectory for the F + H<sub>2</sub> reaction as a point moving along the potential energy surface of **Figure 8.24**. Such a trajectory might look like that in the upper left-hand panel of **Figure 8.26**, which offers some insight into energy consumption and deposition in chemical reactions.

Note in panels (A) and (B) of **Figure 8.26** that the barrier, like that for  $F + H_2$ , is close to the reactant valley (A + BC, lower right), a so-called *early* barrier. The top left panel shows a typical trajectory for the case when the reactants A + BC approach one another with translational energy. The translational energy propels the reactants toward the barrier, and the energy released as the trajectory leaves the barrier compresses the AB bond and results in vibrational energy of the products. By contrast, if an equivalent amount of energy were placed in the vibration of the BC reactant rather than in translation, the trajectory might be similar to that shown in panel (B), where not enough energy is provided along the A–B coordinate to attain the top of the barrier. We thus conclude that *early* barriers favor production of vibrationally excited products and require that the reactant energy be in translation rather than vibration.





From J. C. Polanyi, Acct. Chem. Res. 5, 161 (1972). Reprinted with permission from the Accounts of Chemical Research. Copyright 1972 American Chemical Society.

The opposite is true for the *late* barrier depicted in panels (C) and (D) of the figure. In panel (C) we see that, to turn the corner and attain the barrier, the trajectory needs not only to have its energy in BC vibration but also to have the correct phase (dotted trajectory rather than solid one). Translational energy, shown in panel (D), results in deflection back toward the reactant valley. Those trajectories that do react, such as the dotted one in (C), that do react produce primarily translational energy in the products, because much of the reaction exothermicity is released along the B–C direction. We thus conclude that *late* barriers favor production of translationally excited products and require that the reactant energy be in vibration rather than translation.

#### 8.5.2 Semiclassical Calculations

The energy consumption and deposition propensities described in the previous section provide an example where classical calculations give a qualitative and often even quantitative connection between the potential energy surface and the dynamics. On the other hand, more detailed descriptions of the molecular dynamics sometimes require quantum mechanical calculations with the potential as an input function. Unfortunately, the effort needed to achieve the results often far exceeds the amount of understanding gained. An alternative route that couples the simplicity of classical trajectories with the rigor of quantum mechanics is needed.

One such *semiclassical* approach uses the trajectory calculated from classical mechanics to describe the relative motion of reactants and products while treating the internal energy levels quantum mechanically. This approach works well as long as the amount of energy exchanged in the collision or reaction is small compared to the original translational energy; unfortunately this is not always the case. Even so, it is often instructive to examine the results of semiclassical approaches, because they provide a great deal of insight into what controls energy exchange processes.

For simplicity, we consider an inelastic collision  $A + BC(i) \rightarrow A + BC(f)$  taking a molecule initially in state *i* to a final state *f*. Assume that the trajectory R(t) is known from classical mechanics, where *R* here represents the distance of A from the center-of-mass of BC. Then the potential V(R) can be treated as a time-dependent interaction, V(R(t)), and the wave function for the system will then satisfy the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi(r,t)}{\partial t} = H(r,t)\psi(r,t).$$
 (8.18)

Of course, at  $t \to \infty$  and  $t \to -\infty$ , the potential goes to zero, and H(r,t) becomes the time-independent Hamiltonian for the system,  $H_0(r)$ , with solutions

$$H_0(r)\phi_i(r) = E_i\phi_i(r),$$
 (8.19)

where r represents the internal coordinate of BC.

Let us expand the general solution  $\psi(r,t)$  in terms of the solutions to the timeindependent problem with time-dependent amplitudes  $a_k(t)$ :

$$\psi(r,t) = \sum_{k} \phi_{k}(r) a_{k}(t) \exp\left(-\frac{iE_{k}t}{\hbar}\right).$$
(8.20)

Note that at  $t = -\infty$  all the coefficients  $a_k$  are equal to zero except for the one multiplying the initial state of the system  $\phi_i$ , which has a value  $a_i = 1$ . At some later time t the wave function will be a superposition of the basis states, with the probability of finding the system in state f given by the projection of the superposition state,  $\psi(r,t)$ , onto the wave function for state f:

$$\left| \int \phi_f^* \psi(r,t) \, \mathrm{d}r \right|^2 = |a_f(t)|^2, \tag{8.21}$$

where all other terms in the sum for the expansion **equation 8.19** vanish because of the orthogonality of the solutions to the time-independent problem:

$$\int \phi_j^* \phi_k \, \mathrm{d}r = \delta_{jk}. \tag{8.22}$$

The Kronecker delta function,  $\delta_{jk}$ , is equal to unity if j = k and is zero otherwise.

The probability of finding the system at  $t = \infty$  in state f is simply  $|a_f(t = \infty)|^2$ , where the coefficient is determined by the condition that the wave function of equation 8.20 be a solution to equation 8.18.

#### Chapter 8 Molecular Reaction Dynamics

To calculate  $|a_f(t = \infty)|^2$ , let us substitute the expansion of **equation 8.20** into the time-dependent Schrödinger **equation 8.18** using the fact that the Hamiltonian can be written as  $H = H_0 + V(t)$ :

$$i\hbar\frac{\partial}{\partial t}\left\{\sum_{k}\phi_{k}(r)a_{k}(t)e^{-iE_{k}t/\hbar}\right\}=\left[H_{0}+V(t)\right]\left\{\sum_{k}\phi_{k}(r)a_{k}(t)e^{-iE_{k}t/\hbar}\right\}.$$
 (8.23)

Taking the derivative on the left-hand side and operating with  $H_0$  on the right-hand side, we obtain

$$i\hbar\left\{\sum_{k}\phi_{k}(r)\frac{\mathrm{d}a_{k}}{\mathrm{d}t}e^{-iE_{k}t/\hbar}+\sum_{k}\phi_{k}(r)a_{k}(t)\left(-\frac{iE_{k}}{\hbar}\right)e^{-iE_{k}t/\hbar}\right\}$$

$$=\left\{\sum_{k}E_{k}\phi_{k}(r)a_{k}(t)e^{-iE_{k}t/\hbar}+\sum_{k}V(t)\phi_{k}(r)a_{k}(t)e^{-iE_{k}t/\hbar}\right\}.$$
(8.24)

Note that the second summation on the left-hand side when multiplied by  $i\hbar$  is exactly equal to the first summation on the right-hand side, so that

$$i\hbar \sum_{k} \phi_{k}(r) \frac{\mathrm{d}a_{k}}{\mathrm{d}t} e^{-iE_{k}t/\hbar} = \sum_{k} V(t)\phi_{k}(r)a_{k}(t)e^{-iE_{k}t/\hbar}.$$
(8.25)

We now multiply both sides of equation 8.25 by  $\phi_f^*$  and integrate over the internal coordinate r:

$$i\hbar \sum_{k} \left\{ \int \phi_{f}^{*}(r)\phi_{k}(r) dr \right\} \frac{\mathrm{d}a_{k}}{\mathrm{d}t} e^{-iE_{k}t/\hbar}$$
  
$$= \sum_{k} \left\{ \int \phi_{f}^{*}(r)V(t)\phi_{k}(r) dr \right\} a_{k}(t) e^{-iE_{k}t/\hbar}.$$
(8.26)

Because of the orthogonality of the  $\phi_k$  given in **equation 8.22**, the sum on the lefthand side reduces to the single term for which k = f. On the right-hand side, we now make the approximation that, because the probability for excitation is small and because the initial state of the system was characterized by  $a_i = 1$ , the only coefficient in the sum likely to be important is  $a_i$ ; all the rest will remain close to zero. Thus,

$$i\hbar \frac{\mathrm{d}a_{f}}{\mathrm{d}t}e^{-iE_{f}t/\hbar} = \left\{ \int \phi_{f}^{*}(r)V(t)\phi_{i}(r)\,\mathrm{d}r \right\}e^{-iE_{i}t/\hbar},$$

$$\frac{\mathrm{d}a_{f}}{\mathrm{d}t} = \frac{1}{i\hbar}V_{fi}(t)e^{-i(E_{i}-E)_{f}t/\hbar},$$
(8.27)

where

$$V_{fi}(t) \equiv \int \phi_f^*(r) V(t) \phi_i(r) dr.$$
(8.28)

Letting  $\hbar \omega = E_f - E_i$ , integrating both sides of equation 8.27 from  $t = -\infty$  to  $t = \infty$ , and squaring both sides, we obtain the time-dependent perturbation theory result known as the Born approximation:

$$|a_f(\infty)|^2 = \left|\frac{1}{i\hbar}\int_{-\infty}^{\infty} V_{fi}(t)e^{-i\omega t} dt\right|^2.$$
(8.29)

We will find that this equation is quite important in helping to understand energy transfer.

# Answers and Solutions to Selected Problems

#### Chapter 1

1.1 (a)

1.3 Zero.

1.5 7.

1.7  $x_{\rm mp} = L/2; <x> = L/2.$ 

1.9 The average molecular energy,  $\langle \epsilon \rangle$ , will be given by

$$<\epsilon>=\int_0^\infty\epsilon G(\epsilon)d\epsilon,$$

where

$$G(\epsilon) d\epsilon = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \sqrt{\epsilon} \exp\left(-\frac{\epsilon}{kT}\right) d\epsilon$$

We can simplify the integral by letting  $a \equiv \sqrt{\epsilon}$ , so that

$$<\epsilon> = 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \int_0^\infty \epsilon \sqrt{\epsilon} \exp\left(-\frac{\epsilon}{kT}\right) d\epsilon$$
$$= 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} \int_0^\infty a^3 \exp\left(-\frac{a^2}{kT}\right) d(a^2)$$
$$= 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} 2 \int_0^\infty a^4 \exp\left(-\frac{a^2}{kT}\right) da$$
$$= 2\pi \left(\frac{1}{\pi kT}\right)^{3/2} 2 \frac{1}{2} \sqrt{\pi} \frac{3}{4} (kT)^{5/2} = \frac{3}{2} kT,$$

where the integral was evaluated using Table 1.1.

- 1.11  $f(\epsilon^*) \approx 10^{-100,000,000,000}$ .
- 1.13  $2.95 \times 10^3$  independent of T.
- 1.15 0.673[kT/m]<sup>1/2</sup>.
- 1.17 \$1/molecule, independent of T.

#### Chapter 2

2.1 (c)

2.3 The reaction is first order.

- 2.5 The Arrhenius form of the rate law is  $k = A \exp(-E_a/kT)$ . A can be evaluated by (a) measurement of the rate at infinite temperature, because as  $T \to \infty$ ,  $-E_a/RT \to 0$  and the exponential  $\to 1$ , or (d) or (e) measurement of the intercept of a plot of  $\ln k$  versus 1/T:  $\ln k = \ln A - (E_a/RT)$ . Thus, the correct answer is (f).
- 2.7 (c)
- 2.9 (b)
- 2.11 The substrate concentration must be small.
- 2.13 (a) and (c) are both true, so the correct answer is (d).
- 2.22  $B = E_0 = 1.13 \times 10^{-5} M; A = 1.27 \times 10^{-9} M/s; b = 1.05 \times 10^{-2} s^{-1}; k_3 = 1.12 \times 10^{-4} s^{-1}. k_2 = 0.304 s^{-1}.$
- 2.26  $E_a = 48.1$  kJ/mol.
- 2.27  $E_a = 112.21$  kJ/mol.
- 2.28  $k = 5.04 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ . The activation energy is 1250 times R, or (1250)(8.314 J mol<sup>-1</sup> K<sup>-1</sup>) = 10.4 kJ mole<sup>-1</sup>, while the preexponential factor is  $A = 5.41 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ .
- 2.32  $k_v = 0.014 \ \mu \text{s}^{-1} \text{ torr}^{-1} = 1.4 \times 10^4 \text{ s}^{-1} \text{ torr}^{-1}; k_1 = 714 \text{ s}^{-1} \text{ torr}^{-1}; k_2 = 61 \text{ s}^{-1} \text{ torr}^{-1}.$
- 2.34 The rate constant is  $0.46 \times 10^{-3} \text{ s}^{-1}$ .

#### Chapter 3

- 3.1 Nine coordinates.
- 3.3 (d)
- 3.5 The activated complex for elimination of HBr would be more "ordered" than that for elimination of Br, so the elimination of HBr has a more negative entropy of activation and thus a smaller rate constant.
- 3.6 (b) is true.
- 3.10 (b) 8.8%; 4.6%; 25%.

- 3.11 (a)  $A = 1.28 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ . (b)  $p = 7.82 \times 10^{-4}$ .
- 3.13 (a)  $k = 2.4 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1} \exp(-2.67) = 1.7 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ . The preexponential factor from collision theory,  $2.4 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ , agrees well with the experimentally observed result,  $2 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ . (b)  $A = 0.67 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ , as compared to the experimental value of  $2 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ .
- 3.14 (a)  $A(T) \propto T^{3/2}$ . (b)  $A(T) \propto T^2$ . (c)  $A(T) \propto T^3$ .
- 3.16 (b) The values of  $k_{\rm H}/k_{\rm D}$  calculated for the given vibrational frequencies are CH, 7.78; OH, 10.3; NH, 8.96; SiH, 6.29.

#### Chapter 4

- 4.1 The viscosity coefficient, like the thermal conductivity coefficient, is independent of the molecular density because the mean free path depends inversely on density, whereas the amount of the quantity carried (momentum in this case and energy in the case of thermal conductivity) depends linearly on density. Thus, the density cancels in the final expression, provided, of course, that the density is high enough so that the mean free path is small compared to the macroscopic dimensions of the system.
- 4.3 The correct answers are (b), (d), and (e).
- 4.5 The coefficient  $\kappa$  is proportional to the average molecular speed, and helium is faster than argon because it is lighter. Although N<sub>2</sub> is lighter than argon, it has rotational degrees of freedom, so that its heat capacity is larger. Recall that  $\kappa$  is proportional to  $C_v$ .
- 4.7 (b) increases; (c) decreases.
- 4.9 The correct answer is (d).
- 4.11 800 W.
- 4.13 (a)  $5.56 \times 10^{-2}$  W m<sup>-1</sup> K<sup>-1</sup>. (b)  $J_z A = (44.4$  W m<sup>-2</sup>) (1 m<sup>2</sup>) = 44.4 W. (c)  $6.34 \times 10^{-3}$  torr.
- 4.15 0.635 J.

#### Chapter 5

- 5.1 Independent of size.
- 5.3 The differential equation for the system is

....

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k_f[\mathrm{A}][\mathrm{B}] - k_r[\mathrm{C}].$$

Let x = x(t) be  $A(t) - A_e$ , or equivalently  $B(t) - B_e$  or  $C_e - C(t)$ . Then

$$-\frac{\mathrm{d}x}{\mathrm{d}t} = k_f (x + \mathrm{A}_e)(x + \mathrm{B}_e) - k_r (\mathrm{C}_e - x)$$
$$= k_f \mathrm{A}_e \mathrm{B}_e - k_r \mathrm{C}_e + k_f x (\mathrm{A}_e + \mathrm{B}_e) + k_r x + k_f x^2$$

In the last equation, the first line is zero by the definition of the equilibrium and the last line can be neglected if we assume that the perturbation is small. The resulting equation is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -[k_f(\mathrm{A}_{\mathrm{e}} + \mathrm{B}_{\mathrm{e}}) + k_r]x,$$
$$= x(0)\exp\{-[k_f(\mathrm{A}_{\mathrm{e}} + \mathrm{B}_{\mathrm{e}}) + k_r]t\}.$$

Substitution of this equation into  $A(t) = A_e + x$  gives the desired result.

5.5 
$$k = 9.08 \times 10^9 \,\mathrm{L \ mol^{-1} \ s^{-1}}$$
.

х

#### Chapter 6

- 6.1 (a) increases monotonically.
- 6.3 Only (b) or (d) could possibly be correct. Usually the barrier to diffusion is about 25% of that for desorption, so (d) is most nearly the correct answer.
- 6.5 Answer (c) is correct.
- 6.7 This is a case where one of the products of the reaction occupies sites needed by the reactant. In the presence of both NH<sub>3</sub> and H<sub>2</sub> in the gas phase and at temperatures where both adsorb to any appreciable extent, the surface coverage of NH<sub>3</sub> is given by **equation 6.5**, where "A" here refers to ammonia and "B" to hydrogen. In the limit when  $K_{\rm B}[{\rm B}] >> K_{\rm A}[{\rm A}] >> 1$ , the equation gives the surface coverage of ammonia as  $\theta_{\rm A} \approx K_{\rm A}[{\rm A}]/K_{\rm B}[{\rm B}]$ . The rate for the unimolecular reaction is simply  $k\theta_{\rm A}$ , which is first order in ammonia pressure but inversely proportional to hydrogen pressure.
- 6.9 The activation energy is assumed to be zero and we have already noted in the text that the partition function for the unoccupied site,  $q_s$ , can be taken as unity. Thus the rate constant is given simply by  $k = (kT/h) q^{\sharp'}/q_g$ . For atomic adsorption,  $q_g$  contains only translational motion:  $q_g = (2\pi mkT/h^2)^{3/2}$ . For the activated complex, by assumption there are (in addition to the vibrational coordinate perpendicular to the surface—that is, the reaction coordinate) two degrees of translational motion. Thus  $q^{\sharp'} = (2\pi mkT/h^2)^{2/2}$ . The rate constant is thus

$$k = \frac{kT}{h} \frac{1}{(2\pi m kT/h^2)^{1/2}}$$
$$= \frac{(kT)^{1/2}}{(2\pi m)^{1/2}}$$

$$= \frac{(1/4)(16kT)^{1/2}}{(2\pi m)^{1/2}} = \frac{1}{4}\sqrt{\frac{8kT}{\pi m}}$$
$$= \frac{1}{4} < v >.$$

Since this equation gives the rate constant for adsorption, the rate of adsorption is simply  $\frac{1}{4} < v >$  times the concentration of the gaseous reactants,  $n^*$ ; or rate  $= \frac{1}{4}n^* < v >$ . This is also the rate at which atoms hit the surface, as we have seen in Sections 6.1 and 4.3.2.

6.10 D = 
$$4.0 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$$
.

#### Chapter 7

- 7.1 (a), (c), (d), and possibly (e) are correct.
- 7.3 The basic assumption is that the electrons move much more rapidly than the nuclei, so that the molecule can change its electronic configuration on a time scale short compared to any changes in nuclear arrangement. Note that the assumption here is the same as that used in the Born-Oppenheimer approximation.
- 7.5 All of these processes depend on the density of states.
- 7.7 The differential equations for the three species are

$$\begin{aligned} \frac{\mathrm{d}n_1}{\mathrm{d}t} &= 2j_{\mathrm{a}}n_2 - k_{\mathrm{b}}n_1n_2n_{\mathrm{M}} + j_{\mathrm{c}}n_3 - k_{\mathrm{d}}n_1n_3,\\ \frac{\mathrm{d}n_2}{\mathrm{d}t} &= -j_{\mathrm{a}}n_2 - k_{\mathrm{b}}n_1n_2n_{\mathrm{M}} + j_{\mathrm{c}}n_3 + 2k_{\mathrm{d}}n_1n_3,\\ \frac{\mathrm{d}n_3}{\mathrm{d}t} &= k_{\mathrm{b}}n_1n_2n_{\mathrm{M}} - j_{\mathrm{c}}n_3 - k_{\mathrm{d}}n_1n_3. \end{aligned}$$

Summing the first and third of these equations and applying the steady-state principle we obtain

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} + \frac{\mathrm{d}n_3}{\mathrm{d}t} = 2j_\mathrm{a}n_2 - 2k_\mathrm{d}n_1n_3 \approx 0$$

Neglecting all but the second and third terms in the differential equation for  $n_1$  and application of the steady-state equation to this intermediate yields

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} \approx 0 \approx -k_\mathrm{b}n_1n_2n_\mathrm{M} + j_\mathrm{c}n_3$$
$$n_1 = \frac{j_\mathrm{c}n_3}{k_\mathrm{b}n_2n_\mathrm{M}}.$$

Substitution of this last equation into the equation for  $dn_1/dt + dn_2/dt$  gives

$$j_{a}n_{2} - k_{d}n_{1}n_{3} \approx 0,$$
$$j_{a}n_{2} - k_{d}\frac{j_{c}n_{3}}{k_{b}n_{2}n_{M}}n_{3} \approx 0,$$

$$n_3 = n_2 \sqrt{\frac{j_{\rm a} k_{\rm b} n_{\rm M}}{j_{\rm c} k_{\rm d}}}.$$

- 7.10  $\mathbf{v}_{0_2} = (2714) \times [\sin(141.5)]/\sin(30) = 3379$  m/s, for an arrival time of 101  $\mu$ s. The difference in arrival times is 90  $\mu$ s.
- 7.11 (a) Estimating the spacing between the peaks in the upper plot in **Figure 7.35** gives about 1300 fs;  $\nu = 1/t =$  $1/(1300 \times 10^{-15} \text{ s}) = 7.7 \times 10^{11} \text{ Hz}$ . (b) To find a rate, assume an exponential rise and estimate the time,  $\tau$ , at which a concentration of (maximum conc)  $\times [1 - (1/e)]$  is reached. Take the inverse of this time to get the rate constant, k = $1/\tau$ . The rise time is about 580 fs, so  $k = 1/(580 \times 10^{-15} \text{ s}) = 1.7 \times 10^{12} \text{ s}^{-1}$ .
- 7.13 One method is to solve equation 7.5 for  $1/\rho(\nu)$ , substitute in the blackbody result for  $\rho(\nu)$ , and equate terms with the same temperature dependence. Let  $BF \equiv (g_2/g_1) \times \exp(-h\nu/kT)$ . Then

$$B_{12}\rho(\nu) = B_{21}\rho(\nu)BF + A_{21}BF,$$
  

$$\rho(\nu) = \frac{A_{21}BF}{(B_{12} - B_{21}BF)},$$
  

$$\frac{1}{\rho(\nu)} = \frac{B_{12}}{A_{21}BF} - \frac{B_{21}}{A_{21}},$$
  

$$\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]\frac{c^3}{8\pi h^3} = \frac{B_{12}}{A_{21}BF} - \frac{B_{21}}{A_{21}}.$$

The first term on the left-hand side and the first term on the right-hand side of the last equation depend on temperature, while the second terms do not. Equating the temperature independent terms we obtain the second equation of **equation 7.6.** Equating the temperature dependent terms we find that

$$B_{12} = A_{21} \frac{g_2}{g_1} \exp\left(-\frac{h\nu}{kT}\right) \exp\left(\frac{h\nu}{kT}\right) \frac{c^3}{8\pi h\nu^3}$$
$$= \frac{g_2}{g_1} B_{21},$$

where in obtaining the last line we have used the second equation of **equation 7.6** obtained above.

7.15 Let the two fragments have center-of-mass recoil velocities of  $u_1$  and  $u_2$  and internal energies of  $\epsilon_1$  and  $\epsilon_2$ . Let the energy of the photon be  $E = h\nu$  and the bond dissociation energy be  $D_0^0$ . Then the total energy available to the photofragments following dissociation is  $\epsilon = h\nu - D_0^0$  and is known. By conservation of energy,  $\epsilon = \epsilon_1 + \epsilon_2 + \frac{1}{2}\mu u_r^2$ , where  $u_r$  is the relative velocity of recoil and is related to  $u_1$ and  $u_2$  by the equation  $\frac{1}{2}\mu u_r^2 = \frac{1}{2}m_1u_1^2 + \frac{1}{2}m_2u_2^2$ . Putting these equations together gives  $h\nu - D_0^0 = \epsilon_1 + \epsilon_2 + \frac{1}{2}m_1u_1^2 + \frac{1}{2}m_2u_2^2$ .  $\frac{1}{2}m_2u_2^2$ . By conservation of linear momentum,  $m_1u_1 = m_2u_2$ , so that  $u_2 = (m_1/m_2)u_1$ . Substitution yields  $h\nu - D_0^0 = \epsilon_1 + \epsilon_2 + \frac{1}{2}m_1u_1^2 + \frac{1}{2}m_2(m_1/m_2)^2u_1^2$ . Solving for  $\epsilon_2$ , we find that  $\epsilon_2 = h\nu - D_0^0 - \epsilon_1 - \frac{1}{2}m_1u_1^2 - \frac{1}{2}m_2(m_1/m_2)^2u_1^2 = h\nu - D_0^0 - \epsilon_1 - \frac{1}{2}m_1[1 + (m_1/m_2)]u_1^2$ . Thus, if all the quantities on the right-hand side of this equation are known,  $\epsilon_2$  can be calculated.

7.20 The square root dependence on light concentration suggests that there is an initiation step in which light dissociated  $Br_2$  into

$$Br_2 + h\nu \rightarrow 2 Br.$$

It is then likely that some sort of chain reaction takes place:

$$Br + CH_4 \rightarrow HBr + CH_3$$
,

$$CH_3 + Br_2 \rightarrow CH_3Br + Br$$
,

with a likely termination step as

 $Br + Br(+M) \rightarrow Br_2(+M).$ 

Note that this is the same mechanism as the  $Br_2/H_2$  reaction, except for the initiation step, so that we would expect the same result: linear dependence on the  $CH_4$  concentration and square root dependence on the initiation step; that is, the rate should be proportional to the square root of light intensity and the square root of  $Br_2$  concentration.

#### Chapter 8

- 8.1 The answers (a) and (d) are correct.
- 8.3 The correct answer is (b).
- 8.5 The answers (a) and (d) are correct.
- 8.9 The cross section will be proportional to the total probability given in **equation 8.47:**  $P = 2 P_{12}(1 - P_{12})$ , where  $P_{12}$ is given in **equation 8.46.** Note that as  $P_{12}$  approaches either zero or unity, the total probability *P* will approach zero. This is because there are two possibilities for crossings, one on the way in and one on the way out. For the process to occur, one and only one surface hop must occur. Thus, *P* will be a maximum when  $P_{12} = 0.5$ . Because  $P_{12}$  increases as the velocity increases, *P* will at first increase as  $P_{12}$ increases, but will then decrease as  $P_{12}$  becomes greater than 0.5. A more quantitative treatment is discussed by A. P. M. Baede, *Adv. Chem. Phys.* **30**, (1975), see in particular section IA3 and Figure 5.
- 8.11 Substituting equation 8.11 into the left-hand side of the first equation of equation 8.10, we find that

$$\frac{1}{2}m_3\left(\frac{m_4}{M}\mathbf{v}_{\rm r}'\right)^2 + \frac{1}{2}m_4\left(\frac{m_3}{M}\mathbf{v}_{\rm r}'\right)^2$$

$$= \frac{1}{2} \frac{m_4}{M} \left( \frac{m_3 m_4}{M} \mathbf{v}_r'^2 \right) + \frac{1}{2} \frac{m_3}{M} \left( \frac{m_3 m_4}{M} \mathbf{v}_r'^2 \right)$$
$$= \frac{1}{2} \left( \frac{m_3 m_4}{M} \mathbf{v}_r'^2 \right)$$
$$= \frac{1}{2} \mu' \mathbf{v}_r'^2.$$

Thus, equation 8.10 is satisfied. Equation 8.11 also satisfies equation 8.9:

$$m_3 \mathbf{u}_3 + m_4 \mathbf{u}_4 = -m_3 \frac{m_4}{M} \mathbf{v}'_r + m_4 \frac{m_3}{M} \mathbf{v}'_r = 0$$

8.13 (a) From what we are given, the distance from the center of mass to the peak marked 1 is 3000/2 = 1500 m/s. By measuring with a ruler, we find that the distance between peaks 0 is 1.3 times the distance between peaks 1, so the distance from the center of mass to peak 0 is (1.35)(1500 m/s) = 2025 m/s. These then are radii of the Newton spheres that we are asked to show belong to OH(v = 1)and OH(v = 0). We need to show that these velocities make sense given the energetics of the reaction. If the collision energy is 45 kJ mol<sup>-1</sup> and the exothermicity is 46 kJ  $mol^{-1}$ , then there are 91 kJ  $mol^{-1}$  available to the OH and  $F^-$  products. For OH(v = 0, J = 0), all of this energy would be in translation, so the relative velocity of the products, *u*, would be given by  $\frac{1}{2}\mu' u^2 = 91$  kJ/mole. With  $\mu' =$ (17)(19)/(17 + 19) = 8.97 g/mole, we find that the relative velocity is u = [(2 \* 91 kJ/mole)(1000 g/kg)/(8.97)g/mole)]<sup>1/2</sup> = 4504 m s<sup>-1</sup>. The diagram shows the F<sup>-</sup> products, and this velocity is 17/(17 + 19) of u, or 2126 m s<sup>-1</sup>, somewhat larger than the 2025 m/s calculated for the v =0 peak above. On the other hand, there may be some rotational excitation of the OH, and this would reduce the size of the product sphere. Note that a measurement (with a ruler) of total width of the diagram shows that all the scattering is within a sphere corresponding to  $4416 \text{ m s}^{-1}$ , in rough agreement with the total calculated value of 4054 m  $s^{-1}$ . For OH(v = 1), there is less energy available by 43 kJ  $mol^{-1}$ , so that the total available is  $91 - 43 = 48 \text{ kJ mol}^{-1}$ . The relative velocity is calculated as u = (2 \* 48)kJ/mole)(1000 g/kg)/(8.97 g/mole)]<sup>1/2</sup> = 3271. The F<sup>-</sup> velocity would then be 1545. Since this is again a bit larger than the measured value of 1500, there is probably some rotational excitation for the v = 1 products. In general, however, the assignment seems realistic. (b) Note that the reaction is peaked in both the forward and backward directions, suggesting that a long-lived complex is likely formed.

## INDEX

### **Index Terms**

<u>Links</u>

Page numbers followed by t, f, and n indicate tables, figures, and notes, respectively.

#### A

Ab initio potential energy calcula-				
tion	227			
Absorption, frequency-dependent				
cross-section ( $\sigma(v)$ )for	205	216	245	
Absorption coefficient ( $\alpha$ )	205			
Acetaldehyde, decomposition of				
Arrhenius parameters for	49t			
Rice-Herzfeld mechanism for	74	79		
Acetone, photodissociation of	228	229f	230f	
Acetylene				
bond dissociation energy of	253			
photodissociation of	253			
Acid-base catalysis	63			
Acid rain	221	225		
ACT. See Activated complex theory				
Activated complex (‡)	93	112	113	
Activated complex theory	91	102	109	113
	153	165		
See also Debye-Hückel theory				
calculation of reaction rate of two atoms	107	108		
estimating rate constant orders of				
magnitude with	105			
and RRKM theory	234	238	247	
and simple collision theory,				
connection between	107			
of surface reactions	181	195		
thermodynamic interpretation of	109			
and "width" of reaction channel				
leading over activation barrier	102	106		
Activation energy $(E_a)$	48	49	50t	87
	99	109	112	114

This page has been reformatted by Knovel to provide easier navigation.

Index Terms	Links			
Adatom(s)	172	172f	194	
diffusion of, field ion imaging of	184	184f		
Adiabatic [term]	299n			
Adiabatic collision(s)	292	296	297	
Adiabaticity parameter	294			
Adiabatic potential energy				
curves	298			
Adsorbate(s), number of				
per number of				
sites $(\theta)$	186	186n	195	199
per unit area (Γ)	186	186n		
Adsorption	171	174	194	195
	199			
competitive	177			
equilibrium constant (K) for	195			
heats of	178	178f		
Langmuir model	176	177f	195	198
Alcohol(s), gaseous, dehydrogena-				
tion of, at surfaces	179			
Aligned distribution of vectors	303	303f		
Alignment, of photofragment	243			
Ammonia				
decomposition of, on platinum	179	199		
H/D isotope exchange in	180	181f		
viscosity coefficient for, at 273 K	128t			
Angular distribution(s), of scattered				
molecules, in surface collision	189	190f	191f	196
Anisotropy	242			
Anisotropy parameter ( $\beta$ )	240	247	250	
Anthracene, fluorescence spectrum				
of, at various levels of vibra-				
tional excitation	212	213f		
Argon. See also ArHF system				
molecular diameter of, calcula-				
tion of from viscosity coefficient	129			
scattered from platinum surface				
angular distribution of	190	191f		
thermal conductivity coefficient ( $\kappa$ ) for	142			
	112			

This page has been reformatted by Knovel to provide easier navigation.
Index	Terms

Argon (Cont.)			
at 273 K and 1 atm	124t		
viscosity coefficient for, at 273 K	128t		
Argon plus krypton			
elastic scattering of	273	274f	275f
potential energy function for	275	275f	
Argon plus nitric oxide			
differential cross section for	279	280f	
Newton diagram for	278	279f	
Newton sphere for	281		
Argon plus xenon			
elastic scattering of	274	275f	
potential energy function for	275	275f	
ArHF system			
potential energy surface for	306	307f	
spectrum of, obtained using			
direct absorption of infrared			
light by molecular beam	306	306f	
Arrhenius, Svante August	48n		
Arrhenius law	48	82	
Arrhenius parameters	50		
for first-order reactions	48	49t	
for second-order reactions	48	50t	
Arrhenius preexponential factor (A).			
See Preexponential factor (A)			
Atmospheric chemistry	221	247	
Autocatalysis	70	88	
Average(s), calculation of	5	24	31
from probabilities	6		
speed distribution used in	13		
В			
Backward scattering	270	308	
Beer-Lambert law	205		
for gases	205		
for solutions	205		
Belousov-Zhabotinsky reaction	71		

Index	Terms

Benzene, fluorescence lifetime of				
as function of excitation				
energy	217	217f		
radiative and nonradiative	218			
Bernoulli, Daniel	2			
Bimolecular reactions	51			
activated complex theory of	106			
in solution	144			
surface	180	181f	195	
1, 1'-Binaphthyl				
isomerization of				
pump-probe investigation of	162			
in solvents of varying viscosity	162	162t		
structure of	162	162f		
Binning	284			
Blackbody radiation				
density	206	252		
Boltzmann constant (k)	4	17	36n	97
Boltzmann distribution	206	252	261	
Boltzmann factor $(\exp(-\epsilon^*/kT))$	99	106		
Bond dissociation energy	253			
Bond-selective chemistry, of reactive				
collisions	304	305f		
Born approximation	287	308		
Born-Oppenheimer approximation	207	216	218	246
	282	283	298	
Boyle	2			
Branched chain reaction(s)	74	83	88	
chain branching step in	75			
initiation of	75			
propagation step in	75			
termination of	75			
Branching ratio	55	84	261	
Briggs-Rauscher reaction	71			
Bromine, excited (Br*), plus				
hydrochloride	89			
Brownian motion, equation for	146			

<u>Links</u>

Brownian particle, macroscopic, in		
solution		
Langevin's model for	146	
mean squared displacement of	147	
Butadiene, Diels-Alder condensation of	41	42f
С		

## U

Cage effect	145	146f	147	164
Carbon dioxide				
thermal conductivity coefficient				
$(\kappa)$ for, at 273 K and 1 atm.	124t			
viscosity coefficient for, 142 at 273 K	128t			
Carbon dioxide-carbon dioxide,				
diffusion coefficient (D) for, at 273 K and 1 atm	131t			
Carbon monoxide				
adsorption on polycrystalline				
transition-metal surfaces, heats of	178	178f		
on iron, surface diffusion coefficient of	185			
laser-induced fluorescence spec-				
trum of	228	229f		
scattered from platinum(111)				
surface, angular distributions of	189	190f		
self-diffusion of	142			
Catalysis	82			
See also Auto-catalysis				
acid-base	63			
enzyme	64			
homogeneous	63	82		
surface	179			
Catalyst, definition of	63			
Center-of-mass frame	28	264	264f	266
collisions in	28			
relative velocities for two				
particles in	29	30f		
vector relationships	28	29f		
velocity of one particle in	29			
Center-of-mass to laboratory				
conversion	251	251f		

<u>Links</u>

CF <sub>3</sub> Br, unimolecular dissociation of	255		
$C_2 H_2$ See Acetylene			
C <sub>2</sub> H <sub>5</sub> decomposition, Arrhenius			
parameters for	49t		
$C_2 H_{6}$ . See Ethane			
CH <sub>2</sub> (COOH),. See Malonic acid			
CH <sub>3</sub> . See under Methyl radical			
CH <sub>4</sub> . See Methane			
C <sub>4</sub> H <sub>6</sub> . See Butadiene			
Chain reactions	72	78	84
chain steps of	72		
initiation step of	72		
termination step of	72		
Challenger (space shuttle)	75		
Chaos theory	70		
Chapman mechanism	222	247	249
(COOH)CH&dbCH(COOH). See			
Fumaric acid			
(COOH)CH <sub>2</sub> CH <sub>2</sub> (COOH).See			
Succinic acid			
CH <sub>3</sub> CHO. See Acetaldehyde			
Chemical kinetics			
definition of	xi		
importance of	xi		
instrumental techniques for	xii		
Chemical laser	258		
as weapon	258	259f	
Chemical reaction(s). See Reaction(s)			
Chemiluminescence	258		
Chemisorption	175	195	
activated	175f	176	
potential energy curves for	175	175f	
Chemistry, definition of	xi		
Chlorine monoxide, stratospheric,			
and ozone depletion	224	225f	
Chlorine plus methyl iodide reaction	87		
Chlorine plus ozone reaction	223		
Chlorofluorocarbons	224	247	

Index	Terms

CH <sub>3</sub> NC. See Methyl isocyanide				
CH <sub>3</sub> OH. See Methanol a-Chymotrypsin	85			
Cl. See under Chlorine				
Classical trajectory calculations	283	285f	286f	308
Clausius-Clapeyron equation	178	195		
Co-error function (erfc( <i>x</i> ))	28	28f		
Collinear collisions	292	293f	310	311f
Collision(s)				
adiabatic	292	296	297	
in center-of-mass frame	28			
collinear	292	293f	310	311f
elastic	273			
hard-sphere approximation	290			
Newton diagram for	273	274f		
inelastic	202	278	279f	
Newton spheres for	281			
internal conversion caused by	215			
intersystem crossing caused by	215			
molecular	260			
reactive				
bond-selective chemistry of	304	305f		
cross-section for	95	96f		
energy dependence of	95	96f	98f	
relative energy dependence of	96			
orientation and	302			
surface, angular distributions of				
scattered molecules in	189	190f	191f	
and unimolecular decomposition	61			
vertical distance between	122			
Collision complex	271	272f		
Collision energy( $\epsilon_r$ )	95	111		
Collision rate(s) (Z)	2	19		
between dissimilar species	21	95		
for molecules behaving as hard spheres	19	24	96	
number of possible collision pairs and	20			
relative speed of molecules and	20			
size of molecules and	20			

Index Terms	Links			
Collision theory	01	95	109	113
modified	99	101n	110	115
probability of reaction in	96	97f	110	111
simple	95	110	111	113
and "width" of barrier to reaction	102	110	111	115
Concentration gradient (1)	148			
Concurrent reactions. See Parallel	110			
reactions				
Consecutive reaction(s)	56	82	84	90
Conservation of energy	266		0.	
Conservation of mass	267			
Conservation of momentum	266			
Continuous wave ( <i>cw</i> ) radiation	210			
Contour diagram. See also Potential				
energy surface(s)				
of collinear reaction	92	93f	94f	
Convection, heat transport by	125			
Copper, thermal conductivity coeffi-				
cient ( $\kappa$ ) for, at 273 K and 1 atm	124t			
Coumarin 153, fluorescence spectral				
shift, as function of time follow-				
ing excitation	163	164f		
Crossed molecular beam				
reaction	258			
apparatus for	265	265f		
Cross-section, for reactive collisions	95	96f		
energy dependence of	95	96f	98f	
relative energy dependence of	96			
Cyclobutane, decomposition of,				
Arrhenius parameters for	49t			
Cyclopropane, decomposition of,				
Arrhenius parameters for	49t			
D				
Deactivation probability, of $Ca({}^{1}P_{1})$				
by helium	300	301f		
Debye, Peter	153n			
Debye-Hückel limiting law	154	165		

Debye-Huckel theory153Detlection angle $(\chi)$ 275276277f310See also Stating angle214246Density of vibrational states $(\Lambda_n)$ 214246Deprotomation rates, measured by159160trelaxation techniques159160tDescoption171174194195first-order, rate of186199199gecond-order, rate of186195199Debta'led balance, principle of53101102Differential cross section267266f105for argon plus intric oxide279280f101for f + D <sub>2</sub> reaction312312f101for f + D <sub>2</sub> reaction312312f101for f hithium plus iodine reaction312312f101for down plus intric oxide269102101for f - t HF ceation314314f144for down plus intric oxide108105102for for or - t HF ceation312312f101for fithinup lus iodine reaction312312f101for fithinup lus iodine reaction118104105inwar166117131132inwar166117131132inwar166117131132inwar166117131132inwar166117131132inwar184184f19814	Index Terms	<u>Links</u>			
Debye-Huckel theory153Deflection angle ( $\chi$ )27276f277f3.10See also Scattering angle214246Deprotonation rates, measured byrelaxation techniques1591601Desorption171174194195jirsl-order, rate of186199199second-order, rate of187195199cender-during escience200200199Detailed balance, principle of53197198Differential cross section267268f196for a good plus intric oxide279280f198of or y = Dynamic order312312f198of or y = Dynamic order312312f198of or order plus intric oxide269198198of order order312312f198of order order plus intric oxide269198198of order order order312312f194of order plus intric oxide269198198indicion of velocity312312f194of ordium plus indine reaction312312f194offerential equations196198198infar166117131132infar178194195194infar184194195198infar184194195198infar184194195198infar184194 <th></th> <th></th> <th></th> <th></th> <th></th>					
Deflection angle (y)275276f277f310See also Seattering angleDensity of vibrational states (p.)214246Density of vibrational states (p.)214246Density of vibrational states (p.)214246Density of vibrational states (p.)214246Despinon1591600Despinon171174194195first-order, rate of186199199colspan="2">Descond-order, rate of185186f195199Descond-order, rate of267268f195199Descond-order, rate of267268f196198Descond-order condensation, of butadiene212312f107108107108Second-order volvelity312312f312f106117131132for lot volvelity312312f312f106116117131132Mithele crustoform312312f312f106116117131132Mithele crustoforms316116117131132132Mithele crustoform in for198124195196Differential counters for116117131132for of - + HF reaction312312116117131 <td>Debye-Hückel theory</td> <td>153</td> <td></td> <td></td> <td></td>	Debye-Hückel theory	153			
See also Scattering angle         214         246           Deprotonation rates, measured by         relaxation techniques         159         1600           Desorption         171         174         194         195           first-order, rate of         186         199         199           second-order, rate of         187         194         195           temperature-programmed         183         1867         195         199           Dotated balance, principle of         53         195         2687         195         196           Differential cross section         267         2687         195         196         195         196           for F + D, reaction         270         307         307         312         312f         197         196         195         196         196         196         196         196         196         196         196         196         196         196         196         196         196         197         198         196         196         197         198         196         196         197         198         196         196         196         197         198         196         196         196         196	Deflection angle $(\chi)$	275	276f	277f	310
Density of vibrational states (p_a)       214       246         Deprotution rates, measured by	See also Scattering angle				
Deprotonation rates, measured by         159         160;           relaxation techniques         159         160;           Desorption         171         174         194         195;           first-order, rate of         186         199         199;           comparition         183         186f         195         199;           Detailed balance, principle of         53         100;	Density of vibrational states $(\rho_{\nu})$	214	246		
relaxation techniques         159         160t           Desorption         171         174         194         195           first-order, rate of         186         199         199           second-order, rate of         185         186f         195         199           temperature-programmed         185         186f         195         199           Detailed balance, principle of         53         196         195         199           Differential cross section         267         268f         195         199           for argon plus nitric oxide         279         280f         196         198         196         198         196         198         196         198         196         198         196         198         196         198         196         198         196         198         196         198         196         198         196         198         196         198         196         198	Deprotonation rates, measured by				
Desorption         171         174         194         195           first-order, rate of         186         199         185         186f         195         199           temperature-programmed         185         186f         195         199         195           Detailed balance, principle of         53	relaxation techniques	159	160t		
first-order, rate of       186       199         second-order, rate of       187         temperature-programmed       185       186f       195       199         Detailed balance, principle of       53       53       53         Diels-Alder condensation, of butadiene       41       42f       42f       42f         Differential cross section       267       268f       44       42f         Differential cross section       279       280f       45 </td <td>Desorption</td> <td>171</td> <td>174</td> <td>194</td> <td>195</td>	Desorption	171	174	194	195
second-order, rate of         187           temperature-programmed         185         186 f         195         199           Dotaled balance, principle of         53         53         55           Diels-Alder condensation, of butadiene         41         42r         42r           Differential cross section         267         268r         53           for argon plus nitric oxide         279         280r         53           for F + D <sub>2</sub> reaction         270         307         54           as function of velocity         312         312r         54           for lithium plus iodine reaction         312         312f         54           for O <sup>+</sup> + HF reaction         314         314r         54         54           for of - + HF reaction         312         312f         54         54           for of - + HF reaction         312         312f         54         54           linear         167         171         131         132           utansport equation for         198         195         195         195         195           asfunction of coverage         116         117         131         132         132           utansport equatio for	first-order, rate of	186	199		
temperature-programmed         185         186f         195         199           200	second-order, rate of	187			
200           Detailed balance, principle of         53           Diels-Alder condensation, of butadiene         41         42f           Differential cross section         267         268f           for argon plus nitric oxide         279         280f           for argon plus nitric oxide         279         280f           for f-b_r creation         210         312f           for lithium plus iodine reaction         312         312f           measurement of         269         100           for O <sup>-</sup> + HF reaction         314         314f           for O <sup>-</sup> + HF reaction         312         312f           bilinear         30         312f           inferential equations         30         312           bilinear         116         117         131         132           function of coverage         116         117         131         132           fursport equation for         118         194         195           as function of coverage         118         184f         198           potential energy barrier and         184         198         198           in three dimensions         148         198         198           in th	temperature-programmed	185	186f	195	199
Detailed balance, principle of       53         Diels-Alder condensation, of butadiene       41       42f         Differential cross section       267       268f         for arg on plus nitric oxide       279       280f         for F + D <sub>2</sub> reaction       270       307         as function of velocity       312       312f         for If + D <sub>2</sub> reaction       312       312f         measurement of       269       700°         for O <sup>-</sup> + HF reaction       314       314f         for sodium plus iodine reaction       312       312f         Differential equations       90       90         linear       16       117       131       132         transport equation for       118       14       142f         surface       171       183       194       195         as function of coverage       185       15       15         potential energy barrier and       184       184f       198       15         offusion coefficient (D)       141       198       15       15         surface       171       183       194       195         as function of coverage       184       184f       198       16<		200			
Diels-Alder condensation, of butadiene       41       42f         Differential cross section       267       268f         for argon plus nitric oxide       279       280f         for F + D <sub>2</sub> reaction       270       307         as function of velocity       312       312f         for lithium plus iodine reaction       312       312f         measurement of       269	Detailed balance, principle of	53			
Differential cross section267268ffor argon plus nitric oxide279280ffor F + D2 reaction270307as function of velocity312312ffor lithium plus iodine reaction312312fmeasurement of269	Diels-Alder condensation, of butadiene	41	42f		
for argon plus nitric oxide279280ffor F + D2 reaction270307as function of velocity312312ffor lithium plus iodine reaction312312fmeasurement of269	Differential cross section	267	268f		
for $F + D_2$ reaction270307as function of velocity312312ffor lithium plus iodine reaction312312fmeasurement of269	for argon plus nitric oxide	279	280f		
as function of velocity312312ffor lithium plus iodine reaction312312fmeasurement of269for $O^-$ + HF reaction314314ffor sodium plus iodine reaction312312fDifferential equations9090linear196198Laplace transforms for196197Diffusion116117131132with electrostatic potential167118t195as function of coverage118t194195as function of coverage185184184f198potential energy barrier and184184f198195in three dimensions148144197131132potential of r139139118139139and friction coefficient164118118118118	for $F + D_2$ reaction	270	307		
for lithium plus iodine reaction312312fmeasurement of269for $O^-$ + HF reaction314314ffor sodium plus iodine reaction312312fDifferential equations901linear1961definition of1981Laplace transforms for1961Diffusion116117131with electrostatic potential1671in gases116117131surface171183194surface171183194optential energy barrier and temperature and184184f198Diffusion coefficient (D)141141141equation for139148144in three dimensions148144144in three dimensions148	as function of velocity	312	312f		
measurement of         269           for O <sup>-</sup> + HF reaction         314         314f           for sodium plus iodine reaction         312         312f           Differential equations         90         1           linear         198         1           definition of         198         1           Laplace transforms for         196         1           Diffusion         167         1           with electrostatic potential         167         1           in gases         116         117         131         132           surface         171         183         194         195           as function of coverage         185         1         1         15           potential energy barrier and         184         184f         198         1           in three dimensions         148         1         1         1           potential energy barrier and         184         1         1         1           in three dimensions         148         1         1         1           potential energy barrier and         184         1         1         1           in three dimensions         148         1         1<	for lithium plus iodine reaction	312	312f		
for O <sup>-</sup> + HF reaction       314       314f         for sodium plus iodine reaction       312       312f         Differential equations       90       90         linear       90       90         definition of       198       90         Laplace transforms for       198       90         Diffusion       196       117         with electrostatic potential       167       131         in gases       116       117       131       132         transport equation for       118t       183       194       195         as function of coverage       185       184f       198         potential energy barrier and       184       184f       198         Diffusion coefficient (D)       141       141       141         equation for       139       118       118	measurement of	269			
for sodium plus iodine reaction312312fDifferential equations90linear198definition of198Laplace transforms for196Diffusion167with electrostatic potential167in gases116117131132transport equation for118tsurface171183potential energy barrier and184temperature and184in three dimensions148Diffusion coefficient (D)141equation for139and friction coefficient164	for $O^-$ + HF reaction	314	314f		
Differential equations       90         linear       198         definition of       198         Laplace transforms for       196         Diffusion       196         with electrostatic potential       167         in gases       116       117       131       132         transport equation for       118t       195         surface       171       183       194       195         as function of coverage       185       198       195         potential energy barrier and       184       184f       198         Diffusion coefficient (D)       141       141       141         equation for       139       118       118	for sodium plus iodine reaction	312	312f		
linear       198         definition of       198         Laplace transforms for       196         Diffusion       196         with electrostatic potential       167         in gases       116       117       131       132         transport equation for       118t       194       195         as function of coverage       185       194       195         potential energy barrier and       184       184f       198         Diffusion coefficient (D)       141       141         equation for       139       139         and friction coefficient       164       198	Differential equations	90			
definition of       198         Laplace transforms for       196         Diffusion       196         with electrostatic potential       167         in gases       116       117       131       132         transport equation for       118t       195       195         surface       171       183       194       195         as function of coverage       185       198       198         potential energy barrier and       184       184f       198         temperature and       184       184f       198         Diffusion coefficient (D)       141       141         equation for       139       139         and friction coefficient       164       118	linear				
Laplace transforms for       196         Diffusion       167         with electrostatic potential       167         in gases       116       117       131       132         transport equation for       118t       194       195         surface       171       183       194       195         as function of coverage       185       184       198         potential energy barrier and       184       184f       198         temperature and       184       184f       198         Diffusion coefficient (D)       141       141       141         equation for       139       139       131         and friction coefficient       164       118       118	definition of	198			
Diffusion with electrostatic potential in gases 116 117 131 132 transport equation for 118t surface 171 183 194 195 as function of coverage 185 potential energy barrier and 184 184f 198 Emperature and 184 Diffusion coefficient (D) 141 equation for 139 and friction coefficient 164 in gas 118	Laplace transforms for	196			
with electrostatic potential       167         in gases       116       117       131       132         transport equation for       118t       183       194       195         surface       171       183       194       195         as function of coverage       185       184f       198         potential energy barrier and       184       184f       198         temperature and       184       184f       198         Diffusion coefficient (D)       141       141       141         equation for       139       116       118         in gas       118       118       118       118	Diffusion				
in gases116117131132transport equation for118t118t194195surface171183194195as function of coverage185184f198potential energy barrier and184184f198temperature and184184f198Diffusion coefficient (D)141141equation for139118	with electrostatic potential	167			
transport equation for       118t         surface       171       183       194       195         as function of coverage       185       184       198       198         potential energy barrier and       184       184f       198       198         temperature and       184       184f       198       198         Diffusion coefficient (D)       141       141       141       141         equation for       139       146       141       141         in gas       118       118       118       118	in gases	116	117	131	132
surface171183194195as function of coverage185184f198198potential energy barrier and184184f198198temperature and184148148198198Diffusion coefficient (D)141141199141equation for139164118118	transport equation for	118t			
as function of coverage185potential energy barrier and184184f198temperature and184184198in three dimensions148141141Diffusion coefficient (D)141149141equation for139149141in gas118141141	surface	171	183	194	195
potential energy barrier and184184f198temperature and184184198in three dimensions148148141Diffusion coefficient (D)141141141equation for139149141and friction coefficient164141in gas118148141	as function of coverage	185			
temperature and184in three dimensions148Diffusion coefficient (D)141equation for139and friction coefficient164in gas118	potential energy barrier and	184	184f	198	
in three dimensions148Diffusion coefficient (D)141equation for139and friction coefficient164in gas118	temperature and	184			
Diffusion coefficient (D)141equation for139and friction coefficient164in gas118	in three dimensions	148			
equation for139and friction coefficient164in gas118	Diffusion coefficient (D)	141			
and friction coefficient164in gas118	equation for	139			
in gas 118	and friction coefficient	164			
	in gas	118			

<u>Links</u>

Diffusion coefficient (D) (Cont.)			
for various substances, at 273 K and 1 atm	131t		
for motion in liquid, friction			
coefficient and	147		
for surface reactions	183	195	199
temperature-dependent	184	184f	
Diffusion-controlled rate constant	148	169	
calculation of	152		
for ionic reactants	152	164	
for uncharged (nonionic) reactants	151	164	
Diffusion-controlled reactions	147	149f	164
simple model for	148		
<i>p</i> -Difluorobenzene, emission			
spectrum of	253	253f	
Dihydrogen (H <sub>2</sub> ). See Hydrogen			
Dimethyether, thermal decomposition of	90		
Dinitrogen oxide			
decomposition of, Arrhenius			
parameters for	49t		
photodissociation of	231	232f	
Dinitrogen pentoxide, decomposi-			
tion of			
Arrhenius parameters for	49t		
mechanism for	86		
Dispersion forces	175		
Dissipation	147		
Distribution(s)	5		
of molecular speeds	8		
Distribution function(s)			
definition of	7		
determination of	7		
Doppler profile, of photofragment	241		
Doppler width	208	208f	246
Ε			
Eigen, Manfred	159		
Einstein coefficients	252		
for two-level system			

## <u>Links</u>

Einstein coefficients (Cont.)				
for absorption $(B_{12})$	205	205f	246	
relation to absorption				
cross-section	205	216	245	
relation to transition dipole				
moment	207	246		
for spontaneous emission $(A_{21})$	205	205f	246	
for stimulated emission $(B_{21})$	205	205f	246	
Einstein-Smoluchowski				
equation	138	143		
Elastic collision(s)	273			
hard-sphere approximation	290			
Newton diagram for	273	274f		
Elastic scattering	190	190f	289	
Electrical charge, transport equation for	118			
Electronic energy, calculation of	282			
Electronic energy transfer	297	298f	299f	308
Electronic motion, partition function for	104	104t		
Electronic-to-vibrational energy transfer	89			
Electron transfer reaction(s)	153	155		
energy dependence, as function				
of reaction coordinate for				
electron on donor or acceptor	156	156f		
intramolecular rate constants, as				
function of free energy change	157	158f	165	
rate constant for	157	165		
solvation dynamics of, ultrafast				
laser investigation of	163	163f	164f	
Electrostatic potential, diffusion with	167			
Eley-Rideal mechanism, for bimo-				
lecular reaction	180n	200	200f	
Encounter rate $(k_{enc})$ , in solutions	148	152		
Energy. See also Threshold energy				
$(\epsilon^*)$ ; Zero-point energy				
as function of reaction coordinate for				
endothermic reaction	94	95f		
transport	117	119		
See also Thermal conductivity				

Energy (molecular)				
average of $(\epsilon)$	24	31		
calculation of	4			
temperature and	4			
Energy distribution(s)	17			
Energy transfer	89			
See also Molecular energy transfer				
between different degrees of freedom	289	289t	308	
electronic	297	298f	299f	308
rotational	296	296f	308	310
translational	289	290f	308	310
vibrational	292	293f	308	310
Entropy of activation	109			
Enzyme(s)				
inhibition of	68			
competitive	68	69f	82	84
	85			
noncompetitive	68	69f	82	84
	85			
turnover number of	66			
Enzyme catalysis	64			
Enzyme reaction(s)	64			
rate of	65	84	85	
Equilibrium	52	82	84	
Equilibrium constant				
for ratio of activated complexes to				
reactants	106	111		
between reactants and activated				
complexes, in activated com-				
plex theory	103	110		
Equipartition principle	18			
Error function (erf( <i>x</i> ))	27			
values of, as function of x	28	28f		
Ethane, decomposition of	86			
Arrhenius parameters for	49t			
to ethylene and hydrogen	73			
Ethyl iodide, photodissociation of	255			
Ethyne. See Acetylene				

**Index Terms** 

Index Terms	Links		
Even function(s)	8	8n	
Exchange reaction, path of	92	93f	
Exothermic reactions	258	313	
Explosion(s)	74		
thermal	74		
F			
Faraday, M.	174		
$F + D_2$ reaction	313		
chemical laser based on	258	259f	
differential cross section for	270	307	
energetics of	258	259f	
final vibrational levels	258	259f	259t
potential energy surface for	283		
product contour map for	270	270f	
$F + H_2$ reaction, potential energy			
surface for	282	282f	
Fiberglass insulation, heat flow through	125		
Fick's law			
first	118t	131	132
second	135		
Field emission microscopy	183	184f	
Firefly flashing	87		
First-order reaction(s)	37	38f	81
Arrhenius parameters for	48	49t	
opposing	52		
Flash photolysis. See hmp-probe			
technique			
Flow. See also Flux			
of liquid through tube	117	117f	
Fluid, transport equation for	118t		
Fluorescence	209	246	
See also Laser-induced fluorescence			
Fluorescence decay	214	215f	246
Fluorescence intensity (I)	38	39f	210
definition of	39		
Fluorescence lifetime, as function of			
excitation energy	216	217f	

<u>Index Terms</u>	<u>Links</u>			
Fluorine plus hydrogen reaction	113	113t		
Arrhenius parameters for	50t	1150		
Flux	16	16n		
of atoms or molecules to surface	172	194		
definition of	117			
general flux equation	122			
molecular	116	120	120f	
across a surface	138			
of momentum	128			
units of	128			
of property through a plane	120			
time-dependent	134	134f		
of volume	130			
Formic acid, adsorbed on nickel				
surface at 325 K, temperature-				
programmed desorption of	187	188f		
Forward convolution	277			
Forward scattering	271	308		
Fourier's law	118t	124		
Franck-Condon principle	207	207f	209	217
	228	246	252	
Free radical reactions	72	83		
Frequency of modulation ( $\omega$ )	193	194f	195	
Friction coefficient (ζ), 147	164			
and mean squared displacement	166			
$\beta$ -Fructofuranidase. <i>See</i> Invertase				
Fumaric acid, formation of	68			
G				
Gas(es). See also Ideal gas				
density of, pressure and	131			
kinetic theory of	1			
historical perspective on	2			
integrals of use in	9	10t		
Gas-liquid interface, study of,				
molecular beam techniques for	201	201f		
Gas-solid interface(s). See Solid-gas				
interface(s)				

Index Terms	<u>Links</u>			
General flux equation	122			
Gibbs free energy	109			
Global warming	221	225		
Glory impact parameter $(b_g)$	275			
Glycerol				
collisions of various gases with,				
time-of-flight distributions for	202	203f		
viscosity coefficient for, at 273 K	128t			
Gradient operator $(\nabla)$	148			
Н				
H, H <sub>2</sub> . See Hydrogen				
Half-life, of reactant	38	40		
Hamiltonian	209	212	213	249
	298	299n		
Hard spheres, collision cross section for	290			
Harpoon mechanism	271	300	301	
Hartley band	222	222f		
Heat, transport. See also Thermal				
conductivity				
by convection	125			
by radiation	125			
Heat flow	4			
through fiberglass insulation	125			
Helium				
most probable speed of, and most				
probable speed of oxygen,				
comparison of	14			
thermal conductivity coefficient				
$(\kappa)$ for	142			
at 273 K and 1 atm	124t			
viscosity coefficient for,				
at 273 K	128t			
Herschbach, D. R.	263n			
Herzfeld, K. F.	73			
Higher-order reactions	47			
HNO <sub>3</sub> . See Nitric acid				
H <sub>2</sub> O. See Water				

Index Terms	Links		
Hönl-London factor	229	252	
l'Hônital's rule	85	232	
Hydrogen	05		
desorbed from polycrystalline			
iron angular distribution of	100	101f	
thermal conductivity coefficient	190	1911	
(r) for at 273 K and 1 atm	124+		
(k) 101, at 275 K and 1 atm	124t		
Hudrogen atom exchange reaction	02	100	
Hydrogen hydrogen, diffusion coef	52	100	
figure (D) for at 273 K and 1 atm	121+		
Hudrogen ovugen flame	76		
Hydrogen perovide plus jodide reaction	160		
Hydrogen plus bromine reaction	36	78	86
chain mechanism of	50	78	80
Hydrogen plus carbon dioxide	12		
reaction Arrhenius parameters for	50t		
Hydrogen plus dipitrogen monoxide	501		
reaction Arthenius parameters for	50t		
Hydrogen plus fluorine reaction	113		
Hydrogen plus methane reaction	115		
Arrhenius parameters for	50t		
Hydrogen plus nitric oxide reaction	500		
Arthenius parameters for	50t		
Hydrogen plus oxygen reaction	000		
Arthenius parameters for	50t		
Arrhenius plat of	48	49f	
as branched chain reaction	75	76f	
Hydrogen plus ozone reaction		, 01	
Arrhenius parameters for	50t		
Hydrogen plus water reaction			
Arrhenius parameters for	50t		
Hydrogen sulfide, decomposition of.			
Arrhenius parameters for	49t		
Hydroxyl plus carbon monoxide reaction	51		
Hydroxyl plus hydrogen reaction	114		
Arrhenius parameters for	50t		

Hydroxyl plus methane reaction,				
Arrhenius parameters for	50t			
Hydroxyl plus oxygen reaction,				
Arrhenius parameters for	50t			
Hydroxyl plus ozone reaction	223			
I				
Ideal gas				
monoatomic, thermodynamics of	17			
pressure of	2			
Ideal gas law	1	34	5	24
average square of velocity < <i>v</i> >				
and	8	9		
Impact parameter	20	20f		
and deflection angle	276	276f	277f	310
scattering angle and	277	278f		
Impact parameter(s)	275	276f		
glory	275			
rainbow ( <i>b</i> <sub>r</sub> )	275	310		
Induction period, of consecutive				
reactions	58			
Inelastic collisions	202	278	279f	
Newton spheres for	281			
Inhibition, enzyme				
competitive	68	69f	82	84
	85			
noncompetitive	68	69f	82	84
	85			
Integrals, of use in kinetic theory of gases	9	10t		
Integral transforms	196			
Interference	276			
Internal conversion	215	216f	247	249
induced by collisions	215	247		
intramolecular	216	247		
Intersystem crossing	215	216f	247	249
induced by collisions	215	247		
intramolecular	216	247		

**Index Terms** 

Index Terms	Links			
Intramolecular vibrational energy				
redistribution	211	213f	214f	215f
	246	249		
Invertase, reaction catalyzed by	64			
Iodine				
electronically excited				
deactivation by collision with NO	55			
radiative decay of	38	39f	51	55
as pseudo-first-order				
reaction	45			
fluorescence of, quenching of	210	211f	252	
fluorescence spectrum of	210	211f		
Iodine plus oxygen chloride				
reaction	90			
Ionic strength, of solutions				
increasing, change in activation				
energy with	155	165		
and reaction rates	153	165		
for ions of varying charges	154	154f	165	169
Iron, thermal conductivity coefficient				
( $\kappa$ ) for, at 273 K and 1 atm	124t			
Isothermal compressibility coeffi-				
cient ( $\kappa$ )	124n			
Isotropic distribution of				
vectors	302	303f		
K				
Ketene, photolysis, photofragment				
yield of CH <sub>2</sub>	250	250f		
Kink(s)	172	172f	194	
Knudsen cosine law	190			
Kronecker delta function				
$(\delta_{jk})$	287			
L				
Laboratory to center-of-mass				
conversion	307			

Index Terms	<u>Links</u>			
Tester median edular dia	(7			
Lactase, reaction catalyzed by	67			
Laminar now, or inquid	130	205		
Landau-1 eller equation	294	295		
Landau-Teller model	292	200		
Landau-Zener equation	300	308	165	
Langevin equation	145	164	165	
Langmuir, Irving	176			
I-Langmuir exposure, definition of	174			
Langmuir-Hinshelwood model, for				
bimolecular reaction	180n			
Langmuir isotherm	176			
Langmuir model, for adsorption	176	177f	195	198
Laplace transform(s)	57n	196	197t	
Laser(s)	206	249		
See also Chemical laser; Multiphoton ioniza-				
tion; Ultrafast laser techniques				
excitation using, and control of				
reaction outcome	304	305f	308	
hydrogen fluoride	113			
Laser-induced fluorescence	226	227	228	228f
	229f	247	251	
Lee, Y. T.	263n			
Lennard-Jones	6			
potential	291	292f		
Lifetime, of reactant	38	40		
Lifetime width	208	246		
Light				
absorption of	205	249		
energy density per unit frequency $(\rho(v))$	205	205f	246	
interactions with matter	205	245		
Lindemann, F. A.	61			
Lindemann mechanism	60	77	82	84
	113	233		
high-pressure result for	61			
low-pressure result for	62			
Lineweaver-Burk plot				
for enzyme reaction obeying				
Michaelis-Menten mechanism	66	67f		

## <u>Links</u>

Lineweaver-Burk plot (Cont.)				
for noncompetitive				
inhibition	69			
Liquid				
flow through tube	117	117f		
laminar flow of	130			
Liquid solution(s)				
ionic strength of, and reaction rates	153			
reactions in	144			
of charged species	152			
rate constant determination for				
by relaxation techniques	159	160t		
by temperature jump technique	159	160f		
by ultrafast laser				
techniques	161			
and reactions in gas phase,				
comparison of	144			
Lithium plus iodine				
reaction	312	312f		
Lorentz-broadened line shape	208	208f		
Lotka mechanism	70	90		
Μ				
Mach number	14			
Malonic acid	68			
Marcus, R.	159n			
Marcus inverted region	157	165		
Marcus theory	153	155		
Mass spectrometry, of photofrag-				
ments	241	241f	242f	
Mass-weighted coordinates	313			
Maxwell-Boltzmann distribution	116	265	265f	289
Maxwell-Boltzmann distribution law	119			
Maxwell-Boltzmann energy				
distribution	24			
Maxwell-Boltzmann speed distribution	1	11	14f	24
	31			
experimental verification of	15			

# <u>Links</u>

Maxwell-Boltzmann speed distribution (Cont.)		
as function of temperature	12	12f
measurement of, methods for	15	16f
Maxwell-Boltzmann velocity distri-		
bution, one-dimensional	10	11f
Mean free path $(\lambda)$	2	31
	133	
in liquid	145	
for molecules behaving as hard spheres	23	25
of nitrogen	23	
transport between layers sepa-		
rated by	122	123f
Mean speed	13	14f
Mean squared displacement		
expression for	166	
friction coefficient and	166	
long-time	166	
Mechanism(s). See Reaction mecha-		
nism(s)		
Menten, Maude	65n	
Mesosphere	221f	222
Methane		
thermal conductivity coefficient		
( $\kappa$ ) for, at 273 K and 1 atm	124t	
viscosity coefficient for, at 273 K	128t	
Methanol, decomposition of, Arrhe-		
nius parameters for	49t	
Methemoglobin reductase	69	
Method of initial slopes	37	
Methyl alcohol. See Methanol		
Methyl bromide, formation of	255	
Methyl iodide, photolysis of	239	239f
Methyl iodide plus rubidium		
reaction, steric aspects of	303	304f
Methyl isocyanide, decomposition		
of, Arrhenius parameters for	49t	
Methyl radical plus hydrogen reaction	100	
Arrhenius parameters for	50t	

122

116

<u>Links</u>

Methyl radical plus methyl radical reaction	114			
Methyl radical plus oxygen reaction,				
Arrhenius parameters for	50t			
Michaelis, Leonor	65n			
Michaelis-Menten constant, for				
lactase-catalyzed hydrolysis of				
synthetic substrate	67			
Michaelis-Menten equation	65			
Michaelis-Menten mechanism	65	66n	67n	82
Microscopic reversibility, principle of	52			
Milk, spoilage of	87			
Minimum energy path	94			
Mobility ( $\mu$ )	167			
Modulated molecular beam methods.				
See Molecular beam methods				
Molecular beam methods				
apparatus for	189	189f		
crossed				
alignment of reactants in	302	303f		
orientation of reactants in	302	303f		
for study of gas-liquid interactions	201	201f		
for surface reactions	187	196	200	
in determination of angular				
distribution of scattered species	189	190f	191f	196
in determination of kinetic				
parameters	192	193f	194f	200
Molecular collisions	260			
Molecular diameter				
calculation of, from viscosity coefficients	129			
estimation of	129			
Molecular energy transfer	289			
Molecular flux. See Flux, molecular				
Molecular reaction dynamics	257			
examples of	302			
Molecular scattering	263	307	310	
backward	270	308		
cylindrical symmetry	269	269f		
elastic	289			

Index Terms	Links			
Molecular scattering (Cont.)				
forward	271	308		
inelactic	271	508		
reactive	278			
symmetric	270	272f		
Moleculer trensport	271	2721		
See also Diffusion	11/			
Momentum				
transport	117	110		
See also Viscosity	117	119		
transport equation for	118t			
Monte Carlo method	284			
Montreal protocol	204			
Most probable speed (c*)	13	14	14f	24
Miller F W	184	17	171	24
Multiphoton ionization	226	229	231f	232f
	247		2311	2521
	217			
Ν				
NADH (nicotinamide adenine dinucleotide)	69			
Naphthalene, molecule of, root-				
mean-squared (rms) distance				
traveled by, in a day	136			
Newton diagram	264	266f	268f	307
for argon plus nitric oxide	278	279f		
for elastic collisions	273	274f		
Newton's equations of motion	2			
Newton's law, of viscosity	128			
Newton's laws of motion	283			
Newton spheres, for inelastic collisions	281			
NH <sub>3</sub> . SeeAmmonia				
Nitric acid, decomposition of, Arrhe-				
nius parameters for	49t			
Nitric oxide (NO)				
and ozone, collision rate of	22			
rotational excitation of, by collision with argon	278	279f		
Nitric oxide (NO) plus ozone reaction	113	223		

<u>Links</u>

Nitrogen				
diffusion coefficient (D) for calculation of	133			
at 273 K and 1 atm	131t			
mean free path of	23			
rotational distribution	231	232f		
thermal conductivity coefficient (K) for	142			
at 273 K and 1 atm	124t			
thermal conductivity of	142			
viscosity coefficient for, at 273 K	128t			
Nitrogen dioxide				
photodissociation of, photofrag-				
ment angular distribution for	241	241f		
unimolecular dissociation of	231	233f	234f	237
Nitrogen-nitrogen, diffusion coeffi-				
cient (D) for, at 273 K and 1 atm	131t			
Nitrous oxide. See Dinitrogen oxide				
N <sub>2</sub> O. See Dinitrogen oxide				
N <sub>2</sub> O <sub>5</sub> .See Dinitrogen pentoxide				
Normalization	5			
Normalization constant (K)	7	31		
Norrish, R.G.W.	225	225n	226	
Number density ( <i>n</i> *)	129	132	134	142
0				
O <sub>3</sub> . See Ozone				
Odd function(s)	8			
OH. See under Hydroxyl				
Ohm's law	118	118t		
Olive oil, viscosity coefficient for, at 273 K	128t			
One-dimensional random walk	142			
and molecular diffusion in gas	136	137f	139	
Opposing reactions	52	54f	82	
Order. See Reaction(s), order of				
Orientation, and reactive collisions	302			
Orientation requirement, in collision				
theory	100	110		
Oriented distribution of				
vectors	303	303f		

<u>Links</u>

Oscillating reaction(s)	70	
Oscillator, vibrational excitation of	292	
Oxygen		
diffusing through nitrogen, calcu-		
lation of number of molecules		
crossing an area per second during	132	
dissociation of	222	
most probable speed of, and most		
probable speed of helium, comparison of	14	
thermal conductivity coefficient		
( $\kappa$ ) for, at 273 K and 1 atm	124t	
triplet valence states of, calcu-		
lated potential energy curves for	220	220f
ultraviolet absorption spectrum of	219	219f
viscosity coefficient for	142	
at 273 K	128t	
Oxygen-carbon dioxide, diffusion		
coefficient (D) for, at 273 K and 1 atm	131t	
Oxygen-nitrogen, diffusion coeffi-		
cient (D) for, at 273 K and 1 atm	131t	
Oxygen-oxygen, diffusion coeffi-		
cient (D) for, at 273 K and 1 atm	131t	
Oxygen plus acetylyne reaction,		
Anhenius parameters for	50t	
Oxygen plus bromine reaction, prod-		
uct contour plot for	271	272f
Oxygen plus ethene reaction, Arrhe-		
nius parameters for	50t	
Oxygen plus hydrogen reaction,		
Arrhenius parameters for	50t	
Oxygen plus methane reaction,		
Arrhenius parameters for	50t	
Oxygen plus nitrogen dioxide reac-		
tion, Arrhenius parameters		
for	50t	
Oxygen plus nitrogen reaction	114	
Oxygen plus ozone reaction	223	
Arrhenius parameters for	50t	

Index	Terms

Ozone				
absorption spectrum of	222	222f		
Chapman mechanism for	223	247	249	
chlorine and	221	223	225f	247
decomposition of, Arrhenius parameters for	49t			
dissociation of	222			
time-of-flight distribution of				
O <sub>2</sub> , fragment from	242	242f	243	
formation of	220			
hydroxyl and	223	247		
light absorption by	220			
and nitric oxide (NO), collision rate of	22			
nitrogen oxides and	221	222	223	247
production of	59			
steady-state concentration of	249			
regulation of	223	247		
stratospheric, destruction of	223	247		
determination of, using steady-				
state approximation	59			
Ozone hole	224	247		
Р				
Parallel reactions	54	82	84	90
	260			
Partition function(s)	111	112		
for activated complex	106			
in activated complex theory	103	110		
definition of	103			
electronic	104	104t		
for molecular degrees of freedom	104	104t	105	112
physical interpretation of	103			
rotational	104	104t		
translational	104	104t	112	
vibrational	104	104t	105	
Pascal	128			
Persoz, Jean-Francois	65n			
Phase shift	193	196		
Phosphorescence	209			

<u>Index Terms</u>	Links		
Photochemical smog	221	225	
Photochemistry	204		
on short timescales	244	244f	245f
Photodissociation	218	219f	247
direct	218	219f	247
indirect	218	247	
unimolecular	231	233f	255
Photodissociation dynamics	225	247	
Photofragment			
alignment of, in laboratory frame	243		
rotation vector of, and velocity			
vector, correlation between			
(v-J correlation)	243		
Photofragment angular distributions	239	239f	247
measurement of	241	241f	
Photophysical processes	209	246	
Photopredissociation	255	256f	
Physical chemistry, definition of	xi		
Physisorption	175	195	
potential energy curves for	175	175f	
Poise	128		
Poiseuille formula	130	139	
use of	130		
Poiseuille's law	117	118t	
Polanyi, John	258	258n	263n
Polar vortex	224		
Population inversion	258		
Porter, G.	225	225n	226
Potassium plus iodine reaction, prod-			
uct contour map for	271	271f	
Potential energy curves			
adiabatic	298		
for discussion of harpoon mecha-			
nism	301	301f	
Potential energy function	111		
calculation of	282		
for elastic collisions	275	275f	281
and rate constant	91		

Potential energy function (Cont.)				
for reactive collisions	281			
Potential energy surface(s)	92	93f	94f	95f
	109	281	313	
for ArHF system	306	307f		
for BrHI system	310	311f		
for collinear reaction	92	93f		
for $F + H_2$ , reaction	282	282f		
from spectroscopic information	305	306f	307f	
Predissociation	218	219f	220	
Preexponential factor (A)	48	49t	50t	83
	87	102	109	111
	113	114		
for desorption	185			
temperature dependence of	114			
Pressure, of ideal gas	2			
Pressure gradient	117			
Primary kinetic isotope effect	114			
Primary salt effect	155	170		
Principle of detailed balance	53			
Principle of microscopic reversibility	52			
Product contour diagram	269	270f	271f	272f
Proportionality constant	36	117		
Protonation rates, measured by				
relyation techniques	159	160t		
Pseudo-first-order reaction(s)	44	82		
rate constant for, evaluation of	46			
Pump-probe technique	161	161f	225	247
Q				
Quantum beats	212	215f	246	
Quantum mechanics, definition of	xi			
Quantum yield, for photochemical				
process	209			
Quenching, fluorescence	210	246	252	

**Index Terms** 

# R

Radiation, heat transport by	125		
Radiationless transition	215		
promoting mode for	217	217f	
Rainbow angle	274	276	
Rainbow impact parameter $(b_r)$	275	310	
Random walk, one-dimensional, and			
molecular diffusion in gas	136	137f	139
Rate constant(s) ( $\kappa$ )	36	36n	82
calculation of	109		
collision theory	95	110	
as function of energy	95		
at given temperature $(k(T))$	261		
calculation of, from $\sigma(\varepsilon, i, f)$	262		
for hard-sphere collisions	99		
orders of magnitude, estimation			
of, with activated complex theory	105		
potential energy function and	91		
prediction of, theoretical basis for	109		
for pseudo-first-order reaction,			
evaluation of	46		
second-order, units for	47		
for state-to-state reactions	260		
temperature dependence of	48		
at two temperatures	82		
relationship between	50		
Rate law(s)	35	81	
definition of	35	35f	
determination of mechanisms from	77		
differential			
for first-order reactions	37	81	
for higher-order reactions	47		
for second-order reactions	40	43	81
integrated	81		
for fist-order reactions	37		
for second-order reactions	40		
macroscopic, reaction mechanism and	51		

Index Terms	<u>Links</u>		
Rate-limiting step	88		
and reaction rate	77	79	83
Rate of reaction. <i>See</i> Reaction rate(s)			
Reactant(s)			
half-life of	38	40	
lifetime of	38	40	
Reaction(s)			
bimolecular	51		
branched chain	74	83	
chain	72	78	
chain steps of	72		
initiation step of	72		
termination step of	72		
consecutive	56	82	
diffusion-controlled	147	149f	164
simple model for	148		
exothermic	258	313	
first-order	37	38f	81
Arrhenius parameters for	48	49t	
opposing	52		
free radical	72		
harpoon	271	300	
higher-order	47		
in liquid solutions	144		
opposing	52	54f	82
order of	81	83	
definition of	36		
experimental determination of	37		
oscillating	70		
overall order of, definition of	36		
parallel	54	82	260
pseudo-first-order	44	82	
rate constant for, evaluation of	46		
rebound	270		
second-order	81		
Arrhenius parameters for	48	50t	
first order in each of two			
reactants	40	43	

## <u>Links</u>

Reaction(s) (Cont.)			
with nonstoichiometric start-			
ing conditions, general solution for	43		
opposing	54		
rate constants for, units for	47		
in single reactant	40	41f	
stripping	271		
termolecular	51		
third-order	47	83	
unimolecular	51		
activated complex theory of	104	107	110
reaction rate for, with reactant			
molecules of same energy	107		
surface	179	195	
temperature-dependent rate of	107		
Reaction coordinate	94	95f	
Reaction cross section	260	262	
See also Differential cross section			
Reaction dynamics	257		
definition of	xi		
Reaction intermediate(s)	35	84	
Reaction mechanism(s)	34	51	89
determination of, from rate laws	77		
elementary steps of	34	51	82
order of, molecularity and	52	84	
microscopic processes of	51		
Reaction order. See Reaction(s), order of			
Reaction rate(s)	34	90	106
See also Rate law(s)			
factors affecting	34		
isotopic substitution and	114		
measurement of	35		
prediction of, theoretical basis for	91		
See also Activated complex			
theory; Collision theory			
rate-limiting step and	77	79	83
temperature dependence of	48		
of two atoms, activated complex			

## <u>Links</u>

107	108		
107			
304	305f		
302			
270			
270			
22	31		
96			
32			
20	20n	25	95
29	30f		
159	160t	165	
159	160t		
157	165		
73			
73	83		
74	79		
135			
137	137f	142	143
142			
183			
136			
12	14f		
296	296f	308	310
104	104t		
281			
	107 107 304 302 270 270 22 96 32 20 29 159 159 159 159 159 157 73 73 74 135 137 142 183 136 12 296 104 281	$   \begin{array}{ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

Index Terms	Links			
RRKM theory	212	233	255	304
energy definitions for	234	235f		
RRKMWSU computer program	255			
Rubidium plus methyl iodide reaction	100			
Ruthenium(0001) surface, dissocia-				
tion of nitric oxide on, catalytic sites of	182	183f		
Rutherford scattering experiments	263	263f		
S				
Saddle point, in contour diagram	93			
"width" of barrier over	110			
Salicylate ion	69			
Salt effect, primary	155	170		
Scaling law(s)	297			
exponential energy-gap	297			
statistical power-gap	297			
Scattering, molecular. See Molecular				
scattering				
Scattering angle. See also Deflection				
angle $(\chi)$				
for elastic collisions	290			
and impact parameter	277	278f		
Schrodinger equation	282			
Schumann continuum	219f	220		
Schumann-Runge bands	219f	220		
Second-order reaction(s)	81			
Arrhenius parameters for	48	50t		
first order in each of two reactants	40	43		
with nonstoichiometric starting				
conditions, general solution for	43			
opposing	54			
rate constants for, units for	47			
in single reactant	40	41f		
Self-diffusion	133	142		
Semiclassical trajectory calculations	286	308		
Silver, thermal conductivity of	142			
Skewed coordinates	313			
Sodium iodide, photodissociation of	244	244f	245f	251

Index	Terms

Sodium plus iodine			
reaction	312	312f	
Solid-gas interface(s)), reactions at	171		
processes of	172		
Solid surfaces			
catalytic sites of	182	183f	
flux of atoms or molecules to	172	194	
flux of reactants to	172		
number of molecules striking, at			
1-langmuir exposure, com-			
pared to number of surface sites	172	174	
reactions at	171		
activated complex theory of	181		
bimolecular	180	181f	195
bimolecular elementary step			
in, rate constant for	182		
catalytic	179		
mechanisms for	179		
unimolecular	179	195	
unimolecular elementary step			
in, rate constant for	182		
structure of	172	172f	173f
study of, techniques for	172	185	
Solution(s). See Liquid solution(s)			
Solvation, energy of, for reactants			
versus products	155		
Solvent cage. See Cage effect			
Spectroscopic information, potential			
energy surfaces from	305	306f	307f
Spectroscopy, definition of	xi		
Specular scattering	190	190f	
Speed (molecular)			
average	24		
as function of mass	15	15f	
distribution of	8		
mean	13	14f	
most probable (c*)	13	14f	24
for oxygen and helium, comparison of	14		

<u>Links</u>

Speed (molecular) (Cont.)				
relative, and collision rate	20			
root-mean-squared (rms)	12	14f		
and speed of sound, relationship of	13			
Speed distribution (molecular)	24.			
See also Maxwell-Boltzmann				
speed distribution				
used to determine averages	13			
Speed of sound, and molecular				
speed, relationship of	13			
Spherical coordinates	11f	26	26f	
volume element in	26	27f		
S( <sup>1</sup> D) plus argon				
collision cross sections for	290	291t		
speed distributions for sulfur,				
as function of number				
of collisions with argon	289	290f		
State-to-state rate constants	260	307	310	
State-to-state reaction				
rates	257			
Statistical mechanics	110			
definition of	xi			
Steady-state approximation	56	82	83	84
	86			
and enzyme reactions	63			
for free radical reactions	72			
and Lindemann mechanism	60			
Steady-state hypothesis	77			
Step(s), on surface	172	172f	194	
as catalytic sites	182	183f		
Step-adatoms	172	172f		
Steric factor ( <i>p</i> )	100	109	110	111
	302			
estimation of	100			
formula for, in activated complex theory	107			
Stern-Volmer equation	210	246		
Stirling's approximation	143			
Stoichiometry	36	81	89	

<u>Index Terms</u>	<u>Links</u>			
Stokes-Einstein relationship	169			
Stratosphere	221	221f		
ozone balance in	59			
photochemistry of	221	222		
Stream velocity	265			
Stripping reactions	271			
Succinic acid	68			
Succinic dehydrogenase, inhibition of	68			
Supersonic expansion technique	212n	264	264f	306
velocity distribution for	265	265f		
Surface coverage	186	186n	195	199
Surface reactions. See Solid surfaces, reactions at				
Т				
Taylor series expansion	123	123n	126	
Temperature				
definition of	4			
and energy	4			
probability of vibrational reaction				
as function of	292	293f	294	
Temperature dependence				
of preexponential factors, in gas-				
phase reactions	114			
of rate constant $(k(T))$	33	95	98	
derivation of, from $P(\epsilon_r, b)$	97			
of reaction rate	48			
Temperature jump technique	159	160f		
Temperature-programmeddesorption	185	186f	195	199
Termolecular reactions	51			
Terrace(s)	172	172f	194	
crystallography of	172	173f		
Terrace vacancies	172	172f		
Thermal conductivity	116	117	124	142
quantity (property) carried in	118	119		
transport equation for	118t			
Thermal conductivity coefficient ( $\kappa$ )	118	124n	141	142
equation for	138			
of nitrogen, at 273 K and 1 atm	126			

Index	Terms

Thermal conductivity coefficient ( $\kappa$ ) ( <i>Cont.</i> )				
for various substances at 273K and 1 atm	124t			
Thermal explosion(s)	74			
Thermal rate constant	111			
Thermodynamics				
definition of	xi			
of ideal monoatomic gas	17			
Thermosphere	221f	222		
Third-order reactions	47	83		
Threshold energy $(\epsilon^*)$	94	95f	99	110
in activated complex theory	103	103f		
orientation dependence of	101	102f		
Time-dependent diffusion				
equation	135			
Time-dependent transport	133			
Time-of-flight measure-				
ment	16	17f		
at gas-liquid interface	201	203f		
for photodissociations	241	241f	242	242f
Time-resolved laser absorption	226			
Tolman's theorem	114			
Total reactive cross section	269			
Trajectory calculations				
by classical mechanics	283	285f	286f	308
semiclassical	286	308		
Transfer function $(t(\omega))$	193	193f	200	
Transition dipole moment $(\mu_{12})$	207	246		
Translational energy transfer	289	290f	308	
Translational motion, partition func-				
tion for	104	104t		
Transport equation	117			
for diffusion	118t			
for electrical charge	118t			
for fluid transport	118t			
functional form of	117			
for momentum	118t			
for thermal conductivity	118t			

<u>Index Terms</u>	<u>Links</u>			
Transport law(s)				
microscopic basis for	119	138		
simplifying assumptions for	119	150		
Tranning-desorption collisions	202			
Troposphere	202	221f		
nhotochemistry of	221	2211		
Turnover number, of enzyme	66			
runover number, or enzyme	00			
U				
Ultrafast laser techniques, for mea-				
surement of rapid rate constants	161	161f	163f	164f
	165			
Unimolecular decomposition	61	82	113	
mechanism of	60			
Unimolecular dissociation	231	233f	255	
Unimolecular reactions	51			
activated complex theory of	104	107	110	
reaction rate for, with reactant				
molecules of same energy	107			
surface	179	195		
temperature-dependent rate of	107			
V				
van der Waals, J. D.	305n			
van der Waals clusters, spectroscopy of	305	306f	307f	309
van der Waals complexes	305			
van der Waals forces	175			
Vector correlation, in molecular dynamics	242			
See also Photofragment angular distributions				
Velocity (molecular), squared, aver-				
age of $(\langle v^2 \rangle)$	2	4		
calculation of, 4 and ideal gas law	8	9		
Velocity distribution(s)				
as even function of v	8			
of fluid in cylindrical tube	140	140f		
functional form of	25			
independent	8	9		
## <u>Links</u>

Velocity distribution(s) (Cont.)				
one-dimensional	10	11f		
three-dimensional	10			
depends only on speed	8	11		
uncorrelated	8	9		
Vibrational energy transfer	292	293f	308	
Vibrational frequency	104	112	114	
Vibrational motion, partition func-				
tion for	104	104t	105	
Vibrational relaxation	209	210f		
Vibration-translation energy transfer	292	310		
mass dependence of	295			
Vibration-vibration energy				
transfer	292			
Viscosity	116	117	118t	127
	127f			
Newton's law of	128			
quantity (property) carried in	118	119		
Viscosity coefficient (η)	118	128	141	
calculation of molecular diameter from	129			
equation for	139			
of fluid, measurement of	130			
independence of pressure	128			
for motion in liquid	147			
units of	128			
for various substances, at 273 K	128t			
v-J correlation	243			
Volume flux	130			
W				
Water				
dissociation dynamics of	226	227f		
potential energy curves for, as				
function of R	226	226f		
viscosity coefficient for, at 298 K	128t			
Waterston, John James	2			
Wilhelmy, L.	35			

## **Index Terms**

<u>Links</u>

94

## X

Xenon bromide, fluorescence energy		
spectrum of	254	254f
Xenon-xenon, diffusion coefficient		
( <i>D</i> ) for, at 273 K and 1 atm	131t	
Ζ		

Zero-point energy

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