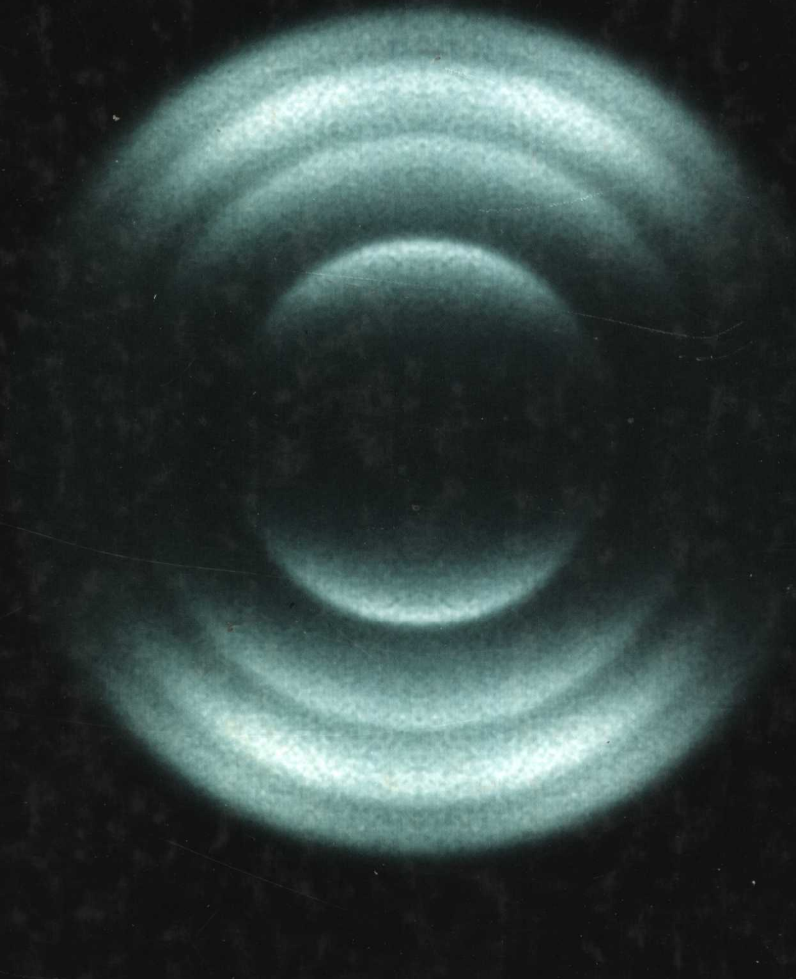
Chemical Kinetics and Reaction Dynamics



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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.

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

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

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

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

TABLE 2 Reactions in Liquid Solutions

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

TABLE 3 An Introduction to Surface Kinetics

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

TABLE 4 Photochemistry and Atmospheric Chemistry

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

TABLE 5 Reaction Dynamics

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

Contents

1

Kinetic Theory of Gases

Chapter Outline

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, $<v^2>$, or equivalently to the average molecular translational energy ϵ. In order for this result to be consistent with the observed ideal gas law, the temperature T of the gas must also be proportional to $<v^2>$ or $<\epsilon>$. 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 $<v^2>$ to determine the Maxwell-Boltzmann distribution of speeds. This distribution, $F(v)\,dv$, tells us the number of molecules with speeds between v and $v + dv$. The speed distribution is closely related to the distribution of molecular energies, $G(\epsilon)\,d\epsilon$. Finally, we will use the velocity distribution to calculate the number of collisions Z that a molecule makes with other molecules in the gas per unit time. Since in later chapters we will argue that a reaction between two molecules requires that they collide, the collision rate Z provides an upper limit to the rate of a reaction. A related quantity λ is the average distance a molecule travels between collisions or the *mean free path.*

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

1.2 PRESSURE OF AN IDEAL GAS

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

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

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

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[a] The history of the kinetic theory of gases is outlined by E. Mendoza, *Physics Today* **14,** 36–39 (1961).

[b] 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.

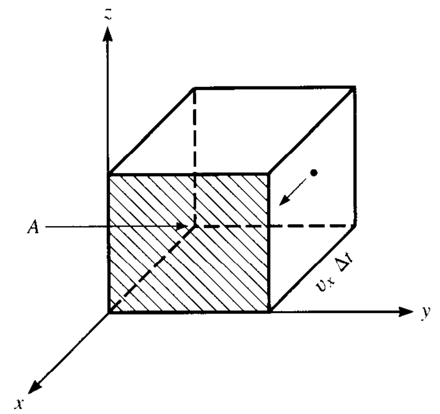

Figure 1.1

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

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

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

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

$$pV = \frac{1}{3}nN_Am\langle v^2\rangle. \tag{1.2}$$

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

$$pV = \frac{2}{3}nN_A\langle\epsilon\rangle. \tag{1.3}$$

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

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

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

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

1.3 TEMPERATURE AND ENERGY

Consider two types of molecule in contact with one another. Let the average energy of the first type be $<\epsilon>_1$ and that of the second type be $<\epsilon>_2$. If $<\epsilon>_1$ is greater than $<\epsilon>_2$, 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 $<\epsilon>_1 = <\epsilon>_2$ will the temperatures of the two macroscopic systems be the same. In mathematical terms, we see that $T_1 = T_2$ when $<\epsilon>_1 = <\epsilon>_2$ and that $T_1 > T_2$ when $<\epsilon>_1 > <\epsilon>_2$. Consequently, there must be a correspondence between $<\epsilon>$ and T so that the latter is some function of the former: $T = T(<\epsilon>)$.

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

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

or

$$<\epsilon> = \frac{3}{2}kT, \tag{1.5}$$

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

$$<v^2> = \frac{3kT}{m}. \tag{1.6}$$

Example 1.1

Calculation of Average Energies and Squared Velocities

Objective Calculate the average molecular energy, $<\epsilon>$, and the average squared velocity, $<v^2>$, for a nitrogen molecule at $T = 300$ K.

Method Use **equations 1.5** and **1.6** with $m = (28 \text{ g/mole})(1 \text{ kg}/1000 \text{ g})/(N_A \text{ molecule/mole})$ and $k = 1.38 \times 10^{-23}$ J/K.

Solution $<\epsilon> = 3kT/2 = 3(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})/2 = 6.21 \times 10^{-21}$ J.

$$<v^2> = \frac{3kT}{m}$$