

Berry / Rice / Ross

PHYSICAL CHEMISTRY

Physical & Chemical Kinetics

Part 3

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PART THREE

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Physical
and
Chemical Kinetics

John Wiley & Sons

New York • Chichester • Brisbane • Toronto

To our families

This book was printed and bound by Halliday. It was set in Times Roman by Universities Press. It was designed by Blaise Zito Associates. The Drawings were designed and executed by John Balbais with the assistance of the Wiley Illustration Department. Deborah Herbert was the copyeditor. Claire Egleiski supervised production.

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Library of Congress Cataloging in Publication Data:

Berry, R Stephen, 1931-
Physical chemistry.

Includes indexes.

CONTENTS: pt. 1. The structure of matter—pt. 2. Matter in equilibrium—pt. 3. Physical and chemical kinetics.

1. Chemistry, Physical and theoretical. I. Rice, Stuart Alan, 1932- joint author. II. Ross, John, 1926- joint author. III. Title.

QD453.2.B48 1980 541 79-29676

ISBN 0-471-05824-6 (V. 1)

ISBN 0-471-05825-4 (V. 2)

ISBN 0-471-05823-8 (V. 3)

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

Preface to Part Three

The textbook, *Physical Chemistry*, is published as a single volume. It consists of three parts:

Part One The Structure of Matter

Part Two Matter in Equilibrium: Statistical Mechanics and Thermodynamics

Part Three Physical and Chemical Kinetics

This book is a reproduction of Part Three. Our purpose, our approach to the subject, and the levels of treatment for all three parts are given below in the preface to the complete volume.

R.S.B.
S.A.R.
J.R.

Preface to PHYSICAL CHEMISTRY

Soul of the world, inspired by thee,
The jarring seeds of matter did agree,
Thou didst the scatter'd atoms bind,
Which, by the laws of true proportion joined
Made up of various parts one perfect harmony
Henry Purcell, *Ode on St. Cecilia's Day*, 1692

We started thinking about this book almost twenty-five years ago. As graduate students we began to realize that undergraduate physical chemistry as it had been presented to us, and physical chemistry as a field of scholarly scientific endeavor, differed greatly in content, emphasis, style, expectation of achievement, and even in the nature of what was considered explanation. We began then to outline an approach that would bring the undergraduate into the subject in a manner consistent with the conceptual structure and the values that characterize physical chemistry as a contemporary discipline. Over the years that followed we talked, planned, and then started to write. There were fruitful periods of gestation, and exciting periods when new research showed that entire sections had to be revised or written from viewpoints altogether different from our original conceptions. Even as we complete this book we see new results appearing in the scientific journals that would have been incorporated in the text had they appeared in time.

Physical chemistry is an empirical science. A science is a set of constructs, called theories, that link fragments of experience into a consistent description of natural phenomena. The adjective "empirical" refers to the common experiences from which the theories grow; that is, to experiments. Simple working hypotheses are guessed by imaginative insight or intuition or luck, usually from a study of experiments. This repetitive interplay in time leads to the formulation of theories that correlate the accumulated experimental information, and that can predict new phenomena with accuracy. As scientists we have, throughout our careers, endeavored to combine both experimental and theoretical work. In this book we try to knit these two inseparable parts of the science into a coherent structure that represents accurately the way they interact in physical chemistry today.

Our goal is the presentation of the three major areas of physical chemistry: molecular structure, the equilibrium properties of systems, and the kinetics of transformations of systems. The theoretical foundations of these subjects are, respectively, quantum mechanics, thermodynamics and equilibrium statistical mechanics, and chemical kinetics and kinetic theory. These theories, firmly based on experimental findings, constitute the structure required for the understanding of past accomplishments and a basis for recognition and development of significant new areas in physical chemistry.

The presentation of the theories of physical chemistry requires careful discussions at several levels of exposition. Our approach aims toward depth of understanding of fundamentals more than toward breadth of recognition of the multitude of activities that go on under the name of physical chemistry. The organization of the book, with its three principal sections, should make this clear. The mathematical level begins with elementary calculus, and rises to the use of simple properties of partial differential equations and the special functions that enter into their solutions. Our intention is to keep the reader's mind on the science rather than on the mathematics, especially at the beginning. This procedure also corresponds to the pattern, followed by many students, of taking physical chemistry and advanced calculus concurrently. Appendices develop the details of the mathematical tools as they are needed.

The text discussion contains more material than can be covered in the traditional one-year physical chemistry sequence; it is designed to fulfill the dual purposes of providing a clear and incisive treatment of fundamental principles at a level accessible to all students while broadening the perspectives and challenging the minds of the best students. Individual instructors will wish to make their own selections of material for inclusion and

exclusion, respectively. We have provided guidance on this matter by having the more advanced sections of the book printed in smaller type on shaded paper. These sections can be omitted without breaking the flow of argument from chapter to chapter. It is also easy to use the material discussed in a different order than in the text, and to omit or downplay classes of topics deemed unsuitable to a particular group of students. For example, we have taught the junior-level physical chemistry course both as organized in this text and with the material of Part Two preceding that of Part One. To invert the order of Parts Two and One, it is only necessary to ask the student to accept the existence of quantized energy levels and a few specific examples of energy level spectra. This has proved quite easy for students who have at least heard of these matters in current freshman chemistry courses. Students with strong backgrounds will have seen the material in the first chapter and parts of the second chapter. Chapter 10, on intermolecular forces, and Chapter 11, on the structure of solids, contain large blocks of material that could be passed over in a traditionally oriented one-year course. The thermodynamic description of matter can be emphasized and the statistical molecular description de-emphasized, or vice versa, by selection of the relevant sections of Chapters 21 to 26. Chapter 20, dealing with hydrodynamic phenomena and negative temperature, can easily be omitted if so wished by the instructor. In Part Three, the elements of physical kinetics (transport theory) are contained in Section 27.1 to 28.8 and 29.1; the elements of chemical kinetics are contained in Chapter 30. The specialized topics in the remaining sections may be used for more extensive treatments of these subjects, either in a three-semester physical chemistry sequence or in a senior-graduate course on these topics.

At the other end of the scale there is sufficient material in this book for a first-year graduate course for students whose undergraduate preparation in physical chemistry did not emphasize modern aspects of the subject.

At the end of each chapter we have suggested extra reading for the interested student. The book contains about 700 problems. A few of these problems are designed to acquaint the reader with dimensions, units, and simple manipulations. More are intended to develop intellectual skills, to enable students to master the material of the text discussions by the difficult process of thinking through the kinds of questions encountered in the laboratory. Some of the problems are designed to extend the theoretical analysis of the text to special but interesting situations.

Part One opens with a review of the elementary quantities of the atomic world and how they are measured. Many readers will find some or all of the material in Chapter 1 familiar; they may choose to read quickly through this chapter and start their more intensive study with Chapter 2, where we develop the experimental evidence for the quantum structure of matter at the molecular level. In the process, we examine the harmonic oscillator, the primitive model for many kinds of behavior examined later, and the concept of action. Chapter 3 is more theoretical and mathematical than its predecessors, but begins at a level the well-prepared student will find quite elementary. Waves and wave equations are introduced and are used to describe only very simple situations: the states of particles in boxes of various sorts, and of rigid rotators.

Chapter 4 brings us back to the more realistic problems of the quantum-mechanical oscillator and the simplest atom, hydrogen. In Chapter 5, we further develop the concepts (such as orbitals and transitions between quantum states) that are introduced for hydrogen in Chapter 4. Chapter 5 treats atoms with more than two electrons, in particular their electronic states and the interactions among the electrons.

Molecules are first introduced in Chapter 6, which is almost analogous to Chapter 4, in that Chapter 6 goes in depth into the description and behavior of the simplest molecules, H_2^+ and H_2 , just as Chapter 4 examined the H atom. The concepts developed in Chapter 6 are then extended to more complex diatomic molecules in Chapter 7. Chapter 6 deals almost exclusively with electronic states; Chapter 7 introduces molecular vibration and rotation, and discusses concepts used to correlate and unify our observations regarding diatomic molecules.

Chapter 8 begins with the primitive triatomic species H_3^+ and H_3 and then goes on to ideas that begin to be important with three or more nuclei: hybrid orbitals and delocalized molecular orbitals at the level of electronic states, and normal modes of vibration. Larger molecules are discussed in Chapter 9; here we introduce the concepts of chirality and optical activity, and explore some aspects of ligand field theory and the magnetic properties of molecules.

Chapter 10 is the first in which we go beyond the properties of individual molecules. The discussion of intermolecular forces describes the interactions between charge distribu-

tions and how one molecule behaves when it collides with another. The material in this chapter is based wholly on the framework of molecular structure, but becomes especially useful to us in Parts Two and Three, where we study the behavior of matter in the aggregate. Part One concludes with another structural aspect of aggregated matter, the structure of solids. Here, we extend the various concepts of bonding previously developed to include the concept of metallic bonding, to describe the structure and states of periodic condensed phases.

Part Two is concerned with the equilibrium properties of bulk matter. Our presentation simultaneously develops the statistical molecular theory and the classical thermodynamic theory in a mutually reinforcing fashion. Despite use of this "mixing" of microscopic and macroscopic points of view, no compromise is made with respect to the rigor and generality of classical thermodynamics, and if desired the two points of view can be separated.

In Chapter 12, we begin with a discussion of the zeroth law of thermodynamics and the concept of temperature. By examining the phenomenological bases for the equation of state and the definition of temperature, together with the elements of the kinetic theory of perfect gases, we establish a first connection between macroscopic and microscopic descriptions. The building of additional generally useful and powerful bridges between the two classes of description is a principal theme of succeeding chapters.

Chapters 13 and 14 treat the first law of thermodynamics and some of its many applications. Particular care is devoted to the precise definition of work and heat, and to how the nature of these quantities exemplifies the differences between the thermodynamic and mechanical descriptions of matter.

Chapter 15 introduces the concept of entropy by way of the microscopic structure of matter. The principle used is that every sample of matter has an energy-level spectrum, the details of which need not be known. It is shown that there exists a function of the energy-level density that behaves like a function of the bulk properties of the system, despite its definition in terms of the microscopic energy-level spectrum.

Chapter 16 develops the second law of thermodynamics via the classical Clausius and Kelvin principles, and Chapter 17 is devoted to examples of the use of the second law to solve problems of chemical interest. These chapters contain a careful discussion of the nature of irreversibility and its interpretation in terms of thermodynamic and statistical molecular theories.

Chapter 18 introduces, discusses, and gives applications of the third law of thermodynamics.

In Chapter 19 we examine the central problem of describing equilibrium as a function of the external constraints on the system. The thermodynamic theory of open systems is developed and is used to derive the several criteria of equilibrium that are suitable to different external constraints. With this background, the notion of ensemble is introduced, and the classical thermodynamics of equilibrium is related to the development of the grand canonical, canonical, and microcanonical partition functions of statistical mechanics. The theory is illustrated by analyzing the velocity distribution in a perfect gas.

Chapter 20 introduces a new point of view into the analysis—it deals with the description of systems whose properties vary slowly in time, and with the fascinating extension of thermodynamics to systems with negative temperature.

Chapters 12 through 19 establish the principles and develop the tools needed to study the bulk properties of matter. This study is carried out systematically in Chapters 21 through 26. Chapter 21 deals with gases, Chapter 22 with solids, Chapter 23 with liquids, Chapter 24 with phase transformations, Chapter 25 with solutions of nonelectrolytes, and Chapter 26 with solutions of electrolytes. In each chapter the thermodynamic theory is developed first, then the statistical molecular theory. Extensive use is made of the details concerning molecular behavior that are provided by computer simulation studies. In addition, the principles developed are illustrated with data from experimental situations wherever that is appropriate.

The simultaneous development of classical and statistical thermodynamics, employed through Part Two, is designed to overcome the difficulties associated with the very abstract nature of purely thermodynamic reasoning, and also to illustrate the richness of the phenomena that can arise from molecular interactions. Nevertheless, for any given problem, the rigor and generality of the thermodynamic approach are made evident, as are the wealth of detail and dependence on assumed models of statistical molecular approach.

Part Three is concerned with time-dependent processes, especially the approach to equilibrium. The topic of physical kinetics (transport processes) is introduced in Chapter 27

with a discussion of the mechanics of molecular collisions, mostly binary collisions. We present as simply as possible the elements of kinematics and dynamics, including the concept of scattering, which is illustrated with the hard-sphere model. In Chapter 28 we consider the kinetic theory of gases, beginning with how velocity distribution functions change with time because of collisions. We present an elementary discussion of the time-dependent transport equations and show how they govern a gas's approach to equilibrium. With these results we can discuss fluxes of mass, momentum, and energy, and study the process of effusion and the simple transport properties (diffusion, viscosity, and thermal conduction) in dilute gases. We conclude with a brief treatment of energy exchange processes, and sound propagation and absorption in gases.

The transport properties of dense phases are taken up in Chapter 29. Transport in liquids is approached with a discussion of Brownian motion, leading to the relation of transport coefficients to autocorrelation functions. A brief discussion of transport in solids concludes the chapter.

Chemical kinetics is treated in a parallel manner to physical kinetics, with an elementary development followed by selected advanced applications. We begin in Chapter 30 with a presentation of the mechanics of reactive collisions, including both kinematics and dynamics. The emphasis is again on the simple hard-sphere model. The collision-theory approach is compared with the activated-complex theory, and both theories are used for an analysis of kinetics in gases and solutions. After a brief survey of experimental methods, we discuss complex reactions and provide an elementary discussion of chemical reaction mechanisms. Chapter 31 is devoted to various advanced topics in chemical kinetics, including the RRKM theory of unimolecular reactions, symmetry rules in chemical reactions, chain reactions, oscillatory reactions, photochemistry, and homogeneous and heterogeneous catalysis.

Our educational and professional associations have obviously influenced the way we wrote this book, as have a few remarkable volumes. In particular, the books by H. Reiss (*Methods of Thermodynamics*, Blaisdell, N.Y., 1965) and F. Reif (*Statistical Physics*, McGraw Hill, N.Y., 1965) helped to clarify our independently developed presentations. Dr. G. P. Flynn (M.I.T.) and Professor J. N. Kushick (Amherst College) painstakingly read, corrected, and made innumerable improvements to the methods and details of presentation. John Hansen and Donald Jordan assisted Professor Kushick in working and checking many of the problems following the chapters. We are grateful to Professor E. Heller (U.C.L.A.), to Professor R. Jarnigan (University of North Carolina), Professor Rodney J. Sime (California State University, Sacramento), and to many students who used this text during its development, for helpful comments.

To the readers, we say that we hope that you will have as much delight in using and creating physical chemistry as we have.

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John Ross

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PART THREE

Physical and Chemical Kinetics

In the first part of this book we studied the structure of atoms and molecules. We investigated the electronic structure of such systems and found it necessary to use quantum mechanics. Solutions of the Schrödinger equation gave us the maximum allowable amount of information about the mechanical system, usually consisting of a small number of particles. For the most part we were interested in stationary solutions of the Schrödinger equation, which can yield information about energies, force constants, bond strengths, molecular geometry, and other time-independent properties. However, we were also concerned with time-dependent behavior of mechanical systems, and here we sought solutions for transition probabilities of a given system from one stationary state to another.

In the second part, on statistical thermodynamics, we studied aggregates of atoms and molecules for the purpose of finding the equilibrium properties of macroscopic systems. In order to do so we needed some information on the mechanical behavior of the system, such as the energy spectrum of the harmonic oscillator, for instance, or in general the density of energy states. For some of the discussion we found classical mechanics sufficient, in which case we could replace summations over energy states by integrations over phase space. Although we found it necessary to define reversible and irreversible processes, we carefully calculated thermodynamic changes along reversible paths only.

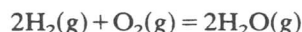
In this third part of the book, we turn to the evolution in time of processes in aggregates of molecules. This subject is called *kinetics*.

Let us discuss a few examples of such processes. Consider water in a container open to the atmosphere at room temperature. We know that in time the water will evaporate, and we know how to calculate the changes in thermodynamic state functions for the evaporation. Such changes depend only on the initial and final states of the process, and not on the particular path or the time required to complete the process. But often we also want to know such things as how quickly the evaporation occurs, that is, what the *rate* of the process is. On what variables does this rate depend? It is easy to guess that the rate of evaporation depends on the temperature of the water; does it depend on the humidity of the air in the room?

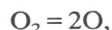
Suppose that a gas of diatomic molecules, for example nitrogen, is heated very rapidly to a high temperature. The heating can be accomplished so rapidly, say by the passage of a shock wave through the gas, that the average kinetic energy of the molecules is increased within 10^{-6} s; within that interval, however, the average vibrational energy of

the molecules will not change. How long will it take for complete equilibrium to be achieved by the transfer of energy from translational to vibrational (or other) degrees of freedom? On what variables does this process depend? Does it depend on temperature, pressure, structure of the molecules, the surface of the container? Is it sensitive to impurities present in the gas?

Suppose H_2 and O_2 gases are present in a vessel at 20°C and a given pressure. We can calculate the Gibbs free energy change for conversion of these gases to water vapor at the same temperature and pressure. Since the Gibbs free energy of the water vapor is lower than that of the reactants, the process is "spontaneous" and "irreversible." But one would grow impatient standing in front of that vessel waiting for the reaction to occur, because essentially nothing will happen. Make an electric spark in the mixture, however, or put into it some platinum powder, and the reaction will occur quickly, even explosively. In any case, what we often want to know is the rate of the reaction, how it depends on temperature, on the structure of the molecules, on the presence of foreign substances. In still more detail, how many molecules have to collide, and in what particular way, in order to bring about the reaction? We ask, "What is the mechanism of the reaction?" The net stoichiometric equation



may or may not tell us anything about the mechanism. Do two hydrogen molecules collide with one oxygen molecule simultaneously, and two water molecules leave the collision zone? If so, the stoichiometric equation tells us all the chemical species involved in the reaction process. Does an oxygen molecule have to dissociate first to atoms, and these then collide with H_2 ? If so, then we have a two-step mechanism,



but the stoichiometric equation tells us nothing about the possible presence of oxygen atoms. What are the forces between the various species? How do these forces determine the collision dynamics? What is the rate of each reaction step in the mechanism, and how is this *average* rate related to the nature of the individual collisions?

The student will see, from just the few examples cited, how complicated time-dependent processes can be. The study of such processes involves a number of important topics which we shall discuss: first, the simple geometric aspects of molecular motion (kinematics), forces between molecules, collisions of molecules, and other subjects properly classified under mechanics; second, the average rate of change of properties such as the concentration, temperature, pressure, entropy (all representative of many-molecule systems), and other subjects belonging to a time-dependent statistical thermodynamics.

Molecular Motion and Collisions

The three processes cited in the introduction, and others like them, can be described in terms of the change with time of some macroscopic observable quantity: the amount of liquid evaporating per unit time, the change of translational temperature per unit time, and the change of concentration of chemical reactant per unit time. In each case the change in the macroscopic quantity is descriptive of the averaged molecular behavior. If there were no molecular motion and no molecular collisions, no macroscopic change could occur. If the molecules of a vapor do not collide with the surface of a liquid, there can be no condensation. Or if a molecule in a liquid does not acquire, through collision with other molecules, enough kinetic energy to escape from the surface, there can be no evaporation. Transfer of energy from one degree of freedom to another, for example, from translation to vibration, can occur only by collisions. Chemical reactions occur upon collisions between molecules of reactants, collisions that usually must be relatively violent if the reactant molecules are to approach each other closely enough for rearrangements of chemical bonds to occur.

It is clear that the detailed dynamics of molecular collisions must determine the rate of a process. Therefore, unlike the study of the equilibrium properties of matter, where we needed only the stationary energy spectrum of a system, the study of time-dependent properties requires a detailed study of molecular dynamics.

We consider the simplest case first: a molecule represented as a point moving in a given direction with a given speed. A collision of one molecule with another is defined as an event during which the velocity of each particle is changed. If we consider the motion of the molecules to be described by classical mechanics, then Newton's laws imply that an interaction must occur between the particles; that is, a force must act between them for any change of velocity to occur. A change of velocity implies an acceleration $d\mathbf{v}/dt$, which, according to Newton's second law of motion, is proportional to the force acting on the particle.

Consider now two point particles, one of mass m_1 , the other m_2 , with corresponding velocities \mathbf{v}_1 , \mathbf{v}_2 . These velocities are measured relative to some fixed frame of reference, and so are called *laboratory* velocities. What can be said about a collision between these two particles without knowing the particular forces between them? The statements that follow, taken to be postulates, form the content of *kinematics*. First, we assume conservation of mass; the total mass $m_1 + m_2$ is the same before and

27.1 Kinematics

after collision,

$$m_1 + m_2 = m'_1 + m'_2 \quad (27.1)$$

(primes are used to designate quantities after a collision), and also we must have

$$m_1 = m'_1, \quad m_2 = m'_2 \quad (27.2)$$

if no reaction takes place. This is a trivial observation once the conservation of mass is accepted. (Actually mass and energy are jointly conserved, with the changes related by Einstein's equation $\Delta m = \Delta E/c^2$. But the mass change Δm is negligible in ordinary chemical reactions, becoming significant only in high-energy nuclear reactions.) Second, we assume the conservation of linear momentum, implying that

$$m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 = m'_1 \mathbf{v}'_1 + m'_2 \mathbf{v}'_2. \quad (27.3)$$

By using the conservation of mass, we can rewrite Eq. 27.3 in the form

$$m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 = m_1 \mathbf{v}'_1 + m_2 \mathbf{v}'_2. \quad (27.4)$$

Of course, a vector equation such as Eq. 27.4 is shorthand for three equations:

$$\begin{aligned} m_1 v_{1x} + m_2 v_{2x} &= m_1 v'_{1x} + m_2 v'_{2x}, \\ m_1 v_{1y} + m_2 v_{2y} &= m_1 v'_{1y} + m_2 v'_{2y}, \\ m_1 v_{1z} + m_2 v_{2z} &= m_1 v'_{1z} + m_2 v'_{2z}. \end{aligned} \quad (27.5)$$

Third, we assume the conservation of energy. Before the collision, the two particles are sufficiently far apart that there is no interaction between them, and the two-particle system has only kinetic energy. The same is true after the collision has occurred and the particles have separated. Thus we have

$$\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{1}{2} m_1 v_1'^2 + \frac{1}{2} m_2 v_2'^2. \quad (27.6)$$

Note that energies are scalar quantities. A fourth set of conditions can be obtained from the principle of conservation of angular momentum, but we are not yet ready to consider this.

We can transform the description of the motion of two particles into that of one particle in a field of force. Let the position coordinate of particle 1, relative to some arbitrary origin, be \mathbf{r}_1 , and the force exerted (by particle 2) on particle 1 be \mathbf{F}_1 , both of these quantities being vectors; we similarly define \mathbf{r}_2 and \mathbf{F}_2 . Newton's third law requires that

$$\mathbf{F}_1 = -\mathbf{F}_2, \quad (27.7)$$

and by Newton's second law we can write the equations of motion

$$\mathbf{F}_1 = m_1 \frac{d^2 \mathbf{r}_1}{dt^2}, \quad \mathbf{F}_2 = m_2 \frac{d^2 \mathbf{r}_2}{dt^2}, \quad (27.8)$$

$d^2 \mathbf{r}_1/dt^2$ and $d^2 \mathbf{r}_2/dt^2$ being the accelerations. By combining Eqs. 27.7 and 27.8, we obtain

$$\frac{d^2 \mathbf{r}_2}{dt^2} - \frac{d^2 \mathbf{r}_1}{dt^2} = \frac{d}{dt} \left(\frac{d \mathbf{r}_2}{dt} - \frac{d \mathbf{r}_1}{dt} \right) = \left(\frac{1}{m_2} + \frac{1}{m_1} \right) \mathbf{F}_2. \quad (27.9)$$

At this point it is convenient to define the relative position vector

$$\mathbf{r} \equiv \mathbf{r}_2 - \mathbf{r}_1, \quad (27.10)$$

as shown in Fig. 27.1, and its time derivative, the relative velocity

$$\mathbf{v} \equiv \mathbf{v}_2 - \mathbf{v}_1. \quad (27.11)$$

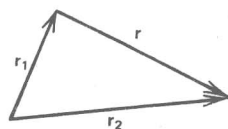


FIGURE 27.1
Definition of relative position vector \mathbf{r} .

If we now drop the subscript on \mathbf{F}_2 , and understand \mathbf{F} to be the force between particles 1 and 2, we obtain the simple result

$$\mu \frac{d\mathbf{v}}{dt} = \mathbf{F}, \quad (27.12)$$

where

$$\mu \equiv \frac{m_1 m_2}{m_1 + m_2} \quad (27.13)$$

is the reduced mass. Now, what does Eq. 27.12 tell us? It is the equation of motion of a single particle with mass μ in the field of force \mathbf{F} . In fact, we can go a bit further along this line. Recall that linear momentum is conserved (cf. Eq. 27.3). Let us consider a point of mass $M \equiv m_1 + m_2$ moving with a velocity \mathbf{V} such that its momentum equals the total momentum of our two particles:

$$m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2 = (m_1 + m_2) \mathbf{V}. \quad (27.14)$$

The motion of this point corresponds to that of the center of mass of the two-particle system. The center-of-mass motion is usually uninteresting. It is the *relative* motion of the two particles that counts in a collision. Having started with velocities \mathbf{v}_1 and \mathbf{v}_2 , and having defined the velocities \mathbf{v} and \mathbf{V} , we can solve Eqs. 27.11 and 27.14 for one set of variables in terms of the other set, obtaining

$$\begin{aligned} \mathbf{v}_1 &= \mathbf{V} - \frac{m_2}{m_1 + m_2} \mathbf{v}, \\ \mathbf{v}_2 &= \mathbf{V} + \frac{m_1}{m_1 + m_2} \mathbf{v}. \end{aligned} \quad (27.15)$$

These vector equations have an easy pictorial interpretation. Consider the simple case that \mathbf{v}_1 and \mathbf{v}_2 are perpendicular to each other. Then Fig. 27.2 shows the vector relations embodied in Eqs. 27.15.

Next let us substitute Eqs. 27.15 into the expression for the total energy,

$$\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2,$$

where v_1 and v_2 are given by equations of the form

$$v_1^2 = v_{1x}^2 + v_{1y}^2 + v_{1z}^2. \quad (27.16)$$

We find that

$$\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{1}{2} (m_1 + m_2) V^2 + \frac{1}{2} \mu v^2. \quad (27.17)$$

The kinetic energy of the two-particle system is just the sum of the kinetic energy arising from the center-of-mass motion and the kinetic energy arising from the relative motion. For our purposes, we can often neglect the center-of-mass motion and concentrate on the relative motion, because the center-of-mass velocity is not changed in a collision between the two particles. The velocity \mathbf{V} can change only if outside forces are brought to bear on the two-particle system. Thus the relative kinetic energy is itself conserved,

$$\frac{1}{2} \mu v^2 = \frac{1}{2} \mu v'^2, \quad (27.18)$$

so that $v = v'$.

What is changed in a collision? In a collision between two point particles, only their velocities can be changed, because they have no internal structure in which to store energy. The magnitude of the relative

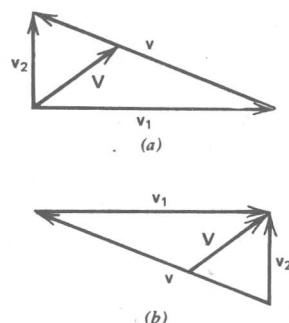


FIGURE 27.2

Relation of laboratory velocities \mathbf{v}_1 , \mathbf{v}_2 to center-of-mass velocity \mathbf{V} and relative velocity \mathbf{v} ; parts (a) and (b) are equivalent representations.

velocity is invariant, by Eq. 27.18. We can draw, as in Fig. 27.3, the velocities of particles 1 and 2 before and after a collision. Remember that \mathbf{V} remains the same, as does the magnitude of \mathbf{v} . In general, the direction and magnitude of both \mathbf{v}_1 and \mathbf{v}_2 are changed by the collision. Thus, in a collision between structureless point particles, momentum and kinetic energy can be transferred from one particle to another. Any collision in which *only* momentum and kinetic energy are transferred is called "elastic." In the elastic collision shown in Fig. 27.3, particle 1 changes its direction of motion through an angle α_1 and particle 2 through an angle α_2 . If we could observe a single particle (as in principle can be done in classical mechanics), we would see particle 1 before the collision traveling in the direction of \mathbf{v}_1 and after the collision in the direction of \mathbf{v}_1' . We say that particle 1 is *scattered*¹ through the laboratory angle α_1 . The relative velocity vector is turned by the collision through an angle χ , the relative scattering angle.

To illustrate the advantage of using relative coordinates, let us plot a collision as shown in Fig. 27.4. (Compare Fig. 2C.1, which illustrates the limiting case of one particle much heavier than the other.) We again show the relative velocities \mathbf{v} and \mathbf{v}' and the relative scattering angle χ . Now, however, we have placed these vectors in alternative positions corresponding to the actual collision trajectory. Initially, before the collision, a fictitious particle with mass μ and velocity \mathbf{v} moves in the direction indicated toward a center of force located at O . This particle then may be pulled toward O by attractive forces or pushed away by repulsive forces, but the net effect of the collision is the deflection of the velocity vector \mathbf{v} into \mathbf{v}' through an angle χ . If there were no forces of interaction, the fictitious particle would pass point O (or the real particles each other) in a straight line. The distance of closest approach would then be some value b , which we call the *impact parameter*; similarly, we can define b' by extrapolating the final trajectory backwards.

Now, what role does the angular momentum play in the collision process? We have mentioned that angular momentum is conserved in a collision. The initial relative angular momentum around point O has a magnitude μvb (cf. Appendix 2C). Since both μ and v are the same before and after the collision, this must also be true for the impact parameter b , if angular momentum is to be conserved. We thus have $b = b'$.

It is clear that the impact parameter is an important quantity in the specification of a collision. If b is large relative to the range of the force between the molecules, then the molecules hardly interact and are but little deflected from their original paths. If the impact parameter is small, the interaction and deflection may be large.

In summary, if we have two point particles of masses m_1 and m_2 , what other variables are at our disposal for studying their collisions? The velocities \mathbf{v}_1 and \mathbf{v}_2 , or, equivalently, the center-of-mass velocity \mathbf{V} and relative velocity \mathbf{v} ; and the impact parameter b . If we are not interested in how fast the two particles move through space but only in the collision itself, there remain only two variables: v and b , or $E = \frac{1}{2}\mu v^2$ and \tilde{b} .

Finally, we note that for elastic scattering there are only three quantities whose sums for the two particles remain invariant before and after the collision. These quantities are the mass, Eq. 27.1, the linear momentum, Eq. 27.3, and the kinetic energy, Eq. 27.6; they are called *summational invariants*.

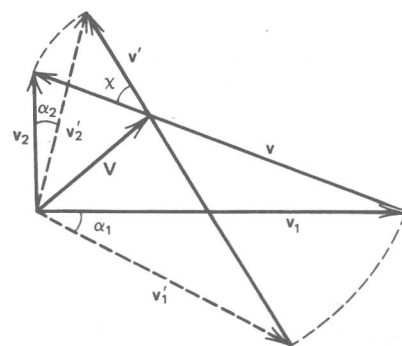


FIGURE 27.3 Velocities before and after an elastic collision.

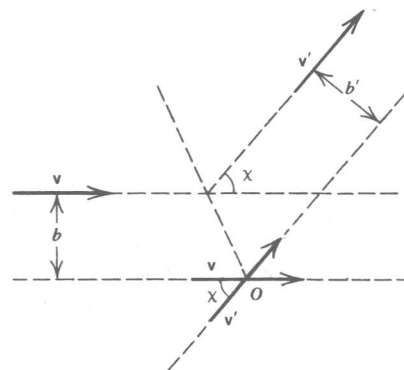


FIGURE 27.4 Relative velocity vector before (\mathbf{v}) and after (\mathbf{v}') an elastic collision. The relative scattering angle is χ , and the impact parameter is b .

¹ Scattering is the general term used to describe the results of collisions.

We have gone about as far as we can with the pure kinematics of the two-particle system; to proceed further, we must give the particles more properties, so that we can discuss forces between molecules and the effect of these forces on collisions. This is the subject of *dynamics*.

We shall use the concepts of forces and potentials (of interaction); let us now review their meaning. Suppose that two particles repel each other, that is, they interact with a force of repulsion. Let that force be zero when the two particles are infinitely far apart, and vary with distance as they are brought together. For this example we take the initial relative kinetic energy to be zero. It is clear that work must be done to bring the two particles together from infinity to some distance R . Thus the energy of the two-particle system at a separation R is greater than the energy at infinite separation, by an amount exactly equal to the work done on the system. The zero of potential energy is conveniently chosen at infinite separation of the pair, so that

$$V(R) = E(R) - E(\infty), \quad (27.19)$$

where $E(R)$ is the energy of the system at separation R . This equation of course applies equally well if the interaction is attractive. The force required to bring the particles together is in the opposite direction to the force of interaction between them. Hence the work done on the system (cf. Eq. 2.55) is

$$W = - \int_{\infty}^R F(R) dR = V(R), \quad (27.20)$$

equal to the potential energy. The relation between force and potential energy is thus

$$F(R) = - \frac{dV(R)}{dR}. \quad (27.21)$$

Note that we have assumed the force and potential energy to depend only on the distance R between the particles, with the force vector directed along the line between them; such a force is called a *central force*.

In principle, as we outlined in Section 10.1, one can calculate the potential energy of two molecules by means of quantum mechanics. Consider two helium atoms. At infinite separation one can calculate the electronic energy of each atom. Even this calculation cannot be expressed in terms of known mathematical functions, but can be carried to completion numerically. If this calculation is repeated for a finite separation between the atoms, account must be taken of the Coulomb interaction of each electron, not with one nucleus, but rather with two nuclei. The system under consideration consists of two nuclei at a fixed separation and four electrons around them. Second, there is a nucleus-nucleus Coulomb repulsion, and electron-electron Coulomb repulsions between all possible electron pairs. Thus the interaction is quite complex, and it is not surprising that an accurate calculation of the energy at a given internuclear distance is an elaborate procedure requiring high-speed computers. Calculations have been made, to various approximations, for simple systems such as He-He. For more complicated cases theoretical predictions, although still meager, are becoming increasingly available. Information about intermolecular forces can be obtained from experimental studies of scattering; and many macroscopic properties, which can be expressed in terms of averages over molecular interactions and collisions, can be used to obtain information about the intermolecular potential.

27.2 Forces and Potentials