Berry/Rice/Ross

Physical Chemistry

PHYSICAL CHEMISTRY

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To our families

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Preface

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

Text by Nicholas Brady for the *Ode on St. Cecilia's Day, 1692* by Henry Purcell

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 or 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 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 bridges between the two classes of description is a prinicipal 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. Given only that every sample of matter has an energy-level spectrum, it is shown that there exists a function of the density of states, the entropy, that behaves like a property only of macroscopic variables 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 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 generality of the thermodynamic approach is made evident, as is the wealth of detail and dependence on assumed models of the 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 manner parallel 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, Donald Jordan and David J. Zvijac 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), Professor Edward I. Solomon (M.I.T.), Professor Jeffrey I. Steinfeld (M.I.T.), Professor Mark S. Wrighton (M.I.T.) 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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Suggested Topic Selections for Various Courses

The following table illustrates possible choices of subject matter for a variety of physical chemistry courses.

Chapter	One-Year Course (initial emphasis on macroscopic approach)	One-Year Course (initial emphasis on microscopic approach)	Three-Semester Course	Senior or Graduate Course
1	Start with Chapters 12 through 26, with emphasis placed on the thermodynamic analysis. Keep only such elements of the statistical molecular analysis as fits with the instructional goal. Then return to Chapter 2 and follow the outline for the one-year course with initial emphasis on microscopics, going rapidly to Section 3.3.	Start with Chapter 1, setting pace as fast as students can absorb	All, as introduction	Omit
2		Chapters 1 and 2, and Sections 3.1 and 3.2.	All	Read quickly
3		Touch lightly or omit Section 3.10 and Appendix 3A	All	Read Sections 3.1 and 3.2 quickly
4		All	All	All
5		All, but Section 5.5 may be omitted for very well-prepared students	All	Touch lightly on Section 5.5
6		All	All	All
7		Section 7.8 may be dropped	All	All
8		All	All	All
9		Omit Sections 9.6 and 9.7	All	All
10		Omit	All	All
11		Sections 11.1 through 11.5, 11.8, and 11.10	All	All
12		All	All	All
13		All	All	All
14		Omit Section 14.6, Only touch lightly on Sections 14.9, 14.10	All	All
15		Omit optional Section 15.1	Omit optional Section 15.1	All
16		Omit optional Sections and Appendix 16A	Omit Appendix 16A	All
17		All	All	All
18		All	All	All
19		Omit Section 19.3	All	All
20		Omit	Touch lightly on Sections 20.1–20.4, keep 20.5	All
21		Omit Appendices 21A, 21B, 21C	All	All
22		Omit Section 22.5 and Appendix 22A	All	All
23		Omit Section 23.4	All	All
24		Omit Section 24.3 touch lightly on Section 24.4	All	All
25		Omit latter half of Section 25.8. Touch lightly on Section 25.9	All	All
26		Omit Section 26.6	All	All
27		27.1–4	All	All
28		28.1, 4, 6, 7, 8	28.9, 10 optional	All
29		29.1	29.2–6	All
30		Omit 30.5, 6, 9	All	All
31		As time permits Assign as special topics	31.3, 6–11 and as time permits	All

Contents

PART ONE

The Structure of Matter

1

The Microscopic World: Atoms and Molecules

We begin our study of the microscopic properties of matter by considering the properties of atoms and molecules. But first, what *are* atoms and molecules? For the moment, let us simply use a working definition: For any of the hundred-odd substances (the chemical elements) listed on the inside cover of this book, an *atom* is the smallest bit of matter that can be identified as that substance; for any other chemical substance, a *molecule* (made up of atoms) is the smallest recognizable bit of the substance. Admittedly, definitions like these are somewhat vague, so we shall begin by reviewing some of the evidence that led to the formulation of these concepts.

Granting the existence of atoms and molecules, what do we want to know about them? In this chapter we deal with some of the simplest properties that can be described in gross terms. When one investigates a macroscopic object, it is natural to ask first about its size and its weight. By the same token, how big and how heavy is an atom or a molecule? On the atomic scale, the electrical charges carried by the various bits of matter are central to their behavior, so we must also consider the charges of the atom's components. We shall describe a number of methods for determining these various atomic magnitudes. Although these are not the only possible methods, nor in general the most precise,[1] they are the most straightforward conceptually, in that the quantities measured are related in very simple ways to the properties desired. Finally, we review some of the basic facts of macroscopic chemistry, the atomic weight scale and the periodic table, which must be related to the properties of atoms.

1.1 Development of the Atomic Theory: Relative Atomic Weights

Chemistry began as a qualitative study of the properties and transformations of the substances found in nature. It evolved into an exact science when quantitative regularities (laws) were found to underlie these properties and transformations. Its goal became the construction of theories to correlate and predict the regularities. The most important of these regularities was the *law of conservation of mass*, which states that the total mass (quantity of matter) present is the same before and after a chemical reaction. Once this law was recognized, one could keep track of the amounts of various kinds of matter involved in reactions and thus determine the composition of substances. A small number of substances—elements—could not be broken down into anything simpler, whereas other substances—compounds—could be separated into two or

[1] In practice it often turns out that the most direct way of doing something is not in fact the most accurate. For example, the review that established the fundamental constants listed in Table 1.1 actually used none of the methods cited here, although some were examined in great detail before it was decided to use less direct but more accurate methods.