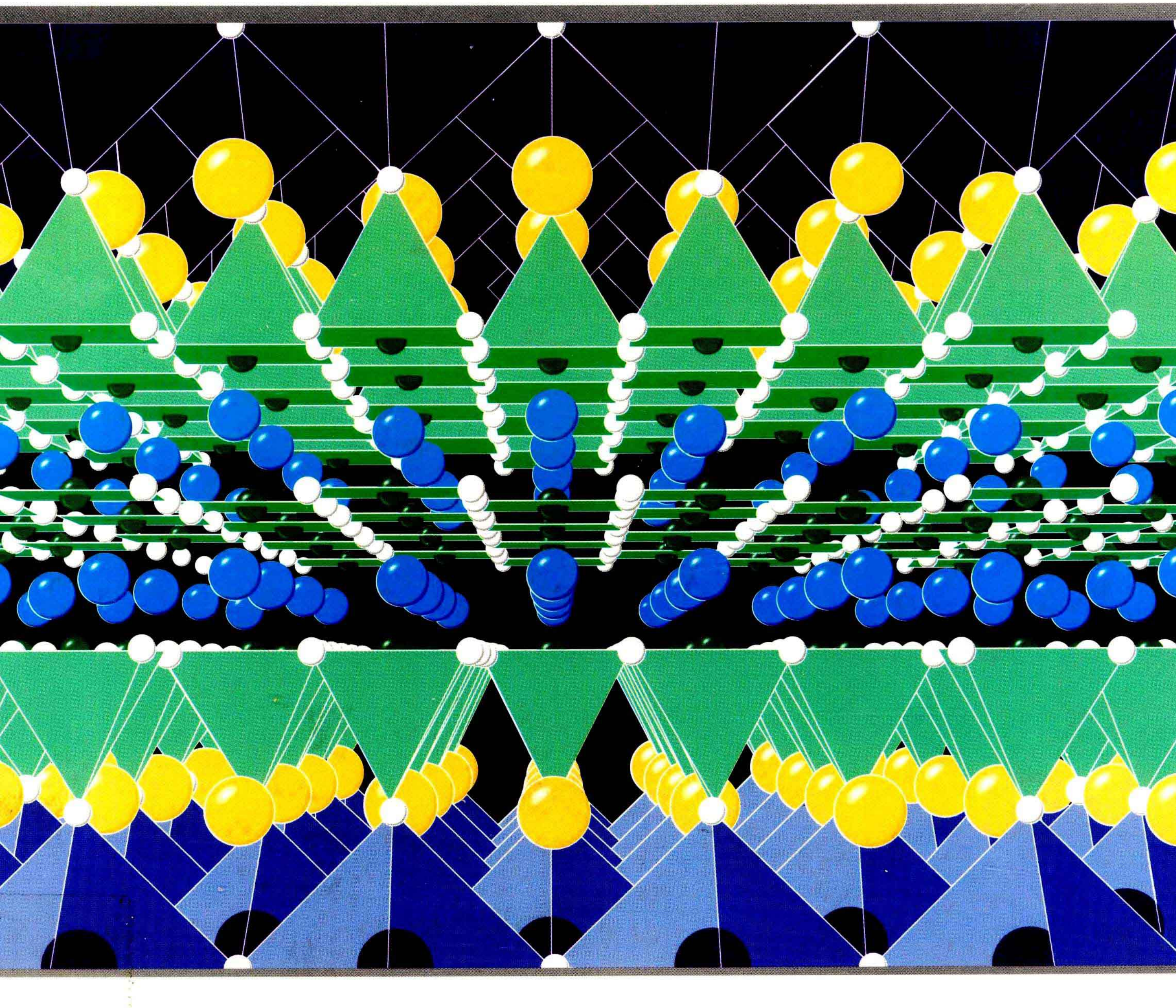
PHYSICAL CHEMISTRY



GEORGE WOODBURY

Physical Chemistry

GEORGE WOODBURY
University of Montana

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This book is dedicated to my family—my sustenance and joy

ABOUT THE AUTHOR

George Woodbury was raised in New York State and Idaho and graduated from the University of Idaho with a B.S. in chemistry. He received his Ph.D. at the University of Minnesota, where Stephen Prager introduced him to theoretical work in quantum chemistry and transport phenomena, and he received a postdoctoral appointment at Cornell University, where he worked with Ben Widom in equilibrium statistical mechanics. Dr. Woodbury's subsequent research concerned the statistical description of liquid and solid interfaces; this work eventually evolved into empirical thermodynamic descriptions of the adsorption of liquid mixtures onto solid surfaces.

Dr. Woodbury's teaching experience spans thirty years in the University of Montana Chemistry Department, a small department that has taken pride in educating ever increasing numbers of undergraduates and supporting a Ph.D. program. Dr. Woodbury's teaching rotation covers freshman chemistry, undergraduate physical chemistry, and all areas of graduate physical chemistry.

Montana's recreational opportunities have not been lost on the author. He and his wife, Carolyn, have taken great pleasure in raising their children, Joan and David, to love the outdoors and to enjoy physical activity.

Preface

In undertaking this project, my goal was to create a text that would make it easier for students to attain a deeper understanding of physical chemistry so as to establish a firm base for practical problem solving and subsequent courses. Strategies that I have used as guiding principles include the following.

- Make more extensive use of models
- Present physical chemistry as a connected subject
- Include molecular pictures in the thermodynamic topics
- Streamline developments to avoid bogging down in unessential details
- Treat selected mathematics topics systematically

Both students and professional physical chemists like the solid feeling of thinking in terms of definite models. All physical chemistry texts use a common list of well-known models such as the ideal gas, ideal solution, particle in a one-dimensional box, etc. I have attempted to make full use of the standard models by introducing techniques and concepts in the context of a specific model. For example, I have introduced perturbation theory, the variation principle, the Hartree method, and the idea of electron correlation all in the context of the helium-atom model (as defined by a specific approximate Hamiltonian)—see Chapter 18, Sections 6, 7, 8, 9, and 10. I have used the van der Waals fluid as a model for the liquid-vapor transition, the critical point, and the law of corresponding states (Chapter 6, Sections 5 and 6). Models not ordinarily seen in physical chemistry texts include a detailed model for collision theory (Chapter 29, Section 1) and the regular solution, which is a model for non-ideal solutions (Chapter 11, Section 6).

In my experience, the students who have the most trouble with physical chemistry are those who treat the material as a collection of unconnected or loosely connected subjects. Texts often exacerbate the problem, in my opinion, by not making sufficient effort to show connections. All too commonly, a derivation that produces the correct equation hides the train of thought that shows the result to be a natural consequence of assumed models or basic principles. Thus, you will see in this text expanded explanations for key results. For example, Chapter 8, Sections 1–4 carefully develop the links between first principles of thermodynamics and practical equilibrium-constant calculations. Chapter 5, Section 4 establishes the result that is the basis of the minimum-free-energy principles (Eqs. 5.35 and 5.38). I have taken pains to explain the connected ideas of basis functions, altenative basis functions for degenerate levels, and complete sets of wave functions (Chapter 16, Sections 9 and 11) because they are so important in comprehending standard approximation methods for describing chemical bonds. In Chapter 16, Section 6, I make the explicit connection between a diatomic molecule and simple models so that the student has the basis for understanding the necessity, and the strategy, for the improvements described in Chapter 16, Section 7. Rather than using the standard trick derivation of the Maxwell distribution, which makes the result appear to be an orphan, I use a derivation that makes the connection to standard statistical mechanics (Supplement 26.1 at the end of Chapter 26).

Another strategy that emphasizes the connected nature of physical chemistry is the consistent use of powerful tools. Two especially important ones are the chemical potential and commutators. The properties of the chemical potential are developed in Chapter 7, Sections 2, 4, and 5 and used as the central organizing idea for chemical equilibrium, phase equilibrium, solution thermodynamics, and electrochemical cells (Chapters 8–12). Commutators (introduced in Chapter 19, Section 1) are used to systematize the description of atomic states (Chapter 19, Section 6) and molecular states (Chapter 21, Sections 2 and 4).

Although thermodynamics does not in principle require accompanying molecular pictures, it is much easier to grasp thermodynamic results if they are related to molecular behavior. Furthermore, we chemists study thermodynamics primarily because of the information it tells us about molecules. Therefore, I have included molecular pictures (i.e., results from statistical mechanics) whenever I thought they would aid comprehension. Molecular pictures of thermodynamic energy and entropy are given in Chapter 2, Section 4, and in Chapter 3, Section 4, respectively. The relationship between the van der Waals equation of state and the intermolecular potential is described in Chapter 6, Section 5. The second virial coefficient is viewed as a window on the intermolecular potential in Chapter 6, Section 7.

A danger associated with presenting physical chemistry in some depth is bogging down the development to the point that students lose interest and essential topics are not discussed for lack of time. Consequently, I have made every effort to streamline developments so as to reach results that students recognize as important in a timely fashion. In this spirit, I have developed the discussion of the first law and second laws of thermodynamics so as to make unnecessary the discussion of the Joule experiment, the Joule-Thomson coefficient, and detailed properties of adiabatic processes. Subtle and difficult discussions of the second law of thermodynamics are avoided by giving the entropy form of the law (the most powerful form) top billing; the heat-engine form of the law is treated as an aside (Chapter 3, Section 5). Because the results of spectroscopic experiments most directly display the features of quantum theory, I have introduced spectroscopy (Chapter 17) early: It appears right after the chapter on the translational, rotational, and vibrational structure (Chapter 16) and before chapters on the electronic structure (Chapters 18–22).

I recognize that the average student (to whom this text is directed) in a first course in physical chemistry often has difficulty in mathematics. Students typically have had the requisite calculus courses and have performed satisfactorily in them, but they lack experience in applying mathematics to chemical problems. Because students feel this handicap acutely—particularly in the early part of the course—I have included a short chapter (Chapter 4) in which important mathematical topics are treated systematically. The emphasis is on presenting mathematical topics as physical scientists, rather than mathematicians, use them. Students consider Chapter 4 a confidence builder. Additional mathematical topics and results are introduced on a need-to-know basis in the text (for example, probability distributions in Chapter 26, Section 1), and in Appendixes B.1–B.8 at the end of the text.

Problems

This text contains approximately 1,000 problems. Many are embedded within the chapters and are designed to be worked by the student when encountered. I consider these problems to be the bare minimum to be worked by the student. Many additional problems are found at the end of each chapter. For the convenience of the instructor assigning problems and the student seeking additional unassigned problems, the end-of-chapter problems are keyed to the appropriate sections. Answers are included at the end of the text for all problems, except of course those whose answers are given initially (such as proofs).

A separate solutions manual contains detailed solutions to all the problems. Most of the manual was produced using problem-solving software (MATHCAD), which has helped to eliminate errors due to faulty arithmetic and incorrect unit conversions. Students have no difficulty following the MATHCAD output because it looks like normal mathematics. I hope the manual encourages students to learn how to use problem-solving software.

Throughout the text, problems have been included that require the manipulation of considerable data. These are designed to be worked by means of spreadsheet or other problem-solving software. Examples showing how to carry out spreadsheet calculations are given in the early chapters; examples follow a progression from simple to complex in order to build skills systematically. Here are some of the early spreadsheet examples, discussions, and problems: Example 2.2 (Chapter 2, Section 6), Problem 2.8, Example 5.3 (Chapter 5, Section 7), Supplement 5.1 (end of Chapter 5), Problem 5.31, Example 6.4 (Chapter 6, Section 7), Problem 6.31, Problem 7.19, and Problem 7.20.

Flexibility

A number of features make the text especially flexible. Because of the expanded discussions in the text, I feel less need to fill in the blanks (do derivations) in class. I like to use class time to establish a dialogue in which we pursue the consequences of text results.

The structure of the text allows considerable choice in course content and in the order of presentation. A not-too-ambitious two-semester course might cover Chapters 1–11 (thermodynamics), Chapters 14–21 (quantum chemistry), and Chapters 27–28 (empirical chemical kinetics and mechanisms); these three topics can be covered in any order.

To fill out a more ambitious course, I suggest adding Chapter 22 (electronic structure of polyatomic molecules), Chapter 31 (transport properties and diffusion-controlled reactions), Chapter 25 (statistical mechanics), Chapter 26 (kinetic theory), and Chapter 29 (theories of elementary rate processes). Chapter 22 should follow Chapter 21, Chapter 31 can be inserted any time after Chapter 27, and Chapter 29 should be preceded by Chapters 25–28.

Instructors with very competent students, or who have the luxury of a course that extends over more than two semesters, will want to consider including some of the remaining chapters: Chapter 12 (electrochemistry), Chapter 13 (surface thermodynamics), Chapter 23 (magnetic resonance spectroscopy), Chapter 24 (electronic properties of crystals), and Chapter 30 (molecular beams).

Thanks to my colleagues Richard Field and John Scott, who have read portions of my manuscript and made many useful comments. The reviewers have been indispensable in guiding the development of this text during its long period of gestation. They are: Paul Davidovits, Boston College; Thomas Dunn, University of Michigan; Lee Pederson; David W. Pratt, University of Pittsburgh; Don Secrest, University of Illinois at Urbana-Champaign; Leonard Spicer, Duke University; Edward Walters, University of New Mexico; and David Williamson.

George Woodbury

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Appendixes

1

Preliminaries

The challenge of physical chemistry is to discover and apply basic physical principles to the broad class of topics that constitute chemistry. In the 19th century physical chemists used primarily thermodynamic tools. Their studies led them to be able to predict whether particular reactions were spontaneous, to develop efficient chemical separation processes such as distillation, to establish the basic laws of electrochemistry, and to predict the amount of heat and work available from chemical processes. By the 1930s the subject matter of physical chemistry had expanded enormously as the establishment of quantum mechanics made it possible to create an electronic theory of chemical bonding and to invent the many types of spectroscopy from which we now investigate molecular structure and dynamics.

Thermodynamics and quantum mechanics continue to be the main windows through which physical chemists view nature. The two perspectives are very different. Quantum mechanics is a **microscopic** theory, meaning that its concepts center on small things: electrons, photons, atoms, and molecules. Thermodynamics, by contrast, is **macroscopic.** It describes properties that depend on the collective behavior of large numbers of molecules, and its great principles are independent of detailed atomic and molecular characteristics.

The theoretical link between thermodynamics and quantum mechanics is statistical mechanics. Statistical-mechanical principles allow one to start with a molecular model and predict, in principle at least, thermodynamic properties of systems containing many molecules. The importance of statistical mechanics to chemists is that it allows one to make molecular sense of thermodynamic measurements; thus, for example, one can use the theory of statistical mechanics and thermodynamic measurements of pressure, volume, and temperature to obtain a detailed description of the intermolecular interactions in a gas.

The order in which this text treats these topics is first thermodynamics, then quantum mechanics, and then statistical mechanics. However, we frequently break this order in the early sections in order to give molecular interpretations of macroscopic, thermodynamic quantities. When this occurs, the student should understand that the molecular *explanations* are the province of statistical mechanics and will be justified later in the text. Chemical kinetics—the study of