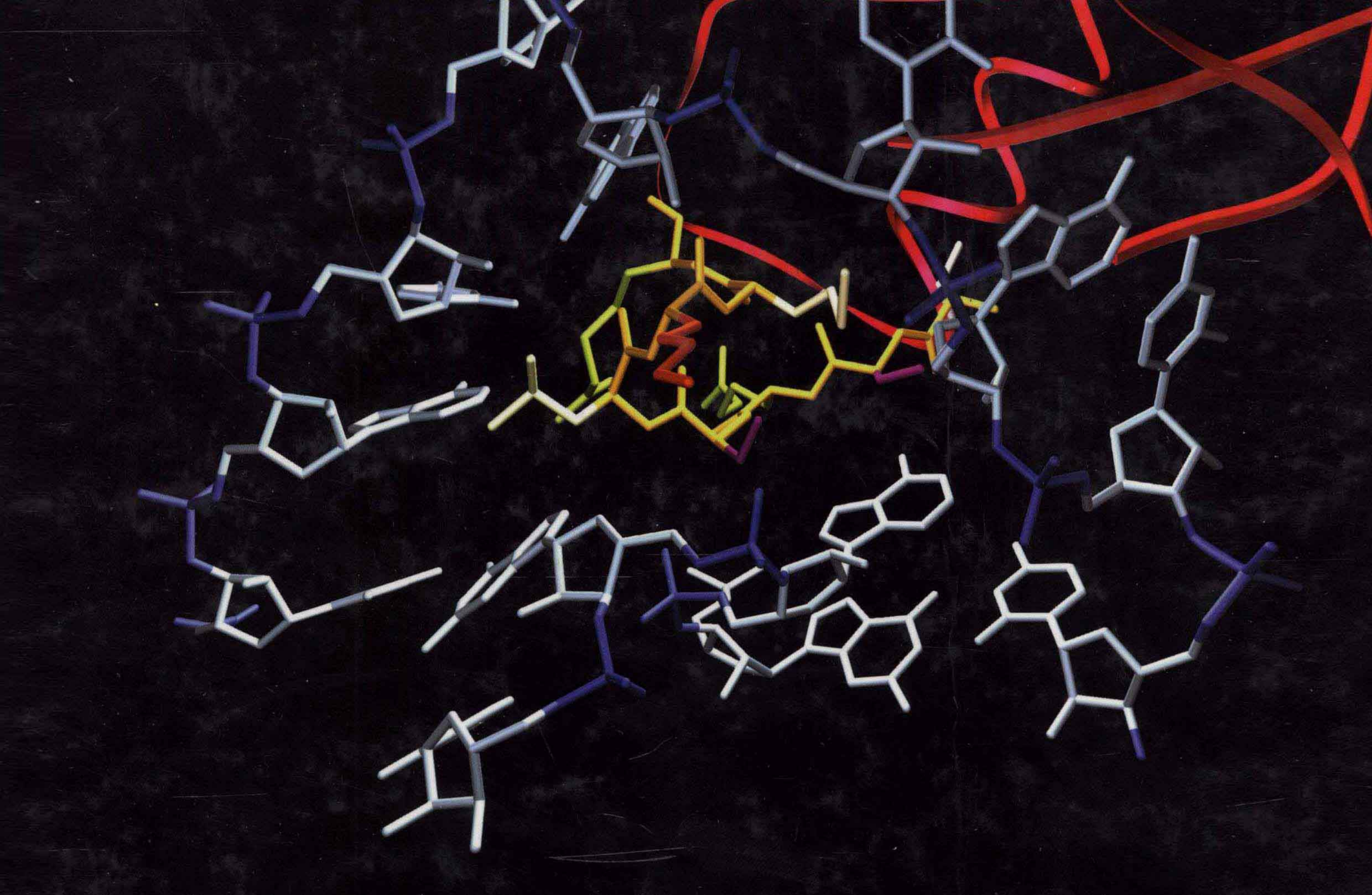

Physical Chemistry for the Life Sciences

Thomas Engel
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for the Life Sciences

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This book is dedicated to my parents, Walter and Juliane, who were my first teachers, and to my cherished family, Esther and Alex, with whom I am still learning.

—Thomas Engel

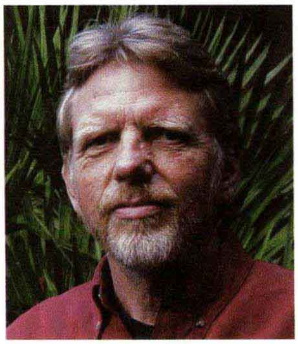
This book is dedicated to my family: Annika, Joshua, and Elizabeth

—Gary Drobny

This book is dedicated to my friends for their faith in me.

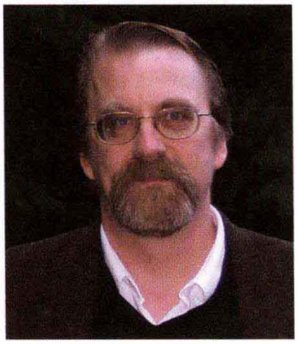
—Philip Reid

About the Authors



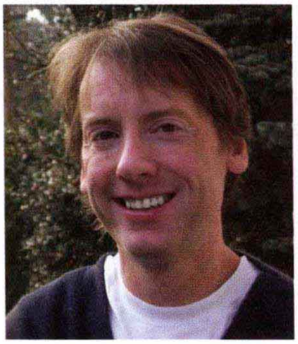
Thomas Engel has taught chemistry at the University of Washington for more than 20 years, where he is Professor Emeritus of Chemistry. Professor Engel received his bachelor's and master's degrees in chemistry from the Johns Hopkins University, and his Ph.D. in chemistry from the University of Chicago. He then spent 11 years as a researcher in Germany and Switzerland, in which time he received the Dr. rer. nat. habil. degree from the Ludwig Maximilians University in Munich. In 1980, he left the IBM research laboratory in Zurich to become a faculty member at the University of Washington.

Professor Engel's research interests are in the area of surface chemistry, and he has published more than 80 articles and book chapters in this field. He has received the Surface Chemistry of Colloids Award from the American Chemical Society and a Senior Humboldt Research Award from the Alexander von Humboldt Foundation. When not writing, he is likely to be hiking, sea kayaking, or cross-country skiing.



Gary Drobny has taught chemistry at the University of Washington since he joined the chemistry faculty in 1985. Professor Drobny received his bachelor's degree in chemistry from San Francisco State University in 1976, and his Ph.D. in chemistry in 1981 from the University of California at Berkeley.

Professor Drobny's interests are in the areas of solution and solid-state nuclear magnetic resonance, protein-nucleic acid recognition, biomaterials, biomineralization, and structural studies of proteins at biomaterial interfaces. He has published more than 120 articles in these fields.



Philip Reid has taught chemistry at the University of Washington since he joined the chemistry faculty in 1995. Professor Reid received his bachelor's degree from the University of Puget Sound in 1986, and his Ph.D. in chemistry from the University of California at Berkeley in 1992. He performed postdoctoral research at the University of Minnesota, Twin Cities, campus before moving to Washington.

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Preface

This book grew out of our experience in teaching physical chemistry to undergraduate students majoring in chemistry, biochemistry, and the biological sciences. The following objectives, illustrated with brief examples, outline the distinctive features of this book:

- **Focus on teaching core concepts.** The central principles of physical chemistry are explored by focusing on core ideas, and then extending these ideas to a variety of problems. For example, the Gibbs energy, bioenergetics, and chemical equilibrium are at the heart of thermodynamics and are explored in depth in this text. Similarly, a very good understanding of quantum mechanics can be obtained from a few basic systems: the particle in a box, the harmonic oscillator, and the hydrogen atom. Therefore, care is taken to fully explain and develop these key systems in order to provide a solid foundation for the student. A similar approach has been taken in other areas of physical chemistry. The goal is to build a solid foundation of student understanding rather than cover a wide variety of topics in modest detail.
- **Illustrate the relevance of physical chemistry to the world around us.** Many students struggle to connect physical chemistry concepts to the world around them. To address this issue, example problems and specific topics are tied together to help the student develop this connection. Biological membranes and the energetics of ion transport are discussed in a chapter focused on bioenergetics. Fuel cells, refrigerators, and heat pumps are discussed in connection with the second law of thermodynamics. Glycolysis, the Krebs cycle, and the electron transport chain are discussed in a chapter on biochemical equilibria.
- **Demonstrate the importance of quantum mechanics in the biological sciences.** Many everyday phenomena cannot be understood without quantum mechanics. The particle-in-a-box model is used to explain why metals conduct electricity and why valence electrons rather than core electrons are important in chemical bond formation. The real-world applications of quantum mechanics are in chemical spectroscopy. In-depth discussions of structural determinations of biomolecules using multidimensional NMR, the use of Raman spectroscopy to image living cells with chemical specificity, the use of fluorescence spectroscopy to sequence the human genome, and the use fluorescence resonance energy transfer (FRET) as a spectroscopic ruler to measure donor–acceptor distances show the student the importance of having a solid foundation in quantum mechanics.
- **Present exciting new science in the field of physical chemistry.** Physical chemistry lies at the forefront of many emerging areas of modern chemical research. Examples discussed in this text include the use of atomic force microscopy to obtain nanometer-scale structural information about biological systems *in situ* and in real time, the use of single-molecule spectroscopy to understand kinetics at a molecular level, the use of FRET to determine the magnitude of the structural change introduced by substrate binding to an enzyme, and the use of multidimensional NMR to determine biomolecular structures in solution.

- **Use Web-based simulations to illustrate the concepts being explored and avoid math overload.** Mathematics is central to physical chemistry; however, the mathematics can distract the student from "seeing" the underlying concepts. To circumvent this problem, Web-based simulations have been incorporated as end-of-chapter problems throughout the book so that the student can focus on the science and avoid a math overload. These Web-based simulations can also be used by instructors during lectures. More than 50 such Web-based problems are available on the course Web site. An important feature is that each problem has been designed as an assignable exercise with a printable answer sheet that the student can submit to the instructor. The course Web site also includes a graphing routine with a curve-fitting capability, which allows students to print and submit graphical data.
- **Show that learning problem-solving skills is an essential part of physical chemistry.** Many example problems are worked through in each chapter. The end-of-chapter problems cover a range of difficulties suitable for students at all levels. Conceptual questions at the end of each chapter ensure that students learn to express their ideas in the language of science.
- **Use color to make learning physical chemistry more interesting.** Color is used to enhance both the pedagogy and content of the text. For example, four-color images are used to enhance the understanding of biochemical cycles, to display atomic and molecular orbitals both quantitatively and attractively, and to make complex images such as multidimensional NMR spectra understandable.

This text contains more material than can be covered in a one- or two-semester course, and this is entirely intentional. Effective use of the text does not require one to proceed sequentially through the chapters, or to include all sections. Many sections are self-contained so that they can be readily omitted if they do not serve the needs of the instructor. The text is constructed to be flexible to your needs, not the other way around. We welcome the comments of both students and instructors on how the material was used and on how the presentation can be improved.

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Many individuals have helped us to bring the text into its current form. Students have provided us with feedback directly and through the questions they have asked, which has helped us to understand how they learn. We especially thank our colleagues at the University of Washington including Rachel Klevit, Mickey Schurr, and Gabriele Varani who contributed valuable advice about biological NMR spectroscopy and transport. The help of Nicholas Breen, Gil Goobes, and Dirk Stueber, who reviewed Chapter 20, is also gratefully acknowledged. The help of William Parson and Ronald Stenkamp in critically reading Chapter 21 has been invaluable. Our own approach to thermodynamics and statistical thermodynamics has been influenced by the excellent textbooks of Lennard Nash and Gilbert Castellan. The biologically oriented physical chemistry texts by Eisenberg and Crothers and Tinoco, Sauer, Wang, and Puglisi influenced some of our approaches to topics in transport and spectroscopy. We are also fortunate to have access to some end-of-chapter problems that were written by Joseph Noggle and Gilbert Castellan in their physical chemistry textbooks. The reviewers, who are listed separately, have made many suggestions for improvement, for which we are very grateful. All those involved in the production process have helped to make this book a reality through their efforts. Special thanks are due to Jim Smith, who helped us initiate this project, and to Katie Conley and Jeff Howard who have guided the production process.

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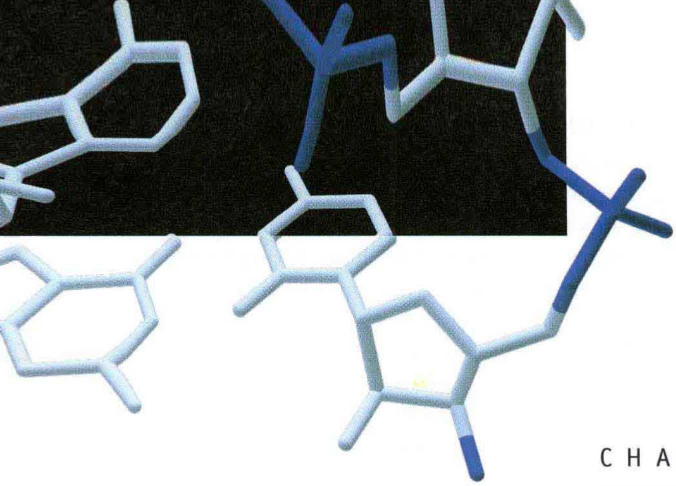

CHAPTER 1

Fundamental Concepts of Thermodynamics

CHAPTER OUTLINE

Thermodynamics provides a description of matter on a macroscopic scale. In this approach, matter is described in terms of bulk properties such as pressure, density, volume, and temperature. The basic terms employed in thermodynamics, such as system, surroundings, intensive and extensive variables, adiabatic and diathermal walls, equilibrium, temperature, and thermometry, are discussed in this chapter. The usefulness of equations of state, which relate the state variables of pressure, volume, and temperature, is also discussed for real and ideal gases.

1.1 What Is Thermodynamics and Why Is It Useful?

Thermodynamics is the branch of science that describes the behavior of matter and the transformation between different forms of energy on a **macroscopic scale** (i.e., the human scale and larger). Thermodynamics describes a system in terms of its bulk properties. Only a few such bulk property variables are needed to describe the system, and these variables are generally obtained via measurements. A thermodynamic description of matter does not make reference to its structure and behavior at the microscopic level. For example, 1 mol of gaseous water at a sufficiently low density is completely described by two of the three **macroscopic variables** of pressure, volume, and temperature. By contrast, the **microscopic scale** refers to dimensions on the order of the size of molecules. At the microscopic level, water is a dipolar triatomic molecule, H_2O, with a bond angle of 104.5° that forms a network of hydrogen bonds.

Given that the microscopic nature of matter is becoming increasingly well understood using theories such as quantum mechanics, why is a macroscopic science like thermodynamics relevant today? The need to approach problems from a macroscopic point of view may seem debatable. Indeed, an argument exists for describing physical problems from a microscopic point of view using quantum or classical mechanics, then deriving macroscopic properties statistically. Such a strategy, commonly called the "bottom-up" approach, is often justifiable in a field such as chemistry where nature is frequently investigated at the molecular level, but in many fields of engineering and biology, nature is not viewed exclusively in detail at the molecular level. In these cases, a "top-down" strategy is followed wherein macroscopic properties are investigated without reference to the underlying microscopic composition or mechanics of the system. Even if an engineer