

THIRD EDITION

# PHYSICAL CHEMISTRY

IRA N. LEVINE

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## PHYSICAL CHEMISTRY

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# PREFACE

This textbook is for the standard undergraduate course in physical chemistry.

In writing this book, I have kept in mind the goals of clarity, accuracy, and depth. To help make the presentation easy to follow, the book gives careful definitions and explanations of concepts, full details of most derivations, and reviews of relevant topics in mathematics and physics. I have avoided a superficial treatment, which would leave the student with little real understanding of physical chemistry. Instead, I have aimed at a treatment that is as accurate, as fundamental, and as up-to-date as can readily be presented at the undergraduate level.

The following improvements, directed mainly at making the book easier for students to follow, have been made in the third edition:

- The number of worked-out examples in the text has been increased from 86 to 107.
- Eighty-nine new figures have been added, and many old figures revised.
- A checklist of important kinds of calculations has been added to most chapter summaries.
- Overly long and complex derivations have been made shorter and simpler. Examples are the derivations of freezing-point depression in Sec. 12.3 and electrochemical potential in Sec. 14.3.
- A few nonessential derivations have been dropped from the text and made into problems with abundant hints. Examples are the derivations of Poiseuille's law, the Einstein-Smoluchowski equation, and the number of available translational states.
- Long sections have been divided into subsections.
- More-difficult material has been moved toward the ends of chapters. For example, the initial discussion of line integrals in Chapter 2 has been simplified, and the section on line integrals and state functions has been moved near the end of Chapter 2. Chapter 5 has been rewritten to emphasize enthalpies and Gibbs energies of formation and de-emphasize the less-used conventional enthalpies and Gibbs energies; calculation of the difference between real-gas and ideal-gas enthalpies has been moved later in Chapter 5. The Gibbs-Duhem equation was moved from Chapter 9 to Chapter 10. The material on fast reactions and relaxation kinetics has been moved from early in Chapter 17 to late in Chapter 17.
- The need for readers to refer back to previous sections for cited equations has been greatly reduced by repeating the equations instead of referring to them by number.

- More drill problems have been added.
- For problems where a computer solution is recommended, BASIC programs have been given in the solutions manual.
- Section 2.12 on problem solving has been expanded.
- More material on experimental methods has been included. For example, the discussion of calorimetry in Chapter 5 has been expanded, material on pressure measurement has been added to Sec. 1.5, and a discussion of the Ostwald viscometer has been added to Sec. 16.3.
- Additional common student errors and misconceptions are pointed out.
- A list of references for further reading has been added to each chapter, and many chapters have a list of data sources.
- The thermodynamic data in the Appendix table have been converted to joules, and the 1 bar standard state has been adopted.
- To avoid a major increase in length, excessively wordy material has been rewritten and irrelevant material dropped. A few specialized topics (photoacoustic spectroscopy, ultrasonic relaxation, pulse radiolysis, biological membranes) have been dropped, and the section on nuclear chemistry has been shortened.
- Throughout, the text has been revised to clarify, simplify, and update material.

The following new material has been included in the third edition:

- A subsection on lasers has been added to Sec. 21.2.
- The material on surface science has been expanded and modernized. Section 13.5 on adsorption of gases on solids was expanded. Section 17.17 on heterogeneous catalysis was expanded and updated to include a subsection on the kinetics of adsorption, desorption, and surface migration of gases on solids. Section 21.9 was expanded to include discussion of electron-energy-loss spectroscopy and infrared absorption spectroscopy of chemisorbed species. Section 24.10 on the use of low-energy electron diffraction and the scanning tunneling microscope to determine structures of surfaces and chemisorbed species was added.
- A subsection on the kinetics of free-radical addition polymerization was added to Sec. 17.12.
- The discussion of the AM1, MNDO, and MINDO/3 methods and the molecular mechanics method in Sec. 20.9 has been expanded and updated.

Although the treatment is an in-depth one, the mathematics has been kept at a reasonable level and advanced mathematics unfamiliar to the student has been avoided. Since mathematics has proved to be a stumbling block for many students trying to master physical chemistry, I have included reviews of aspects of calculus that are important to physical chemistry.

The book is organized so that students can see the broad structure and logic of physical chemistry rather than feel that they are being bombarded with a hodgepodge of formulas and ideas presented in random order. In line with this, the thermodynamics chapters are grouped together, as are those on quantum chemistry. Statistical mechanics is taken up after thermodynamics and quantum chemistry.

To avoid the impression that thermodynamics deals mainly with ideal gases, I have included substantial thermodynamic treatments of nonideal systems so that students can see that thermodynamics is useful in systems of real chemical interest.

In many applications of physical chemistry, approximations are necessary. In developing theories and equations, I have clearly stated the assumptions and approxi-

mations made, so that students will be aware of when the results apply and when they do not apply. Conditions of applicability of important thermodynamic equations are explicitly stated alongside the equations.

The equation numbers of important equations are starred to help the student realize which are the key equations.

The presentation of quantum chemistry steers a middle course between an excessively mathematical treatment that would obscure the physical ideas for most undergraduates and a purely qualitative treatment that does little beyond repeating what the student has learned in previous courses. The book discusses modern *ab initio* and semiempirical calculations of molecular properties so that students can appreciate the practical value of such calculations to nontheoretical chemists.

The content of physical chemistry courses has expanded greatly in recent years. In a one-year course, not enough time is available for a detailed presentation of all the required material. Because this book gives derivations in full detail, the instructor is freed from the necessity of presenting them in class; the class can be devoted to discussing concepts and answering questions, and more material can be covered.

Each chapter has a wide variety of problems, and answers to many of the numerical problems are given. The class time available for going over problems is usually limited, so a manual of solutions to the problems has been prepared and can be purchased by students upon authorization of the instructor.

A fair number of biological applications are included. Material on polymers is integrated into sections on osmotic pressure, transport properties, and solids.

The book uses both SI and non-SI units so that students are made familiar with both the officially recommended SI units and widely used non-SI units. For the most part, the symbols recommended by the International Union of Pure and Applied Chemistry are used.

Professors Gene B. Carpenter, Howard D. Mettee, Roland R. Roskos, Theodore Sakano, and Peter E. Yankwich reviewed various portions of the manuscript of the first edition; reviewers for the second edition were Professors Alexander R. Amell, Paul E. Cade, Jefferson C. Davis, Jr., George D. Halsey, Denis Kohl, John P. Lowe, Peter Politzer, John L. Ragle, Richard E. Wilde, John R. Wilson, and Peter E. Yankwich; reviewers for the third edition were Professors Alexander Amell, University of New Hampshire; C. Allen Bush, Illinois Institute of Technology; Luis Echegoyen, University of Miami; George D. Halsey, University of Washington; David O. Harris, University of California, Santa Barbara; Leonard Kotin, University of Illinois, Chicago; Alfred Mills, University of Miami; Mary J. Ondrechen, Northeastern University; Peter Politzer, University of New Orleans; Thomas H. Walnut, Syracuse University; Grace Wieder, Brooklyn College; and Richard E. Wilde, Texas Tech University. Professors Fritz Steinhardt and Vicki Steinhardt provided helpful mathematical advice; Professors Thomas Allen, Fitzgerald Bramwell, Dewey Carpenter, Norman C. Craig, John N. Cooper, Thomas G. Dunne, Hugo Franzen, Darryl Howery, Madan S. Pathania, J. L. Schreiber, John C. Wheeler, and Grace Wieder and my students provided me with many valuable comments and suggestions. I thank all these people for their very considerable help.

I welcome any suggestions for improvement that readers may have.

Ira N. Levine

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# THERMODYNAMICS

## 1.1

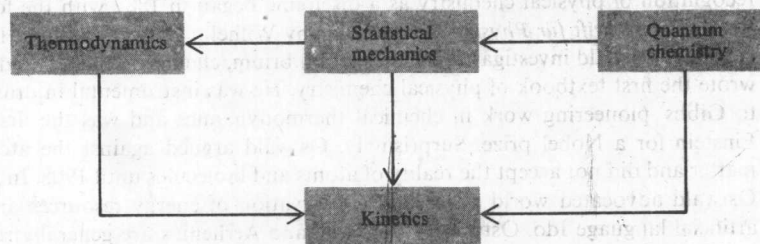
### PHYSICAL CHEMISTRY

**Physical chemistry** is the study of the underlying physical principles that govern the properties and behavior of chemical systems.

A chemical system can be studied from either a microscopic or a macroscopic viewpoint. The **microscopic** viewpoint makes explicit use of the concept of molecules. The **macroscopic** viewpoint studies large-scale properties of matter without explicit use of the molecule concept. The first half of this book uses mainly a macroscopic viewpoint; the second half uses mainly a microscopic viewpoint. The term **chemical physics** denotes those aspects of physical chemistry that study phenomena at the molecular level.

We can divide physical chemistry into four main areas: thermodynamics, quantum chemistry, statistical mechanics, and kinetics (Fig. 1.1). **Thermodynamics** is a macroscopic science that studies the interrelationships of the various equilibrium properties of a system and the changes in equilibrium properties in processes. Thermodynamics is treated in Chaps. 1 to 14.

FIGURE 1.1



The four branches of physical chemistry. Statistical mechanics is the bridge from the microscopic approach of quantum chemistry to the macroscopic approach of thermodynamics. Kinetics uses portions of the other three branches.

Molecules and the electrons and nuclei that compose them do not obey classical mechanics; instead their motions are governed by the laws of quantum mechanics (Chap. 18). Application of quantum mechanics to atomic structure, molecular bonding, and spectroscopy gives us *quantum chemistry* (Chaps. 19 to 21).

The macroscopic science of thermodynamics is a consequence of what is happening at a molecular (microscopic) level. The molecular and macroscopic levels are related to each other by the branch of science called *statistical mechanics*. Statistical mechanics gives insight into why the laws of thermodynamics hold and allows calculation of macroscopic thermodynamic properties from molecular properties. We shall study statistical mechanics in Chaps. 15, 16, 22, 23, and 24.

*Kinetics* is the study of rate processes such as chemical reactions, diffusion, and the flow of charge in an electrochemical cell. The theory of rate processes is not as well developed as the theories of thermodynamics, quantum mechanics, and statistical mechanics. Kinetics uses relevant portions of thermodynamics, quantum chemistry, and statistical mechanics. Chapters 16, 17, and 23 deal with kinetics.

The principles of physical chemistry provide a framework for all branches of chemistry.

Organic chemists use kinetics studies to figure out the mechanisms of reactions, use quantum-chemistry calculations to study the structures and stabilities of reaction intermediates, use symmetry rules deduced from quantum chemistry to predict the course of many reactions, and use nuclear-magnetic-resonance (NMR) and infrared spectroscopy to help determine the structure of compounds. Inorganic chemists use quantum chemistry and spectroscopy to study bonding. Analytical chemists use spectroscopy to analyze samples. Biochemists use kinetics to study rates of enzyme-catalyzed reactions, use thermodynamics to study biological energy transformations, osmosis, and membrane equilibrium, and to determine molecular weights of biological molecules, use spectroscopy to study processes at the molecular level (for example, intramolecular motions in proteins are studied using NMR), and use x-ray diffraction to determine the structures of proteins and nucleic acids.

Chemical engineers use thermodynamics to predict the equilibrium composition of reaction mixtures, use kinetics to calculate how fast products will be formed, and use principles of thermodynamic phase equilibria to design separation procedures such as fractional distillation. Geochemists use thermodynamic phase diagrams to understand processes in the earth. Polymer chemists use thermodynamics, kinetics, and statistical mechanics to investigate the kinetics of polymerization, the molecular weights of polymers, the flow of polymer solutions, and the distribution of conformations of a polymer molecule.

Although the term "physical chemistry" was used occasionally in the 1700s, widespread recognition of physical chemistry as a discipline began in 1887 with the founding of the journal *Zeitschrift für Physikalische Chemie* by Wilhelm Ostwald with J. H. van't Hoff as coeditor. Ostwald investigated chemical equilibrium, chemical kinetics, and solutions and wrote the first textbook of physical chemistry. He was instrumental in drawing attention to Gibbs' pioneering work in chemical thermodynamics and was the first to nominate Einstein for a Nobel prize. Surprisingly, Ostwald argued against the atomic theory of matter and did not accept the reality of atoms and molecules until 1908. In his later years, Ostwald advocated world peace and conservation of energy resources and created the artificial language Ido. Ostwald, van't Hoff, and Arrhenius are generally regarded as the founders of physical chemistry.



## THERMODYNAMICS

**Thermodynamics.** We begin our study of physical chemistry with thermodynamics. *Thermodynamics* (from the Greek words for “heat” and “power”) is the study of heat, work, energy, and the changes they produce in the states of systems. In a broader sense, thermodynamics studies the relationships between the macroscopic properties of a system. A key property in thermodynamics is temperature, and thermodynamics is sometimes defined as the study of the relation of temperature to the macroscopic properties of matter.

We shall be studying *equilibrium thermodynamics*, which deals with systems in equilibrium. (*Irreversible thermodynamics* deals with nonequilibrium systems and rate processes.) Equilibrium thermodynamics is a macroscopic science and is independent of any theories of molecular structure. Strictly speaking, the word “molecule” is not part of the vocabulary of thermodynamics. However, we won’t adopt a purist attitude but will often use molecular concepts to help us understand thermodynamics. Thermodynamics does not apply to systems of molecular size; a system must consist of a large number of molecules for it to be treated thermodynamically. The term “thermodynamics” in this book will always mean equilibrium thermodynamics.

**Thermodynamic Systems.** The macroscopic part of the universe under study in thermodynamics is called the *system*. The parts of the universe that can interact with the system are called the *surroundings*.

For example, to study the vapor pressure of water as a function of temperature, we might put a sealed container of water (with any air evacuated) in a constant-temperature bath and connect a manometer to the container to measure the pressure (Fig. 1.2). Here, the system consists of the liquid water and the water vapor in the container, and the surroundings are the constant-temperature bath and the mercury in the manometer.

An *open system* is one where transfer of matter between system and surroundings can occur. A *closed system* is one where no transfer of matter can occur between system and surroundings. An *isolated system* is one that does not interact in any way with its surroundings. An isolated system is obviously a closed system,

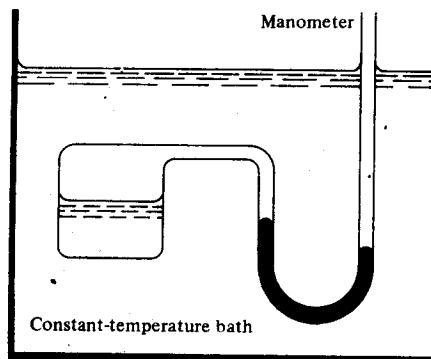


FIGURE 1.2

A thermodynamic system and its surroundings.