Physical Chemistry

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To the Instructor

The order of topics in this text is, for the most part, the traditional one found in most physical chemistry texts and, apparently, the one preferred by most instructors—namely, thermodynamics, kinetics, then quantum theory. However, as always, the instructor has the option of teaching the chapters in any order. Those who prefer another order may also find this book useful; the chapters on quantum theory and spectroscopy, 11 through 14, are relatively self-contained. One of the problems with teaching thermodynamics before quantum theory is the placement of statistical mechanics. On one hand, one would like to teach it with thermodynamics, where its utility is more immediately apparent to the student. On the other hand, the foundations of this topic cannot be understood without a firm background in quantum theory. *Physical Chemistry* attempts to resolve this dichotomy by placing statistical mechanics in *both* places. In Chapter 5, the major emphasis is on the calculation of thermodynamic functions. This not only provides a deeper insight into the molecular significance of macroscopic thermodynamics, but also gives an important motivation to the student for the coverage of quantum theory to come. Then, in Chapter 15, statistical mechanics is revisited with more rigorous derivations and additional applications. Those who do not like this approach can, with small loss, simply omit Chapter 5 and cover it later, together with Chapter 15; the subsequent applications (mostly in Chapter 6) can be avoided by a judicious choice of material and problems.

One of the things you will no doubt notice when reading the Table of Contents is the absence of the usual topical chapters such as "Solids," "Liquids," "Polymers," "Spectroscopy," "Surfaces," and the like. The reason for this absence is that *Physical Chemistry* is organized around theoretical principles, and such chapters would cut cross-grain. Closer inspection will reveal that many of these topics are there, but are distributed into various chapters. For example, surfaces are discussed in Chapters 4 and 10, and polymers are discussed in Chapters 3, 5, 7, 9, 10. Spectroscopy is integrated into the teaching of quantum theory. In the matter of choice of topical material and examples, physical chemistry is so broad that only an encyclopedia could cover all of the material that is interesting, relevant, and important. The choices are somewhat arbitrary, so, since I was the author, I made them. Generally, I tried to choose topics and applications that, in my judgment, would best fit in with the principal subject of the chapter and that would best provide an illustration of the theoretical principles the student could follow at that point. It is likely that you may disagree in some cases, or that your favorite topic has been omitted—on the other hand, I'm certain you will find some way to put it back in. This book is intended to be a teaching text, not an encyclopedia, and the students should not be left to think that any one book contains all they will need to know about physical chemistry; they should be encouraged to explore other resources. A major objective in this book is developing the students' vocabulary so that they can read more specialized books in the various areas of physical chemistry.

The coverage of quantum mechanics (Chapters 11 to 14) may, at first glance, appear to be excessively difficult and deep. However, closer inspection will reveal that many derivations are worked out in detail that in many other texts is left to the imagination of the student or to the travail of the instructor. The principal difficulty that students find with this approach is its linearity — each chapter must be understood well before the next one makes much sense. You can help them with this by encouraging them to review frequently; for example, it is a good idea to reread parts of Chapter 11 while studying Chapters 12 and 13. There has been a deliberate effort to limit the level of mathematics in these chapters. Operator algebra is used because it is relatively easy to teach and learn at this level. Differential equations and matrix algebra are avoided as much as possible.

With electronic calculators, not to mention computers, today's students have more computational power available than G. N. Lewis ever dreamed of — yet few of them know how to use this power effectively. For that reason, this text emphasizes numerical analysis to an unusual degree. Throughout, the student is encouraged, even required, to use techniques such as numerical integration, differentiation, root finding, and linear regression. These techniques are easily implemented with pocket calculators costing scarcely more than this book. Since they are used in a number of different chapters, they are discussed together in a general way in Appendix I. The use of numerical methods together with "real" data is, I believe, helpful in showing the student the relevance of mathematical formulas and abstract functions to experimental results. Particularly in thermodynamics, this approach permits the use of realistic models and avoids leaving the student under the impression that the world is an ideal gas.

Although the problems in this text take full advantage of the capabilities of the electronic calculator, they do not take into account the now ubiquitous microcomputer. This deficiency will be remedied by a separate volume, *The Microcomputer in Physical Chemistry,* which will be published in early 1985. A *Solutions Manual* with worked out solutions to most of the problems is also available.

Acknowledgments

Two people deserve credit for having encouraged me to write this book — my wife Carol and my friend Cecil. Far be it from me to choose between two redheads, so let them share the credit equally; however, it was Carol who had to bear the brunt of the execution, and I am most grateful for her patience and help. Also, major credit should go to the students of the University of Delaware who, through their insistent curiosity and probing questions, made me learn the subject better. Those who struggled through the early drafts deserve special mention. In the line of redheads, I would also like to thank Don Wetlaufer for his support and encouragement throughout the trying period in which this book was written.

A number of colleagues and students have critically read parts of the manuscript, made useful suggestions, and gratuitously corrected my errors. In particular, I would like to thank Cecil Dybowski, Bob Wood, Don Wetlaufer, Doug Ridge, and students Seth Digel, Eric Scharpf, John Townsend, Suzie Kretchmar, Ellen Yurek, and John Nahay. Many others contributed to a lesser extent, and I thank them together. Despite their efforts, I am certain that some errors remain, and can only hope that they are minor. The manuscript was typed efficiently and accurately by Rose O'Neill.

The referees also made numerous useful suggestions. They include Thomas J. Murphy, University of Maryland; David W. Pratt, University of Pittsburgh; Roland Roskos, University of Wisconsin, La Crosse; Don Secrest, University of Illinois at Urbana-Champaign; C. Daniel Cornwell, University of Wisconsin—Madison; Clifford E. Dykstra, University of Illinois at Urbana-Champaign; Sherril D. Christian, University of Oklahoma; Charles E. Reid, University of Florida; Charles S. Johnson, University of North Carolina at Chapel Hill; Richard L. Snow, Brigham Young University; Dewey Carpenter, Louisiana State University; Peter C. Jordan, Brandeis; Alan G. Marshall, Ohio State University.

Finally, when I began this book, Jim Moore told me to be sure to mention the parachor—I just did.

Physical chemistry is not a variety of chemistry; it is the chemistry of the future.

–Wilhelm Ostwald

. . . lecture courses that consisted of descriptive facts and recipes for separations bored me; my desire was to understand phenomena. I discovered physical chemistry on my own and was inspired.

–Joel H. Hildebrand

To the Student

Physical chemistry, like a table with four legs, is built upon four major theoretical principles; thermodynamics, kinetics (or, more generally, transport processes), quantum mechanics, and statistical mechanics. This is not all of physical chemistry, no more than a table is all legs. Physical chemistry is a widely diverse subject that cannot be summarized adequately in any brief definition; certainly there are important parts of physical chemistry that do not fit neatly into this quadrivium. But it is not a bad place to start, and certainly no education in the subject can fail to provide some foundation in each of these four areas. However, they do not, in this or any other text, receive equal time; usually thermodynamics and quantum theory, in that order, are covered more thoroughly than the other two subjects. This is because these two are, to some extent, prerequisite to kinetics and statistical mechanics. This emphasis does not reflect the relative importance of these areas within physical chemistry, let alone within chemistry as a whole, but only the exigencies of teaching an introductory course.

But a first course in physical chemistry is more than an introduction to four, or a hundred subjects. It is, in addition, a course on mathematical problem solving, with emphasis on chemical problems. This is a two-edged sword. Mathematics is the feature of this course that, for the majority of students, is the most difficult—and is in no small part responsible for the frightful reputation of physical chemistry courses in general. It is also the part of the course that is of greatest value—you may never need to integrate a heat capacity, measure a reaction rate, or analyze a spectrum, but the experience in quantitative problem solving will be of constant value.

But how does one learn to solve problems? There are some who feel that this is a subject in itself that can be taught in the abstract; this area is called *heuristics* (see, for example, G. Polya, "How to Solve It," 1957: Garden City, New York, Doubleday & Company, Inc.). Be that as it may, it is certain that problem solving is something that can also be learned by example and by practice. This book provides numerous worked-out examples to introduce you to the subject; these should be studied carefully as you encounter them in the text. The exercises in the text and the problems at the end of each chapter serve two purposes: to make you think about and review the material just covered and to provide you with practice in problem solving. You may have available worked-out solutions to some (or perhaps all) of these problems — but beware: You cannot learn to swim by watching, you must get into the water, and you cannot learn physical chemistry by reading other people's problem solutions. The effort in solving them yourself may be ten times greater, but the benefit will increase in proportion. It can be stated as a certainty that, as this text is written, if you read the words without doing the problems, you will receive only half of what is intended.

In connection with the question of mathematics, there are appendices at the end of the book covering a number of areas that cause problems for many students. You should, before beginning, familiarize yourself with what is there, and then use them as needed. When an appendix is referred to in the text, you should, unless you are confident of your background in that area, review the appropriate material before proceeding.

Good luck!

Contents

Let curious minds
Who would the air inspect,
On its elastic energy reflect.
–Sir Richard Blackmore (1712)

1
Properties of Matter

In large part, "properties of matter" is the subject of this entire book. This chapter broaches several important fundamentals. It also introduces a number of basic concepts, models, and techniques that will be used and, in some cases, developed further in subsequent chapters.

The properties of matter may be discussed on two levels, the macroscopic and the microscopic. At the *microscopic* level, we examine the properties of atoms and molecules such as molecular size, shape, velocity, momentum, and intermolecular forces. At the *macroscopic* level we investigate properties of bulk matter, such as temperature, pressure, or viscosity, which may have no meaning whatever at the atomic-molecular level. Making the connection between microscopic and macroscopic is a major mission for physical chemistry. In this book we shall first be concerned mostly with macroscopic properties; then, beginning with Chapter 11, we look into the properties of atoms and molecules. Even when we are focusing on macroscopic properties, however, the microscopic picture will never be far in the background, since it can give us an insight into the "why" in the behavior of nature which would otherwise be unavailable.

1.1 Equations of State

The macroscopic properties of matter may be classified as either extensive or intensive. *Extensive* properties are proportional to the amount of material — for example: mass (W), volume (V), number of moles (n), heat capacity (C). In subsequent chapters we shall encounter many other extensive properties, such as energy and entropy.

Intensive properties depend on the nature of the material but not on the amount. Temperature and pressure are the most obvious examples, but there are many others, including viscosity, thermal conductivity, electrical conductivity, dielectric constant, magnetic susceptibility, and compressibility. In addition, any ratio of extensive properties is intensive; some important examples include density ($\rho = W/V$), specific volume ($v = V/W$), molar volume ($V_m = V/n$), and specific heat (C/W).

These properties are interrelated; their mutual relationships can be expressed as a functional dependence in the mathematical sense, as, for example, $\rho(T)$, the "density as a function of temperature." (It would probably be useful to read the first section of Appendix I at this point.) In fact, for a pure, homogeneous material, only two intensive variables can be independent; the remaining variables must then be a function of these two. ["Pure" means that the entire material has a single chemical identity; by chemical standards, water is a pure substance and not a mixture of hydrogen and oxygen (let alone, a mixture of protons, neutrons, electrons, and so on). "Homogeneous" means that the entire material is uniform throughout with respect to all intensive properties; this implies that there is only one physical phase — solid, liquid, or vapor.]

This idea is expressed in the concept of the *state* of a material; we define the state of a pure, homogeneous material by giving the values of *any* two intensive properties (which then become the *independent variables*). The functional dependence of any