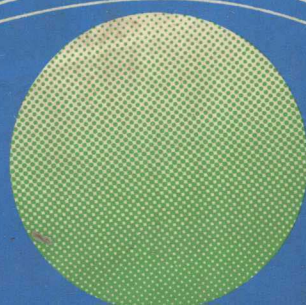
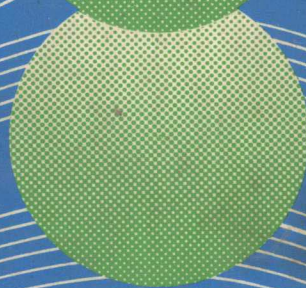
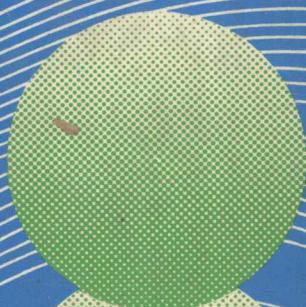
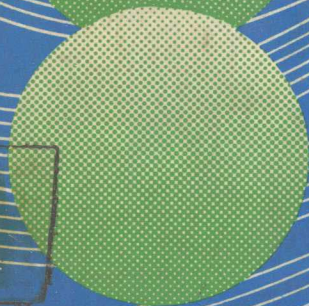
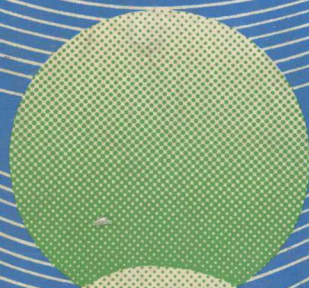
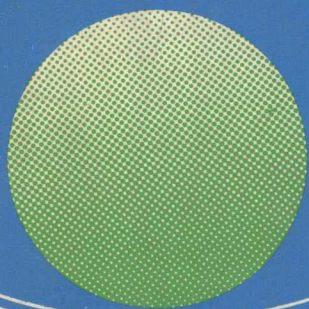


Physical Chemistry with Applications to Biological Systems

Second Edition

Raymond Chang



PHYSICAL CHEMISTRY

**with Applications to
Biological Systems**

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Preface

This text is designed for use in a one-semester or one-quarter physical chemistry course at the junior level. In writing the second edition, I have retained the original aim of placing the emphasis on understanding the physical concepts rather than on precise mathematical development or on actual experimental detail. The principles of physical chemistry are presented from the viewpoint of their applications to chemical and biochemical problems. The text is also suitable for a full-year physical chemistry course where a more rigorous text would be inappropriate.

Many topics from the first edition have been extensively rewritten and a number of changes, corrections, and additions have been made. For example, the chapter on thermodynamics has been expanded into three separate chapters. In response to the request of many instructors, I have altered the sequence of the chapters so that thermodynamics and related material now precede chemical bonding and spectroscopy. The number of end-of-chapter problems has been more than doubled. These problems are divided into two categories: those marked with a star are more challenging, while the unmarked ones are relatively straightforward. In most chapters the references have been expanded to include more up-to-date articles and texts. A new feature in this edition is the appendices at the end of some chapters, which provide mathematical derivations of equations and/or extensions of material discussed in the chapters.

The case of SI units versus CGS units has not changed noticeably since the first edition. For this reason, I have decided to continue with the practice of presenting most physical quantities in both units. An important change is the replacement of angstrom (\AA) with nanometer (nm) for wavelength.

I have greatly benefited from the suggestions and criticisms of many instructors who have used the text, as well as a number of reviewers and colleagues. In particular I would like to thank the following individuals: Jesse S. Binford, Jr. (University of South Florida), Robert E. Blankenship (Amherst College), Donald Boerth (Southeastern Massachusetts University), Luther K.

Brice, Jr. (Virginia Polytechnic Institute and State University), B. J. Chapman (University of Southampton, England), John N. Cooper (Bucknell University), Allen A. Denio (University of Delaware), George E. Ewing (Indiana University), James Franzen (University of Pittsburgh), Chien Ho (Carnegie-Mellon University), Gary W. Hunt (Shorter College), Richard S. Myers (Delta State University), Gerald Nagahashi (Williams College), Richard F. Olivo (Smith College), Reeves B. Perry (Southwest Texas State University), Douglas D. Radtke (University of Wisconsin), John S. Ricci, Jr. (Williams College), and Edmund C. Shearer (Fort Hays State University). Thanks are also due Bolesh J. Skutnik (Fairfield University) and William J. Zaks (Williams College) for help in checking the accuracy of many problems.

Finally, I would like to express my appreciation to Gregory W. Payne, the chemistry editor at Macmillan, for his assistance in general; to Elaine W. Wetterau for editorial supervision; and to Eileen Sprague and Holly Andrews for typing the manuscript.

I welcome comments and suggestions from readers.

R. C.

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1

Introduction

And it's hard, and it's hard, ain't it hard, good Lord.
Woody Guthrie*

Nature of Physical Chemistry 1.1

Physical chemistry can be described as a set of characteristically quantitative approaches to the study of various chemical problems. A physical chemist is a person who seeks to predict chemical events using certain models and postulates. Because the problems encountered are often both diversified and complex, a number of different approaches must be employed. For example, in the study of thermodynamics and rates of chemical reactions, we employ the phenomenological, macroscopic approach. On the other hand, a microscopic, molecular approach is required for an understanding of the kinetic behavior of molecules and reaction mechanism. Ideally, it would be best to study all the phenomena at the molecular level, because it is here that one learns what really occurs. Now, however, this is not possible—our knowledge of atoms and molecules is neither extensive enough nor thorough enough. Fortunately, there are some areas in which we are beginning to have good, semiquantitative understanding. As each topic is developed, it is well to keep in mind the scope and limitation of the approaches involved.

To see how physiochemical principles can be applied to study a biochemical system, let us consider the binding of oxygen with hemoglobin. This is one of the most important biochemical reactions and may be the most extensively studied. Hemoglobin is a protein molecule that has a molecular mass of about 65,000. The molecule contains four subunits, made up of two α chains (141 amino acids each) and two β chains (146 amino acids each). Each of the chains contains a heme group to which an oxygen molecule can be bound. The main function of hemoglobin is to carry oxygen in the blood from the lungs to the tissues, where it unloads the oxygen molecules to myoglobin.

* "Hard Ain't It Hard." Words and Music by Woody Guthrie. TRO—© Copyright 1952 Ludlow Music, Inc., New York, N.Y. Used by permission.

Myoglobin, which possesses only one polypeptide chain (153 amino acids) and one heme group, stores oxygen for metabolic processes.

The hemoglobin system has many interesting aspects. To begin with, we are interested in the size, shape, and detailed structure of the molecule. A number of techniques that have been developed in recent years, such as viscosity measurement, electrophoresis, ultracentrifugation, and light scattering, enable us to measure the molecular mass and/or to estimate the shape of macromolecules. The best technique for determining structure is X-ray diffraction, but this can be quite difficult. Nevertheless, the complete or almost complete structure of a number of protein molecules has been determined by the X-ray method. Two such molecules are myoglobin and hemoglobin. A detailed understanding of the three-dimensional structure of a protein molecule is perhaps the single most important factor in revealing the secrets of its various functions.

The next questions concern the binding of oxygen. To understand how oxygen and other molecules, such as carbon monoxide and nitric oxide, bind to the heme group, we need to investigate the coordination chemistry of transition-metal ions in general and complexes of iron in particular. For example, it is important to know which orbitals are involved in the complex, as well as the reasons why the binding constant for CO is some 200 to 300 times stronger than that for oxygen. Knowledge of the molecular orbitals involved will also help to explain the spectral properties.

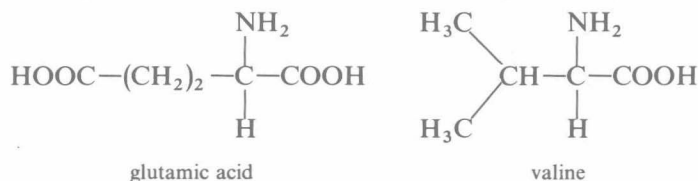
A very important phenomenon is the cooperative nature of binding. It was noticed many years ago that oxygen molecules did not bind to the four heme groups independently; rather, the presence of the first molecule facilitates the binding of the second, and so on. The biological function of cooperative binding is that it results in the more efficient transport and release of oxygen. The kinetic and thermodynamic details of this phenomenon have been successfully accounted for, at least in broad outline, by current theories based on the allosteric model, which is also applicable to many other regulatory enzymes.

Another function of hemoglobin is the transportation of carbon dioxide from the tissues to the lungs. The pH dependence of the oxygen equilibrium, the Bohr effect, is coupled to this role. The maintenance of proper physiological pH is of paramount importance, because the function and efficiency of most proteins and enzymes depend critically on the hydrogen-ion concentration. The CO_2 - O_2 transport process in blood is buffered by the bicarbonate-carbonic acid system. Being amphoteric,* hemoglobin itself can also act as a buffer. Here the problem is dealt with in terms of acid-base equilibria.

Finally, we may raise the following point: Of the very large number of possible structures that a molecule this size can assume, why is it that only one predominant structure is observed for hemoglobin? We must realize that in addition to the normal chemical bonds, many other types of molecular interaction, such as electrostatic forces, hydrogen bonding, and van der Waals forces, are also present. In principle, a macromolecule can fold up in many different ways; the native conformation represents the minimum-energy structure or is in the neighborhood of the minimum-energy structure. The specificity in binding depends precisely on the environment at and near the active site which is maintained by the rest of the three-dimensional molecule.

* An amphoteric substance can react either as an acid or as a base, depending on reaction conditions.

To appreciate how delicate the balance of these forces must be in some cases, consider the replacement of a glutamic acid by valine in the β chains:



This seemingly small alternation is sufficient to result in a significant conformational change—an increase in the attraction between protein molecules, resulting in polymerization. Insoluble polymers so formed will then distort red blood cells into a sickle shape, causing the disease that we call sickle-cell anemia.

All these problems can be understood, at least in theory, by application of the principles of physical chemistry. Obviously, very different approaches are needed if a thorough investigation of the chemistry of hemoglobin is desired. We could easily have chosen another example, such as photosynthesis, to demonstrate our point. It is not the purpose of this text to present a detailed explanation for each of the phenomena described above; however, the hemoglobin example serves to illustrate that a student must first understand the basic principles of physical chemistry before embarking on the study of many exciting biochemical phenomena.

Units 1.2

Students are frequently confused by the variety of units used in physical chemistry. Since people in vastly different disciplines have contributed to the development of this science, it is not surprising that different units are often used to express the same quantity. A case in point relates to the quantity of heat, which can be expressed in terms of calories, joules, or British thermal units (Btu). To add to the confusion, the calorie unit used to measure the fuel value of food is 1000 times greater than that for measuring bond energies and heats of chemical reactions.

The CGS (centimeter–gram–second) system, which was developed in France after the French Revolution, has been widely adopted throughout the world, with the notable exception of the United States. The advantage of metric units lies in their convenience and simplicity, in contrast to such native units as the foot and the pound. Physicists, on the other hand, have long favored the MKS (meter–kilogram–second) system.

In 1960, the General Conference of Weights and Measures, an international authority on units, agreed to adopt the International System of Units (SI). This system has now been endorsed by scientists in many countries. The advantage of the SI system is that many of the units employed are derivable from natural constants. For example, the CGS unit of length is the meter (strictly the centimeter; 1 meter is exactly equal to 100 cm), which is defined to be the distance between two marked lines on a bar kept in Sèvres, near Paris. On the other hand, the SI system defines meter as the length equal to 1,650,763.73 wavelengths of radiation corresponding to a particular electronic transition from the 6d to the 5p orbital in krypton. The unit of time, second, is defined as 9,192,631,770 cycles of the radiation associated with a certain elec-