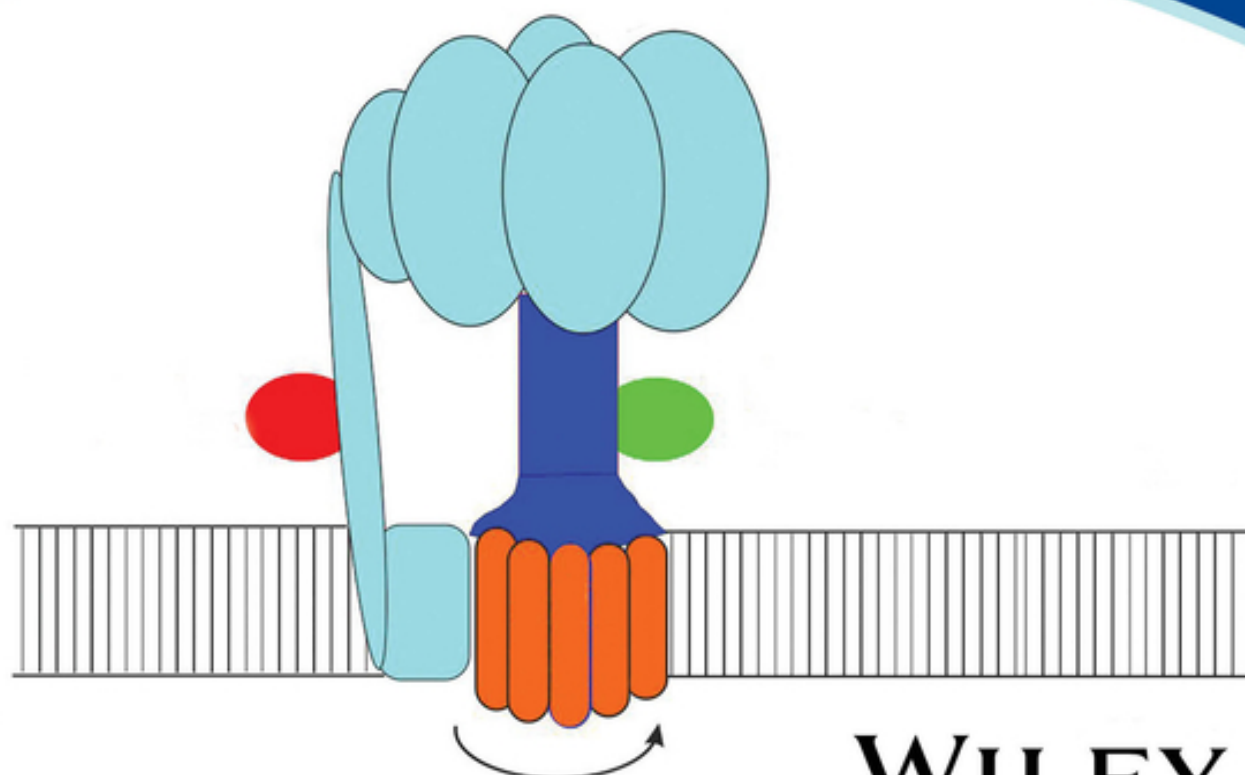


HANS KUHN  
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PRINCIPLES OF  
**PHYSICAL  
CHEMISTRY**

THIRD EDITION



**WILEY**



## Principles of Physical Chemistry



# Principles of Physical Chemistry

Third Edition

*Edited by Hans Kuhn, David H. Waldeck, and Horst-Dieter Försterling*

**WILEY**

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## Preface Third Edition

Chemistry comprises the structure, interaction, and transformation of atoms and their assemblies into molecules, solids, and supramolecular structures. With the notable exception of nuclear chemistry, chemists regard matter as a collective interaction of atoms and molecules, and consider the macroscopic properties of matter to arise from a few fundamental principles. In this book on physical chemistry, we emphasize this view by first exploring the nature of atoms and chemical bonds, and then proceeding to a discussion of complex molecules and, subsequently, to more and more complex forms of matter. This sequence of topics is chosen to aid the student in developing a systematic and coherent understanding of the subject. Because it proceeds from the fundamental principles which govern the arrangement of electrons and nuclei into atoms and molecules, this textbook in physical chemistry should be accessible to biologists, chemical engineers, materials scientists, and physicists, as well as chemists.

As a discipline physical chemistry attempts to understand chemistry, in all its complexity, as a consequence of a few fundamental physical laws. This fascinating enterprise includes chemical processes in physics, biology, and engineering, as well. On a deeper level, physical chemistry aims to understand and quantify the tremendous variety that matter takes in our world, from individual atoms to complex life forms. The unifying nature of physical chemistry is emphasized by the book's organization—beginning with atoms and molecules, proceeding to molecular assemblies of increasing complexity, and ending with the emergence of matter that carries information, i.e., the origin of life, a physicochemical process of unique importance. The aim is to show the broad scope and coherence of physical chemistry.

The book begins with the most basic and central question in physical chemistry, “Why do atoms and molecules form from a collection of electrons and nuclei?” The answer to this question requires a fundamentally different way of thinking about the world than we are used to from our common human experiences; and we need the fascinating and strange predictions of quantum mechanics to guide us. In Chapter 1 we consider some astonishing experimental facts that require this new way of thinking, and we show how these facts can be considered to arise from a few fundamental postulates. On this basis Chapter 2 explains the existence of the simplest atom (hydrogen atom H) and the simplest molecule (hydrogen molecule ion  $\text{H}_2^+$ ) in terms of a simple model for an electron confined to a region of space (particle-in-a-box model). Next the book explores the quantum mechanical basis of chemical bonding (Chapters 3–8 and 13) and how we use light to probe molecular structure, a field of study called spectroscopy (Chapters 9–12). We emphasize  $\pi$  electron systems in Chapters 8–10, because they illustrate particularly well how one can use simple theoretical models to understand molecular properties. Throughout these chapters the particle-in-a-box model is used as a touchstone to reinforce and develop the understanding of chemical bonding.

Although some modern experimental methods can probe the properties of individual atoms and molecules, most experiments are performed with collections of atoms and/or molecules. Chapter 13 provides an introduction and overview of some essential aspects of how to think about such collections. This part considers a second fundamental question in physical chemistry, “What is the connection between molecular (or atomic) properties and the macroscopic properties of matter?” Chapters 14–18 show how our atomistic view of matter can be used to predict the properties of a large collection of molecules quantitatively in terms of macroscopic system variables, such as temperature and pressure. In order to present this description most clearly we use simplified models that ignore intermolecular forces, e.g., the ideal gas law. With this fundamental understanding in hand, Chapters 19–21 show how these ideas can be extended to macroscopic chemical systems in which the intermolecular forces are included. Chapters 22 and 23 apply these developments to chemical equilibria in aqueous solutions, biosystems, and electrochemistry.

“How do molecules and atoms (reactants) transform into different molecules and atoms (products)?” For many practicing chemists, this question is the most exciting part of chemistry. We consider chemical reaction rates and reaction dynamics, in Chapters 24 and 25. While much progress has been made in providing a quantitatively accurate picture of reaction dynamics, this area remains a frontier of physical chemistry.

The final chapters of the book address the question, “Why do molecules aggregate into organized assemblies and how does the organization of molecules give rise to new properties?” The treatment of organized systems of molecules, including supramolecular machines, is a fast developing subject which lies at the nexus of biology, chemistry, and physics. Methods and ideas from physical chemistry are a powerful approach to exploring this current frontier, and we develop some of the primary physicochemical considerations for understanding organized molecular assemblies in Chapters 26–29. Chapters 26 (macromolecules) and 27 (interfaces) illustrate different ways of organizing molecules, or molecular subunits, in space. Chapter 28 describes principles for organizing functional molecules to create new behaviors that are characteristic of the supramolecular assembly, distinct from the individual molecule behaviors, and introduces this fascinating and dramatically growing field by discussing selected examples. This part of the book culminates in the final chapter which considers the basic processes in the origin of life and explores some of the underlying physicochemical principles that are important for chemical and biological evolution.

The book aims to develop an intuition for how research is performed by presenting many exciting original ideas and providing instructive examples to inspire thinking. Studying typical examples is an excellent opportunity for learning how to design simple experiments and theoretical models. For these reasons, original research findings and current research findings are included in the examples or as part of problems and exercises to be worked. Rather than always aiming for rigor, we use simplified models and approximations that promote intuition and guide one’s thinking at the boundaries of knowledge. Inventing idealized theoretical descriptions of real situations is crucial for understanding new research and developing new knowledge. Lastly, we recommend that you consider the text as a tool through which you can explore and discover the rich field of physical chemistry.

Although the presentation of subject matter is logical and hierarchical, the chapters in the book can be used in almost any order because they are relatively self-contained. The book starts with a simplified introduction to quantum mechanics because it is so important in all parts of physical chemistry and is essential for understanding the nature of the chemical bond. Nevertheless, students in chemistry and biochemistry are trained to think in terms of chemical bonds and processes at the atomic level in their first year classes, so many of the more advanced topics can be explored without the full rigor of the early chapters. Where possible, the logical sequence in a given chapter is constructed to evolve from the more basic and simple picture to a more sophisticated treatment for the more experienced students. If such a section is too difficult in a first reading to study with excitement, consider skipping it and returning at a later stage. Although the sequence of chapters in the book need not determine the sequence of topics in a physical chemistry lecture course, the organization of the chapters in the book and its broad scope aims to emphasize the logical progression and unity of physical chemistry. Whatever order of topics is chosen, it is important to appreciate the unified nature of physical chemistry.

In order to save space in the printed book, part of the material is only provided electronically. These are most of the foundations (containing more basic derivations) and justifications (containing detailed calculations), and the computational exercises (Fortran, MathCad, and Mathematica).

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We dedicate this book to Hans Kuhn (1919–2012). We have made every effort to present physical chemistry with Hans' spirit of curiosity, enthusiasm, and incisive explanation. As a chemistry student, H.D.F. attended the inspiring lectures on physical chemistry held by Hans since 1953, guided by the idea that quantum theory is the key to understand the whole field of physical chemistry. Moreover, using simplifications and instructive models rather than complicated formalisms, his lectures became a highlight among the chemistry students. Later, these lectures gave rise to a textbook on experimental courses<sup>1</sup> and an introduction into the basic ideas of physical chemistry<sup>2</sup>. Finally, after Hans' retirement and a visit of H.D.F. to his home in Switzerland, on a walk through a wonderful small valley, the idea of a more comprehensive textbook on physical chemistry was born, leading to the first edition of this book. During all the time of this cooperation, H.D.F. enjoyed the hospitality and patience of Hans' family, first of all of his wife Elsi, when discussing the topics of the book in his home, mostly working together from early in the morning until late in the evening.

1 H.D. Försterling, H. Kuhn, *Physikalische Chemie in Experimenten, Ein Praktikum*, Verlag Chemie, Weinheim 1971.

2 H.D. Försterling, H. Kuhn, *Moleküle und Molekülanhäufungen*, Springer Verlag Berlin, Heidelberg, New York 1983.

