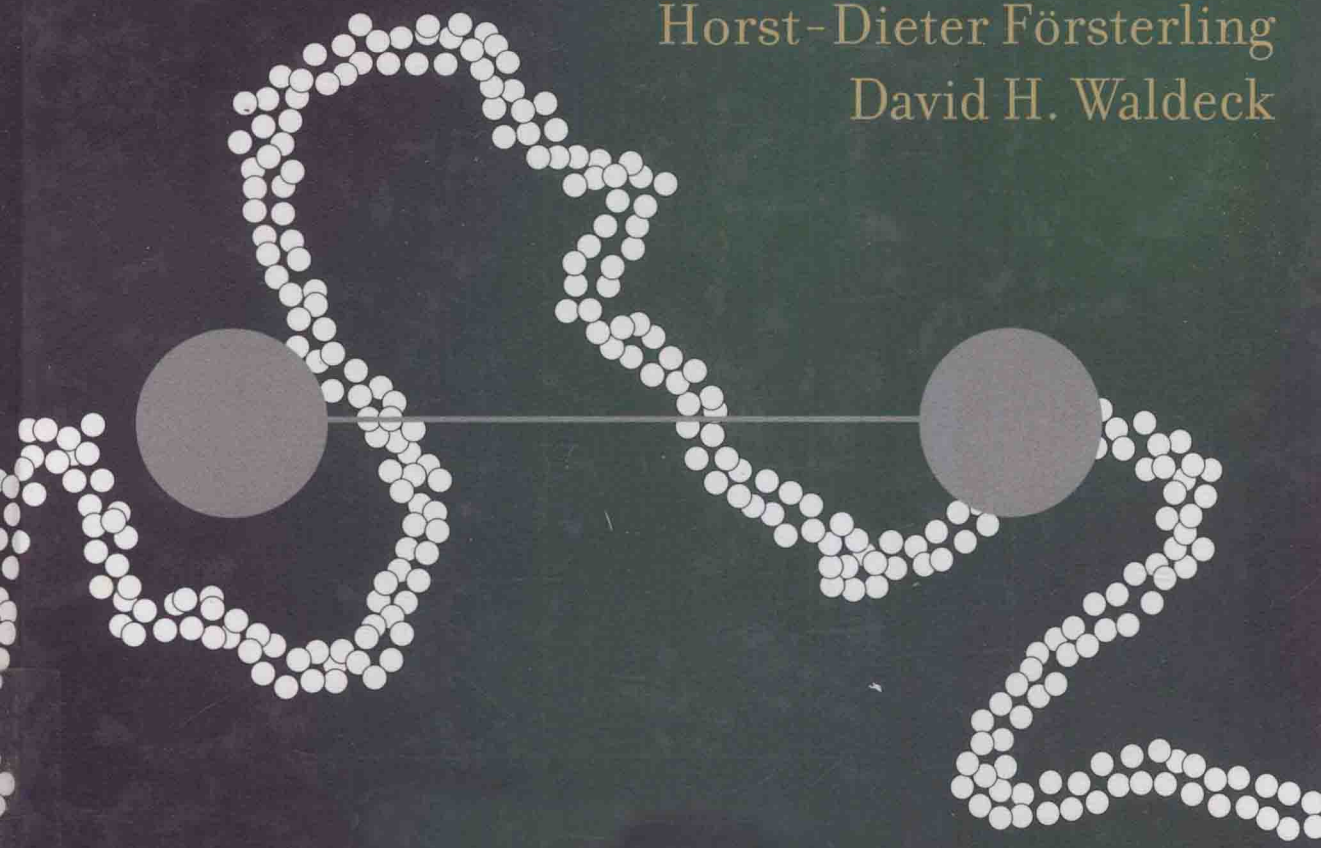
SECOND EDITION

PRINCIPLES OF PHYSICAL CHEMISTRY

Hans Kuhn
Horst-Dieter Försterling
David H. Waldeck



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Preface

The interplay of atoms and molecules produces the rich and diverse phenomena of our world, from the inanimate to the animate. As a discipline physical chemistry explains these phenomena in terms of a few fundamental principles. Because of this broad scope, this physical chemistry textbook is addressed equally to chemists, polymer chemists, biologists, chemical engineers, material scientists, and physicists. To emphasize the unified nature of the discipline, the book treats atoms and chemical bonds first, followed by a discussion of how these building blocks lead to molecules and, subsequently, to more and more complex manifestations of matter, ending with the structure of self-propagating matter that carries information (life). This logical structure guides and motivates the student to develop a systematic understanding of the subject.

The self-contained chapters allow the course to proceed in almost any order (see "Introduction"). Simplified theoretical models illustrate many of the important concepts. The book starts with a simple introduction to quantum mechanics that aims to develop intuition for this somewhat counterintuitive subject. We feel that an early confrontation with quantum mechanics is important because quantum mechanics is needed throughout physical chemistry and explains the nature of the chemical bond. In this way students will appreciate the origins of simplified bonding models that are used in biochemistry, inorganic chemistry, organic chemistry, and materials chemistry. The need and benefit of making key approximations is shown further in the description of molecular assemblies and macroscopic systems. By emphasizing the atomistic approach to matter, the origin of thermodynamic quantities (such as heat capacity) in atomic and molecular properties and the understanding of kinetics and its parameters (such as the rate constant) in terms of molecular properties becomes apparent.

Inventing idealized theoretical descriptions of real situations is crucial for describing complex organized systems, and ingenious experiments are of particular importance in modern physical chemistry. In order to illustrate this feature of the scientific process, we emphasize examples that show how to design simple experiments and theoretical models, rather than provide a full survey of this vast field. Nevertheless, details of the experimental methods must be left in the background. We emphasize selected cases in order to focus on fundamental aspects, for example, π electron systems are discussed in more detail than other subjects because they illustrate the power of simple theoretical models. Beyond illustrating this approach in well understood areas, we show the student that physical chemistry is a living and rapidly growing field of study. To this end, we treat organized systems of molecules, including supramolecular machines. We attempt to introduce the student to this fascinating and dramatically growing field in physical chemistry by discussing selected examples. The final chapter is reserved for the uniquely important example of understanding some of the basic physical processes underlying the origin of life.

This second edition (with David H. Waldeck as a coauthor) differs from the first edition by changes throughout the text, improvement of the organization, and the inclusion of new topics. Some chapters have been split and new ones added so that the number of chapters increased from 24 to 29. In the first 13 chapters, changes include a more formal presentation

of quantum-mechanical principles, a more modern development of molecular orbital theory, a more extensive discussion of the spectroscopy of polyatomic molecules, and the inclusion of new material discussing quantum wires, soliton conductors, and semiconductors. The chapters on thermodynamic assemblies (Chapters 14 to 23) were reorganized and expanded to include formal thermodynamics with applications to real gases, real solutions, and an expanded discussion of electrochemistry. While the first edition had one chapter on chemical change (reaction kinetics), this edition has two such chapters (Chapters 24 and 25) and provides a more extensive description of transition states and reaction dynamics. Chapters 26 to 29, develop a systematic and principles based understanding of macromolecules, organized molecular assemblies, supramolecular machines, and the origin of life. These chapters include new topics and applications of current research.

In order to keep the book length manageable, part of the material is provided on the accompanying CD. These are the foundations (fundamental derivations and proofs that are necessary for a graduate level course), the justifications (containing detailed calculations), the problems and exercises (a separate printed solution manual is available), searchable data tables and program modules for MathCAD.

HANS KUHN, HORST-DIETER FÖRSTERLING, DAVID. H. WALDECK
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David Waldeck thanks his wife, Janet, and children, Aaron and Anna, for their support and understanding during the five years of this endeavor.

Authors Biography

HANS KUHN, Dr. phil, became a Professor at the University of Basel in 1951. From 1953–1970 he was on the chair of the Institute of Physical Chemistry at the Philipps-University at Marburg, and in 1970 he became Director at the Max Planck Institute for Biophysical Chemistry (Karl-Friedrich-Bonhoeffer-Institut) until he retired in 1985. Professor Kuhn has published papers in such fields as polymer science, quantum chemistry, organized molecular assemblies, and the origin of life.

HORST-DIETER FÖRSTERLING, Dr. phil., was a Professor in the Department of Physical Chemistry at the Philipps-University of Marburg from 1972 until his retirement in 1999. Professor Försterling has taught physical chemistry courses and laboratory courses at all levels, including graduate and advanced graduate courses in spectroscopy, statistical mechanics, reaction kinetics, and quantum mechanics. His research interests include quantum chemistry, reaction mechanisms, oscillating chemical reactions, and chemical waves.

DAVID H. WALDECK, PhD, is Professor and Chair in the Department of Chemistry at the University of Pittsburgh. Professor Waldeck has taught chemistry courses at all levels, including graduate and advanced graduate courses in statistical mechanics, reaction dynamics, and quantum mechanics. His research interests include condensed-phase reaction dynamics (homogeneous and heterogeneous), solute-solvent interactions (structural and dynamical characteristics), relaxation processes in solids, and electron transport at the nanometer scale.

List of Symbols

$P^{\ominus}$	standard pressure = 1 bar
$c^{\ominus}$	standard concentration = 1 mol L^{-1}
$\hat{P}$	$= P/P^{\ominus}$
$\hat{c}$	$= c/c^{\ominus}$
$\boldsymbol{n}$	amount of substance
$U^{\ominus}$, $H^{\ominus}$	U, H under standard conditions
$S^{\ominus}$	S under standard conditions
$G^{\ominus}$	G under standard conditions
$C_V^{\ominus}$, $C_P^{\ominus}$	C_V, C_P under standard conditions
$\Delta_f H$	molar enthalpy of formation
$\Delta_f G$	molar Gibbs energy of formation
$\Delta_r H$	molar change of H in reaction
$\Delta_r S$	molar change of S in reaction
$\Delta_r G$	molar change of G in reaction
$\Delta_{vap} H$	molar enthalpy of evaporation
$\Delta_{fus} H$	molar enthalpy of melting
$C_{V,m}$	molar heat capacity at constant volume
$C_{P,m}$	molar heat capacity at constant pressure
$\hat{n}$	refractive index
$\hat{\varepsilon}$	relative permittivity

Note that the symbols $\hat{P}$ and $\hat{c}$ denote dimensionless quantities: $\hat{P} = P/P^{\ominus}$, $\hat{c} = c/c^{\ominus}$. The symbols $\hat{n}$ and $\hat{\varepsilon}$ are used for the refractive index and the relative permittivity.

a	coefficient
a	activity
a	distance
a_0	Bohr radius
b	coefficient
b	contour length per monomer unit
c	coefficient
c_0	speed of light in vacuum
d, d_0	distance, bond length
e	elementary charge
f	force
g	number of quantum states
h	Planck's constant
$\hbar = h/(2\pi)$	
h	distance between chain ends
i, j	indices