

Fifth Edition

PHYSICAL CHEMISTRY

An abstract geometric design on the book cover. It features a large, irregular shape on the left side, colored in a gradient from red at the top to yellow at the bottom. This shape is overlaid with a network of thin, white, curved lines that intersect to form a grid-like pattern. The background of the entire cover is a solid dark blue.

Peter Atkins

PHYSICAL CHEMISTRY

FIFTH EDITION

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The cover as illustrated by Ian Worpole, is based on Peter Atkins' representation of the amplitude of the antibonding orbital formed from the overlap of two H1s orbitals.

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Preface

A fifth edition of a text has all the advantages of maturity: it represents the accumulated wisdom of all readers who have taken the trouble to suggest variations in former editions and ideas on organization and content. At the same time it stands in danger of succumbing, perhaps unwittingly, to one of the problems of maturity: an unwillingness to change. Although the advantages of maturity will be perceived throughout the text, I hope the danger has been avoided. From their familiarity with successive editions, users will be aware that in each case I have provided not a slight tinkering with the text but a wholesale rewrite. This edition is no exception, for yet again I have considered every word. Moreover, to quash the charge of sameness, I have introduced a number of innovations in this text which I hope will improve its pedagogical value.

The most obvious new feature of the text is the use of a second colour. It has been considered for some time now that students who are introduced to chemistry through the glitter of freshman texts and their equivalents in various parts of the world, are suddenly confronted with grey again when they move on to more advanced courses. The books look dull after encounters with the expensive texts of introductory chemistry. Partly to offset this attitude and to make the text look more lively and enticing, I have redrawn all the art with the systematic use of a second colour. Broadly speaking, I have used the second colour for emphasis, or for an abstract aspect of a diagram (for example, showing the symmetry axis of an object). Only rarely is it used just for decoration. The use of colour entailed redrawing nearly 1000 illustrations, and I have taken the opportunity to do so in a more consistent, modern style using the electronic aids that are now available.

The second major innovation is the use of *Justifications*. I explored the use of this device in my *Elements of physical chemistry*, where it proved

popular, and have made extensive use of *Justifications* in this text. Briefly, the format of a *Justification* is that a conclusion (typically a mathematical formula) is stated in the text, and the derivation then follows the statement of the result. There are several advantages in this approach. One is that a result is immediately presented, and not lost in a thicket of other equations. Another is that a *Justification* captures the manner in which lectures are often given, where the *result* is presented and discussed, and the detailed derivation is left to private study. Thirdly, *Justifications* allow the text to be used at different levels: some students will find that they need not grapple with some derivations, or find that they can return to them later when their ideas have matured. The *Justifications* help to make the subject more digestible and accessible without damaging the authoritative completeness of the text. Some background material which I consider to be important but too intrusive to appear in the body of the text is present as *Further information* at the end of the volume. (The *Further reading* sections are now collected there too.)

In keeping with the general aim to make the text more accessible I have introduced several more changes. Thus, in the Examples that occur throughout the text, I have introduced a *Method* section. The most difficult part of answering a problem is knowing where to start; the *Methods* suggest how to collect one's thoughts, what expressions to use, where to find the data, and generally how to think strategically about the problem. Keen-eyed, long-memored readers will remember that I used *Methods* in the third edition, but dropped them from the fourth; these *Methods*, though, are more extensive and more structured than in the third edition.

Another feature is the introduction of *Molecular interpretations*, which are new to this edition. These sections, which are found in Part 1, stemmed from the views that have been expressed concerning the question of whether to start from classical thermodynamics or from atomic properties. I have always maintained that instructors can easily use Part 2 of this text before Part 1 (indeed, few instructors consider themselves bound by the order of a text at this level), but I wanted to find a way of introducing atomic concepts (which have a strong intuitive appeal and an undeniable instructive value) without damaging what I perceive to be the intellectual self-sufficiency of thermodynamics. So, interspersed into the text of Part 1 are optional *Molecular interpretations*, which show (as their name suggests) the interpretation of a bulk result in terms of atomic and molecular properties. I believe that this approach enriches and deepens thermodynamics without damaging its integrity.

I have introduced a number of devices for helping readers to keep the subject in mind. First, I have reinstated an entirely new version of Chapter 0, which gives an overview of the whole subject and introduces some fundamental concepts by way of review. Chapter 0, now called the *Introduction*, gives the big picture. Secondly, I have moved the *Key ideas* to the ends of their respective chapters. I consider that they act better as a check list after the topics have been introduced than as a somewhat daunting list of terms at the head of a chapter. In their place at the start

of the chapter, I have put a paragraph of introduction, an abstract of the chapter, which maps out the sequence of ideas that the reader will encounter, and highlights the key issues.

There are a considerable number of changes within the text. For example, I have responded to the advice that suggested that the kinetic theory of gases came far too late. It now comes in Chapter 1, where it augments the phenomenological aspects of gases. I have shifted several sections on the properties of surfaces from their original location in Chapter 7 to a chapter that now deals with all aspects of surfaces, both liquid and solid (Chapter 28). Some chapters have been completely rewritten. An example is Chapter 15 on group theory: it has been urged on me that it is inappropriate to attempt to give a formal introduction to group theory in a single chapter. Now I give a highly pragmatic introduction—essentially confined to showing how character tables are used—but a lot of the background is still present in several *Justifications*. The material on transport properties has been combined with the material on ionic motion and diffusion into a single chapter; this reorganization brings out more clearly the unity of the ideas underlying molecular migrations of various kinds.

While rewriting a text keeps the narrative young (at the risk of ageing the author), I know that it is important to try to ensure accuracy. In this edition I have called on the good offices of a number of colleagues who have scrutinized the text at several stages of its production. The typescript was read by over 50 people in part or in its entirety, and I have corrected all the errors and infelicities of expression they found. We took particular care at proof stage. Galley proofs were read several times by Michael Clugston (the whole) and Dixie Goss and Stephen Davis (sharing the whole), and we collectively tried to perfect the proofs at that stage. The entire set of page proofs was then read again, with a fresh eye, by Carmen Giunta, who happily found few points to correct at that stage. Charles Trapp, who has been largely responsible for compiling the *Solutions Manual* for this edition, also provided many helpful suggestions and corrections. We are very conscious of the need to perfect a text, and have put a considerable effort into cleansing this edition of irritating typographical slips, cross-references, and the like.

To these readers I owe my very special thanks. I also owe a great debt to all those colleagues, users, students, and translators around the world who sent me the distillation of their wisdom. If a book is a monument to anyone, then it is a monument to its well-wishers who have done so much to ensure that it is exactly what is needed for modern courses in physical chemistry.

As always, I wish to record my thanks to my publishers for the understanding and unstinting assistance they have provided at all stages of the massive and complex task of producing a book such as this.

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Conclusion

Physical chemistry establishes and develops the principles that are used to explain and interpret the observations made in the other branches of chemistry. The subject is characterized by three main approaches: the discussion of bulk properties in terms of thermodynamics, the use of spectroscopy to explore the behaviour of individual atoms and molecules, and the analysis of the rates and mechanisms of chemical change. This opening chapter surveys these approaches and puts them in a general context. It also reviews some basic ideas on which the entire text hinges. All the new material will be dealt with in greater detail later in the text.

SOME BASIC IDEAS

Certain concepts are common to the whole of the subject (and to other branches of science too), and here we review some of them.

The structure of science

The observations that physical chemistry (like other branches of science) organizes and explains are summarized by scientific laws. A **scientific law** is a summary of experience. Thus, we shall encounter the laws of thermodynamics, which are summaries of the relations between bulk properties and particularly observations on the transfer of energy. We shall also encounter the laws of quantum mechanics, which summarize observations on the behaviour of individual particles. The first step in accounting for a law is to propose a **hypothesis**, which is essentially a guess at an explanation in terms of more fundamental concepts. Dalton's atomic hypothesis, which was proposed to account for the laws of chemical composition in terms of atoms, is an example. When the hypothesis has become established, perhaps as a result of the success of further experiments it has inspired or by a more elaborate formulation

(often in terms of mathematics) that puts it into the context of broader aspects of science, it is promoted to the status of a **theory**. We shall encounter a number of theories in this text: among them will be the theories of atomic structure and the chemical bond.

A characteristic of physical chemistry (like other branches of physical science) is that, to develop theories, it adopts **models** of the system it is seeking to describe. A model is a simplified version of the system that focuses on the essentials of the problem. That is, a model seeks to identify the heart of the problem and ignores possible complications that are considered to be of only secondary importance. Once a successful model has been constructed (and tested against known observations and any experiments it inspires), it can be made more sophisticated so as to incorporate some of the complications the original model ignored. Thus, models provide the framework for discussions, and reality is captured rather like a building is completed, decorated, and furnished. We shall encounter a number of such models. One example is the **kinetic model** of gases, in which a gas is regarded as a collection of particles in ceaseless, chaotic motion. Another example is the **nuclear model** of an atom, and in particular a hydrogen atom, which is used as a basis for the discussion of the structures of all atoms. A third very important type of example is that of a **perfect gas**, which is an idealized model of the gaseous state of matter in which the pressure is related to the volume, temperature, and amount of substance by the relation

$$pV = nRT$$

where R is a constant called the **gas constant**. This expression, which is the starting point of the discussion of **real gases** (that is, actual gaseous chemical species) is one of the most important equations in physical chemistry, and a wide variety of thermodynamic expressions are based on it. It is introduced in Chapter 1.

It is commonly the case that the form of equations developed on the basis of a simple model is maintained in the elaboration of the model. The advantage of such a procedure is that the appearance of many equations is then preserved, and the equations remain familiar. An example of such a modification is the replacement of a concentration term in certain thermodynamic expressions (such as an equilibrium constant) by an effective concentration called an **activity**. To make this a practically useful procedure it is then necessary to find the relation between this effective concentration and the true concentration. That step is often done by proposing a more detailed model of the behaviour of the system that takes into account the interactions between molecules.

The amount of substance: moles

Another preliminary idea we need is that in chemistry we are normally concerned with enormous numbers of atoms. The number of atoms in 1 g of matter is of the order of 10^{22} to 10^{23} , which is larger than the number of stars in the visible universe. To express these large numbers it is conventional in chemistry to refer to the **amount of substance** n and to express that amount in the unit called the **mole**. The formal definition