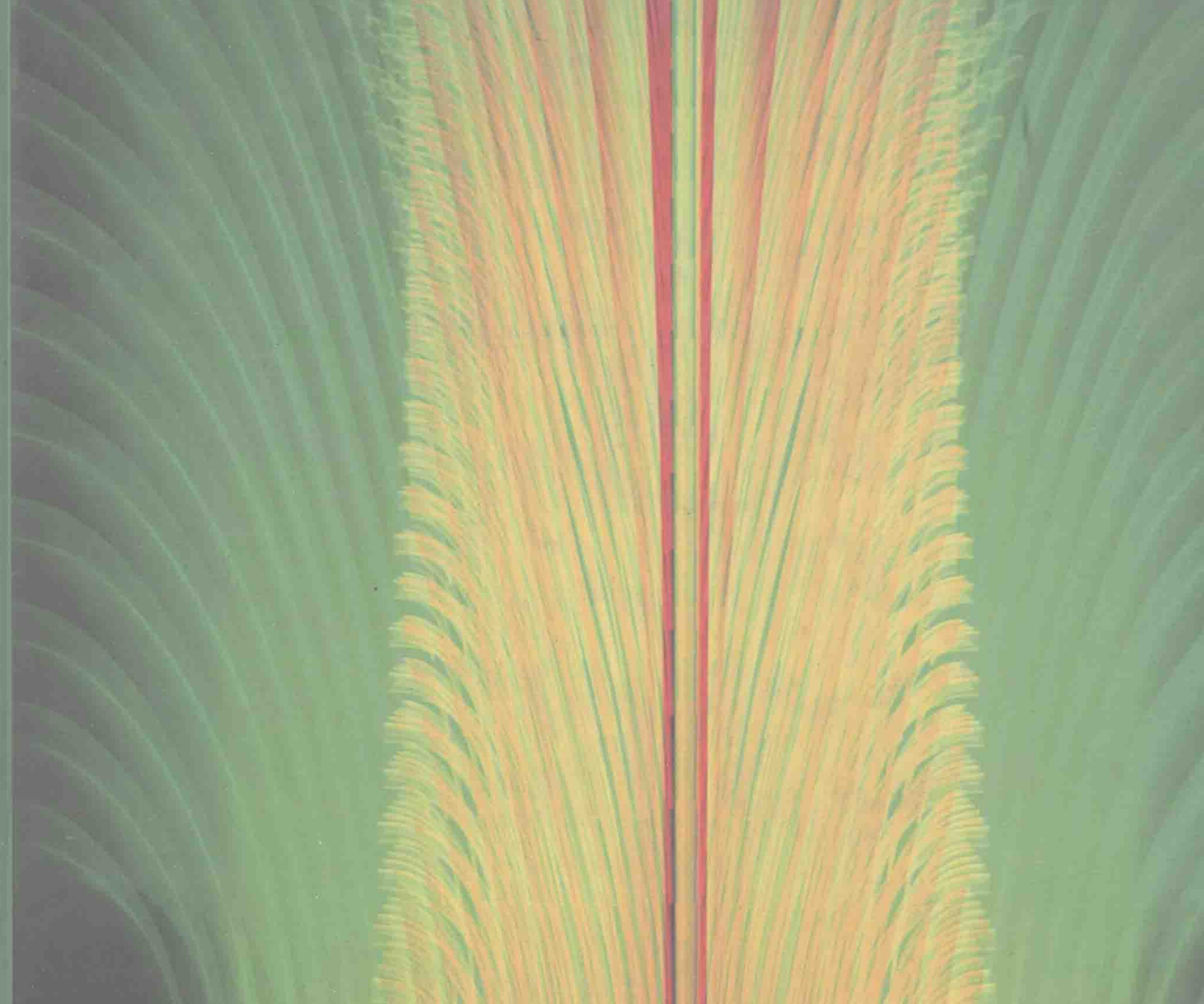
PHYSICAL CHEMISTRY

FIFTH EDITION

GORDON M. BARROW



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About the Author

Gordon M. Barrow is a physical chemist with a career in education, research, and administration. He grew up in Vancouver, B.C., attended the University of British Columbia, and received a Ph.D. degree from the University of California. He has been on the faculties of Northwestern and Case Western Reserve, with visiting appointments at Dartmouth and U.C. Santa Cruz. He was executive director of the Advisory Council on College Chemistry.

Dr. Barrow is the author of several texts and creator of a major set of computer-based support materials for the physical and general chemistry courses. He now is developing instructional materials and teaching at Royal Roads Military College in Victoria, B.C.

Preface

Much reorganization of the material of the preceding edition of Physical Chemistry and many changes in the development of individual topics have resulted from changes in my own understanding of physical chemistry and from the suggestions of users of the earlier editions. Unchanged is the general attitude toward physical chemistry that guided the previous editions. The unity of many topics of physical chemistry is emphasized. The principal common thread remains the interrelation of macroscopic and molecular-level phenomena. The preface of the previous edition expresses the attitude that underlies this edition.

> Physical chemistry is a unit in the undergraduate chemistry program that introduces, or develops, many distinct topics. Some, such as thermodynamics and kinetics, are long-recognized as major areas of study. Others, such as quantum mechanics, spectroscopy, statistical mechanics, and photochemistry, have come into the physical chemistry course more recently. A single course in which such varied areas are treated is valuable if it provides coherence to the study of these different topics. A textbook for such a course must make it clear that the whole is greater than the sum of the parts. This has been the goal of previous editions, and it remains the goal of this fifth edition.
>
> Each topic is treated in such a way that the knowledge of the entire subject of physical chemistry, as well as that of the particular area, is advanced. But what is the subject of physical chemistry if it is not just a collection of distinct topics? We see it as the quantitative interpretation of the macroscopic world in terms of the atomic-molecular world. To achieve this interpretation, we must organize our observations of macroscopic phenomena, as we do in thermodynamics and in parts of kinetics. We must advance our studies of atoms and molecules, as we do, for example, in quantum mechanics and spectroscopy. Then we must bring these studies together. This coming together is woven into much of the fabric of a modern physical chemistry course.
>
> Earlier it was necessary to argue that studies of the atomic-molecular world belonged, along with the traditional topics, in the physical chemistry course. Now it seems necessary to insist that the traditional macroscopic studies not be completely driven out. Physical chemistry should offer much more to the undergraduate student than an introduction to the specialized topics that now constitute the research frontier.

In this edition the material has been reorganized so the students can see more clearly the unity and development of the entire subject. The chapters are now organized into six major parts. The close relation, or common goal, of the several chapters in each part is now more evident, and the six major parts make the overall order of the text easily recognizable.

Some of the reorganization helps to tie applications or extensions more closely to the principles on which they are based. For example, some aspects of photochemistry are now dealt with along with spectroscopy, while other aspects are treated along with the elementary reactions of chemical kinetics. The detailed atomic-level structure of macromolecular systems is now taken up as part of the structural studies based on x-ray diffraction, and only the special shape features of the molecules of these materials are given separate treatment in studies of dynamic solution phenomena.

Some of the topics of physical chemistry are now developed in a way that is nontraditional. The basic ideas of quantum mechanics and statistical mechanics are introduced early, as the motions of the molecules of a gas are studied. This early introductory treatment is followed, in later chapters, by the more formal development of statistical thermodynamics and by the application of quantum mechanics to the electrons of atoms and molecules. This two-stage development makes both the statistical and the quantum-mechanical methods appear as general methods, not as procedures required only in rather special circumstances.

Thermodynamics is developed in terms of changes in the properties of the system and the changes in the energy and entropy of its thermal and mechanical surroundings. A great conceptual simplification results when no heat "flows" and no work "is being done." Students find this treatment of thermodynamics to be concrete and immediately understandable. Instructors share this view—once they set aside their old familiar struggles with q's and w's.

My objective is, as in earlier editions, to help students deal with the various concepts of physical chemistry without an obscuring mathematical screen. Those students who go on to more advanced studies in physical chemistry will have a conceptual base that they can develop as they become more mathematically sophisticated. Those students who go on to work in other, perhaps applied, work will have the appreciation of physical chemistry principles that they will need. Help with the specific calculations that must be done to appreciate the principles is provided by the many worked-out examples, which are now set off from the text material.

The move toward SI units has continued and is now nearly complete. Only the liter, which is not referred to as a cubic decimeter, remains!

The atmosphere unit of pressure has been replaced by the *bar*, equal to 10^5 Pa. (The atmosphere unit still occasionally appears when earlier measurements and the normal boiling point are referred to.) Atomic and molecular distances are now expressed in picometers rather than angstroms. Wavelengths of visible and ultraviolet radiation are expressed in nanometers. The standard-state pressure for thermodynamic properties is taken to be 1 bar. This pressure and the thermodynamic reference temperature of 25°C are now implied by $\not{S}$TP and are used in gas PVT calculations in place of the old 0°C and 1 atm. The result is that 24.789 L replaces the old $\not{S}$TP molar gas volume of 22.4 L. (The approximate value of 24.8 L is as easily remembered as is the value of 22.4 L.) Students readily accept this common basis for ideal-gas and thermodynamic quantities. They also more easily recognize the relation of R as the gas constant, with the value of 0.08314 L bar K^{-1} mol^{-1}, to R as a measure of energy, with value 8.314 J K^{-1} mol^{-1}.

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Gordon M. Barrow

Contents

ONE

GASES—AN INTRODUCTION TO PHYSICAL CHEMISTRY

1

Physical Properties of Gases

The study of gases provides an ideal introduction to physical chemistry. The two principal components of physical chemistry are clearly identified. One is the organization of the experimental results obtained from studies of the "ordinary," or macroscopic, world. The other component is the study of the atomic-molecular world that underlies this macroscopic world. Physical chemistry consists of studies of these aspects *and* the bringing of them together to give a molecular-level interpretation of the observed macroscopic phenomena.

In this chapter we shall study the pressure-volume-temperature behavior of gases. These studies provide a base from which many practical and penetrating studies stem. The practical aspects will be apparent when we go from the behavior of "ideal" gases to real gases, next to the vapors in equilibrium with liquids and solids, and then to liquids and solids themselves. Much use will be made of simple ideal-gas relations when we take up thermodynamics, a very practical method for dealing with macroscopic phenomena. The penetrating aspects will be apparent when you see how we can use the behavior of gases to learn about some of the intimate details of the molecular world.

In this chapter the results of experimental studies of the pressure-volume-temperature behavior of gases are described and organized. In Chap. 2 a molecular model is developed that explains the empirical relations obtained here.

You will better appreciate the nature of empirical studies of gases if, in your studies of this chapter, you set aside your sophisticated knowledge that the material world is made up of atoms and molecules. The empirical studies of this chapter did precede the theoretical atomic-molecular interpretations of the following chapter. You might notice some of the early dates mentioned in this chapter and have in mind that the molecular view of matter was not born until the early 1800s and did not mature and become respectable until near the end of that century.