Gordon M. Barrow

PHYSICAL CHEMISTRY

Third Edition

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PREFACE

One of the two time-dependent phenomena leading to a textbook revision, such as this third edition, is the development of the field itself. Physical chemistry has now clearly outgrown its original limitation to the study and organization of the macroscopic chemical world. It now includes, on an equal footing, the study of the atomic and molecular world. The heart and enduring character of the subject is the bringing together of these worlds. The student of the subject acquires the conviction that, on a broad front, knowledge of these two worlds can be coupled and that remarkable insights into both worlds result. This was the view of physical chemistry presented in the first edition of this book, and it remains the guiding attitude for this edition. It is in the extension of our knowledge of the molecular world, and thus our increased ability to develop encounters with the macroscopic world, that updating of the content has been made.

The second motivation for a revision is the added insight that an author receives—from students, other teachers, and reviewers, and from very general experience. On this basis a large part of the second-edition material has been rewritten and reorganized. While the goals and scope are not changed, I hope that the clarity of presentation has been improved and the unity of the various aspects of the subject will be more readily appreciated.

I have continued, in this revision, to try to resolve the conflict between the use of developments that stay close to the physical approach, and are at all stages understandable on this basis, and the introduction of concise mathematical treatments that provide elegant paths to the desired result. As in the second edition, I have attempted to get the best of both approaches. Thus, where additional mathematical formalism appears, it is because I now think the treatment that is carried out reveals more clearly the physical nature of the relation that is established.

An easily noticed change throughout the text is the use of SI units. Although it is hard for a chemist to give up his long-remembered quantities—that R is 1.987 calories per degree mole, for example—the student will probably find SI units easier to deal with. In any case, the trend is toward SI units in most branches of science, both in the United States and abroad. I have, however, been unwilling at this stage to give up the pressure unit of atmospheres, which serves as the basis of standard states, or the angstrom, which will likely be used for some time for the wavelength of light and for scaled molecular models. Also, the treatment of magnetic properties has not been changed, since conversion to SI units involves more than a unit change and would lead too far from current and past chemical practice.

One of my delights in the development of the revision has been the receipt of detailed and incisive reviews on many parts of the manuscript. I particularly would like to acknowledge the very great help that James W. Richardson of Purdue University has given me, as he did when the previous edition was being prepared. I am also greatly indebted to DeWitt Coffey, Jr., San Diego State College; Benjamin P. Dailey, Columbia University; A. James Diefenderger, Lehigh University; Eugene Hamori, University of Delaware; and Alan S. Rodgers, Texas A & M University. Their efforts have, in many places, put me on the right track, and I am sure the instructors and students who use this textbook would share my appreciation if they could recognize their contributions.

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1

PROPERTIES OF GASES

The study of the nature of gases provides an ideal introduction to physical chemistry. This study, undertaken in the first two chapters, has three clearly recognizable aspects. One is the organization of the experimental results that are obtained from studies of the world around us, the macroscopic world, into general statements, or *laws*. Second is the development of a molecular model, i.e., a study of the microscopic, or molecular, world. Finally, these aspects are brought together to give a molecular-level interpretation of the observed macroscopic phenomena.

A considerable appreciation of the world of molecules can be obtained from the second and third steps, and this comes about without recourse to the more elaborate, and more powerful, theories and experiments that will be encountered later in this text. The deduction of some of the innermost details of the molecular world from the simple experimental results of Chap. 1 and the equally simple theory of Chap. 2 should be appreciated as an elegant accomplishment of science.

Seldom are the experimental and theoretical aspects of a study so neatly separated as they are here. A clear illustration is provided of how these two aspects of scientific study go hand in hand to lead to a more profound interpretation of our physical world. The division of the subject into its empirical and theoretical aspects, it must be admitted, ignores the historical sequence of events. However, most of the results reported in this chapter predate the theoretical deductions of the following chapter. For reference one can recall that the molecular view of matter was born with the nineteenth century and became quite mature and respectable by the end of that century. The earlier dates

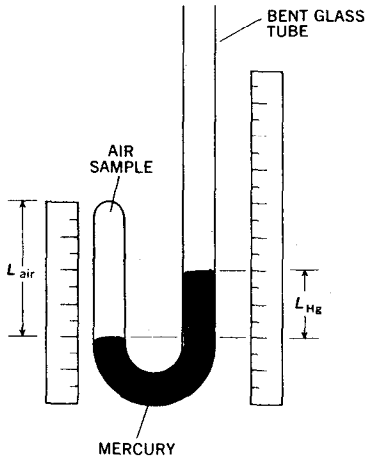

FIGURE 1-1 Apparatus for the measurement of the relation between the pressure and the volume of a sample of air.

attached to some of the empirical studies should emphasize the fact that these studies were indeed purely empirical and were not appreciably guided by any existing theory.

1-1 The Dependence of the Volume of a Gas on Pressure: Boyle's Law

As early as the year 1660 Robert Boyle performed a series of experiments in which he determined the effect of pressure on the volume of a given amount of air with the apparatus illustrated in Fig. 1-1. A little mercury was added through the open end of the tube to seal off a quantity of air in the closed end. The volume of the enclosed air, for various amounts of mercury added through the open end, could then be measured. Table 1-1 shows some of the results that Boyle obtained.

Qualitatively, it is immediately obvious that, as the pressure on the air increases, the volume of the air decreases. Such data prompt one

TABLE 1-1 Data of Boyle on the pressure-volume relation for air

L_{air} (arbitrary units)	L_{Hg} (inches)	$L_{Hg} + 29\frac{1}{8}$ (inches)	$(L_{Hg} + 29\frac{1}{8})L_{air}$
12	0	$29\frac{2}{16}$	349
10	$6\frac{3}{16}$	$35\frac{5}{16}$	353
8	$15\frac{1}{16}$	$44\frac{3}{16}$	353
6	$29\frac{11}{16}$	$58\frac{13}{16}$	353
4	$58\frac{2}{16}$	$87\frac{4}{16}$	349
3	$88\frac{7}{16}$	$117\frac{9}{16}$	353

to go further and see if there is a simple quantitative relation between the pressure P and the volume V. One tries the relation

$$V \propto \frac{1}{P} \qquad \text{or} \qquad V = \frac{\text{const}}{P} \qquad \text{or} \qquad PV = \text{const} \qquad [1]$$

The data are easily compared with the final form of this relation, and included in Table 1·1 is the calculated product of the effective length of the column of mercury and the length of the air column. (The units used are not pertinent since it is only the constancy of the result that is of interest.) Within experimental error a constant value is obtained, and so Boyle was able to conclude that the volume of air varies inversely as the pressure. Later experiments showed that this relation required the temperature to be maintained constant and, furthermore, that many gases, as well as air, conformed quite closely to this behavior. Boyle's law can now be written as follows: *The volume of a given quantity of a gas varies inversely as the pressure, the temperature remaining constant.*

Processes which are performed at constant temperature are said to be *isothermal*. The pressure-volume data obtained at constant temperature in demonstrating Boyle's law are frequently exhibited on a plot of P versus V. The hyperbolic curve obtained, as in Fig. 1·2, at any given temperature, is an example of what is called an *isotherm*.

According to Boyle's law, the pressure and volume of a given amount of gas, at a fixed temperature, vary so that the product PV always has the same value. Sometimes one deals with an isothermal process which takes the gas from the initial values P_1 and V_1 to some new values P_2 and V_2. Since the product of P and V is constant, one can write a frequently convenient form of Boyle's law as

$$P_1V_1 = P_2V_2 \qquad [2]$$

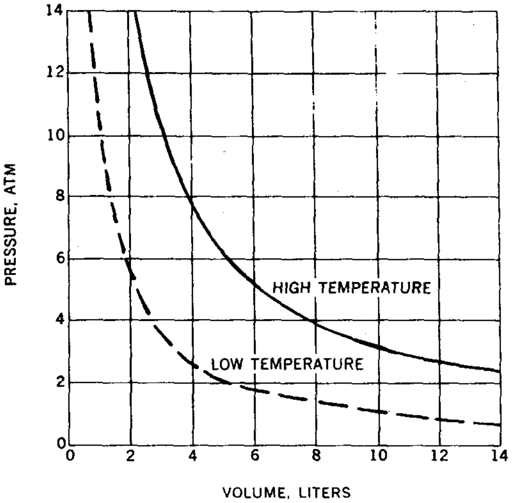

FIGURE 1·2
Isotherms for a gas obeying Boyle's law.

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