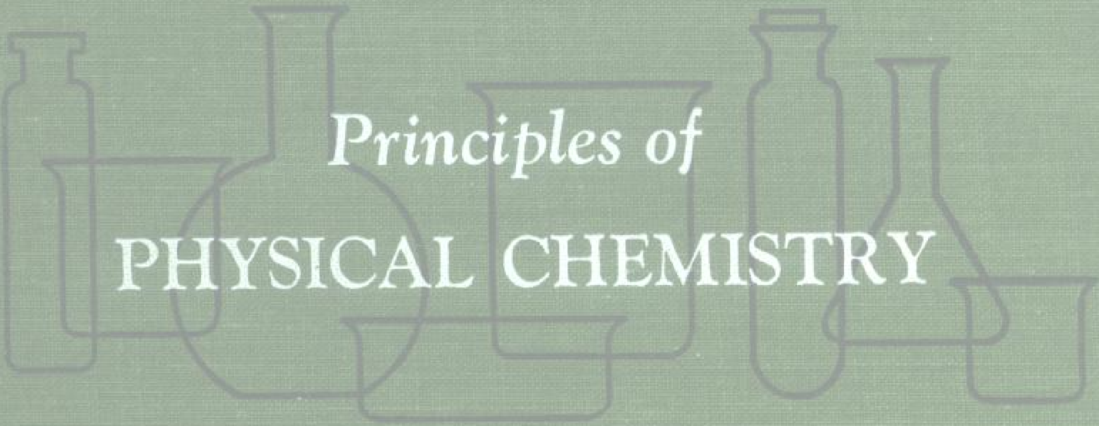

Principles of
PHYSICAL CHEMISTRY

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Preface

In the preface to the first edition the authors stated that their "aim in writing this text on elementary physical chemistry is to place in the hands of teachers and students a book which covers the fundamental principles of the subject in a thorough, sound, up-to-date, and clear manner.

"In deciding what constitutes the fundamental principles the authors were continually guided by the needs of the chemist and chemical engineer for a sound grounding in physical chemistry. Although physical chemistry is offered to various students with various purposes in mind, the fact remains that those who expect to be engaged in any branch of chemical or related work must be conversant with the principles of this subject, and they must be able to use and apply these principles effectively and correctly. In order to do this they must be exposed to a basic training sufficiently complete to permit them to understand the subject, not only in a general and qualitative way, but also in its more intimate experimental and quantitative aspects. To achieve such mastery the authors feel that use of mathematics and some thermodynamics is absolutely essential. For this reason the necessary calculus is employed here without any apology, and the elements of thermodynamics are introduced early and are used throughout the book as an integral part of the subject. . . .

"Throughout the book considerable attention is devoted to the experimental aspects of physical chemistry. This is done expressly, because it is felt that a student can better understand what he is dealing with when he has some idea how the quantities involved are obtained. At the end of each chapter are given bibliographies, to which the student may turn for further details, and extended lists of exercises to test his familiarity with the subject matter and to develop in him facility in handling equations and data.

"The book as a whole is intended primarily for a full year course in physical chemistry for students of chemistry and chemical engineering. By judicious selection of various portions of the contents, this book should be readily adaptable to any one-semester course for students in other branches of science, such as physics, metallurgy, biology, and biochemistry. What is to be omitted and what is not is largely a matter of circumstances and needs, and can be left safely to the discretion and decision of each individual teacher."

The above aims and philosophy have been followed in preparing the present edition. Although the general order of presentation is the same as used before, extensive changes have been made in the organization of the subject matter and in the discussion of some topics. Thus, Chapter 2 is now devoted exclusively to the first law of thermodynamics and its application to gases, while Chapter 10 deals with both the second and third laws. Again, discussion of nonelectrolytes and electrolytes has been combined under the head of "Colligative Properties of Solutions," and the exposition of molecular structure and properties has been consolidated into a single chapter titled "Molecular Structure." On the other hand, the chapter on surface phenomena and colloids has been divided into separate chapters dealing with these topics, and each of these subjects has been considerably expanded and brought up to date.

To avoid increasing the size of the book, all changes and additions have been made at the expense of less significant subject matter. At the same time the number of problems has been increased to 634, the largest number in any book of this type.

In conclusion the authors wish to express their appreciation to colleagues, friends, and teachers who have been kind enough to offer us their suggestions and criticisms for improvement of the text, and who have called to our attention the inevitable errors which, despite all efforts, still manage to escape attention. Particular thanks are due to Professor Walter Kauzmann of Princeton University for the trouble he has taken to send us extensive comments and suggestions for improvement, and to Professor Irvin M. Krieger of Case Institute for his continual interest and willingness to read and criticize the entire manuscript. Finally, we also wish to acknowledge our deep gratitude to the publishers, The Macmillan Company, and their staff for their ever-present cooperation, courtesy, and desire to go to any length to produce a book satisfactory to the authors.

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Introduction

SCIENCE AND THE SCIENTIFIC METHOD

Science is organized and systematized knowledge relating to our physical world. This knowledge did not spring into being full blown, but has been accumulated painstakingly through the efforts of many researchers and observers. In its inception this cumulative process was quite simple. It involved merely the observation of phenomena as they occur in nature and their faithful recording. As the facts and observations multiplied, regularities were sought and discovered in them which were then formulated into *laws*. Each law was capable of embracing a number of facts and of summarizing them in succinct form.

However, natural laws do not constitute an interpretation of nature, but rather a description. To supply the reason for the operation of a law scientists began to propose purely suggestive explanations, or *hypotheses*, in terms of which the operation of the law could be accounted. From these hypotheses logical predictions were then derived and compared with the observed phenomena. If the two tallied fairly well, the hypothesis was accepted, provisionally at least, and became a *theory*. On the other hand, if the logical deductions of a hypothesis did not agree with experimental facts, the hypothesis was discarded to await a more satisfactory explanation.

At present we do not rely on purely fortuitous observation for our information. With the state of scientific knowledge as advanced as it is, experiments are carefully planned and conducted to yield the specific data sought. It is thus possible to arrive at desired facts more rapidly and efficiently. Again, with planned research hypotheses and theories may be subjected to deliberate test by arranging experiments designed to answer directly the specific point in question. By such means faulty concepts can be eliminated, incomplete theories refined, and new principles discovered.

This modus operandi of science is called the *scientific method.* It will be noticed that in its operation the scientific method involves essentially four stages, namely: (a) the accumulation of facts; (b) the organization of facts into laws; (c) the postulation of hypotheses to account for the facts and the laws; and (d) the comparison of the hypothetical deductions with the experimental results. Whenever possible, facts and their correlations, as well as their explanations, are expressed in mathematical terms. It is this precision of language more than any other single factor which differentiates the physical sciences from more purely descriptive sciences such as biology or medicine.

The intimate combination of experiment and theory embodied in the scientific method has proved very fruitful, and has led to the development of our present highly advanced state of science and technology. It must be emphasized, however, that the function of theory and hypothesis in this advance has not been merely to explain what is already known. Were this the only contribution of theory, speculation would have been more of interest than value. The real function of theory and speculation lies much more intrinsically in its ability to define the experimental variables, and in its ability to foretell phenomena and effects that are as yet unknown. When thus used, theory and hypothesis may serve not only as powerful guides in the interpretation of phenomena, but also as effective tools for the advancement of our knowledge of the physical world and its control for our benefit.

PHYSICAL CHEMISTRY

The branch of chemistry which concerns itself with the study of the physical properties and structure of matter, with the laws of chemical interaction, and with the theories governing these is called *physical chemistry*. The purpose of physical chemistry is, first, to collect the appropriate data required to define the properties of gases, liquids, solids, solutions, and colloidal dispersions, to systematize them into laws, and to give them a theoretical foundation. Next, physical chemistry is interested in establishing the energy relations obtaining in physical and chemical transformations, in ascertaining the extent and speed with which they take place, and in defining quantitatively the controlling factors. In this connection must be considered not only the more common variables of temperature, pressure, and concentration, but also the effects of the intimate interaction of matter with electricity and light. Finally, matter itself must be examined to determine its nature and structure. This is necessary in order that we may be able to arrive at a basic understanding of physical and chemical behavior in terms of the properties of the fundamental constituents of matter.

To accomplish its purposes physical chemistry must rely to a large degree on experiment. Experimental methods and techniques play thus a very important role. The subject also draws generously on the laws and methods of physics and mathematics. In fact, physical chemistry may be looked upon as the field where physics and mathematics are applied extensively to the study and solution of problems of prime chemical interest. With the appropriate data at hand, physical chemistry then proceeds to its correlational and theoretical goal through two general modes of attack, namely, the *thermodynamic* and the *kinetic.* In the thermodynamic approach the fundamental laws of thermodynamics are utilized to yield deductions based on the energy relations connecting the initial and final stages of a process. By circumventing the steps intervening between the start and end of a process, thermodynamics enables us to arrive at many valuable deductions without our knowing all the intimate details of the intermediate stages. Consequently, although this approach is able to tell us what can happen, and to what extent, it is unable, by its very nature, to give us information on *how*, or *how rapidly,* a change will actually occur. On the other hand, the kinetic approach requires for its operation an intimate and detailed "picture" of the process. From the mechanism postulated may be deduced then the law for the over-all process and its various stages. Evidently the kinetic approach to a problem is more explanatory in character, but unfortunately it is generally more complicated and difficult to apply. These two modes of attack will be illustrated at various stages in the text. From the examples given there the student will be able to differentiate more clearly between them and come to appreciate their respective powers and utilities.

HISTORY OF PHYSICAL CHEMISTRY

The roots of physical chemistry lie in the fields of both chemistry and physics. At first these two branches of science developed more or less independently. However, in the nineteenth century it was found that the discoveries in physics had important bearing on and application to chemistry, and hence need arose for a distinct field dealing primarily with the application of physical laws to chemical phenomena. This need finally impelled Wilhelm Ostwald, van't Hoff, and Arrhenius to organize and systematize the subject matter generally included now under the head of physical chemistry, and led them in 1881 to found the *Zeitschrift* *für physikalische Chemie.* The inception of physical chemistry as a formal branch of chemical science may be dated from the appearance of this journal.

Stimulated by this publication, and fostered by the contributions of the men mentioned, physical chemistry entered a period of very rapid growth. Aiding this progress were not only advances in chemistry, but also the remarkable series of discoveries in physics which started with the discovery of the electron, and which include the discovery of x rays and radioactivity, the establishment of the quantum theory, and the unfolding of our understanding of subatomic phenomena. Thanks to these contributions, physical chemistry has developed in the past 80 years or so to a position of importance and utility not only to chemistry but to other sciences as well.

IMPORTANCE OF PHYSICAL CHEMISTRY

Since physical chemistry deals with the principles and theories of chemistry, it goes without saying that any student or practitioner of this science must be familiar with physical chemistry in order to understand his own subject. The same applies also to the chemical engineer. The essential difference between a chemist and a chemical engineer is that whereas the former conducts his reactions and operations on a small scale, the chemical engineer carries them out in large commercial units. To transfer an operation from the laboratory to a plant the chemical engineer must of course be able to apply engineering and economic principles. However, at the same time he must understand also the fundamentally chemical nature of the processes he is dealing with, and for that he needs physical chemistry. As a matter of fact, chemical engineering has frequently been described as applied physical chemistry. Viewed in this light, many of the aspects of chemical engineering fall within the realm of physical chemistry and can be handled in terms of well-established and familiar physicochemical laws. On the other hand, any attempt to consider chemical engineering as a purely empirical pursuit robs it of the attributes of a science and translates it into an art.

What has been said about the importance of physical chemistry to the chemist and chemical engineer applies equally well to the metallurgist and metallurgical engineer. The latter two perform essentially the same functions as the two former, except that their attention is confined primarily to metals. From this point of view the prominent position of physical chemistry, whether under this or other titles, in these subjects becomes clear, and accounts for the valuable contributions made to these fields by the application of physicochemical principles.

Finally, physical chemistry finds application also in physics, geology, and in the various ramifications of the biological sciences. To appreciate the extent of its utility it is only necessary to compare a book on chemical physics, geology, or biochemistry with one on physical chemistry. From such a comparison it becomes quite evident why physical chemistry is often included in curricula in these subjects, and why it can be applied with effect in these sciences.

1

Gases

All matter exists in one of three states of aggregation, solid, liquid, or gaseous. A solid may be defined as a body possessing both definite volume and definite shape at a given temperature and pressure. A liquid in bulk, on the other hand, has a definite volume but no definite shape, while a gas has neither definite shape nor volume. Liquids and gases are both termed *fluids*. A liquid, insofar as it fills the container, will always adopt the shape of the container in which it is placed, but will retain its definite volume, while a gas will always fill completely any container in which it may be confined.

The distinctions among the three states of matter are not always as clear cut as the above definitions would imply. For example, a liquid at the critical point is indistinguishable from its vapor. Again, such substances as glass or asphalt, although exhibiting many of the properties of a solid, will, under certain conditions of temperature, become plastic and exhibit properties not ascribed to pure solids. For this reason such substances are usually considered to be supercooled liquids with very high viscosity.

The particular state of aggregation of a substance is determined by the temperature and pressure under which it exists. However, within certain limits of temperature and pressure a substance may exist in more than one state at the same time. In fact, under special conditions a substance may exist in all three states simultaneously. Thus at 4.57 mm Hg pressure and at 0.0099°C, ice, water, and water vapor may all be present simultaneously, and all be stable. This subject of simultaneous existence in more than one state will be discussed more completely in subsequent chapters.

NATURE OF GASES

A gas may be regarded as consisting of molecules traveling in straight lines at random and at high rates of speed within the containing space, and colliding frequently with other molecules or the walls of the container. The force exerted per unit area on the walls of the container by the colliding molecules is known as the *pressure*—a force present at all times and distributed uniformly over the entire surface. The fact that small molecules produce a considerable bombarding force upon container walls suggests that the number of collisions with the walls must be large and that the molecules must be moving with high velocities.

The space occupied by the molecules themselves within a gaseous volume is a small fraction of the total volume of the gas under ordinary conditions of temperature and pressure. Thus, if all the air in a room 20 by 10 by 10 ft were liquefied, the volume of the liquid would be approximately 2.4 cu ft, or about 0.1 per cent of the volume of the room, and yet the molecules would not be touching each other. Hence we may conclude that molecules generally are separated from each other by distances which are large compared to molecular diameters, and that within a gas the space actually occupied by molecules is very small, most of the volume being "free" space. This accounts for the much lower densities of gases as compared to liquids and solids.

Also, this large amount of "free" space within a gas makes compression of the gas fairly easy. The compression process merely reduces the large "free" space and, by reducing the average distance between the molecules, brings them closer together. When there is no attraction between the molecules, the decrease in "free" space on compression is equal to the observed decrease in the total volume of the gas. Similarly, on expansion the average distance between molecules is increased, and thereby also the "free" space of the gas. In any case the random motion of the molecules will give the effect of completely filling any containing vessel in which the gas is placed.

In terms of the structure of a gas outlined above it is easy to understand why gases interdiffuse or mix. Two different gases such as nitrogen and oxygen, or any number of nonreactive gases, when placed in a container will by their motion mix with one another very quickly regardless of density. This mixture of gases will in many respects behave like a single gas, and the molecules of the various gases will collide with each other regardless of similarity or dissimilarity. Further, the total pressure exerted by the mixture will be determined by the total number of collisions between the molecules of all kinds and the walls of the container, a pressure to which each particular kind of molecule contributes its share.

IDEAL AND REAL GASES

For purposes of discussion, it is convenient to classify all gases into two types, namely, (a) *ideal* gases, and (b) *nonideal* or *real* gases. An ideal gas is one that obeys certain laws which will be presented shortly, while a real gas is one that obeys these laws only at low pressures. The deviations from the ideal laws are due in general to two factors of which the ideal laws take no account, namely, the volume actually occupied by the molecules themselves, and the attractive forces existing between the molecules.

An ideal gas is one in which the volume occupied by the molecules themselves is negligible compared to the total volume at all pressures and temperatures, and one in which the intermolecular attraction is extremely small under all conditions. In a nonideal or real gas both of these quantities are appreciable, the magnitude of each depending on the nature, the temperature, and the pressure of the gas. We can easily see that an ideal gas must be a hypothetical gas, as all actual gases must contain molecules which occupy a definite volume and exert attractions between each other. However, very often the influence of these factors becomes negligible, and the gas then may be considered to be ideal. We shall find that the latter condition will obtain in particular at low pressures and relatively high temperatures, conditions under which the "free" space within the gas is large and the attractive forces between molecules small.

EMPIRICAL GENERALIZATIONS OF IDEAL GAS BEHAVIOR

Through the study of gases there have been evolved certain laws or generalizations which are always the starting point in any discussion of gas behavior. These are: (a) Boyle's law, (b) Charles's or Gay-Lussac's law, (c) Dalton's law of partial pressures, and (d) Graham's law of diffusion. Another generalization is Avogadro's principle, but this will be considered later.

BOYLE'S LAW

In 1662 Robert Boyle reported that the volume of a gas at constant temperature decreased with increasing pressure, and that, within the limits of his experimental accuracy, *the volume of any definite quantity of gas at constant temperature varied inversely as the pressure on the gas.* This highly important generalization is known as *Boyle's law.* Expressed mathematically, this law states that at *constant temperature* $V \propto 1/P$ or that

$$V = \frac{K_1}{P}$$