PHYSICAL CHEMISTRY
FOR COLLEGES

A Course of Instruction Based
upon the Fundamental Laws of Chemistry

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SEVENTH EDITION

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INTERNATIONAL CHEMICAL SERIES

Louis P. Hammett, Ph.D., *Consulting Editor*

PREFACE TO THE SEVENTH EDITION

This seventh edition is another attempt to present the complex subject of physical chemistry in language of simple accuracy that is within the understanding of students who have completed the usual courses in inorganic chemistry, physics, and calculus. The required compromise between a precision of statement that will satisfy a professional chemist and an unqualified statement that will meet the expectation of a student has been difficult, as it will always remain in the presentation of an elementary text. The author has tried to favor the student point of view, while saying nothing that will have to be retracted or greatly revised in more advanced study. He has not avoided qualifying statements when they were required to show the limitations of any "law," and he has maintained the distinction between an exact law and a useful approximation.

Much of the text has been written anew, and all of it has been carefully studied in a search for errors or omissions. New illustrative material has been included in the text and problems on the topics that students commonly find difficult. The chapter on thermochemistry now follows that on introductory thermodynamics, in order to provide longer contact with thermodynamic concepts before turning to other topics. Otherwise, the order of chapters, the scope, and the precision are the same as in the sixth edition.

Additions have been made to the problem lists at the ends of the chapters, and a few problems of a more advanced type have been added. The longer problem lists have been divided into two groups, with the less difficult problems preceding the more mature ones, and within each group the order of topics is that of the material in the text.

Many tables of data have been included, as before, for the dual purpose of presenting the facts of physical chemistry and of providing additional material for class discussion and fresh problems. Many of the references to original work are restricted to the more widely circulated journals, so that students may be encouraged to start their acquaintance with original sources.

It is a pleasure to acknowledge the helpful suggestions of those who teach the text, especially those from my associates at the Massachusetts Institute of Technology.

<div align="right">E. B. MILLARD</div>

CAMBRIDGE, MASS.
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PREFACE TO THE FIRST EDITION

This book has been prepared to bring before college students certain of the more important aspects of physical chemistry, together with accurate modern data which illustrate the applicability of its laws to the phenomena observed in the laboratory. It has been assumed that the student is familiar with inorganic and analytical chemistry, that he has had an adequate course in college physics, and that the simple processes of calculus are familiar to him.

No attempt has been made to cover the whole of physical chemistry in a single volume; its most important topics have been treated at such length as the size of the volume allows, and numerous references to recent periodical literature are included for those who would pursue any given topic further.

The limitations of the orthodox laws of physical chemistry have been emphasized more than is commonly done in beginning courses of physical chemistry. To this end the illustrative data have been carefully chosen from modern experimental work, in order to minimize the "experimental errors" which are so often used to conceal real deviations of a law from the facts it is intended to express. A trusting belief in inadequate physical laws will only retard the scientific progress of a student, and weaken his faith in adequate laws; whereas a wholesome appreciation that physical chemistry is an unfinished and growing science may stimulate thoughtfulness and research. The proper time to encourage a research attitude is in the very beginning of a student's chemical career.

A qualitative treatment of the subject, so-called descriptive physical chemistry, may be obtained from the text alone; but careful consideration and study of the numerous tables of data will be required if anything approaching an appreciation of quantitative physical chemistry is desired. A quantitative point of view has been maintained as far as possible, even in the descriptive material.

Rather more tabulated data have been presented than might seem necessary in a beginning text. This is done to furnish the basis for numerous problems of a quantitative character. Many such problems should be solved in the course of a term, since they stimulate interest and increase the usefulness of the material taught in the class room.

The problems at the end of each chapter will not be sufficient to test the ability of general classes; they are type problems in many instances, and should be supplemented by others designed by the teacher to suit the needs and ability of his particular class. Problems should often be assigned for which data must be obtained directly from tables in the text. Much of the value of problem working is lost when a student knows he must use all of the data given him and no other; this too often results in suggesting the entire solution of the problem. Moreover, fresh problems must be given every year if fresh interest in physical chemistry is maintained; this can be done only when ample data are at hand. Some of the more difficult problems at the end of a chapter should be worked by the instructor in class.

References to original sources are not intended primarily as citations of authority for statements made; they are first of all suggestions for further reading. With this in mind, most of the references are to periodicals in English, and to those which are available in small libraries. The author has not hesitated to draw upon little known periodicals when the material to be obtained in them suited the needs of the text; he has not ignored foreign publications in the search for material; but for obvious reasons much of the best data is published in the widely circulated journals, and to these most of the reference work is confined.

The author is greatly indebted to Prof. James F. Norris and to Mr. Charles R. Park for reading the manuscript and making many helpful suggestions and criticisms based on their teaching experience. Their assistance has aided materially in detecting errors. He is also indebted to many other friends for kindly interest and encouragement during the preparation of the manuscript. It will be considered a favor if those who find errors of any kind in the text will communicate them to the author.

E. B. Millard

Cambridge, Mass.
March, 1921

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CHAPTER 1

INTRODUCTION
DETERMINATION OF ATOMIC WEIGHTS

The growth of all science has been so rapid that its fields, such as biology, medicine, physics, or chemistry, must be subdivided into specialties soon after they mature beyond their separation from "general" science. These specialties of scientific fields may be nearly independent as to subject matter, they may be the theoretical and practical aspects of a science, or they may serve as transitions from one field to another. Physical chemistry partakes of all three classifications, for it is the theoretical basis of all chemistry, the foundation of chemical engineering, and a most practical union of kinetic theory, quantum theory, statistical mechanics, spectroscopy, and thermodynamics with experimental work which suggests new theories and promotes new industries. Among the important aspects of physical chemistry are the influence of temperature, pressure, concentration, and relative proportions of reacting substances upon the rate of their interaction; the heat or work which chemical reactions may produce; the structure of atoms and molecules; prediction of the equilibrium composition of reacting systems from the properties of the individual substances; and in general the scope and limitations of the laws or theories that apply to chemical systems. Even this long list is not a complete description of the field; other topics of almost equal importance could well be added.

As a preliminary to the study of mixtures or of reacting systems, it is convenient to know how the properties of single substances change with pressure or temperature, the conditions under which they are gaseous or liquid or crystalline, the conditions under which they exist at equilibrium in two or more states of aggregation, their heats of formation, and other properties.

Since it is obviously impossible to study experimentally every chemical system at every temperature, every pressure, and every concentration, one of the main functions of physical chemistry is the formulation of laws and theories that show the relations among the properties of chemical systems and the testing and revision of these theories and laws as experimental studies reveal minor or serious faults in them. The laws of thermodynamics, which are in no sense the "property" of chemists, have been most helpful in developing physical chemistry, but they could not

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have given this help to the extent that they have without accurate experimental data of the most varied kind. Notwithstanding the diligent work of thousands of chemists for many years, the supply of data is still inadequate; and notwithstanding the diligent work of many theorists for many years the theoretical foundation of physical chemistry is still inadequate. But research and study are continuing at an increasing rate, and while the prospect of complete theory or of complete experimental solution of the problems is remote, the progress already made is both impressive and useful.

Research opens up new fields in physical chemistry, as in any science, and makes more difficult the choice of materials to be used in a first presentation of the topic. One must still "begin at the beginning," he must obtain an adequate grasp of fundamentals through an orderly approach before turning to more fascinating new developments, he must above all reject the temptation to omit those topics for which his present interest can show no immediate use and hasten on to "applications" that may depend upon intelligent use of these topics.

Physical chemistry correlates mathematics, physics, and chemistry, using general methods of treating specific systems and thus providing a classification that puts less stress on memory. What is said of a selected system may be said of hundreds of particularized systems, almost without modification. It is only for this purpose that "principles" are important and only in this sense that the principles or generalizations of chemistry have come to be called *physical chemistry*.

The following pages are intended to be a first survey of its vast field, with emphasis upon what has been accomplished and with some indication of what yet remains to be done. Of necessity many topics have been treated briefly and others have been omitted entirely in order to keep the length of text within reasonable limits; but numerous references to the original sources are given in the footnotes, and suggestions for further reading are given at the ends of the chapters. Since the experimental facts are more important than theories, we shall speak of the deviations of theories or laws from the facts, rather than the deviations of the facts from the theory.

Use of Symbols. Many of the laws used in physical chemistry are best stated by equations, or through the use of symbols. The notation used in this text is that commonly found in the journals and books of the field, and it is as nearly "standard" as is possible. Students must be aware of the fact that there is no universally accepted set of symbols, and they must be prepared to accept minor differences and some duplication. For illustrations, the energy content of a system is usually designated by U in books on physics, and by E in books on chemical thermodynamics; the Greek letter μ is used for the ionic strength of a solution, for the

Joule-Thomson coefficient of an expanding gas, for the chemical potential, for the deviation of a compressed gas from the ideal state, for the viscosity coefficient of a gas, for 10^{-4} cm., and for other quantities. Many other Greek letters and most of the Latin ones have several uses, and there is of course no connection between the properties so designated. Thus μ approaches zero at low pressure when it is the Joule-Thomson coefficient, and it approaches unity at low pressure when it is the deviation coefficient, and for some of its uses there is no effect of pressure. There are simply more physical quantities than there are letters for designating them.

Laws of Nature (Results of Experience). Some of the general laws of chemistry appear to be absolutely exact; they describe faithfully the results of most carefully conducted experiments, and the apparent deviations of these laws become less and less as the manipulative skill employed in testing them increases. Among these laws may be mentioned the law of the indestructibility of matter (conservation of matter), the law of definite proportions, Faraday's law of electrolysis, and the laws of thermodynamics. Other "laws" do not accurately describe the results of measurements, and their deviations do not show errors in the experiments. Such laws are useful approximations that show the properties of chemical systems with reasonable accuracy under certain conditions, and with larger deviations under other conditions. Thus, within about 1 per cent, the "ideal gas law" $pv = nRT$ shows how the volume of a quantity of gas changes with temperature and pressure, in terms of the quantity n and a universal constant R, for most gases when the pressure is "moderate," and it fails when the pressure is "high." More complex equations show these changes more accurately, and one must decide whether to be content with an approximate result or perform the extra work required for a better one.

As the various laws are stated, we shall also state the experimental facts which confirm them or show their deviations, and so endeavor to learn whether judgment is required in the use of a law. For this purpose a sense of proportion is essential. If a law is exact in all but a few instances among many thousand, as is true of the law of definite proportions, these exceptions may point to a new fact. In these circumstances, one must examine the data more carefully or reconsider the fundamental assumptions or look for an unjustified interpretation. If the exceptions reveal a new fact, as is true here, much detailed work may be required before its full significance is appreciated. But while this study is in progress, it would be absurd to give up the many applications of the law to other than these exceptional systems.

Avogadro's law and Boyle's law are "limiting" laws which become more exact as the gas pressure is reduced. They may be quite inaccurate at high pressures, but they may be adequate approximations for some

purposes at high pressures. Other approximations, such as those for "ideal" solutions, describe the results of experiment accurately under some conditions and deviate from them under other conditions. For all such laws we shall state the conditions under which they are accurate to within 1 or 2 per cent.

The statements put forward as laws of nature are sometimes the result of experience alone (empirical laws). There is always a possibility that some future experiment will demonstrate the untruth of what we have considered as a law, but the probability of this becomes less and less as the number of experiments increases. No change has ever been observed in the total mass of the substances involved in a chemical reaction; *i.e.*, matter is not destroyed in being changed into other forms.[1] As the methods of experiment have become more and more refined, and as the experimenters have become more skilful in their work, this law remains unshaken as a statement of universal experience, and it is now commonly accepted as an exact law of nature. Other simple laws, such as Boyle's law and Charles's law for gases, are also the result of experience; but as the experimental methods have become more refined, real deviations of these laws from the facts observed have been discovered.

Theories are plausible beliefs advanced to explain observed facts. They serve to guide further experiments in a given field. Thus the theory that a gas consists of molecules, separated from one another by considerable distances and in rapid motion, offers a ready explanation of the compressibility of gases, of their diffusion, of their ability to mix with other gases in all proportions, and of practically all their properties. The evidence in favor of the theory is abundant and convincing; no facts are known that contradict it; and deductions based on this theory are in accord with the results of experiment. It is therefore universally accepted as a fact but is referred to as the kinetic *theory* of gases.

The theory that the entropy of a crystal is zero at the absolute zero of temperature was proposed long after the kinetic theory of gases. It is, of course, still a theory; and conclusions based on it are confirmed by experiment, as is true of conclusions from the kinetic theory of gases. Its name has long since lost the word "theory," and it is now known as the third *law* of thermodynamics.

Other theories rest on less secure foundations, and they are accepted only until new evidence shows the need for revision or rejection. Before proceeding to a study of new laws and theories, it will be advantageous to review some of those already studied in earlier courses in chemistry.

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[1] The exception to this statement that became so conspicuous in the summer of 1945 had been known for many years. It was, and still is, so exceptional as to leave the conservation of matter one of the most valuable, if not the most valuable, guiding principle in chemistry.

Indestructibility of Matter. It is a familiar fact that matter may be changed into various forms by combination and rearrangement of the elements in various ways without any loss in the total mass of material. The many operations of analytical chemistry depend on the validity of this fact; but since there is no reason why there *might* not be a change of mass during chemical change, it has been necessary to test this belief experimentally before accepting it. Perhaps the best known tests are Landolt's experiments[1] extending over a period of 20 years and devoted to a careful study of 15 different chemical reactions, which were examined with great skill and patience. The reacting substances were enclosed in the separate arms of sealed vessels, such as that of Fig. 1.1, to prevent the possibility of mechanical loss of material. The tubes were weighed on a very sensitive balance, a counterpoise of the same size and shape being used. Then, by tipping the vessel, the two solutions were brought in contact a little at a time. After the reaction had been completed, the vessel was weighed again. The weighings were made several times, and an average was taken. As a result of

Fig. 1.1.

his work, Landolt concluded that, if there was a change in mass during chemical reaction, it was less than the error of weighing, which was 1 part in about 10,000,000.
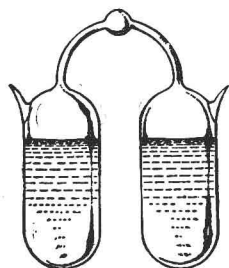
The later work of Manley[2] on the reduction of silver nitrate by ferrous sulfate showed that the change in weight attending this chemical reaction was less than 1 part in 32,000,000, which is less than the probable error in weighing. In another series of experiments Manley showed that the reaction between barium chloride and sodium sulfate was attended by a change in mass of less than 1 part in 100,000,000. In the light of these experiments there is no reasonable doubt that mass is conserved in chemical changes; we may, therefore, state that matter (anything which has mass) does not change in mass during chemical change.

One of the postulates of Einstein's theory of relativity states that matter is converted into energy under certain circumstances. The extraordinary velocities of some of the particles produced in nuclear reactions (which are briefly discussed in Chap. 16) confirm experimentally the conversion of minute quantities of matter into energy. The astonishing amount of energy radiated by the sun is also claimed to be due to the conversion of matter into energy, with the loss of 3.6×10^{11} tons of mass per day required. Recently a few grams of matter were converted into an enormous amount of energy under circumstances that attracted world-

[1] *Z. physik. Chem.*, **12,** 1 (1893); *Sitzber. preuss. Akad. Wiss.*, **1908,** 354.
[2] *Phil. Trans. Roy. Soc. (London),* (A) **212,** 227 (1913).

wide attention and set off an equally large amount of speculation, not to say fear, as to future developments. For the purpose of this text, we confine our attention to the common chemical reactions with which chemistry and chemical industry are concerned. In these reactions, mass is conserved within our limits of measuring it. The relation between the loss of mass and the energy produced is $\Delta E = \Delta mc^2$, where c is the velocity of light, 3×10^{10} cm. per sec. Hence, if the total energy evolved by the combustion of 12 grams of carbon to carbon dioxide came from the destruction of matter the loss in mass would be about 10^{-8} gram, which is far beyond the precision of any weighing device yet discovered.

Elements and Compounds. The number of kinds of matter is very great indeed, but attempts to resolve matter into its ultimate constituents by chemical means have brought to light about 92 natural elements that are not resolvable into simpler substances by the ordinary processes of chemistry. Many of the natural elements are indeed mixtures of particles of identical chemical properties and different masses, but they behave as simple substances in the reactions we are to study. The separation of elements into isotopes, which are atoms of different mass and practically identical chemical properties, will be discussed briefly in Chap. 16. We may mention here that deuterium, or hydrogen of atomic weight 2, has been separated in a practically pure state from natural hydrogen,[1] that neon (atomic weight 20.18) has been separated into portions of atomic weight 20 and 22, and that lithium (atomic weight 6.94) has been separated into portions of atomic weight 6.0 and 7.0; there are other instances of more or less complete separation of elements. The separation of chlorine (atomic weight 35.45) into portions of which one contained 99 per cent of the isotope of mass 37.0 has been reported,[2] and the separation of uranium isotopes is well known. The isotopes of hydrogen are called protium and deuterium (symbol D). Deuterium oxide, or "heavy water," contains about 20 per cent of "heavy" hydrogen, as compared with 11 per cent hydrogen in ordinary water; it boils at 101.42°C., freezes at 3.8°C., has a density of about 1.1, and its surface tension, latent heat, and other properties differ from those of ordinary water.

Lead of atomic weight ranging from about 206.0 to 208.0 results from radioactive changes and has been found in small quantities in some rare minerals. These isotopes of lead are the result of "natural" processes in the sense that they have not been produced in the laboratory; they are naturally occurring exceptions to the constancy of atomic mass, and their halides and other compounds have slightly different percentages of lead.

[1] Urey and Teal, *Rev. Modern Phys.*, **7**, 73–94 (1935).

[2] Hirschbold-Wittner, *Z. anorg. allgem. Chem.*, **242**, 222 (1939).

As may be seen from the periodic table in Chap. 14, it is improbable that there are many undiscovered natural elements of atomic weight less than uranium, and there is yet no evidence of *natural* elements of higher atomic weight than uranium. Very small amounts of "transuranium" elements, with atomic weights higher than that of uranium, have been made, as have many "synthetic" elements of lower atomic weight which are isotopes of natural elements.

Law of Definite Proportions. This law states that the quantity of an element that will combine with a given weight of another element to form a pure chemical compound is a fixed quantity, regardless of the method of preparation of the compound. In other words, the percentage of each element in a pure compound is always the same, and the presence of an excess of one element does not result in the formation of a compound containing more of it. The atomic theory was suggested to Dalton by this law, and the theory furnishes a ready explanation of the law. Identical whole atoms of an element, by combining with identical whole atoms of another element, must yield molecules of a fixed composition.

Table 1.1 shows data[1] on the synthesis of silver bromide from carefully purified silver and bromine, together with the weight of bromine combined with each gram of silver. Elaborate precautions were taken to ensure the purity of the substances weighed and to avoid mechanical loss during the synthesis.[2]

The synthesis was conducted by supplying ammonium bromide to a weighed quantity of silver that had been converted into nitrate, until no more bromine would combine with the silver, after which the silver bromide was collected and weighed.

Other examples of the law of definite proportions are shown in Table 1.1. A quantity of iron was converted into ferric oxide and heated with an excess of oxygen until no more would combine with it.[3] The ferric oxide was weighed, then heated in a current of hydrogen until all the oxide has been completely reduced to iron, which was then weighed. The synthesis of tin tetrabromide is also shown in Table 1.1. It will be seen again that the composition of the product is constant, insofar as it is possible for the best quantitative chemistry to determine it.[4]

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[1] Baxter, *J. Am. Chem. Soc.*, **28**, 1322 (1906).

[2] Students will note that six significant figures are given in most of the weights in Table 1.1. This is justified in view of the elaborate precautions that atomic-weight work requires. All the reagents are purified with great care, and manipulative precautions are taken with which students of ordinary quantitative analysis are quite unfamiliar. For an excellent description of such work, see Baxter, *Proc. Am. Acad. Arts Sci.*, **40**, 419 (1904), and **41**, 73 (1905), in connection with the atomic weight of iodine. Students who read these papers with care will find themselves well repaid.

[3] Richards and Baxter, *Proc. Am. Acad. Arts Sci.*, **35**, 253 (1900).

[4] Bongart and Classen, *Ber.*, **21**, 2900 (1888).

TABLE 1.1. DATA ILLUSTRATING DEFINITE PROPORTIONS

Weight of silver	Weight of silver bromide formed	Grams of bromine combined with each gram of silver
5.01725	8.73393	0.74078
5.96818	10.38932	0.74079
5.62992	9.80039	0.74077
8.13612	14.16334	0.74080
5.07238	8.82997	0.74079
4.80711	8.36827	0.74081
5.86115	10.20299	0.74078
6.38180	11.10930	0.74078
6.23696	10.85722	0.74079
9.18778	15.99392	0.74078
8.01261	13.94826	0.74079
8.59260	14.95797	0.74079
8.97307	15.62022	0.74079
		Average 0.74079

Weight of iron	Weight Fe_2O_3	Per cent Fe in Fe_2O_3
2.78115	3.97557	69.956
3.42558	4.89655	69.959
3.04990	4.35955	69.959
4.99533	7.14115	69.951
4.49130	6.42021	69.956

Weight of tin	Weight of $SnBr_4$ formed	Per cent tin in $SnBr_4$
2.8445	10.4914	27.113
4.5735	16.8620	27.123
4.5236	16.6752	27.119
3.0125	11.1086	27.116
2.8840	10.6356	27.113
3.0060	11.0871	27.123

Molecular Theory. The theory that matter of all kinds consists of molecules is now commonly accepted as a fact. This theory is in complete accord with all the known facts of chemistry; it explains in a simple way all our chemical reactions; and it forms the basis of modern chemical thinking. The molecules of which a substance consists cannot be divided into smaller particles without a complete change in the properties of the resulting particles. They are the limit of divisibility for a given kind of matter. When there are two or more kinds of molecules or molecular