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Consulting Editor

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UNIVERSITY CHEMISTRY

Preface to the Second Edition

In accordance with the response to the first edition of *University Chemistry*, I have made no basic changes in my approach to the subject in this second edition. Alternative, increasingly sophisticated, treatments of the kinetic theory of gases have been added, material on solid-state defects and on statistical mechanics has been included, and I have added a chapter on the elementary qualitative description of molecular orbitals and one on biochemistry.

It has always been my opinion that presenting extensive amounts of material on molecular orbitals before the student understands basic quantum mechanics is very difficult and involves certain dangers. I have tried to introduce the basic language and qualitative features of molecular-orbital theory and to emphasize the very approximate nature of the LCAO-MO treatment. The chapter can be used by those who feel their students are ready for it, but it is not necessary to the understanding of the rest of the book.

Biochemistry has been neglected too long in freshman chemistry texts and courses. My chapter is an attempt to provide a brief but coherent picture of this vast and important subject. I have emphasized the importance of fundamental chemical principles in the understanding of the complex processes of metabolism, synthesis, and replication. With this background, the student should be able to approach his more advanced courses with a clearer idea of the connection between chemistry and biology.

Once again it is a pleasure to thank the many colleagues, teachers, and students whose kind comments and encouragement have aided me greatly in writing this book.

November 1968

B.H.M.

Preface to the First Edition

This is a textbook of general chemistry intended for students who have had an introductory high-school chemistry course. Its design is based on my experience with such a group, which included students who had had a "standard" high-school course, one of the two newer courses generated by Chem Study and CBA, and a few who had had a second high-school course designed for advanced placement in college. Writing a book which emphasizes fundamental principles and builds on previous experience presents some difficult problems. It has been my experience, one shared by other university teachers, that at this time there is no one block of the traditional elementary material so well understood by the majority of freshman students that it can be entirely omitted from the beginning college course. On the other hand, it is still possible to take advantage of a student's previous training by assuming a general familiarity with the most fundamental chemical concepts. The ability to assume such a background allows the instructor to treat the elementary material in a critical manner—an approach which is generally appreciated by students who might otherwise consider review material to be boring. This is the course I have followed in writing this book. All the important elementary concepts are discussed, but from what I hope is a more penetrating point of view than the one already familiar to the student.

A further advantage afforded by the student's previous training is that time and space become available for new material, usually treated only in the upper division and graduate physical, inorganic, and organic chemistry courses. The concepts of elementary thermodynamics, reaction rates, and chemical-bond theory are most appropriate in the general chemistry course, for they can be immediately applied to systematize the descriptive material of inorganic and

organic chemistry. There is a danger here to be avoided: there is more material which might be presented than can be assimilated by the average beginning student. Just "covering" a great deal of advanced material can leave the student with no real command of the subject, but instead with a blasé attitude that he has "had all that," which can inhibit his success in more advanced courses. Consequently, I have made an effort to discuss only those advanced concepts which are either useful in the general chemistry course or which help to give a picture of what presently concerns the professional chemist.

The organization of this book departs somewhat from the recent standard of first presenting a detailed description of the electronic structure of atoms. Instead, the first four chapters are principally concerned with the macroscopic properties of matter, the origins of the atomic theory, and chemical arithmetic. Then follow five chapters which emphasize the characterization of chemical reactions and systems. Of these, Chapters 5, 6, and 7 treat, in increasing depth, the problem of chemical equilibrium. Thus the first seven chapters contain virtually all of the fundamental material of quantitative chemistry, and their position is particularly appropriate if the laboratory work in the course is to be quantitative in nature. Chapter 8 is an introduction to chemical thermodynamics which unifies the earlier phenomenological treatments of colligative properties and chemical equilibria. The thermodynamic concepts introduced here are used repeatedly throughout the chapters on descriptive chemistry. Chapter 9 treats the problem of chemical reaction rates and emphasizes the idea of reaction mechanisms.

The next two chapters, 10 and 11, are concerned with the electronic structure of atoms and the nature of chemical bonding. A part of Chapter 10 is devoted to the historical development of the quantum theory in an attempt to show that our knowledge of atomic structure and the quantum theory was gained by deduction from experiments, and not *ex cathedra*, as some elementary texts seem to imply. Deciding what can be said about chemical bonding that is simple, useful, and essentially correct is very difficult. I have tried to present a simplified point of view, while emphasizing its approximate nature and occasional inadequacies.

The final chapters contain the descriptive material of inorganic and organic chemistry. Their general thesis is that chemistry makes sense; that there are relationships, trends, and similarities in chemical behavior which can be understood in terms of chemical bonding, thermodynamics, and the periodic table. These chapters also contain certain extensions of the conceptual material covered earlier; for instance, the bonding in the boron hydrides, and the magnetic properties of matter.

The organization of this book is governed principally by my feeling that students should be supplied with the background that allows them to do quantitative laboratory work as early in the course as possible. I have, however, tried to write in a manner which will accommodate the preferences of others. Chapters 10 and 11 on atomic structure and bonding may be treated immediately after

Chapter 1, if the instructor prefers this organization. The material on thermodynamics can be delayed and presented just previous to the descriptive material of Chapter 13 *et seq.* Much of the discussion in Chapter 3 on the structures of solids can be combined with descriptive chemistry or with the material on chemical bonding.

This book is primarily intended for serious students of science, including those majoring in biology, engineering subjects, and premedicine, as well as physics and chemistry. Calculus is used in and after Chapter 6; concurrent enrollment in the introductory calculus course will provide an entirely adequate mathematical background.

Sincere thanks go to Professors Jerry A. Bell, Francis T. Bonner, and Paul B. Dorain for reading the manuscript and making many kind and helpful suggestions concerning the material. The entire manuscript was typed by Mrs. Nancy Monroe, whose cheerful help and cooperation are greatly appreciated. A considerable portion of this book was written while I was a visitor at Oxford University, and I would like to acknowledge the hospitality extended to me by the fellows of the Queen's College, and particularly the many kindnesses of Dr. and Mrs. J. W. Linnett. It has been my privilege to associate with two outstanding chemistry faculties. I would like to thank my teachers at Harvard University and my colleagues at the Berkeley campus of the University of California for the stimulation and instruction I have received from them.

Berkeley, California
January 1965

B.H.M.

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STOICHIOMETRY AND THE BASIS OF THE ATOMIC THEORY

Our whole understanding of chemical phenomena is based on the atomic theory of matter. It is a theory remarkable for the detailed accuracy with which it describes a seemingly unknowable part of our physical world, and it stands as the most important collection of ideas in science. Throughout this book we will be continually drawing on the theory to help us organize and understand chemical behavior. Faced with a repeated demonstration of the usefulness, detail, and subtlety of the atomic concept, it is natural to wonder how such ideas were generated. In this chapter we will briefly outline the origins of the atomic theory and show how its development was connected with the growth of chemical science.

1.1 THE ORIGINS OF THE ATOMIC THEORY

The “atomism” of the Greek philosophers of 400 B.C. provides an interesting and enlightening contrast to our present-day atomic theory. The Grecian atom was designed to resolve a logical conflict: on one hand there was the *observation* that natural objects are in a constant state of change; on the other there was the unshakable *faith* that there must be a permanence associated with things which are real. The Greeks felt that this philosophical impasse could be avoided if invisible atoms were accepted as the permanent constituents of the universe, and if observable changes were interpreted in terms of their motions.

Now it is clear that the phenomena of mixing, evaporation, erosion, and precipitation can be readily “explained” in terms of an atomic picture which is not at all detailed. With but little elaboration the atomic idea encompasses many properties of matter. The existence of solids requires only that certain atoms have extensions with which they can interlock themselves to form an unyielding mass. The atoms of liquids need only be smooth to flow over one another, while the taste of some chemicals arises from sharp edges of their atoms slashing at the tongue. While some of these ideas are of remarkable accuracy (the enzyme molecules in raw pineapple do indeed “slash” at the tongue by destroying the protein structure), they are nothing but conjecture. The Greek atomism lacked the essential feature of a scientific theory: it was not supported or tested by critical experiments. Since it was a construct of conjecture, it could be demolished by more conjecture. The objections which arose concerned the simplicity of atoms and the complexity of nature. How could something so small and inanimate be responsible for things which live? How could the variety of nature arise from particles which, the Greeks felt, differed only slightly from one another? How could any body, being a collection of particles moving in chaos, have predictable behavior? These are questions which still concern us and which stimulate the constant refinement of the modern atomic theory. They are also questions which, by 40 B.C., led to the abandonment of atomism as an active philosophy. One conjecture had been toppled or seriously shaken by others, and so the situation remained for nearly 2000 years.

Surely it is correct to say that the logical basis for belief in the existence of atoms was supplied by Dalton, Gay-Lussac, and Avogadro, in work published in the early 1800's. What is it, though, that distinguishes the contributions of these men from the ineffectual speculations of the preceding 2000 years? Why is it that Dalton is called the father of the atomic theory, when for a century and a half previous to his work such distinguished men as Boyle and Newton had used the particulate description of matter? The quality which Dalton held in common with Gay-Lussac and Avogadro was a concern for the testing of an idea by performance of a quantitative experiment, and the success he shared with them was the demonstration that diverse experimental data can be summarized by a limited set of generalizations on the behavior of matter. Dalton's contribution was not that he proposed an idea of astounding originality, but that he clearly formulated a set of postulates concerning the nature of atoms; a set of postulates which emphasized *weight* as a most fundamental atomic property.

On the basis of the crude experimental data available to him, Dalton suggested that there are indivisible atoms; the atoms of different elements have different weights; and atoms combine in a variety of simple whole number ratios to form compounds. We recognize today that these postulates are not all exactly correct, but they were the first rationalization of the quantitative laws of chemical combination. Inasmuch as the combining laws comprised the first convincing experimental demonstration that Dalton's ideas were essentially

correct, they form the experimental basis for the atomic theory. Let us examine each of these laws, with respect to both its role in the development of the atomic theory, and the extent to which it is held valid today.

Questions. Do you feel that any of the following phenomena constitute qualitative evidence for the existence of atoms: sharp edges on crystals; dissolution of solids in liquids; high compressibility of gases but not of liquids and solids; the suspension of small particles in liquids and gases; the occurrence of chemical change? Can you think of other models that will explain any or all of them?

The Law of Definite Proportions

In a given compound, the constituent elements are always combined in the same proportions by weight, regardless of the origin or mode of preparation of the compound. To those familiar with the atomic theory this law is in obvious agreement with the principle that each molecule of a given compound contains the same number of atoms of each constituent element. Since the atoms of each element can be assigned a definite average weight, the composition by weight of a given compound is some definite value fixed by the atomic weights and the molecular formula. The law of definite proportions had been established experimentally before Dalton published his atomic theory in 1807, and the consistency of the theory with existing experiments was clearly in its favor and hastened its acceptance. However, the law of definite proportions is by no means a proof of the validity of the atomic theory. Our argument demonstrating the consistency of the atomic theory and the law of definite proportions might be more critically stated by saying that *if* there are atoms, and *if* compound formation involves interaction of these atoms in some specific way, then we might *expect* that all molecules of a given compound contain the same numbers of atoms. Then, *if* all atoms of a given element have the same weight, a compound must have a definite composition by weight. It was Dalton's position that each of these conditional statements was true; but proof of this requires more than just the fact that the consequence of all of them together is consistent with experiment. We can say, however, that it is difficult to imagine any theory not based on the atomic concept which could explain the law of definite proportions without even more serious conjecture.

Considering the importance of the law of definite proportions to the development of the atomic theory, it is surprising to find that this "law" is in many cases only a rough approximation to observed behavior. In the first place, the composition by weight of any compound depends on the atomic weights of its constituent elements. For elements having more than one isotope, the atomic weight is an *average number* whose value depends on the isotopic composition, and this may vary noticeably, depending on the source of the element. Therefore the atomic weight of an element and the weight composition of its compounds are necessarily subject to variations, and consequently the law of definite proportions is not strictly followed. One of the most serious offenders

is boron, whose atomic weight may range from 10.82 to 10.84 as a result of natural variation in the ratio of abundance of the B^{11} and B^{10} isotopes. Fortunately, the variations of natural isotopic composition associated with most elements are smaller than this, and become troublesome only in the most precise work.

There is, however, another source of more serious violations of the law of definite proportions. While it is true that compounds composed of simple discrete molecules display a definite atomic and weight composition, it is also an experimental fact that there is an obvious variation in the relative numbers of atoms in ionic solids such as zinc oxide, cuprous sulfide, and ferrous oxide. For example, the composition of cuprous sulfide can range from $Cu_{1.7}S$ to Cu_2S . Materials in which the atomic composition is variable are called **nonstoichiometric compounds**, and the most extreme examples of this behavior are found among the sulfides and oxides of the transition metals.

Let us see how the atomic theory accommodates the existence both of stoichiometric and nonstoichiometric compounds. First consider a compound which consists of simple, discrete molecules, like nitric oxide, NO. Now it is clear that in order to make the atomic composition of nitric oxide depart from a 1/1 ratio, we must in some way change the atomic composition of *each* nitric oxide molecule. But the smallest possible change which we can make in a nitric oxide molecule is to add to it either one atom of nitrogen or one atom of oxygen. This results in the formation of N_2O or NO_2 , both of which we recognize as compounds whose chemical properties are quite distinct from those of nitric oxide. Accordingly, we conclude that no change in the atomic composition of nitric oxide is possible without creating a new chemical species. The atomic and weight compositions of nitric oxide are therefore constant, and this and other molecular compounds obey the law of definite proportions.

Solid compounds that contain no discrete molecules present an entirely different situation. It is possible to prepare crystals of TiO with an atomic ratio of 1/1, yet if the conditions of preparation are varied, crystals of composition ranging from $Ti_{0.75}O$ to $TiO_{0.69}$ can be obtained. All these crystals have the same spatial arrangement of ions, as x-ray studies show. Depending on the preparation of the crystal, varying fractions of the titanium (II) and oxide ions are absent from sites in the crystal lattice that could be occupied, and titanium (II) oxide does not obey the law of definite composition. Such variation in atomic composition can occur without affecting the chemical properties, because titanium (II) oxide contains no discrete molecules, and the change in the ratio of atoms in the crystal as a whole does not cause a change in its crystal structure. In contrast, the electrical and optical properties of the crystal are sensitive to its atomic composition, for the resistivity and color of nonstoichiometric compounds change markedly as the atomic ratio varies.

Figure 1.1 indicates schematically how nonstoichiometry can occur through lattice vacancies (as in TiO) or through extra interstitial atoms (as in ZnO). Note that the ability of an atom to assume more than one oxidation state