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CHEMISTRY

D. C. HEATH AND COMPANY BOSTON
ENGLEWOOD CHICAGO SAN FRANCISCO ATLANTA
DALLAS LONDON TORONTO

PRINTED IN THE UNITED STATES OF AMERICA

Library of Congress Catalog Card Number: 65-11347

About UNIVERSITY CHEMISTRY —

ILLUSTRATION: R. Paul Larkin

DESIGN: Panagiota Darras

TYPE FACE: Times Roman, designed by Stanley Morison for *The Times* of London.

COMPOSITION: Monotype, by Wolf Composition Co.

MANUFACTURE: Offset printed and bound by W. A. Krueger Co.

PAPER: *Bookman* paper by S. D. Warren Company was especially formulated to complement the colors of the inks used in this book.

UNIVERSITY CHEMISTRY

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UNIVERSITY

PREFACE

To say that we are participating in the most challenging era in the development of chemical science is to state in the most moderate terms what is obvious to all. We see everywhere new technical products, new drugs, new fuels, new materials of construction, new electronic devices, new colors, new fabrics, new weapons, even new modes of existence based upon our developing chemical knowledge. We are aware of the construction of new chemical laboratories, both academic and nonacademic, designed to further the study of chemistry in its theoretical and practical senses. We learn, even from popular sources, of the steadily increasing demand for persons trained in chemistry and of the growing emphasis upon providing this training. We realize that the sum total of available chemical knowledge is large and that additional information is becoming available at a rapidly accelerating rate.

With this realization comes the question of how this knowledge can be imparted to beginning students to best advantage and with the greatest degree of logic and correlation. Should the presentation be encyclopedic or fragmentary? Should it be wholly conceptual, or should it be wholly descriptive? Should it deal only with recent developments, or should it take into account the whole of significant accomplishment down through the years? Should it be completely final, or should it delineate unsolved problems and thus attempt to impart to the student the background, intellectual tools, and abiding curiosity essential to their solution? Should it be designed only for those students who propose to be professional chemists, or should it recognize that a rigorous background is essential to persons who will enter other professions? Should it be sufficient unto itself, or should it be keyed to the presentation of advanced topics and the development of fundamentals in subsequent courses? Obviously there is more than a single way to answer each of these questions, but if a new introduction to chemistry is to be made available to students, its authors must provide a coordinated series of answers through an underlying and consistent philosophy of writing.

It is our firm belief as teachers that general chemistry must be a truly general introduction to the entire science of chemistry. It is our further belief that to provide such an introduction we must offer a rigorous presentation of coordinated fact and principle which is modern in approach but not so modern that those developments that led to present-day ideas are ignored. We must realize fully and impart to the reader the realization that chemistry is an experimental science, that theoretical concepts are valid only if they can be successfully tested by experiment, and that chemistry is a growing science which does not answer all of the questions that can be raised by observation. In preparing this textbook, we have been guided by these beliefs. Our philosophy that general chemistry is a logical combination of fact and theory, which can be developed through interpretations of observations into a coordinated background of either generally useful information or fundamentals for further expansion, is an expression of these convictions.

We have attempted to make the presentation in this book modern but not unmindful of the past, liberal but not radical, conservative but not classical, and broad but not all-inclusive. The presentation is not geared to the high-level honors program that seeks only to train students who hope ultimately to take doctor's degrees in chemistry; it does not include wave mechanics, statistical thermodynamics, or the whole of classical physical chemistry. It is not dedicated to the principle that an acquaintance with concepts is the sole criterion for understanding chemistry. Rather, the presentation is designed to develop logically and reasonably, in terms of observation, the fundamentals of theory and practice that constitute modern chemistry. It is based, primarily, upon the structure of matter and is developed around this theme. We have tried to include in our presentation the modern approaches to structure, to the chemical bond, to equilibrium, to kinetics and reaction mechanisms, to the fundamentals of thermochemistry and thermodynamics, to coordination chemistry, to nuclear chemistry, and to a host of other items, not as subjects sufficient unto themselves, but rather in a context of how they are related to each other and to modern descriptive chemistry. The presentation is designed for either the terminal or prerequisite type of general chemistry course that seeks to offer rigor in breadth and to engender interest. It is adaptable either to students with a background in high-school chemistry or to the better students without such a background. It is the feeling of the authors that it may well be adaptable to many honors courses.

The reader will find special emphasis upon the logical development of the subject from the relatively simple stages to the more complex. In explanations of advanced topics, the reader will find a continuing use of material already presented, a uniform correlation of factual and conceptual items, and a careful balance between descriptive and theoretical chemistry. He will see strong emphasis upon quantitative relationships, extensive reference to periodic relationships, a remarkably close correlation between electrochemistry and the general subject of oxidation-reduction, and a balance in discussion that permits adequate treatment of the representative, the transition, and the inner transition elements. The reader will appreciate, we believe, the continuing emphasis upon the solution of numerical problems by reasoning approaches involving dimensional analysis. He will appreciate, also, the inclusion of a host of new and challenging exercises. He will find a novel approach that develops many ideas in terms of the properties of two well-known substances: water and sodium chloride. Above all, he will encounter discussions that have been developed with due consideration to his own needs and tailored to proven patterns of instruction. A series of imaginatively executed new drawings, that should prove to be highly instructive, supplements the entire presentation.

In writing this book, the authors have drawn heavily upon their experience in the classroom and upon discussion with students and colleagues. They are indebted to those innumerable persons who by these discussions helped in the preparation of this volume. To name all of these persons is impossible; to offer a blanket "thank you" to them is an unsatisfactory but essential alternative. Our thanks are not in the least diminished by this approach. We do express specific gratitude to Miss Janet D. Scott for making the index, and to Mr. R. Paul Larkin for doing the illustrations.

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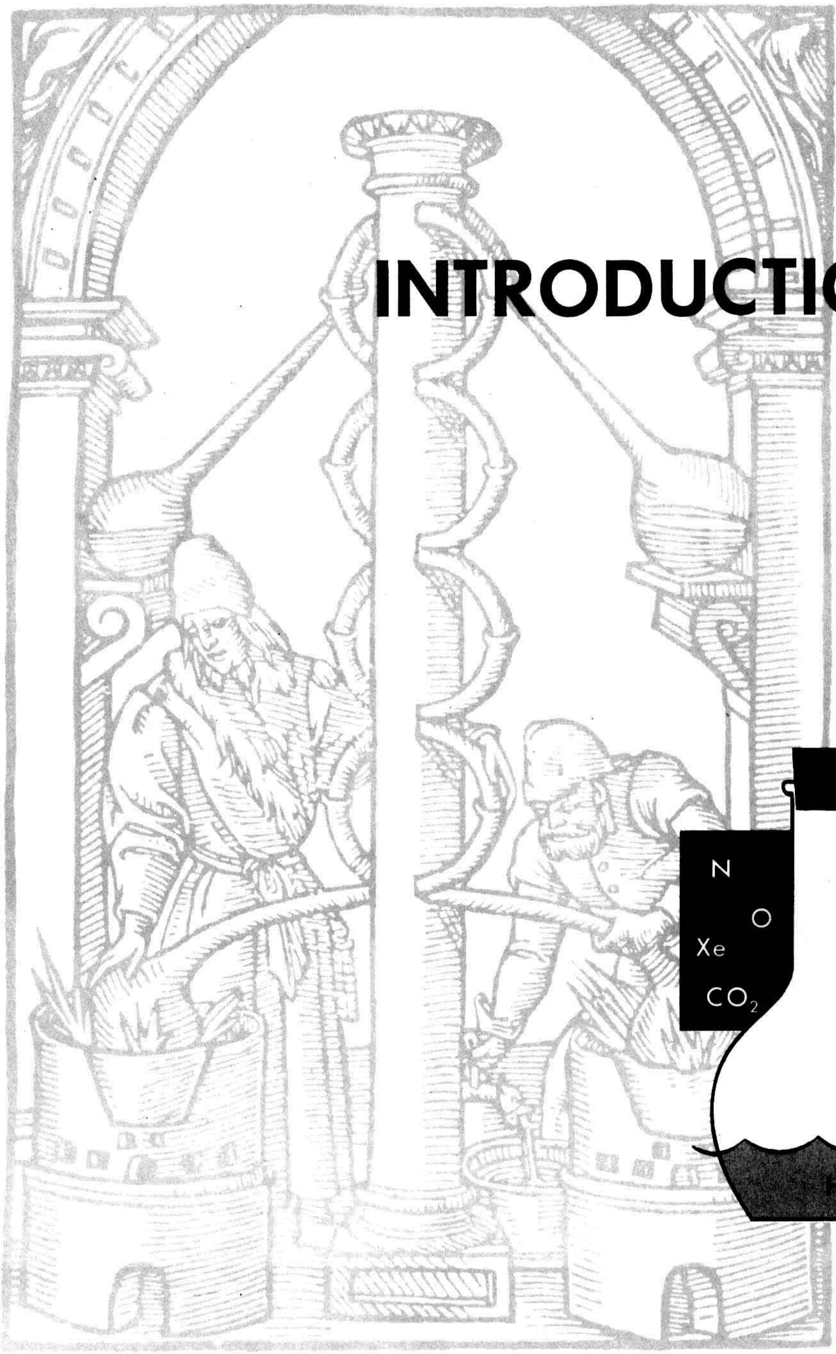
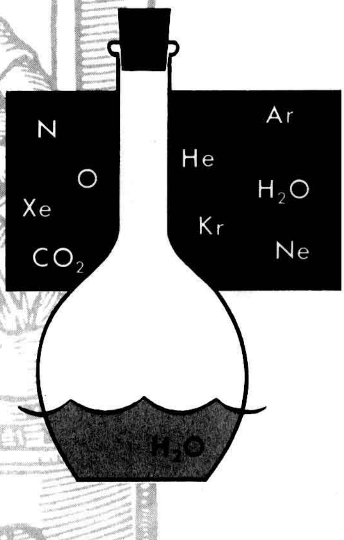
INTRODUCTION





Alchemists at work. From *De Secretis Naturae* by Philip Ulstadt (1544).

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CHAPTER 1

1–1 What Chemistry Is. How It Differs from Physics

The reader will quickly discover that this book presupposes that he has some prior knowledge of scientific terms. The authors believe that nearly all college students have gained such knowledge from their general reading, if not from courses in general science, physics, or chemistry. Most of the chemical terms used in this book are defined, at least in a general way, the first time they are used. Many are defined again, later in the book, in a more detailed and sophisticated manner. In the early chapters, the student may encounter a few chemical words that are not familiar to him. If so, he should learn their meanings by consulting a dictionary, or by finding these words in other parts of this book with the aid of the index. If this habit is developed early, the terminology of chemistry, and hence, the study of all phases of the science, will be greatly simplified.

It is the hope of the authors that the course presented here will not be too difficult for students who have not studied chemistry in high school, but different enough from the high school course that it will challenge and interest those who have studied chemistry in high school.

Chemistry is the science that deals with the composition of matter, and especially with the changes in composition which matter may undergo. Matter is anything that occupies space and has weight. Matter may be classified into three types—elements, compounds, and mixtures. Elements and compounds exist in the form of discrete particles—molecules, ions, and atoms. Atoms, in turn, are composed of protons, electrons, neutrons, and other primary particles. The properties of a substance depend upon the nature, the number, and the arrangement of the particles which constitute it. Thus, chemistry is concerned primarily with the structure of atoms, the way the atoms behave in forming ions and molecules, and the nature of the substances which these particles compose.

Chemistry is concerned only in a secondary way with mixtures, for, in general, the separation of mixtures into compounds and elements does not involve chemical changes; i.e., changes in the composition of matter.

All chemical changes, as far as we know, are accompanied by a loss or gain of energy, usually in the form of heat, light, or electricity. It follows that although chemistry is concerned primarily with the composition of matter, it must also be concerned with the absorption and evolution of energy. Chemistry is therefore intimately related to physics, which is the science concerned primarily with the study of energy. Since energy is a manifestation of the behavior of matter, physics must deal with matter as well as with energy.

There is no real dividing line between chemistry and physics. We think of them as separate subjects as a matter of convenience, but we recognize that the distinction between a chemical property and a physical property, or a chemical change and a physical change, is purely arbitrary. This is well illustrated by the process of solution, which may or may not involve changes in the composition of the materials involved. If a piece of zinc is dissolved in concentrated sulfuric acid, the metal disappears and foul-smelling gases are evolved. Evaporation of the acid by heating leaves a white, powdery residue of zinc sulfate. Clearly, in this case, substances have been changed into other substances—a chemical change has been involved. When water is dissolved in pure sulfuric acid, other kinds of changes take place. A great deal of heat is evolved, and the solution has characteristics which were not possessed by either of the original materials. The solution, for example, is a good conductor of electricity, although neither pure sulfuric acid nor pure water is a good conductor. However, if the solution is boiled, water is removed as vapor, leaving pure sulfuric acid behind. Since the components of the mixture can be separated by physical means (evaporation by heat), the mixing of sulfuric acid and water has long been considered to involve only physical changes. However, we know that this is not strictly correct—the molecules of sulfuric acid break into ions when they are dissolved in water (Table 11–3), and the ions combine with molecules of the water. That a reaction takes place when sulfuric acid is mixed with water is shown by the fact that concentrated and dilute acid have quite different chemical properties. As another example, consider the dissolving of sugar in water. Little heat, if any, is evolved; the solution does not conduct electricity, and, indeed, it does not seem to possess any chemical property which was not shown by one or the other of the components. Yet careful study shows that the molecules of sugar combine with those of water. Whether the bonding here is sufficiently tight to constitute a change in composition is, perhaps, a matter of opinion. This example of dissolving is usually considered to be physical in nature, but one could logically argue that it is chemical. Finally, consider the dissolving of paraffin in gasoline. In this case, there is no evidence that the composition of either component is affected by the presence of the other while they are mixed. We must, then, consider *this* example of solution to be purely physical.

Here we have illustrated, by different kinds of solutions, the fact that there is no absolute dividing line between physical changes and chemical changes. Other examples of borderline cases of quite different sorts might also be mentioned; these would include the conversion of water into steam and the change in color of mercuric sulfide when it is heated.

Chemistry and physics, along with mathematics, are basic sciences. Biology, astronomy, geology, and all of the other natural sciences lean heavily upon these three. Any student who wishes to go very far in any science, or in engineering, or in medicine, must first gain an understanding of these basic three. This was not always true; until recent years it was quite possible for a geologist or a botanist, for example, to be an expert in his profession with little background in chemistry, physics, or mathematics. However, with the rapid advance which science has made in this century, the sciences have intergrown to such an extent that an understanding of chemistry, physics, and mathematics is essential to real progress in any scientific field.

1–1a Subdivisions of Chemistry

Since chemistry is such a broad subject, it is convenient to subdivide it into smaller areas. The dividing lines between these are quite artificial, and the subdivisions of chemistry overlap a great deal, but since they have come to have real meaning, a brief description of the subdivisions of chemistry is in order here. **Organic chemistry** is concerned with the chemistry of carbon compounds. Its name is derived from the fact that in earlier times, its chief concern was with substances which came from living (organic) material. **Inorganic chemistry** deals with all of the elements except carbon (and even includes some carbon compounds). The French call it "Chimie Minérale" but this is too narrow a term, for there are many inorganic substances that are not of mineral origin. **Analytical chemistry,** as the name implies, is concerned with the analyses of materials, that is, the determination of their compositions. **Physical chemistry** includes the study of the physical properties of materials and the theories which relate these properties to the structures of the materials and their chemical behavior. **Biochemistry** deals with the chemical reactions that go on in living systems, for example, in growth, in digestion, and in disease.

Although these are the main subdivisions of chemistry, others are frequently mentioned. These include radiochemistry, sanitary chemistry, food chemistry, ceramic chemistry, geochemistry, and soil chemistry.

Chemical engineering is concerned with the design, construction, and operation of plants in which chemical reactions can be carried out efficiently on a large scale. Essentially, it lies between physical chemistry and mechanical engineering.

1–2 The Importance of Science

The growth of scientific discovery has affected the lives, not only of scientists, but of all people, and has made it desirable that the education of everyone include a knowledge of chemistry and of its importance. Food, of course, is a mixture of chemical substances, and it undergoes changes in composition in the processes of digestion and metabolism. In addition, many of our prepared foods contain chemicals which are added to retard deterioration or to improve the tenderness or the flavor. Our clothing, once made only from natural fibers, is now prepared increasingly from synthetic materials which have special properties to provide special characteristics—longer wear, resistance to wrinkling, elasticity, strength, immunity to moths, or some other characteristic demanded by the use to which the clothing is to be put. The development of new drugs (usually attributed by the public to the medical profession, but actually, largely chemical) has lengthened the span of life and has greatly increased our comfort. Many more examples could be given. Every walk of life has been affected by science within the last few years—the book which you are reading is purely the product of chemistry. The paper, the ink, the cloth of the cover, the adhesive in the binding—all of these are produced by chemical changes, and their preparation is supervised by chemists or chemical engineers. It is too much to expect every citizen to understand the details of the chemicals and the chemical changes which support his life, but it is not too much to hope that every person will have a real understanding of the role of chemistry in modern life and of the methods and philosophy of science.

1–3 The Scientific Method

Natural science proceeds, first of all, through observation. The earliest men observed birth, growth, sickness, and death, and the more curious among them certainly speculated on the causes of these phenomena. Such a speculation, if it is based on observation, and if it tries to give a general explanation, is called a **hypothesis.** It should suggest further observations, and raise questions as to its own validity: "Does sickness always follow the eating of a certain food?" "Is this the only food that produces illness?" "Do different foods produce different kinds of illness?" "Do people sometimes become ill when they have not eaten any of these foods?" Even primitive men must have raised such questions and tried to answer them by repeated observations. Many of their hypotheses were based on superstition and were completely false, but they must not be ridiculed, for they were the beginning of scientific thought. A hypothesis, ancient or modern, is useful if it leads to further observation and to its own refinement and improvement.

When a hypothesis has achieved a status of some probability—that is, when enough observations have been correlated to make the hypothesis seem reasonable and general—it graduates to the status of a **theory.** The ancient Greek philosophers watched the motion of the heavenly bodies and recorded their observations with enough accuracy that they were able to formulate general rules for astronomical phenomena, and to develop theories to account for their observations. A theory is not necessarily a true explanation; it should, however, explain all or most of the observations which have been made. Even if it does not account for *all* of the known observations, it may be useful in correlating a great deal of information, in suggesting new experiments, or in leading scientists to suggest alternative theories. It may be used, even though it is known to be faulty, as long as it is helpful in generating new ideas or in advancing science, but it must be modified or discarded when a more accurate or helpful theory is available. This is not always easy, for scientists, like other people, have a tendency to cling to their ideas and to try to explain away the faults of their hypotheses. In the history of science, many a theory has been modified, patched, and extended, long after it should have been discarded in favor of a quite different theory.

Every theory involves assumptions, and if the theorist is willing to assume enough, he can explain almost anything. For example, during the eighteenth century, it was theorized that combustion involved the loss of a substance called "phlogiston" from the burning material. According to this theory, noncombustible substances do not burn because they contain no phlogiston. Wood contains phlogiston; when it burns the phlogiston escapes, and only the ash is left. The ash weighs less than the wood because of the loss of the phlogiston. When it was pointed out that the combustion of a metal leaves an ash that weighs more than the metal, the phlogistonists theorized that metals must contain a kind of phlogiston which has negative weight! The theory obviously had outlived its usefulness, but even after Lavoisier announced an alternative and much better theory (that combustion is combination with oxygen), many scientists continued to believe in the modified phlogiston theory. Among these, interestingly enough, was one of the discoverers of oxygen, Joseph Priestley.

Everyone now accepts Lavoisier's theory of combustion. So many experiments have been performed, and so much is known about the combustion process, that it is inconceivable to us that combustion does not involve reaction with oxygen. On that account, we no longer refer to Lavoisier's proposal as a theory—it has become a **law**. Of course, even what we regard as a law may not be completely true, for someone may sometime observe a scientific fact which is contrary to it. However, the generalizations which are designated as laws are so very well established that we think it *most* unlikely that any of them will be upset. It may be necessary to modify them slightly as more exact measurements are made. A scientist accepts a law as true if his observations, and those of other scientists, are in accord with it, and if, by such acceptance, he can correlate or understand phenomena which otherwise seem unrelated or unexplainable. He uses the law and relies on it in the belief that it is true. Evidence that the law is not true will doubtless come as an emotional and intellectual shock to him; however, if he is a true scientist, he will modify his beliefs to fit the new state of scientific knowledge. This is the spirit of science.

Scientific theories have undergone several such changes in the last few years, and doubtless will undergo many more in the years to come. For example, the discovery in 1962 that xenon forms stable compounds revolutionized many of our ideas of molecular structure and chemical bonding. Should we lose our faith in science because our theories and laws are continually being upset? Not at all. Our knowledge of molecular structure grew tremendously during the years that we believed xenon and the other noble gases to be inert, and partly *because of* that mistaken belief. We are now ready to discard the idea that these gases are inert and to build a better science on the new observations.

1-4 Compounds

As has already been pointed out, all materials are either mixtures, compounds, or elements. A **mixture** contains **two or more substances not chemically combined with each other.** Each retains its own properties. In some mixtures, the fact that different substances are present may be detected by the eye, perhaps with the aid of a magnifying glass or microscope. A mixture of sand and salt is of this kind. In other mixtures, such as a solution of paraffin in gasoline, it is impossible to distinguish particles of either constituent. This results from the facts that the particles are almost infinitely small and that they distribute themselves uniformly and completely (as individual molecules). A mixture is characterized by variable composition, though the composition may not be infinitely variable. Thus, sand and salt, or alcohol and water, may be mixed in any proportion; on the other hand, the amount of sugar that may be dissolved in a given quantity of water is limited.

A compound is also formed from two or more substances, but in this case, the component materials lose their individual properties, and the compound may have quite different characteristics from the materials of which it is composed. Moreover, substances combine to form a compound in a fixed ratio. For example, if 200 grams of mercury is ground in a mortar with 32 grams of sulfur, complete combination takes place—neither mercury nor sulfur remains. The silver color of the mercury and the yellow color of the sulfur are gone—the new material is a black powder. Although mercury will dissolve in dilute nitric acid, and sulfur will dissolve in carbon disulfide, the newly formed material is not soluble in either of these liquids. If the mercury and sulfur are taken in any other ratio than 200:32, the excess of one or the other will remain uncombined, and can be extracted, either with dilute nitric acid (if the mercury was in excess) or with carbon disulfide (if the sulfur was in excess). When combined in this way, mercury and sulfur unite *only* in the weight ratio 200:32. In many cases, two elements can combine in more than one ratio, forming quite different compounds. This does not violate the **Law of Definite Proportions,** which states that **the composition of any pure compound is always the same.** A compound may be derived from three or four or more elements, but the ratio in which these elements combine is constant. Later, it will be shown that some compounds apparently do not fulfill this requirement; however, the exception is more apparent than real (Sec. 21–4).

1–5 Elements

As has been indicated, compounds are made up of simpler substances called elements. At present, 103 elements are known. Not all of these occur in nature, and some are sufficiently unstable that they can be kept only for relatively short periods of time. The progress chemistry has made in the last sixty years is well illustrated by the fact that the definition of the word "element," which is fundamental to all of chemistry, has had to be changed several times. Chemists once believed that an element could not be decomposed into simpler substances, but the discovery of radioactivity forced a change in this point of view. The substance radium, for example, has the properties of an element. It closely resembles barium and strontium, which clearly are elements, and it fits perfectly into Representative Group II of the periodic system of the elements (Sec. 6–5). It does not fit the conditions of the definition which has just been given, however, for it is constantly decomposing into simpler substances. This decomposition is purely spontaneous; it cannot be started or stopped in the laboratory, or even accelerated or retarded by the methods which chemists ordinarily use to control the rates of reactions. It was quickly seen that if radium was to be considered an element, then the definition of that word had to be changed.

In view of this observation, chemists adopted the definition "An element is a substance that cannot be decomposed into simpler substances *by any known means*." This was not very satisfactory, for the question was immediately raised "What if someone finds a way to produce or regulate such changes?" Indeed, within a very few years, physicists found that they could induce radioactivity into some of the well-known elements, and the definition had to be changed again to indicate that an element could not be decomposed *by chemical means*. This definition, too, was unsatisfactory, for there is no real distinction between "chemical means" and "physical means." Clearly, a new approach to the definition was to be desired.

Such a definition was found in the statement that "An element is a substance in which all of the atoms are alike." This definition avoids any statement concerning the stability of the substance, and for a time it seemed to express a completely satisfactory point of view. However, the discovery of **isotopes** (Sec. 2–7b) showed that all atoms of an element are *not* alike—some are heavier than others. So, again, the definition had to be changed. We now define an **element** as a substance in which **all of the atoms have the same atomic number**; i.e., they contain the same number of protons. We believe this to be a sound definition and without any exception. Our prede-