SOURCEBOOK
ON
ATOMIC ENERGY

BY SAMUEL GLASSTONE

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Consultant to the United States Atomic Energy Commission

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Foreword to the Second Edition

THE Atomic Energy Commission, at the request of the American Textbook Publishers Institute, sponsored the first edition of the *Sourcebook on Atomic Energy* written by Dr. Samuel Glasstone and published in 1950. The worldwide acceptance of the book has fully justified the original expectations that it would provide a source of basic atomic energy information for readers with many different interests. About 50,000 copies of the English language edition have been sold and the book also has been translated into several foreign languages. Its use in schools, colleges and universities has made it a significant contribution to education in atomic science.

The fund of knowledge in the field of nuclear energy has increased rapidly since 1950. Therefore, in keeping with the Commission's policy to distribute information as broadly as possible, Dr. Glasstone was requested to prepare this revised edition.

As in the case of the first edition, the staff of the Commission has assisted in the provision of material for inclusion in the book, but its presentation and scientific evaluation are wholly the work of its distinguished author, Dr. Glasstone.

Lewis L. Strauss

CHAIRMAN, UNITED STATES ATOMIC ENERGY COMMISSION

Acknowledgment

I WISH to thank all those whose names were mentioned in the first edition of this book for help given me in connection with the original manuscript. In particular, I would like to record my very great appreciation of the efforts of the late Dr. Alberto F. Thompson, whose foresight and persistence made the work possible.

In preparing the revised edition, the suggestions and comments of many colleagues and correspondents have been very useful. Special thanks are due to Drs. O. R. Frisch, A. V. Grosse, L. Szilard and H. C. Urey, for interesting historical side lights; to Drs. R. K. Wakerling and H. Bradner, University of California Radiation Laboratory, for the provision of illustrations; to Mr. Bernard M. Fry, Assistant Director for Technical Information Service, A.E.C., and his staff, especially Dr. A. Frank Owings and Mr. Paul S. Feinstein, for their cooperation and encouragement, and Mr. Carl B. Holmes, for assistance with the art work; and to Dr. Norris E. Bradbury, Director, and other members of the Los Alamos Scientific Laboratory for placing the excellent facilities of the Laboratory at my disposal.

Finally, I wish to express my indebtedness to my wife for her continued help in innumerable ways.

Los Alamos, N. M. SAMUEL GLASSTONE
January 1958.

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Foundations of the Atomic Theory

Chapter I

THE ATOMIC CONCEPT

EARLY HISTORY OF THE ATOM

1.1. The broad concept of the atomic structure of matter can be traced back some 2500 years to the scholars of ancient Greece, and even to the Hindu philosophers of a still earlier age. In the fifth century B.C., Leucippus and his pupil Democritus, as founders of the Greek school of atomists, taught that all material things were made up ultimately of small, indivisible units which Democritus called *atoma* (atoms).* Although these teachings were supported by Epicurus, whose ideas were elaborated at length by Lucretius in his famous Latin poem, *De Rerum Natura* (Concerning the Nature of Things), during the early part of the first century B.C., the considerations made little headway, largely because of the objections of the influential Greek philosopher Aristotle (384 to 322 B.C.). Thus, atomistic concepts lay dormant for several hundred years, until they were revived in the active period of learning which followed the Renaissance in Europe. During the sixteenth and seventeenth centuries after Christ, philosophers and scientists, such as Galileo Galilei in Italy, René Descartes in France, and Francis Bacon, Robert Boyle and Isaac Newton in England favored the view that matter was not continuous in nature but was made up of ultimate particles or atoms.

DALTON AND THE ATOMIC THEORY

1.2. It was not until the nineteenth century, however, that the work of the chemist transformed the atom from a somewhat vague philosophical idea to a material reality, while the discoveries of the physicist laid the foundation for the development during recent years of a remarkable body of detailed knowledge concerning its internal structure.

1.3. Credit for originating the modern atomic theory is usually given to the English schoolteacher John Dalton, who became interested in the subject as a result of his investigations of the solubilities of gases in water and other liquids. The part he played in the development of the theory, although of the greatest importance, is frequently misunderstood. In writing of

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* The term *atom,* derived from two Greek words, *a* (not), *temnein* (to cut), implies something that is not divisible.

Dalton's contribution, the German physical chemist W. Nernst stated that "by one effort of modern science, [it] arose like a phoenix from the ashes of the old Greek philosophy." That this is a misconception can be proved by a quotation from Dalton's *New System of Chemical Philosophy,* published in 1808, in which he discussed in detail his ideas concerning the atom as the unit of chemical structure.

1.4. In considering the existence of a substance such as water in gaseous (steam), liquid and solid (ice) states, Dalton said: "the observations have tacitly led to the conclusion which seems universally adopted, that all bodies of sensible magnitude . . . are constituted of a vast number of extremely small particles, or atoms of matter bound together by a force of attraction." The phrase "which seems universally adopted" is significant, for it implies that the atomic concept of matter was already widely accepted. It has been suggested that Dalton was indebted to Newton, whose works he probably studied, for in his notes of a lecture delivered at the Royal Institution, London, in January 1810, he remarked: "Newton had demonstrated clearly . . . that an elastic fluid [i.e., a gas] is constituted of small particles or atoms of matter."

1.5. There is no doubt, also, that the contemporary Irish chemists, Bryan Higgins (1737-1820) and his nephew William Higgins (1769-1825), had expressed themselves very clearly on the subject of combination by atoms some years prior to Dalton. Why then is the latter regarded as the founder of the atomic theory? The answer lies in the fact that John Dalton made the theory quantitative. By showing how the weights of different atoms relative to one another could be determined, he introduced a feeling of reality into a purely abstract idea. In a paper submitted to the Literary and Philosophical Society of Manchester, England, in October 1803, Dalton wrote: "An enquiry into the relative weights of the ultimate particles [atoms] of bodies is a subject, so far as I know, entirely new. I have lately been prosecuting this enquiry with remarkable success." Most of his weights were subsequently proved to be erroneous, but Dalton sowed the seed which grew, where others had previously merely turned over the soil.

1.6. In the Lowell Lectures on *Science in the Modern World,* delivered at Harvard University in 1925, the Anglo-American philosopher and mathematician A. N. Whitehead said: "In considering the history of thought, it is necessary to distinguish the real stream, determining a period, from the ineffectual thoughts casually entertained. In the eighteenth century every well educated man read Lucretius and entertained ideas about atoms. But John Dalton made them efficient in the stream of science; and in the function of efficiency atomicity was a new idea." The atomic theory of the classical thinkers was somewhat in the nature of a vague philosophical speculation, but the theory as enunciated by Dalton was much more specific. It provided an explanation or, at least, an interpretation of many chemical facts and, of greater consequence, it acted as a guide to further experimentation and investigation.

1.7. From the time of Dalton the atomic hypothesis has played an increasingly important role in science, first in chemistry and later in physics. It is true that a few scientists, some of them men of influence like the German physical chemist Wilhelm Ostwald, doubted the existence of atoms, but by the early years of the present century even these objectors were converted. Today the arguments in favor of the atomic structure of matter are so numerous and convincing that the concept is universally accepted as an established fact rather than a theory.*

THE CHEMICAL ELEMENTS

THE FOUR-ELEMENT THEORY

1.8. While the atomic concept was undergoing development, another important principle, also based on Greek philosophy, was being refined in the fire of successive generations of the human mind. In contemplating the make-up of the universe, Empedocles, in the fifth century B.C., entertained the idea that all matter was composed of four "elements," namely, fire, earth, air and water. It is probable that in this respect also, as with the atom, the ancient Hindu thinkers had anticipated the Greeks, but our present views stem more directly from the latter than from the former. Having the influential support of Aristotle and others, the four-element theory was widely accepted for more than two thousand years, in spite of a considerable degree of vagueness concerning its actual implications.

1.9. Some scholars undoubtedly regarded the elements as referring to material earth, air, fire and water, while others thought of them more in the nature of principles or representations of physical attributes. Aristotle, for example, envisaged all matter as consisting of one primordial substance which he called *hyle* (stuff or material);† and this could acquire varying amounts of the four qualities, or "principles," hot, cold, dry and moist. Thus air was hot and moist, water was cold and moist, fire was hot and dry, and earth was cold and dry. The difference between one material and another was regarded as due to variations in the primal qualities, but the fundamental matter was always the same.

1.10. It is apparently on this interpretation of the four-element theory that the ancient alchemists based their vain efforts to change common metals into gold. For hundreds of years all attempts to bring about transmutation met with complete failure, although at the present time, thanks to the accumulated knowledge concerning the behavior of atoms, the deliberate change of one element into another is a daily occurrence in many laboratories (Chapter X).

ELEMENTS AND COMPOUNDS

1.11. Although the Aristotelian theory was widely accepted, even as late as the seventeenth century, doubts began to develop concerning its ability to account for the nature of different forms of matter. Some of the strongest objections were expressed by the Irish-born Robert Boyle in a book entitled *The Sceptical Chymist,* published in London in 1661. In this book he gave his own interpretation of an element; thus, he wrote: "I mean by elements,

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* A fact may be defined as something for the actual existence of which there is definite evidence. A theory or hypothesis, on the other hand, is a purely conceptual attempt to explain or interpret known facts. While facts are presumably established and unalterable, a theory may be altered or discarded if it proves to be inadequate.

† In later years, this was changed, possibly by Roger Bacon in the thirteenth century, to *protyle,* from *protos* and *hyle,* meaning the first or primal matter.

as those chymists that speak plainest do by their principles, certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which . . . mixt bodies are immediately compounded, and into which they are ultimately resolved . . . I must not look upon any body as a true principle or element . . . which is not perfectly homogeneous, but is further resolvable into any number of distinct substances, how small soever."

1.12. It has been argued that the foregoing concept of an element was not original with Boyle, and some support for this contention may be found in his parenthetical remark, "as those chymists that speak plainest do [mean] by their principles," near the beginning of the quotation given above. Be that as it may, the fact remains that Boyle did express clearly the basic ideas from which developed the modern view concerning the nature of an element. However, more than a century was to elapse before these ideas had any real influence on scientific thought. It was only after the French chemist A. L. Lavoisier proved in 1774 that air was not a simple elementary substance, but a mixture of at least two different gases, now called nitrogen and oxygen, and after the work, in 1781, of Joseph Priestley and of Henry Cavendish, in England, established the fact that water was compounded of hydrogen and oxygen, that the four-element theory was finally abandoned. In its place, Lavoisier established, in 1789, the modern concept of an element, thus: "We apply the term elements . . . to bodies to express our idea of the last point which analysis is capable of reaching." An element was thus regarded as a substance containing, as far as was known, only one kind of matter, and which could not be split up in any known way into anything simpler.

1.13. On this basis, Lavoisier substituted for the four elements of the Greek philosophers a list of thirty-three elementary substances, of which more than twenty are still regarded as elements even to this day. By 1819, the Swedish chemist J. J. Berzelius had increased the number of elements to fifty, and at the present time ninety different elements are definitely known to exist on the earth, while several more have been obtained by other means, as will be explained in Chapter XVI. All material things contain at least one of these elements, and when two or more elements unite with one another, by the process referred to as chemical combination, the resulting product is known as a *compound*.

DEFINITION OF AN ELEMENT

1.14. Until the beginning of the present century a chemical element would have been defined simply as a form of matter which could not be split up into other forms of matter. Now, with the discovery of the phenomena of radioactivity, accompanied by the spontaneous change of one element into another (Chapter V), and the development of various means of bringing about transmutation and disintegration of numerous elements (Chapter IX), it is not easy to give such a precise definition. It will be seen, in succeeding chapters, that these processes, whether spontaneous or brought about by artificial means, are associated with very large amounts of energy. Chemical reactions, on the other hand, involve energy changes of a much lower order of magnitude. It is thus possible to describe an element as a form of matter which cannot be decomposed into (or be produced from) simpler forms of matter by means of chemical reactions, that is, by reactions associated with relatively small amounts of energy. In spite of the somewhat vague character of this definition,* there is never any doubt at the present time concerning the elementary or compound nature of a material. Numerous tests, now available, based on characteristic physical properties, such as the optical spectrum, mass spectrum and X-rays, permit elements to be distinguished and identified.

1.15. The atom may now be defined as the smallest possible or ultimate particle of an element, each element having its own characteristic atoms. As will be seen in Chapter IV, the atom itself has an internal structure and can be split up into subatomic particles. But these particles, most of which are electrical in nature, do not have the characteristic properties of the element. In the sense that the identity of the element is to be retained, the atom may therefore be regarded as indivisible.

SYMBOLS AND FORMULAS

1.16. In order to represent pictorially the building up of compounds from elements, Dalton introduced a set of symbols for the atoms. Thus, an atom of oxygen was indicated by a circle, one of hydrogen by a circle with a central dot, and a nitrogen atom was represented by a circle with a vertical line through it. This type of formulation was not only somewhat cumbersome when compounds were being considered, but the discovery of each new element presented the problem of inventing an appropriate symbol. The difficulty was overcome by Berzelius who devised the method which forms the basis for the symbolic representation of elements and compounds in use at the present day.

1.17. In his treatise *On the Theory of Chemical Proportions* (Paris, 1819), Berzelius proposed that "chemical symbols should be letters of the alphabet, in order to be easily drawn and printed without disfiguring the text," and that "the initial letter [or letters] of the Latin name of each element" should be used for this purpose. Consequently, oxygen (oxygenium) was symbolized by O, hydrogen (hydrogenium) by H, copper (cuprum) by Cu, gold (aurum) by Au, silver (argentum) by Ag, and so on.† The symbol, or *formula*, as it is generally called, of a compound is then obtained by combining the symbols for the appropriate elements, with subscripts to indicate the numbers of atoms present. Thus, the formula for water, which involves a chemical union of two atoms of hydrogen with one of oxygen, is H_2O; sulfuric acid, containing two atoms of hydrogen, one of sulfur and four of oxygen, has the formula H_2SO_4, and so on.

THE DETERMINATION OF ATOMIC WEIGHTS

DALTON'S ATOMIC WEIGHT SYSTEM

1.18. As mentioned earlier, perhaps Dalton's most significant contribution to the atomic theory was his attempt

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* An element may be defined more precisely as a form of matter all the atoms of which have the same nuclear charge (Chapter IV).

† Some symbols, e.g., O and H, were obtained from Latinized names of French or other origin. The complete list of modern symbols for the elements is given in § 1.37.

to determine the relative masses or weights* of atoms. The actual atoms are, of course, much too small to be weighed directly, and so it is convenient to express their weights relative to that of a specified atom. For this purpose Dalton chose the atom of hydrogen, the lightest atom known to him and, as it happens, the lightest of all the elements. Hence, to the hydrogen atom was ascribed a weight of unity, and the weights of other atoms were then recorded in terms of that of the hydrogen atom.

1.19. The actual procedures for obtaining the relative atomic weights were then based on certain postulates concerning the nature of atoms and their mode of combination. The following quotations from Dalton's *New System of Chemical Philosophy*, mentioned earlier, give the arguments in his own words.

"Whether the ultimate particles of a body, such as water, are all alike, that is of the same figure [i.e., size and shape], weight, etc., is a question of some importance. From what is known, we have no reason to apprehend a diversity in these particulars: if it does exist in water, it must equally exist in the elements constituting water, namely, hydrogen and oxygen. Now it is scarcely possible to conceive how the aggregates of dissimilar particles should be so uniformly the same. . . . Therefore we may conclude that the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc. In other words, every [ultimate] particle of water is like every other particle; every [ultimate] particle of hydrogen is like every other particle of hydrogen, etc. . . .

"Chemical analysis and synthesis go no further than to the separation of particles from one another, and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. . . . All the changes we can produce consist in separating particles that are in a state of cohesion or combination, and joining those that are previously at a distance. . . .

"If there are two bodies, A and B, which are disposed to combine, the following is the order in which combinations may take place, beginning with the most simple: namely, 1 atom of A + 1 atom of B [= AB] . . . , 1 atom of A + 2 atoms of B [= AB_2] . . . , 2 atoms of A + 1 atom of B [= A_2B], etc."

1.20. Stated briefly, Dalton's conclusions were threefold: that the ultimate particles of a given pure substance, whether element or compound, are alike in size, shape and weight; that chemical reaction does not cause any change in the nature of atoms but results merely in their rearrangement; and, that combination between atoms takes place in the ratio of the simplest numbers, preferably AB, then AB_2, and so on. If, as Dalton supposed, the atoms of a given element are all alike and are unchanged by chemical action, then the relative weight of the atom, as determined from the analysis of a compound, should have a definite and constant value. While the actual determination of relative atomic weights made use of the third of the postulates stated above, the results could have no significance without the first two.

1.21. The procedure used by Dalton may be illustrated by reference to his estimate of the atomic weight of oxy-

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* Although mass and weight are treated here as synonymous, it is, strictly speaking, necessary to make a distinction. Mass is a measure of the quantity of matter in a body, while weight is the force exerted by the body, under the influence of gravity. It has become the practice to speak of "atomic weights" although "atomic masses" would perhaps be more accurate.

gen. At the time only one compound of oxygen with hydrogen—water—was known, and so Dalton, in accordance with the principles he enunciated, assumed it to have the simplest possible composition, namely, the combination of one atom of hydrogen with one of oxygen, i.e., HO. Upon analysis he found that water consisted of one part by weight of hydrogen and seven—later shown to be eight—parts by weight of oxygen. It followed, therefore, that if the weight of hydrogen is taken as unity, the relative atomic weight of oxygen should be seven—actually eight. That is to say, the weight of a single atom of oxygen, according to Dalton, was seven—actually eight—times that of a single hydrogen atom. Similarly, by assuming the formula of ammonia to be NH, the atomic weight of nitrogen appeared to be five—more accurately 4.7—relative to that of hydrogen.

COMBINING OR EQUIVALENT WEIGHTS

1.22. Apart from the errors in Dalton's experimental work, several of his atomic weights, such as those of oxygen and nitrogen given above, were incorrect. The reason for the discrepancies lay in the fact that the postulated simple formulas of the type AB, such as, HO for water and NH for ammonia, were erroneous; water is now known to be properly represented by H_2O and ammonia by NH_3. What Dalton determined was, in general, the *combining weight* or *equivalent weight* of an element, that is, the weight of the element which combines with or replaces—that is, is equivalent to—one part by weight of hydrogen.*

1.23. If the formula of the compound under consideration is actually HX, as is the case, for example, when X is the element chlorine, then the atomic and combining weights are identical. In other instances, however, the atomic weight is a simple multiple of the equivalent weight. It can be readily seen that this multiple must be the same as the number of atoms of hydrogen which unite with, or replace, one atom of the given element. Thus, since the formula of water is H_2O, and two atoms of hydrogen combine with one of oxygen, the atomic weight of oxygen is exactly twice the equivalent weight. If, therefore, Dalton had used the correct formula for water, he would have arrived at an atomic weight of twice seven, i.e., 14, relative to hydrogen, which is in fair agreement with the more accurate value of 16. Similarly, if he had known that ammonia was NH_3, the atomic weight of nitrogen would have been given as three times five, i.e., 15, not very different from the accepted atomic weight of approximately 14.

THE ATOMIC WEIGHT SCALE

1.24. It is evident from the figures just cited that Dalton's experimental work was not too reliable. One of the factors responsible was his choice of hydrogen as the basis of comparison for atomic weights. In the first place, relatively few elements form compounds with hydrogen, and these are not easy to analyze; in the second place, on account of the lightness of hydrogen, a small error in weighing leads to a large over-all discrepancy. Since most elements combine with oxygen, the atom of which is about sixteen times as heavy as that of hydrogen, Berzelius used oxygen as the

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* The modern definition of combining (or equivalent) weight of an element uses 8.000 parts by weight of oxygen, rather than 1 part of hydrogen, as the basis of comparison (§ 1.24).

standard, assigning to it an arbitrary combining weight of 100. Later there was a return to the Daltonian system and the weight of the atom of oxygen was then found to be very close to 16, in comparison with unity for hydrogen. Because of its practical value, as indicated above, chemists therefore agreed to take the atomic weight of oxygen, as it occurs in the air, to be exactly 16.0000, and its equivalent weight to be 8.0000; this is still the basis of modern chemical atomic and equivalent weights.* The atomic weight of hydrogen on this scale is now known to be 1.0080, rather than exactly unity.

Atomic and Equivalent Weights

1.25. In Dalton's time the principles of quantitative chemical analysis were not well understood, and the precision balance had not been developed, so that combining weights of a high order of accuracy could not have been expected. With improvements in the techniques and methods of analytical chemistry during the first half of the nineteenth century, there became available increasingly exact values of the combining or equivalent weights of many elements, for which J. J. Berzelius, in Sweden, and J. S. Stas, in Belgium, were largely responsible. Before these could be converted into atomic weights there still existed the problem of finding for each element the integer by which the equivalent weight was to be multiplied. In this connection, Berzelius obtained guidance from the *law of isomorphism*† proposed by his German pupil E. Mitscherlich in 1819, as well as from the *law of the constant heat capacity* of atoms‡ discovered in the same year by the French scientists P. L. Dulong and A. T. Petit.

ATOMS AND MOLECULES

Early Developments

1.26. A fundamental postulate, which would have been of inestimable value in the early attempts at determining atomic weights, had been proposed independently by the Italian physicist Amadeo Avogadro in 1811, and some three years later by A. M. Ampère, for whom the unit of electric current is named. Unfortunately, the concepts involved were not too clearly expressed nor too well understood until 1858, when Stanislao Cannizzaro, in his *Sketch of a Course of Chemical Philosophy* as given in the University of Genoa, clarified and explained the significance of the ideas of his fellow countryman, Avogadro, published more than forty years earlier.

1.27. In order to appreciate the circumstances at that time, it is necessary to consider the distinction between

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* The reasons for the qualifications "as it occurs in air," applied to oxygen, and "chemical," applied to atomic weight, will be given in § 8.61.

† According to this law, isomorphous substances, i.e., substances which form crystals of similar shape, having similar chemical properties can usually be represented by analogous formulas, e.g., Cu_2S and Ag_2S, Fe_2O_3 and Al_2O_3. The *valence* of an element, i.e., the ratio of the atomic weight to the equivalent weight, can be derived from the formula of an appropriate compound.

‡ The product of the atomic weight and the specific heat has approximately the same value for most solid elements. The specific heat can be readily measured, and hence a rough atomic weight can be estimated. The accurate value can then be obtained from the combining weight.

atom and *molecule.** In the early years of the nineteenth century no very clear differentiation was made. Dalton, for example, occasionally used the term molecule as synonymous with his ultimate particle or atom. Further, he did not discriminate between the particles of an element and those of a compound; he referred to both types as "atoms." Avogadro, on the other hand, went to the other extreme; he did not use the term atom, but applied the general name of "molecule" to various particles. However, a careful reading of Avogadro's writings shows that he distinguished between three different types of molecules, although the distinction is implicit rather than explicit. There is little doubt that the situation was clear in Avogadro's mind, but it is not so certain that his views were expressed plainly enough to be grasped by his contemporaries. In the succeeding decades, efforts were made to define the terms "atom" and "molecule," particularly by the French scientists A. M. Gaudin (1833), A. M. Ampère (1835), A. Laurent (1846) and C. L. Gerhardt (1856). It was Cannizzaro's logical development of the consequences of the distinction between these quantities that resulted in the opening of a new era in the determination of atomic weights.

1.28. A molecule may be defined as the smallest particle of any substance—element or compound—as it normally exists. A molecule of a compound always contains atoms of two or more elements; thus, a molecule of water is represented by H_2O, because it consists of two atoms of hydrogen and one of oxygen. Since an atom of an element is indivisible, it is not possible for a molecule to contain less than one atom of any element. Hence, for the present purpose, an atom may be regarded as the smallest portion of an element that can be found in a molecule of any of its compounds. Alternatively, an atom is described as the smallest particle of an element that can enter into chemical combination. It is no longer permissible to speak of an "atom of a compound," or of a "compound atom," as Dalton did; the ultimate particle of a compound is the molecule. If such a molecule were further subdivided it would break up into the atoms of its constituent elements, and hence would cease to be a compound.

ATOMS AND MOLECULES OF ELEMENTS

1.29. One further point remains to be clarified, namely, the distinction between the atom and molecule of an element. The atom is the smallest *conceivable* particle of an element, as well as the smallest portion that can take part in chemical combination. However, it is not necessarily the smallest unit that can normally *exist* as such; it is the latter which is the molecule of the element.† Consider, for example, the element oxygen, the gas which constitutes about one fifth of the air. The atom would be represented by the symbol O, but the molecule, as present in the atmosphere, is made up of a combination of two such atoms and hence is O_2. It is true that by the use of high temperatures or by means of an electrical discharge some of the molecules could be split up into two atoms, but as soon as normal conditions were restored the atoms would

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* From the diminutive of the Latin word *moles* (mass); hence, molecule means a small mass.

† Avogadro referred to the atoms of elements as "molécules élémentaires," and the molecules of elements he called "molécules constituantes." Molecules of compounds he termed "molécules intégrantes."

reunite in pairs to form molecules. Single atoms of oxygen tend to combine chemically with other atoms; if two atoms of oxygen interact with one another the result is an oxygen molecule, but if one atom of oxygen unites with two atoms of hydrogen the result is a molecule of water.

1.30. Under ordinary conditions of temperature and pressure, most elements, at least those which are gases, such as oxygen, hydrogen, nitrogen and chlorine, form diatomic molecules, that is to say, the molecule contains two atoms. There are, however, some important elements, often referred to as the "inert gases of the atmosphere," for which the atom and the molecule are identical. The element helium, for example, as it occurs in the atmosphere and in certain natural gases, consists of single atoms and these may equally correctly be described as molecules. Thus, helium is said to be a monatomic gas. The atoms of helium, and of its related gases neon, argon, etc., are so inert that they will neither unite with one another nor with the atoms of other elements.

AVOGADRO'S LAW

1.31. Bearing in mind the correct significance of the term molecule, the law of Avogadro states that under the same conditions of temperature and pressure equal volumes of different *gases* contain equal numbers of molecules.* The density of a gas is defined as the weight of a given volume, say 1 liter, and hence is equal to the weight of the molecules contained in that volume. But, since for different gases, this definite volume always includes the same number of molecules, it follows that the density of a gas is directly proportional to the weight of its individual molecules. In the words of Avogadro: "Setting out from this hypothesis [as stated above], it is apparent that we have the means of determining very easily the relative masses of the molecules of substances obtainable in the gaseous state . . . for the ratios of the masses of the molecules are then the same as those of the densities of the different gases at equal temperature and pressure."

DETERMINATION OF MOLECULAR WEIGHTS

1.32. By the comparison of densities it is thus possible to determine the weight of one molecular species with reference to that of another, and hence, for practical purposes, it is desirable to choose a uniform basis of reference for expressing molecular weights. That proposed by Cannizzaro, and now universally adopted, is to use the same standard as is employed for atomic weights. The molecular weight is then recorded as the weight of a given molecule relative to the weight of the oxygen atom taken as 16.0000. Defined in this manner, the molecular weight is equal to the sum of the conventional atomic weights (§ 1.37) of its constituent elements, due allowance being made for the number of atoms of each present in the molecule.

1.33. There are good reasons for believing that the oxygen molecule consists of two atoms, and so the molecular weight of ordinary oxygen is taken as 32.0000. Hence the molecular weight of any substance is the weight of a molecule of that substance compared with the assumed weight of 32.0000 for

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* Dalton had previously (1808) considered this possibility but had rejected it, perhaps because of the confusion between atoms and molecules. He wrote: "I had a confused idea . . . that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous. . . . But . . . I became convinced that the different gases have not their particles of the same size [i.e., do not occupy equal volumes]."

an oxygen molecule. It can be readily seen, therefore, that in view of Avogadro's law, it is possible to write for any *gaseous* substance, element or compound, at the same temperature and pressure, the relationship

$$\frac{\text{Molecular weight of substance}}{\text{Molecular weight of oxygen}} = \frac{\text{Density of substance}}{\text{Density of oxygen}}$$

or,

$$\text{Molecular weight} = \frac{\text{Density of substance}}{\text{Density of oxygen}} \times 32.0000,$$

so that a determination of gaseous density is sufficient to yield the molecular weight of the substance. It may be remarked that the use of ordinary densities does not give results of a high order of accuracy; but by applying certain corrections it is possible to obtain molecular weights with a considerable degree of precision.*

Molecular Weights and Atomic Weights

1.34. It now remains to be seen how the development of a reliable method of determining molecular weights provided a solution for the atomic weight problem. If Dalton had known the molecular weight of water to be 18, with reference to hydrogen as unity, it would have been obvious that its formula could not be HO, as he thought; as stated above, this formula implied an atomic weight of 8 for oxygen, and hence a molecular weight of $1 + 8$, i.e., 9, for water. By taking the formula of water to be H_2O, and making use of the experimental fact that one part by weight of hydrogen is united with eight parts of oxygen, it is readily seen that the atomic weight of oxygen should be 16. In this event, the molecular weight of water would be $2 + 16$, i.e., 18, as is actually found from gas density measurements. This type of argument has been used to determine the atomic weights of several elements.

1.35. Since the atom is the smallest portion of an element that can be present in a molecule, the atomic weight must be the smallest weight of the element that can be found in a molecular weight of any of its compounds. This contention formed the basis of the procedure introduced by Cannizzaro for the evaluation of atomic weights. Volatile compounds of a given element were prepared and their molecular weights derived from gas-density measurements. The various substances were then analyzed so as to find the weight of the element present in the molecular weight of each compound. The smallest of the weights found in this manner or, more correctly, the highest common divisor of these weights, is the atomic weight of the element.

1.36. Other uses have been made of molecular weights in connection with the derivation of the atomic weights of the elements, but sufficient has been stated here to indicate that the proper application of Avogadro's law helped to remove one of the outstanding difficulties that faced the chemists of the early 1800s. In the latter part of the same century methods were developed for determining molecular weights without resort to gas densities, so

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* These corrections are necessary because Avogadro's law is strictly applicable to "perfect" or "ideal" gases, whereas actual gases do not behave ideally at ordinary temperatures and pressures.