

THE ELEMENTS
OF
PHYSICAL CHEMISTRY

By

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PREFACE

As its title implies, the purpose of this book is to present, in the words of Webster's Dictionary, "an outline regarded as containing the fundamental features" of physical chemistry. It is an introductory text intended not only for students who propose to specialize in chemistry, but also for those who require some knowledge of the principles of physical chemistry in connection with their studies of physics, engineering, metallurgy, biology, medicine, geology, etc. Without equivocation, the treatment is meant to be elementary and to be suitable for a first course in physical chemistry for the average, rather than the exceptional, student. The emphasis is, therefore, on simplicity and clarity, the author's purpose being to present the material in such a form as to help the reader obtain an understanding of the essential concepts and ideas of modern physical chemistry.

As an aid to both teacher and student, all new terms, names of laws, and other important topics are printed in bold-face type. The actual statements of laws and of fundamental results and conclusions are given in italics, so that they may be impressed on the mind of the reader. Although the mathematics employed does not go beyond the most elementary calculus, mathematical results are also stated in words, wherever it is feasible, for the benefit of readers with a limited knowledge of the calculus.

Each chapter is provided with a number of review questions covering all the essential points in the text, and two sets of problems to which answers are given at the end of the book. Within each set repetition has been avoided as far as possible, so that every problem serves to illustrate or test a separate point; the two sets, however, duplicate one another fairly closely. Teachers should find that this scheme lends itself to a variety of uses. In addition to these problems, based directly on the material in each chapter, and those worked out in the text, a number of miscellaneous problems of a variety of types have been added.

In order to encourage the beginning student to do some outside reading, without discouraging him by the difficulty of the material, the somewhat novel procedure has been adopted of giving references only to papers published in the *Journal of Chemical Education*. This journal, intended for students as well as teachers, is one to which the student should be introduced at the earliest opportunity. The references are to the fifteen years from 1930 through 1944; they cover a wide range of physicochemical topics, and in them the reader will be directed to papers in other journals. Further information and references to the subjects dealt with in this book may be found, if required, in the writer's "Textbook of Physical Chemistry."

In preparing the present book the author has drawn upon his varied experience as a teacher and writer. In addition, he has had the benefit of advice from two other experienced teachers, his friends Professor A. E. Stearn and Dr. E. B. Sanigar, to whom he is greatly indebted for reading the manuscript and for making many valuable suggestions. To Dr. Sanigar thanks are also due for his careful reading of the galley proofs and for checking the answers to most of the problems. In conclusion, the writer wishes once again to express his gratitude to his wife for reading the proofs and for her continued help in innumerable ways.

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CHAPTER I

INTRODUCTION: ATOMIC THEORY

THE NATURE OF PHYSICAL CHEMISTRY

1a. The Scope of Physical Chemistry.—Although the nature of the problems that fall within the scope of physical chemistry is well recognized, it is nevertheless not an easy matter to give a simple and precise definition of this subject. Chemistry has been described as the science which deals with matter and its transformations, in contrast to physics which is concerned largely with energy and its transformations. Physical chemistry may be regarded as an intermediate field involving the study of the interactions between matter and energy. However, this definition is not complete enough to include all the topics that are generally regarded as being properly in the realm of physical chemistry, and the situation may well be considered from another point of view. Inorganic chemistry and organic chemistry deal primarily with the actual nature of the material changes occurring in chemical reactions. In physical chemistry, on the other hand, the influence of physical factors, such as temperature, pressure, concentration, electricity, light, etc., both on the reacting substances and on the reactions, is of primary interest; the objective is the understanding of the fundamental nature of chemical change. It is thus reasonable to describe physical chemistry as being concerned with the *elucidation or clarification of the principles underlying those transformations of matter known as chemical reactions*, through a study of the physical properties of the reacting substances and of the effect of physical changes on the reactions themselves.

In the light of the foregoing definition, the treatment of physical chemistry as given in this book will commence with a brief review of the basic laws of chemical combination that have been known since the early part of the nineteenth century, and which led to the development of the modern concept of atoms and molecules. The internal structures of these building stones of the chemist will then be considered, and it will be seen that it is possible in this manner to understand the different ways in which atoms can combine to form molecules. Although matter is ultimately composed of molecules and atoms, and these of even smaller units, namely electrons, protons and neutrons, the substances that take part in chemical reactions are generally encountered in the form of gas, liquid or solid, or perhaps in solution. Consequently, in the further study of physical chemistry the properties of the various forms of matter, both in the pure state and in mixtures, will be taken up from a number of different points of view. With this general background, the student will be in a position to consider actual chemical reactions, and to examine the factors which determine the direction, velocity and extent of a chemical change. In

this manner it is hoped to justify the assertion that physical chemistry deals with the fundamental principles that underlie all chemical transformations, irrespective of whether inorganic or organic substances are involved.

1b. Scientific Method.—Before proceeding to the more detailed consideration of the various topics, as just outlined, it is desirable to say a few words about the methods of physical chemistry. Essentially, the study of this subject provides one of the best illustrations of the use of what is called the **scientific method**. To start with, experiments are performed, and the results of the observations, i.e., the empirical data, relating to a particular phenomenon are collected. An attempt is then made to generalize these results in the form of a simple statement or mathematical expression known as a **law**; so long as further experiments bring to light no exceptions, the law is regarded as holding good. Sometimes, as in the case of the influence of temperature and pressure on the volume of a gas, more accurate observations show that the laws which were originally proposed are approximate and are applicable under certain restricted conditions only. In other instances, as, for example, with the laws of thermodynamics, no exceptions are known.

The next stage in the application of the scientific method is to put forward a **hypothesis** with the object of explaining the experimental observations, or of accounting for the general law which summarizes them. It is, of course, doubtful whether a complete "explanation" of observed phenomena is ever possible; after all, the fundamental concepts of matter and energy cannot really be "explained." What a hypothesis generally attempts, therefore, is an *interpretation of the experimental facts in terms of simpler or more easily understood phenomena*. In other words, the purpose of the hypothesis is to state the causes which lead to the observed effects. These causes themselves have underlying causes, and it is the object of science to trace them, step by step, as far back as possible; the ultimate aim is the unification of all phenomena into one scheme. This is being gradually achieved in chemistry, for example, by the use of the concepts of the electron, the proton and the neutron; even though the exact nature of these structural units cannot be explained, the resulting systematization has, nevertheless, proved of great value.

1c. Hypothesis and Theory.—It may happen that two or more alternative hypotheses are proposed to account for certain experimental facts. A familiar illustration is provided by the phenomenon of burning or combustion in air. Two hypotheses, one based on the supposed existence of "phlogiston" and the other on the idea of combination with oxygen, were suggested. In the course of time it became evident that the latter hypothesis offered a more satisfactory interpretation of the observations than did the former. The phlogiston hypothesis of combustion was consequently discarded, and it ceased to have any but historical interest. When a particular hypothesis has withstood the test of many experiments, while the others have been eliminated or proved to be unsatisfactory in one way or another, it is referred to as a **theory**.

Although a distinction should strictly be drawn between the terms hypothesis and theory, it is nevertheless the common practice to regard them as having

the same significance. It is probably true to say that the use of the term "hypothesis" is decreasing in modern scientific writings, and the word "theory" is employed almost exclusively in this connection. One reason for this preference, in spite of its not being strictly correct, lies partly in the fact that the adjective "hypothetical" has acquired the significance of referring to something that is imaginary. The same, objection, however, does not apply to the adjective "theoretical," and such expressions as the "theoretical treatment" of a subject, or the "theoretical approach" to a problem can be used without misunderstanding.

It should be apparent from what has been said that there is nothing that is necessarily permanent about a theory. A satisfactory theory must be able to correlate all the known facts concerning a particular phenomenon or set of phenomena, and also predict new ones. If there exist proven facts which are not in harmony with the theory, or the theory makes predictions which are later found to be incorrect, then that particular theory must be modified or discarded in favor of another. Sometimes an unsatisfactory theory has to be retained, simply because the necessary improvement or alternative is not immediately evident. This was the case, for example, in connection with certain properties of salt solutions, i.e., the strong electrolytes. In the course of time, however, suggestions were made for modifying the theory, which had been known for many years to be inadequate, so as to bring it into better agreement with the observed facts. Even now, in spite of the great advances that have been made, it is realized that the theory is still incomplete. Sometimes a theory can be modified, as just indicated, but in other cases it may have to be discarded altogether. In any event, a theory is retained only as long as it proves useful in the correlation and interpretation of experimental data, for that is its prime function in the operation of the methods of science.

THE ATOMIC THEORY

2a. Elements and Compounds.—Although nearly half a million different chemical substances are known, it is now realized that there are actually only ninety-two distinct species from which these thousands of substances are composed. The simple species or types of matter are known as elements, and the chemical combination of two or more elements in a variety of possible ways leads to the formation of the many compounds which either exist in nature or have been prepared in the laboratory. Until the beginning of the present century, an element could be defined in a simple manner as a form of matter which could not in any way be split up into other forms of matter. The discovery of the phenomena of radioactivity, and the realization of the universal occurrence of electrons (see Chapter II), showed that this definition had to be modified; this necessity has been emphasized in recent years by the development of methods whereby one element can be changed into another. However, as will be seen shortly, radioactive changes are spontaneous and cannot be controlled by any known methods, while most processes used for artificial disintegration and transmutation of elements involve the use of electrically

charged particles moving with high velocity under the influence of potentials of millions of volts. Such procedures can hardly be considered to be in the same category as ordinary chemical changes, and so it is possible to define an element as *a form of matter which cannot be decomposed into, nor be produced from, simpler forms of matter by means of ordinary chemical reactions*. As indicated above, a compound is a substance produced by the union of two or more elements as the result of a chemical reaction.

2b. The Fundamental Laws of Chemical Combination.—The combination of elements to form compounds, and chemical reactions generally, are governed by four simple laws. These laws may be regarded as fundamental, for without them there could have been no science of chemistry as it is to-day. The four laws, which are based on the results of many experiments, will be enunciated and discussed briefly in turn.

I. Law of Conservation of Mass.—Within the limits of experimental error, *the total mass of a reacting system is unchanged as the result of a chemical reaction*. In other words, *there can be no loss or gain of matter accompanying a chemical change*. Every properly balanced chemical equation is based on this law, for since matter can neither be created nor destroyed, every item that appears on one side of the equation must be represented on the other side, and vice versa. Were it not for the experimental fact of the conservation of matter, chemical equations, and the calculations based on them, would not be possible, and the science of quantitative analysis could not have been developed.

It may be pointed out that according to modern views the law of conservation of mass must be interpreted properly in order for its true significance to be understood. It seems certain that if a sufficiently accurate and sensitive balance were available, and all sources of error could be eliminated, it would be found that many chemical reactions were actually accompanied by a loss or gain of weight. This result would, nevertheless, not be contrary to the law of conservation of mass in its complete sense. The reason for this is to be found in the realization that *mass and energy must be regarded as equivalent*. If a chemical change is accompanied by either a loss or gain of energy, for example, in the form of heat, such as is generally the case, there must be a corresponding loss or gain of weight, respectively. The equivalence of mass and energy is expressed by means of the equation

$$E = mc^2, \quad (2.1)$$

where E is the energy and m is its mass equivalent; c is the velocity of light. If m is in grams and c in cm. per sec., i.e., 3×10^{10} cm. per sec., then the energy E will be given in ergs; to convert this to calories, the result should be divided by 4.184×10^7 , as will be seen in § 23a. It follows, therefore, that equation (2.1) may be written in the form

$$\begin{aligned} E &= m \times (3 \times 10^{10})^2 = 9 \times 10^{20} m \text{ ergs} \\ &= \frac{m \times (3 \times 10^{10})^2}{4.184 \times 10^7} = 2.15 \times 10^{13} m \text{ calories.} \end{aligned} \quad (2.2)$$

For a reaction involving about 100 grams of chemical substances, an energy change of 100,000 calories would be moderately large, and the corresponding mass equivalent would be given by equation (2.2) as

$$100,000 = 2.15 \times 10^{13}m$$

$$m = 4.65 \times 10^{-9} \text{ gram.}$$

If the heat is evolved in the given reaction, the weight should consequently be decreased by this amount; on a total mass of the order of 100 grams, or even of 1 gram, this change would, of course, be undetectable by any known means.

It is obvious, therefore, that the law of conservation of mass, in its simple form, will hold for all chemical reactions within the limits of any experimental accuracy that is possible at present. There are certain changes, associated with the transmutation of elements, in which very large amounts of energy are concerned; it will be seen in § 8d that in such cases the corresponding change in weight is no longer insignificant. As already stated, however, these transformation processes cannot be regarded as ordinary chemical reactions.

II. Law of Constant Proportions.—*A given chemical compound always contains the same elements united in the same proportions by weight.* For obvious reasons, this statement is sometimes called the law of definite proportions or of constant composition. Like the law of conservation of mass, this law is of fundamental importance to chemistry; it is based on the fact that the composition of a particular compound is definite, and is independent of the method, time or place of preparation. For example, cupric oxide may be obtained from copper in several ways; in every case, however, the product will be found to contain 79.9 per cent by weight of copper and 20.1 per cent of oxygen.

The existence of many elements in two or more isotopic forms, which will be considered further in § 7c, necessitates some modification in the statement of the law of constant proportions by weight. The isotopes of a given element may be regarded as having identical chemical properties, but equivalent units, i.e., the atoms, differ in weight. Consequently, a specimen of cupric oxide containing a predominating amount of one particular isotope of oxygen will have a composition by weight slightly different from a specimen which contains more of another isotope. As long as the proportions of the various isotopes remain constant, however, the composition by weight of any compound will be quite definite, in agreement with the law enunciated above. Unless deliberate efforts are made to vary the isotopic ratio, the actual value for a given compound, as it exists in nature or is prepared in the laboratory, is virtually constant; hence, in practice the law of constant proportions may be regarded as being obeyed. Nevertheless, it would probably be more satisfactory to modify the statement of the law in the following manner: *a given isotopic form of a chemical compound always contains the same isotopes of the constituent elements united in the same proportion by weight.*

III. Law of Multiple Proportions.—*If two elements A and B combine to form more than one compound, the different amounts of A that unite with a definite amount of B bear a simple ratio to one another.* Without going into details, it

will be evident that here, as in the case of the law of constant proportions, it is supposed that the isotopic nature of the elements A and B is always the same. The law of multiple proportions may be illustrated in a simple manner by reference to three oxides of carbon, namely carbon dioxide, carbon monoxide and carbon suboxide. The compositions by weight and the amounts of carbon that combine with one part by weight of oxygen in each case are given below.

	Carbon	Oxygen	Carbon	Oxygen
Carbon dioxide	27.28%	72.72%	0.3752	1
Carbon monoxide	42.87	57.13	0.7505	1
Carbon suboxide	52.96	47.04	1.126	1

The amounts of carbon that combine with a fixed weight of oxygen are seen to be in the simple ratio of 1 to 2 to 3, in agreement with the law of multiple proportions.

It should be pointed out that the requirement of a "simple ratio," that is to say, one that can be expressed in the form of small integers, can apply only to simple compounds. Consider, for example, two members of the paraffin series of hydrocarbons, viz., methane and triacontane. The amounts of hydrogen in these two substances that unite with a definite quantity of carbon are in the ratio of 60 to 31; this can hardly be regarded as a ratio of small integers. Although the ratio is approximately 2 to 1, it is nevertheless not this simple ratio, but more exactly 1.9355 to 1. Actually the two substances under consideration do not provide an exception to the law of multiple proportions in its fundamental significance. For reasons which will be evident shortly, it would be better if the expression "simple ratio" were replaced by the words "an exact integral ratio"; although the ratio of 60 to 31 is not simple, at least it does involve exact integers.

IV. Law of Combining (or Reciprocal) Proportions.—*The proportions in which any two elements unite with a third element are the proportions, or a simple multiple (or submultiple) of the proportions, in which they combine with each other.* For example, 64 grams of sulfur combine with 12 grams of carbon in carbon disulfide, while this same weight of carbon is combined with 32 grams of oxygen in carbon dioxide. Hence, when sulfur and oxygen unite they should do so in the proportion of 2 parts by weight of the former to 1 part of the latter, or in some simple multiple of this proportion. This is actually found to be the case, for sulfur dioxide contains 1 part of sulfur to 1 part by weight of oxygen, and in sulfur trioxide the corresponding proportions are 2 to 3. These are clearly simple submultiples of the ratio of 2 to 1.

An important consequence of the law of combining proportions is the emergence of the idea of **combining weight** or **equivalent weight**; with every element there must be associated a definite weight, in simple multiples of which it takes part in chemical combination. For the purpose of expressing these combining weights numerically, it is necessary to fix upon a standard of reference; this is taken as 8.000 parts by weight of the element oxygen. The equivalent weight of any element is then defined as *the number of parts by weight of that element which will combine chemically with, or will replace from chemical combination,*

8.000 parts by weight of oxygen. The equivalent weight, like all other properties depending upon weight, will vary with the isotopic composition of the element, but it is the invariable practice to state the result for the particular composition that occurs in nature. On this basis the equivalent weight of hydrogen is 1.0080, that of carbon (in carbon dioxide) is 3.0025, and that of chlorine (in chlorine monoxide) is 35.457. The equivalent weight of oxygen is always 8.000 by definition.

When a given element forms two or more compounds with oxygen, the equivalent weights will differ in the two cases, but the values will bear an integral ratio, generally a simple integral ratio, to one another. As seen above, there are three well known compounds of carbon and oxygen, and from the compositions recorded it can be readily calculated that the weights of carbon that unite with 8.000 parts of oxygen are 3.002 in carbon dioxide, 6.004 in carbon monoxide, and 9.008 in carbon suboxide. It is to be expected from the law of multiple proportions, of course, which these substances are known to obey, that the three equivalent weights will bear a simple ratio to each other.

In accordance with the law of combining proportions, the equivalent weights of different elements give the proportions in which, or in integral multiples of which, they combine with one another. Since the equivalent weights of hydrogen and chlorine are 1.008 and 35.46, respectively, a compound of these two elements would be expected to contain them in precisely this proportion; such is actually the case in hydrogen chloride. The equivalent weight of sulfur in its stable compounds is generally 16.03, and hence a compound containing 16.03 parts by weight of sulfur and 35.46 parts of chlorine is to be anticipated. This compound is known and is called sulfur dichloride; there is, however, another combination of the elements sulfur and chlorine, namely sulfur monochloride, in which there are 32.06 parts of sulfur to 35.46 of chlorine. Since 32.06 is exactly twice 16.03, this result is in complete agreement with expectation.

Attention should be drawn to the fact that the equivalent weight is essentially an experimental quantity. It was at one time defined in terms of combination or replacement of the element hydrogen, but since there are many elements, particularly metals, that do not form stable compounds with hydrogen, the basis of the definition was changed. Of course, there are some elements which do not form compounds with oxygen that are stable and easily purified, two primary requirements for the determination of equivalent weight. In order to maintain the experimental basis of this quantity, therefore, the definition is extended for practical purposes; the equivalent weight is thus taken as the quantity of an element which can combine with or replace 8.000 parts of oxygen, or its equivalent, e.g., 35.457 parts by weight of chlorine. Many elements form stable, easily purifiable chlorides, or other halides, and these have been employed for the experimental determination of equivalent weights.

2c. Dalton's Atomic Theory.—Now that the laws of chemical combination, which summarize the experimental facts, are known, it is desirable to see if a simple scheme can be proposed to account for the observed phenomena. Such

a scheme, known as the **atomic theory**, was put forward by J. Dalton in 1803; this theory may be stated in the form of the following three postulates:

(i) *All matter is composed of small, definite and indestructible particles, called atoms, which are indivisible by ordinary chemical means.*

(ii) *Atoms of the same element are equal in weight and are alike in all respects, but atoms of different elements have different weights and properties.*

(iii) *Compounds are formed by the union of an integral number of atoms of one element with an integral number of atoms of one or more other elements.*

The theory summarized in the foregoing statements, representing the first step in the development of the modern idea of atoms, provides a satisfactory interpretation of the laws of chemical combination. In the first place, since the atoms are definite particles with a definite weight, there should be no change in mass as the result of a chemical reaction. Such a reaction involves merely the interchange of attachments between various atoms of different elements, and so the weight should remain constant. This is, of course, in harmony with the requirements of the law of conservation of mass. The postulate of definite and constant mass also leads directly to the law of constant proportions. If cupric oxide, for example, consists of a combination of an atom of copper with an atom of oxygen, as is very probable, then since each of these atoms has a perfectly definite and constant weight, the composition of the oxide will also be quite definite.

An explanation of the law of multiple proportions can be obtained by considering the chemical interaction of two elements A and B; according to the atomic theory, combination of an integral number of atoms of A will take place with an integral number of atoms of B. The formulae of some of the possible resulting compounds would thus be AB, AB₂ and A₂B₃, so that the amounts of B that unite with a constant quantity of A in these three substances are 2 to 4 to 3, respectively. These small integers bear a simple ratio to one another, as required by the law of multiple proportions. In the three compounds between A and B just suggested, the number of atoms involved is not large; although this is the case for many compounds, it is not necessarily always true. In some organic substances, for example, large numbers of atoms of different kinds may be joined together; thus, in the hydrocarbon triacontane, to which reference was made earlier, 30 atoms of carbon are united with 62 atoms of hydrogen. On the other hand, in the related paraffin hydrocarbon methane, there is one carbon atom to four hydrogen atoms. The amounts of hydrogen that are combined with a constant amount of carbon in these two compounds are thus in the proportion of 31 to 60, as stated in § 2b, III. This is not a simple ratio, but it is nevertheless in complete agreement with the atomic theory, since the theory postulates that chemical combination can occur only between whole numbers of atoms.

Consider the elements B and C, both of which can combine with the element A; according to the atomic theory, such compounds as AB, AB₂, A₂B₃, etc., and AC, AC₂, A₂C₃, etc., are to be expected. If the substance AB, on the one hand, is compared with AC₂, on the other hand, it is seen that one atom of B and two of C, respectively, combine with the same quantity, viz., one atom,

of A. By the law of combining proportions, therefore, the elements B and C should unite in the atomic ratio of 1 to 2, that is, to yield the compound BC_2 , or in some simple multiple of this ratio, which might result in such substances as BC or B_2C_3 . Since these compounds all involve integral numbers of the atoms B and C, their existence would be in accord with the requirements of the atomic theory. This theory, therefore, provides a satisfactory basis for the law of combining proportions, as well as for the three other laws of chemical combination.

It may be noted that if all compounds formed between two elements contained only one atom of each, viz., AB, AC, BC, AD, BD, CD, etc., the ratio of the combining weights of the elements A, B, C, D, etc., would be identical with the ratio of the actual weights of these atoms. However, this is not always true and the ratio of the combining weights may differ from the ratio of the weights of the atoms; as is to be expected from the atomic theory, these ratios if not identical must be simple integral multiples of each other. It may be stated as a general rule that if two elements form a compound of the type AB, BC, CD, etc., the ratio of their equivalent or combining weights in that compound will be the same as the ratio of the weights of the atoms.

ATOMS AND MOLECULES

3a. Gay-Lussac's Law of Combination by Volume.—In addition to the laws of chemical combination considered in the preceding section, there is another important law, known as the **law of combination by volume**, discovered by J. L. Gay-Lussac (1808); this law cannot be explained in terms of the atomic theory alone. The law, which applies only to reactions involving gases, states that *when two gases combine chemically they do so in simple proportions by volume; further, the volume of the gaseous products also bears a simple ratio to that of the reacting gases*. It should be understood, of course, that the volumes are all measured under the same conditions of temperature and pressure.

In the formation of hydrogen chloride gas from hydrogen and chlorine, for example, it is found that

1 volume of hydrogen + 1 volume of chlorine = 2 volumes of hydrogen chloride.

The volumes of the two reacting gases and of the product are thus in the simple ratio of 1 to 1 to 2. Similarly, when hydrogen and oxygen react to form water vapor (steam),

2 volumes of hydrogen + 1 volume of oxygen = 2 volumes of steam;

here again, the ratios of the volumes are simple integers.

As in the case of the law of multiple proportions, the Gay-Lussac law of combination by volume holds strictly for relatively simple compounds; with more complex substances, there are apparent, although not real, exceptions. If the gas butane were completely burnt in oxygen, it would be found that 2 volumes of butane gas required 13 volumes of oxygen gas, and the products—carbon dioxide and water—would occupy 18 volumes in the gaseous state at

the same temperature and pressure. These numbers, 2, 13 and 18, can hardly be said to bear a simple ratio to each other. The essential point here, however, as in other cases, is that the ratio of the volumes can be expressed in terms of integers.

3b. Atoms and Molecules.—The significance of Gay-Lussac's law of volumes was realized by A. Avogadro (1811), and it led him, in the first place, to distinguish between an atom and a molecule. Previously, the word "atom" had been used to describe the smallest conceivable particle of any substance, either element or compound, but Avogadro suggested that this term should be restricted to elements. In addition, he introduced the use of the term "molecule," which could be applied to both elements and compounds. The distinction between an atom and a molecule will be apparent from the following definitions:

An atom is the smallest particle of an element that can take part in chemical change.

A molecule is the smallest particle of an element or compound that can exist in the free state.

The smallest unit of a compound substance is thus seen to be the molecule; this can exist as such in the free state and it can also take part in chemical reaction. With an element, however, it is necessary to distinguish between the atom and the molecule, for the atom may not be capable of any prolonged existence in the free state. In some cases, for example, the inert gases of the atmosphere, i.e., helium, neon, etc., and the vapors of most metals, e.g., mercury, the smallest conceivable particle, which is the atom, is quite stable and is capable of a free and independent existence. For these elements the atom and the molecule are consequently identical. With the great majority of nonmetallic elements, however, the molecule contains two or more atoms, although the number may vary with the temperature.

As in many other instances, an attempt to give a precise definition of a molecule of an element involves some difficulties, for even when it is recognized that the atom and molecule are different, it is not strictly true to say that the atom does not exist in the free state. A hydrogen molecule, to take a simple illustration, normally contains two atoms; as the temperature is raised, the molecules split up into single atoms, and at sufficiently high temperatures hydrogen gas contains an appreciable proportion of atoms which can exist in the free state, alongside molecules containing two atoms. It would seem, therefore, that under these conditions both the atom and the molecule of hydrogen are capable of a free existence. Although this is true, in a sense, it would be more correct to say that at high temperatures there are two kinds of hydrogen molecules; one in which there are two atoms per molecule and the other with but one atom to the molecule. As the temperature is lowered the proportion of the latter type of molecule decreases, but even at ordinary temperatures there are undoubtedly a few that can exist in the free state. Since the number is so small that it can be neglected, hydrogen gas under normal conditions may be regarded as consisting entirely of molecules each of which contains two atoms. The possibility of the existence of different types of

molecules of the same element, and even of a compound, must nevertheless always be borne in mind.

3c. Avogadro's Law.—After making the distinction between an atom and a molecule, Avogadro proposed a hypothesis which is now so universally accepted that it is regarded as one of the established laws of chemistry. According to **Avogadro's law**, *under the same conditions of temperature and pressure, equal volumes of different gases contain equal numbers of molecules.* If it may be supposed, as a consequence of the atomic theory, that when molecules react chemically they do so by simple whole numbers, then Gay-Lussac's law of volumes follows directly from the law of Avogadro. Suppose a small integral number a of molecules of the substance A interact with the integral number b of molecules of B, both being in the gaseous state; suppose further that, in accordance with Avogadro's law, a unit volume of each of these gases, or of any other gas, contains n molecules at the given temperature and pressure. It follows, therefore, that

$$\frac{a}{n} \text{ volumes of A combine with } \frac{b}{n} \text{ volumes of B,}$$

and hence the ratio of the volumes in which the gases A and B interact is equal to a to b . Since a and b are both small integers, this will be a simple ratio, as required by Gay-Lussac's law. The number of molecules c of the product (or products) resulting from the reaction must also be integral, since fractions of molecules cannot exist in the free state; hence, the volume of the gaseous products will bear a simple ratio to that of the reacting substances. It is now easy to understand why the ratio of the volumes of butane gas, oxygen gas, and the gaseous products of complete combustion are 2 to 13 to 18, as noted in § 3a. In the light of Avogadro's law, that equal volumes contain equal numbers of molecules, the explanation lies in the fact that the over-all reaction involves 2 molecules of butane, 13 molecules of oxygen and 18 molecules of products. Such a conclusion is quite in keeping with the atomic theory and its extension by the introduction of the idea of molecules.

There are many important consequences of Avogadro's law, some of which will be referred to here. As already seen, one volume of hydrogen and one of chlorine unite to produce two volumes of hydrogen chloride; consequently, supposing that there are n molecules per unit volume,

$$\begin{aligned} n \text{ molecules of hydrogen} + n \text{ molecules of chlorine} \\ = 2n \text{ molecules of hydrogen chloride,} \end{aligned}$$

or

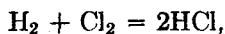
$$\begin{aligned} 1 \text{ molecule of hydrogen} + 1 \text{ molecule of chlorine} \\ = 2 \text{ molecules of hydrogen chloride.} \end{aligned}$$

A single molecule of hydrogen chloride, which is, of course, capable of free existence, thus contains one-half molecule of hydrogen and one-half molecule of chlorine. Since the atom is the smallest particle that can take part in

chemical combination, it is evident that the one-half molecule of hydrogen and of chlorine must consist of a single atom *at least*. In other words, the molecule of hydrogen and the molecule of chlorine must each contain at least two atoms. There are good reasons for believing that, at ordinary temperatures and pressures, these molecules contain no more than two atoms; it follows, therefore, that it is possible to represent the reaction between hydrogen and chlorine gases as

2 atoms of hydrogen + 2 atoms of chlorine = 2 molecules of hydrogen chloride,

or



so that the formula of hydrogen chloride gas must be HCl. Similar conclusions concerning the structures of other gaseous molecules can be reached in an analogous manner.

Before going on to consider other uses of Avogadro's law, brief reference may be made here to the limits of applicability of this law, and of the Gay-Lussac law of combination by volume. Strictly speaking, both of these laws refer to what are known as "ideal" or "perfect" gases, which will be considered more fully in Chapter IV. The nature and extent of the deviations from ideal or perfect behavior exhibited by actual gases will be discussed there, and it will be seen that allowance can be made for the small departures from Avogadro's law; for the present these deviations may be ignored. Incidentally, it should be noted that the conclusions reached above in connection with the hydrogen-chlorine reaction are independent of any failure of the gases to behave ideally; the small departures from Gay-Lussac's law balance those from Avogadro's law. Experiments of the highest precision would show that it is not exactly one volume of hydrogen that combines with one of chlorine to produce exactly two volumes of hydrogen chloride; the actual volumes would be very slightly different. Nevertheless, after allowing for the corresponding deviations from Avogadro's law, it would be found that precisely two atoms of hydrogen and two atoms of chlorine yield precisely two molecules of hydrogen chloride.

3d. Atomic and Molecular Weights.—One of the postulates of the atomic theory is that the atom of any given element has a definite and constant weight; since a molecule of an element or compound contains a definite integral number of atoms, it must also have a definite weight characteristic of the given molecule. These statements are, of course, based on the supposition that a particular isotopic form, or a certain isotopic composition of the element or compound, is under consideration. It should thus be possible to state the weight of an atom or molecule of any substance as a definite quantity. Because atoms and molecules are so small, their actual weights being of the order of 10^{-24} gram, it is more convenient in practice to state the weight of any atom or molecule in terms of that of a standard atom. The so-called atomic and molecular weights are thus really *relative weights*. At one time the hydrogen atom, the lightest known atom, was chosen as the standard of comparison,

so that its atomic weight was taken as precisely unity. Since atomic weights are generally determined from the experimental equivalent weights and the latter, for reasons already given, are expressed in terms of the element oxygen as the standard, atomic weights are now given relative to that of the oxygen atom. The **atomic weight** of an element is thus defined as *the weight of an atom of the element relative to the weight of the oxygen atom taken as 16.0000*.

Oxygen exists in at least three isotopic forms with atoms of different weights; hence, the atomic weight of any element will depend on the isotopic composition of the oxygen employed as the standard of reference. If the value 16.0000 is taken as the mean atomic weight of oxygen having the same isotopic composition as in the atmosphere, the resulting figures for other elements are known as the **chemical atomic weights**.* On the other hand, if 16.0000 is assumed to be the atomic weight of the most abundant isotope, the **physical atomic weights** are obtained. From a study of the masses and relative proportions of the isotopes of oxygen (§ 7e), it is found that

$$\text{Chemical atomic weight} = \frac{\text{Physical atomic weight}}{1.00027}$$

It is evident that the difference between the two sets of atomic weights is not large; nevertheless, it is necessary to distinguish between them. The chemical atomic weights are those employed by chemists in the quantitative study of reactions, but the physical atomic weights are often used in stating the weights of isotopes and in connection with atomic disintegration reactions (§ 8d). Unless a specific statement is made to the contrary, chemical atomic weights will be employed throughout this book.

It was noted earlier that the equivalent weight of oxygen, which is the standard of reference for equivalent weights, is taken as 8.000, whereas the atomic weight is 16.000. It is seen, therefore, that on the basis of the accepted scales, the atomic weight of oxygen is exactly twice the equivalent weight. According to the atomic theory, the weight of an atom of any element must always be a simple integral multiple of its combining weight; hence, it is possible to write the following general relationship:

$$\frac{\text{Atomic weight}}{\text{Equivalent weight}} = \text{a small integer.}$$

This integer, which is *the ratio of the atomic weight of an element to its equivalent weight*, is called the **valence** of the element in the particular compound employed in the determination of the equivalent weight; it is generally 1, 2, 3 or 4, although it is sometimes larger.

If the valence is known, it is possible to obtain the atomic weight from the accurately determined, experimental, equivalent weight; this is the principle most frequently employed in the evaluation of atomic weights. The valence of the element being studied is rarely in doubt, at the present time, but in the

* The familiar chemical atomic weights, like that of oxygen, are actually the mean of the values for the isotopic forms which may be present.