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FORMULATION  
**and**  
STOICHIOMETRY

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# Formulation and Stoichiometry

A  
REVIEW  
OF

## Fundamental Chemistry



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# Formulation<sup>and</sup> Stoichiometry

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## PREFACE

The purpose of this book is to interpret more sensitively some of the offerings of the standard text book of general chemistry. As a supplement thereto, it covers various aspects of formulation and stoichiometry that are frequently treated far too perfunctorily or, in many instances, are not considered at all.

The inadequate attention often accorded by the comprehensive text to many topics within its proper purview arises, understandably enough, from the numerous broad and highly varied objectives set for the first year of the curriculum for modern chemistry in colleges and universities. For the serious student this means, more often than not, the frustrations of questions unanswered.

The amplification that this book proffers in the immediate area of its subject covers the equations representing *internal* redox reactions, not only of the simple but, also, of the multiple disproportionations of which the complexities often discourage an undertaking despite the challenge they offer: distinctions to be observed in the balancing of equations in contrasting alkali-basic and ammonia-basic reaction media; quantitative contributions made by the ionization or dissociation effects of electrolytes to the colligative properties of their solutions; intensive application of the universal reaction principle of *chemical equivalence* to the stoichiometry of oxidation and reduction.

As the endeavor here is always to anticipate the questions most likely to be asked by beginning students, it is deemed prudent not to start in the middle of things on the assumption, as often misconceived by supplemental texts, that what is needed in the way of preparation for comprehension has already been acquired elsewhere. Hence, various rudiments of theory normally taken for granted as understood are emphasized and elaborated whenever an efficacious integration of subsequent chemical themes must be ensured.

The fortifying of the text with significant, and frequently advanced, applications of formulation and stoichiometry establishes its utility not only to supplement a course, or for review, but also its character as a fully independent and self-sustaining primary text for instruction in class.

The varied exercises given—some “routine,” others “challenging”—afford the student ample opportunities to demonstrate a confident understanding and practical mastery of principles, a memory for important

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facts, and a capability with elementary mathematics. Indeed, they do more; for, by pedagogical design and physical construction, many of these exercises feature new chemical information not supplied in the text of the chapter. They thus offer earnest incentives to learn further while demonstrating skills in performance.

The ample amounts of worked-out problems, each interpreted in progressive step-by-step fashion, demonstrate practical methods of solving successfully the numerous mathematical exercises. Answers to all the exercises are fully supplied in the Appendix. Ready opportunity is thus given to corroborate having been on the right track.

E.J.M.



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## CHAPTER 1

# CONCEPTS OF QUANTITATIVE COMPOSITION

The objective of this book is to interpret the chemist's shorthand — chemical symbolism and formulation — and to introduce the subject of *stoichiometry*. Stoichiometry is the branch of chemical mathematics concerned with the relative amounts of substances that interact. Derived from the Greek *stoicheion*, meaning *element*, stoichiometry originally treated only of the different weights of elements that combine to form specific compounds. Modern usage, however, has expanded the generic applicability of the term to any and all aspects of chemical reactivity that can be validly interpreted by a balanced chemical equation. Consequently, stoichiometry encompasses within its purview not only weights but also volumes, gaseous and liquid, and even thermochemical and photochemical quanta of reaction.

The art and practice of calculating the combining weights of chemical elements requires a thorough knowledge of fundamental physical laws and theories.

## LAW OF CONSERVATION — MATTER AND ENERGY

Mass-energy can be neither created nor destroyed. Although matter can be converted from one chemical species to another, energy transformed from one kind to another, and matter and energy mutually interconverted, no over-all losses or gains can occur in a closed system. This is the universal and incontrovertible law of conservation.

That mass and energy are equivalent and can be converted into each other was demonstrated in the classic theory of relativity developed by Albert Einstein in Germany in 1905. The interconvertibility of mass and energy is expressed mathematically as

$$E = mc^2,$$

where  $E$  represents the energy in ergs (fundamental unit of energy) obtained from the rest mass of a given quantity (in grams) of matter  $m$  that disappears; and  $c$ , the velocity of light ( $3 \times 10^{10}$  centimeters a second).



Inherent in this mathematical definition is the recognition that the energy equivalent of any specific quantity of matter is dependent solely upon its total mass and not upon its chemical nature, form, or identity.

In *ordinary* types of chemical reaction — those that do not chemically involve the atomic nuclei — transformations of mass to energy are far too slight to be even detectable. Consequently, total mass remains unchanged in any nonnuclear reaction and the total initial mass of all reactants must equal the total final mass of all products.

## MASS VERSUS WEIGHT

In practice the terms *mass* and *weight* are frequently confused. Despite their marked differentiation, they are loosely regarded as equivalent. Mass is, correctly, the *quantity* of matter ascertainable by the experimental measurement of “weighing” or by the response (change in velocity) that is caused by an unbalanced force.

In determining the mass of an object by weighing it upon a balance, we are actually measuring the magnitude of the force with which it is being attracted by the force of gravitation of the earth. As the force of gravity diminishes as distance from the earth increases, the *weight* of an object must likewise diminish. Mass, however, is completely independent of gravitational force; hence, although the weight of a given object decreases as the altitude of its measurement increases, its mass remains constant. An object is weighed by *counterbalancing* it with the exact number of *standard* units of mass (the “weights”) required to make the gravitational force upon the object on one side equal to the gravitational force upon the standard weights on the other side. We are, in effect, canceling the force of gravitation, and thus we are measuring mass.

## MASS AND VOLUME — THE IMPLICATIONS OF DENSITY

The term *volume*, as the chemist employs it, means precise, minimum amount of space needed to accommodate a specific amount of matter. The fundamental unit of volume in the metric system is the *cubic centimeter* (cc), which term is acceptably interchanged with *milliliter* (ml).

This duality of terms for volume emphasizes not only an error in computation that was originally made in the measurement of volume but also a difference in the units utilized in the respective measurements. Derived from units of *length*, the cubic centimeter represents the volume of a cube one centimeter on edge. An assignment of 1000 cc was made to standardize the space occupied by an intended mass of one kilogram of water at its temperature of maximum density, 3.98°C. It was subsequently determined, however,

that one kilogram of the water actually occupies 1000.027 cc. To rectify this error without compounding a *fait accompli* into utter confusion, the term "liter" was designated to represent this volume of 1000.027 cc. Consequently, 0.001 liter (= 1 milliliter *exactly*) becomes identical in volume with 1.000027 cc. Hence, one gram of water at 3.98°C occupies a volume that may alternately be described as 1 ml or as 1.000027 cc. The quantitative difference between the two is so slight that there is little reason to belabor the inconsistency further; hence, the cc and the ml may be considered identical for all practical purposes.

*Density* is defined as the mass of a unit of volume. Using the metric units already established, the dimensions of density are grams/cc to the cubic centimeter (g/cc), or to the milliliter (g/ml). Density may also be expressed in any other units that properly relate the mass of a substance to the volume it occupies. This may be useful when experiments in weighing require the use of larger volumes, for example, in weighing gases, because reliably weighable quantities of materials so light must be, understandably, large. Thus, the densities of gases are often expressed in dimensions of gram/liter.

## DENSITY VERSUS SPECIFIC GRAVITY

Closely related to density is *specific gravity* — a term of especial convenience when applied to liquids and solids. The specific gravity of a substance is a ratio of the density of that substance to the density of another substance taken as a standard. It thus represents how many times heavier the substance is than the stated standard. If, for instance, the standard is water at 3.98°C (more conveniently, 4°C) where its density is 1.0 g/ml, the specific gravity of the substance in question will be *numerically* equivalent to its density (*but* dimensionless, inasmuch as the units in the ratio will have cancelled out). Thus, for liquid mercury, of which the density is 13.6 g/ml,

$$\text{sp.gr.} = \frac{\text{density of mercury}}{\text{density of water at } 3.98^{\circ}\text{C}} = \frac{13.6 \text{ g/ml}}{1.0 \text{ g/ml}} = 13.6.$$

Although a standard of 1.0 g/ml is a distinct convenience, laboratory practice rarely permits exactitude with respect to this, inasmuch as the temperature is seldom 3.98°C and liquids other than water may occasionally be preferred as standards. In any event, appropriate notation will clarify what is intended. The notation " $1.78_{4}^{25^{\circ}}$ " specifies that the density of the given substance at 25°C is 1.78 times greater than that of water at 4°C and, consequently, the actual density of the given substance (at this temperature) must coincide with its specific gravity. Hence, density here is 1.78 g/ml.

Were the reference standard to have been water at 25°C, the specific gravity of the substance in question (expressed by sp. gr. $_{25^{\circ}}^{25^{\circ}}$ ) could not be

numerically identical to its density, because the density of water at 25°C is something less than 1.0. The value of specific gravity for the given substance is now somewhat larger than the value of 1.78 computed for it when water at 4°C was used as standard — the value of the density ratio having increased because of a decrease in the denominator (the numerator remaining constant).

## LAW OF DEFINITE PROPORTIONS—CONSTANCY OF COMPOSITION

Two or more substances — elements or compounds — which chemically combine to form a specific compound will do so in fixed and unalterable proportions by weight.

This scientific law, first expressed by Joseph Proust (France, 1799), means that the composition of each and every compound is incorruptibly exact and may always be defined in terms of the combining parts by weight of each of the elements therein. Certain contingencies that must, however, be recognized here are as follows:

1. Two elements may combine in different proportions by weight if each new ratio of combination leads to a completely different compound.

Thus, although hydrogen and oxygen, in forming the compound *water*, always combine in the ratio of *one* part by weight of hydrogen to approximately *eight* parts of oxygen — the same two elements may also combine in the ratio of *one* part by weight of hydrogen to *sixteen* parts of oxygen. But, the compound formed here is not water ( $\text{H}_2\text{O}$ ); it is hydrogen peroxide ( $\text{H}_2\text{O}_2$ ).

2. The Law of Definite Proportions does not preclude the possibility that the same elements may combine in identical proportions to form two or more different compounds. Such compounds are called *isomers*. Some isomers may be widely different in physical and chemical properties; for example, the compounds ammonium thiocyanate, empirically described by the molecular arrangement  $\text{NH}_4\text{OCN}$ , and urea, empirically described by the molecular arrangement  $\text{CO}(\text{NH}_2)_2$ .

The properties of other isomers may be so close that only a significant physical property offers an effective and ready means for differentiating them. Thus, *glucose* (grape sugar) and *fructose* (fruit sugar), both identified by the same general formula  $\text{C}_6\text{H}_{12}\text{O}_6$ , have virtually similar chemical and physical properties but they can be readily distinguished on the basis of their opposing optical activities. When polarized light (vibrations confined to a single plane) is transmitted through a solution of glucose, the plane of the polarized light is rotated to the right; when similar light is passed

through a solution of fructose, however, rotation is to the left. The chemical synonyms "dextrose" and "levulose" are thus comprehendingly descriptive of the respective compounds.

3. Another type of chemically different compounds with exactly similar percentage composition are those constituted of precisely the same elements in numbers of atoms that are, in the different compounds, reducible to a common empirical (simplest) unit.

Thus, the compounds *formaldehyde*,  $\text{CH}_2\text{O}$ , and *glucose*,  $\text{C}_6\text{H}_{12}\text{O}_6$ , are both algebraically expressed by different numbers of units of  $\text{CH}_2\text{O}$ . In formaldehyde, only one such unit is present; for the glucose, six such units, formulated for the compound as  $(\text{CH}_2\text{O})_6$ . Clearly, percentage composition, which expresses parts by weight of a constituent element per one hundred parts by weight of the entire compound, is not mathematically altered by the multiple that has been applied to the formula. The ratios  $\text{C}/\text{CH}_2\text{O}$ ,  $2\text{H}/\text{CH}_2\text{O}$ , and  $\text{O}/\text{CH}_2\text{O}$  correspond exactly to  $6(\text{C})/6(\text{CH}_2\text{O})$ ,  $6(2\text{H})/6(\text{CH}_2\text{O})$ , and  $6\text{O}/6(\text{CH}_2\text{O})$ , respectively.

None of these variations compromises in the slightest the precise validity of confirmed law, because percentage composition by weight remains incorruptibly constant for each and every specific compound. When proportions of the elements are the same for different compounds, the numbers and architectural arrangements of their atoms will supply the answers to the different properties.

Another seeming refutation of the Law of Definite Proportions must be reconciled here. References heretofore have been made to naturally occurring substances. In such samples of matter it must be recognized that the percentage distributions of the various *isotopes* (different varieties of atoms of the same element) remain uniform under all normal conditions. It is clear that if one particular isotope of a given element were combined with some single specific isotope of another the analysis might well show a percentage composition for the compound formed that is significantly different from the one shown under reaction conditions of normal mixtures of the isotopes of the element.

In illustration, we have observed that one part of hydrogen will combine with eight parts of oxygen to form water — an analysis reflecting the distributive percentage *average* atomic weight of the three isotopic atoms of natural hydrogen (mass numbers 1, 2, and 3), and of the three isotopic atoms of natural oxygen (mass numbers 16, 17, and 18). Were we to have taken, however, specifically individual isotopes of the respective elements we would have obtained " $\text{H}_2\text{O}$ " of different compositions by weight, in conformity with the possibilities shown in Table 1:1.

Molecules of "heavy water,"  $\text{D}_2\text{O}$ , and the still heavier  $\text{T}_2\text{O}$ , all contribute to the average weight of molecules of water. The latter are standardized in the numerical identity of the ratios of elemental weights solely



TABLE 1:1

Possible Combinations of Hydrogen and Oxygen

Isotopic Combinations		H <sub>2</sub> O: hydrogen to oxygen weight ratios
Protium ( ${}_1\text{H}^1$ ) oxides	$\left\{ \begin{array}{l} {}_1\text{H}^1 \text{ with } {}_8\text{O}^{16} \\ {}_1\text{H}^1 \text{ with } {}_8\text{O}^{17} \\ {}_1\text{H}^1 \text{ with } {}_8\text{O}^{18} \end{array} \right.$	2 : 16 or 1 : 8 2 : 17 or 1 : $8\frac{1}{2}$ 2 : 18 or 1 : 9
Deuterium ( ${}_1\text{H}^2$ or D) oxides	$\left\{ \begin{array}{l} {}_1\text{H}^2 \text{ with } {}_8\text{O}^{16} \\ {}_1\text{H}^2 \text{ with } {}_8\text{O}^{17} \\ {}_1\text{H}^2 \text{ with } {}_8\text{O}^{18} \end{array} \right.$	4 : 16 or 1 : 4 4 : 17 or 1 : $4\frac{1}{2}$ 4 : 18 or 1 : $4\frac{1}{2}$
Tritium ( ${}_1\text{H}^3$ or T) oxides	$\left\{ \begin{array}{l} {}_1\text{H}^3 \text{ with } {}_8\text{O}^{16} \\ {}_1\text{H}^3 \text{ with } {}_{10}\text{O}^{17} \\ {}_1\text{H}^3 \text{ with } {}_8\text{O}^{18} \end{array} \right.$	6 : 16 or 1 : $2\frac{2}{3}$ 6 : 17 or 1 : $2\frac{5}{6}$ 6 : 18 or 1 : 3

because all samples contain virtually constant percentages of admixed H<sub>2</sub>O, D<sub>2</sub>O, and T<sub>2</sub>O. Although the reference to *heavy water* is, in general, intended to distinguish between hydrogen atoms — the protium and the deuterium or tritium — in their chemical associations with the oxygen atom of average weight, the same considerations apply with respect to the isotopic variations that are possible with the oxygen atoms in their chemical associations with a hydrogenation of *average* weight. The abundance of the protium, to the near-exclusion of the other varieties, ensures a practical average atomic weight of hydrogen of 1.

### LAW OF MULTIPLE PROPORTIONS—PRELUDE TO ATOMIC CONCEPTS

Whenever variable weights of one specific element combine with a fixed weight of another specific element in the formation of different compounds of the two, those variable weights will always be found to be simple multiples of one another.

By a “simple multiple” is meant a number expressible by a small whole-number numerator and a small whole-number denominator; for example,  $\frac{1}{2}$ ,  $\frac{3}{1}$  (= 3),  $\frac{2}{3}$ , etc.

The interpretation of this scientific law (first stated by John Dalton, England, in 1803) leads inevitably to the conclusion that in ordinary chemical reaction, whole atoms are nature’s building blocks which must be transferred intact from one substance to another. Any weight of any substance must then represent an integral number of whole atoms, and any removals or additions in the formation of new substances must likewise be in the

ratios of integral numbers of whole atoms. These integral numbers then establish the relative numbers of each of the pertinent atoms present in each of the respective compounds.

## ATOMIC THEORY—IMPLICATIONS OF MULTIPLE PROPORTIONS

John Dalton's interpretations of multiple combining proportions led him to propose a theory of internal constitution of matter that has served as the foundation of our modern developments of atomic concept. Its postulations were, essentially, as follows: (we interpolate certain modernized appraisals):

1. The chemical elements and all the compounds formed from their combinations are composed of discrete and indivisible entities called *atoms*. [The existence of *subatomic* particles — not surmised in Dalton's time — must today represent a qualification of the term "indivisible." For all ordinary (nonnuclear) chemical changes, however, the term remains legitimate.]

2. The chemical and physical properties of all atoms of any specific element are identical, but are different from those of any other element. (Here again the existence of isotopes must qualify the term "identical," at least insofar as identity of the physical property of mass is concerned.)

TABLE 1:2

Different Compounds of Nitrogen and Oxygen

Compound	Parts by Weight		Corresponding Ratios	
	Nitrogen (constant)	Oxygen and the variable Simple Multiples	N : O in Whole Atomic Weights	Molecular Formula
Nitrous Oxide	14.00	$8.00 \left( = \frac{1}{2} \times 16.00 \right)$	$(2 \times 14.00) : (1 \times 16.00)$	N <sub>2</sub> O
Nitric Oxide	14.00	$16.00 \left( = \frac{1}{1} \times 16.00 \right)$	$(1 \times 14.00) : (1 \times 16.00)$	NO
Nitrogen Trioxide	14.00	$24.00 \left( = \frac{3}{2} \times 16.00 \right)$	$(2 \times 14.00) : (3 \times 16.00)$	N <sub>2</sub> O <sub>3</sub>
Nitrogen Dioxide	14.00	$32.00 \left( = \frac{2}{1} \times 16.00 \right)$	$(1 \times 14.00) : (2 \times 16.00)$	NO <sub>2</sub>
Nitrogen Pentoxide	14.00	$40.00 \left( = \frac{5}{2} \times 16.00 \right)$	$(2 \times 14.00) : (5 \times 16.00)$	N <sub>2</sub> O <sub>5</sub>

3. Chemical change involves merely the combinations of different elements to form compounds; and the atoms of the elements involved in such change are merely rearranged without impairment of their identities. (We must qualify "chemical change" as used here as ordinary, or non-nuclear.)

4. The chemical combinations of different atoms that lead to the formation of compounds must occur in simple numerical ratios of whole numbers; that is, 1 : 1, 2 : 1, 2 : 3, etc.).

Let us now illustrate the implications of multiple proportions. In Tables 1:2 and 1:3, the parts-by-weight base for each weight-constant element is expressed in grams; and these, moreover, have been conveniently rounded off for greater visual clarity. It should be borne in mind that the weights represent a judicious refining of experimental, and hence, sensitivity-limited, measurements.

The identical results could have been achieved with equal convenience by making oxygen the element of constant weight, and observing the variations in weight of the nitrogen; and similarly relating the simple multiples to units of whole atomic weights, as shown in Table 1:3.

TABLE 1:3

Alternate Calculations for Oxides of Nitrogen

Compound	Parts by Weight		Corresponding Ratios	
	Nitrogen and the variable Simple Multiples	Oxygen (constant)	N : O in Whole Atomic Weights	Molecular Formula
Nitrous Oxide	28.00 $\left( = \frac{2}{1} \times 14.00 \right)$	16.00	$(2 \times 14.00) : (1 \times 16.00)$	N <sub>2</sub> O
Nitric Oxide	14.00 $\left( = \frac{1}{1} \times 14.00 \right)$	16.00	$(1 \times 14.00) : (1 \times 16.00)$	NO
Nitrogen Trioxide	9.33 $\left( = \frac{2}{3} \times 14.00 \right)$	16.00	$(2 \times 14.00) : (3 \times 16.00)$	N <sub>2</sub> O <sub>3</sub>
Nitrogen Dioxide	7.00 $\left( = \frac{1}{2} \times 14.00 \right)$	16.00	$(1 \times 14.00) : (2 \times 16.00)$	NO <sub>2</sub>
Nitrogen Pentoxide	5.60 $\left( = \frac{2}{5} \times 14.00 \right)$	16.00	$(2 \times 14.00) : (5 \times 16.00)$	N <sub>2</sub> O <sub>5</sub>

As would be mathematically inevitable, the two simple multiples obtained for any specific individual compound, when the weight of one element therein is alternately varied against a fixed weight of the other, are *reciprocally* related to one another.

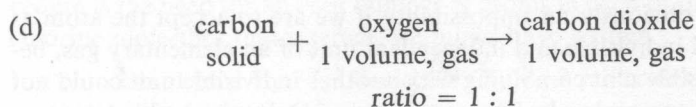
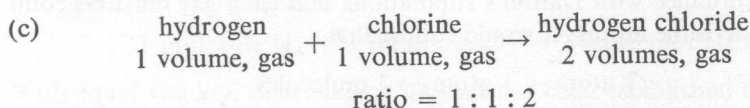
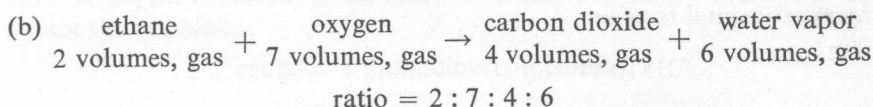
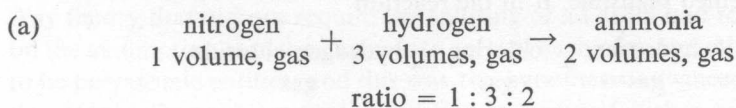
## GAY-LUSSAC'S LAW — WHOLE-NUMBER RELATIONSHIPS

Dalton's atomic theory suggested no clues whatever as to the manner in which the relative weights of atoms might be ascertained. The implications of the integers in the Law of Multiple Proportions not only were to prove inescapable but also, indeed, were to receive additional bolstering from an entirely different experimental direction — again, by the recurrence of integers.

In 1808, J. L. Gay-Lussac (France) observed that the volumes of all gases that combine or are produced in a chemical reaction may always be expressed in ratios of small whole numbers.

This statement, in various forms of its intent, is today called the Law of Combining Volumes. Although their theoretical significance was not understood at the time, the known experimental phenomena proved later to be additional clues to what was being sought; namely, a scale of atomic weight.

A few examples demonstrate the Law of Combining Volumes:



It is to be observed that, unlike the "left hand/right hand" equalities that represent conservation of mass, there is no conservation of volume.

The relationships witnessed hold regardless of the particular units used to express volume — liters, cubic centimeters, cubic feet, etc. — provided that they are uniformly applied to a given reaction. Likewise, it must be evident that any expression of a relationship in fractional fashion — such as  $(\frac{1}{3}) : 1 : (\frac{2}{3})$ , as might be written for example *a* — does not preclude its being translated into integral numbers.



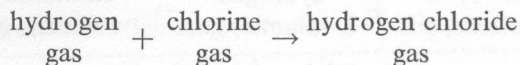
## AVOGADRO'S PRINCIPLE

In 1811, Amadeo Avogadro (Italy) offered an explanation of the yet-to-be-understood theoretical significance of combining volumes of gases. He hypothesized that

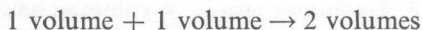
equal volumes of all gases under the same conditions of temperature and pressure contain equal numbers of molecules.

Through lack of experimental evidence to support this contention it was not accepted at the time, and as a result the concept lay dormant for about fifty years — when experimental findings in newly developed areas of physical and organic chemistry exhaustively corroborated it as valid. It has earned, today, the dignity not merely of an educated guess — an hypothesis — but rather, of a firmly established scientific law.

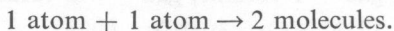
Let us examine, by means of a few examples, the theoretical implications of this concept and the historical objections that it had to surmount. It must be remembered that Dalton conceived of an elementary gas as a collection of solitary monoatomic entities, rather than as the polyatomic units (in virtually all ordinary instances) that today we call *molecules*. Dalton's inability to accept the theoretical premises of Gay-Lussac's laboratory investigations and of Avogadro's interpretations rested upon grounds that then seemed plausible. If in the reaction



the experimental facts are



then, in accordance with Dalton's stipulations that each gas must be composed of indivisible atoms, it would follow that



This last is obviously an impossibility if we are to accept the atom as the fundamental indivisible and independent unit of an elementary gas, because one indivisible unit combining with another indivisible unit could not yield more than one molecule. The carry-over of Dalton's single-atom concept of gases has left us, even up to the present time, with an arbitrary standard of weight combinations of an element — called its *combining weight* (or *equivalent weight*). This stemmed from the theoretically erroneous conclusion that because 1 part by weight of hydrogen combines with 8 parts by weight of oxygen to form water vapor, consequently, with the atomic weight of hydrogen fixed at 1, the relative atomic weight of oxygen should then be 8, and the Dalton equation for the reaction would be  $\text{H} + \text{O} \rightarrow \text{HO}$ .