Third Edition

CHEMISTRY

The Central Science

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3 Stoichiometry

Antoine Lavoisier (Section 1.1) was among the first to draw conclusions about chemical processes from careful, quantitative observations. His work laid the basis for the law of conservation of mass, one of the most fundamental laws of chemistry. In this chapter, we will consider many practical problems based on the law of conservation of mass. These problems involve the quantitative relationships between substances undergoing chemical changes. The study of these quantitative relationships is known as **stoichiometry** (pronounced stoy-key-AHM-uh-tree), a word derived from the Greek words *stoicheion* ("element") and *metron* ("measure").

3.1 LAW OF CONSERVATION OF MASS

Studies of countless chemical reactions have shown that the total mass of all substances present after a chemical reaction is the same as the total mass before the reaction. This observation is embodied in the **law of conservation of mass:** There are no *detectable* changes in mass in any chemical reaction.* More precisely, *atoms are neither created nor destroyed during a chemical reaction;* instead, they merely exchange partners or become otherwise rearranged. The simplicity with which this law can be stated should not mask its significance. As with many other scientific laws, this law has implications far beyond the walls of the scientific laboratory.

The law of conservation of mass reminds us that we really can't throw anything away. If we discharge wastes into a lake to get rid of them, they are diluted and seem to disappear. However, they are part of the envi-

*In Chapter 19, we will discuss the relationship between mass and energy summarized by the equation $E = mc^2$ (E is energy, m is mass, and c is the speed of light). We will find that whenever an object loses energy it loses mass, and whenever it gains energy it gains mass. These changes in mass are too small to detect in chemical reactions. However, for nuclear reactions, such as those involved in a nuclear reactor or in a hydrogen bomb, the energy changes are enormously larger; in these reactions there are detectable changes in mass.

ronment. They may undergo chemical changes or remain inactive; they may reappear as toxic contaminants in fish or in water supplies or lie on the bottom unnoticed. Whatever their fates, the atoms are not destroyed.

The law of conservation of mass suggests that we are converters, not consumers. In drawing upon nature's storehouse of iron ore to build the myriad iron-containing objects used in modern society, we are not reducing the number of iron atoms on the planet. We may, however, be converting the iron to less useful, less available forms from which it will not be practical to recover it later. For example, consider the millions of old washing machines that lie buried in dumps. Of course, if we expend enough energy, we can bring off almost any chemical conversions we choose. We have learned in recent years, however, that energy itself is a limited resource. Whether we like it or not, we must learn to conserve all our energy and material resources.

3.2 CHEMICAL EQUATIONS

We have seen (in Sections 2.2 and 2.6) that chemical substances can be represented by symbols and formulas. These chemical symbols and formulas can be combined to form a kind of statement, called a **chemical equation,** that represents or describes a chemical reaction. For example, the combustion of carbon involves a reaction with oxygen (O_2) in the air to form gaseous carbon dioxide (CO_2). This reaction is represented as

$$C + O_2 \longrightarrow CO_2 \qquad [3.1]$$

We read the + sign to mean "reacts with" and the arrow as "produces." Carbon and oxygen are referred to as **reactants** and carbon dioxide as the **product** of the reaction.

It is important to keep in mind that a chemical equation is a description of a chemical process. Before you can write a complete equation you must know what happens in the reaction or be prepared to predict the products. In this sense, a chemical equation has qualitative significance; it identifies the reactants and products in a chemical process. In addition, a chemical equation is a quantitative statement; it must be consistent with the law of conservation of mass. This means that the equation must contain equal numbers of each type of atom on each side of the equation. When this condition is met the equation is said to be **balanced.** For example, Equation 3.1 is balanced because there are equal numbers of carbon and oxygen atoms on each side.

A slightly more complicated situation is encountered when methane (CH_4), the principal component of natural gas, burns and produces carbon dioxide (CO_2) and water (H_2O). The combustion is "supported by" oxygen (O_2), meaning that oxygen is involved as a reactant. The unbalanced equation is

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O \qquad [3.2]$$

The reactants are shown to the left of the arrow, the products to the right. Notice that the reactants and products both contain one carbon atom. However, the reactants contain more hydrogen atoms (four) than the products (two). If we place a coefficient 2 in front of H_2O, indicating formation of two molecules of water, there will be four hydrogens on each side of the equation:

$$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O \qquad [3.3]$$

Before we continue to balance this equation, let's make sure that we clearly understand the distinction between a coefficient in front of a formula and a subscript in a formula. Refer to Figure 3.1. Notice that changing a subscript in a formula, such as from H_2O to H_2O_2, changes the identity of the chemical involved. The substance H_2O_2, hydrogen peroxide, is quite different from water. *The subscripts in the chemical formulas should never be changed in balancing an equation.* On the other hand, placing a coefficient in front of a formula merely changes the amount and not the identity of the substance; $2H_2O$ means two molecules of water, $3H_2O$ means three molecules of water, and so forth. Now let's continue balancing Equation 3.3. There are equal numbers of carbon and hydrogen atoms on both sides of this equation; however, there are more oxygen atoms among the products (four) than among the reactants (two). If we place a coefficient 2 in front of O_2 there will be equal numbers of oxygen atoms on both sides of the equation:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad [3.4]$$

The equation is now balanced. There are four oxygen atoms, four hydrogen atoms, and one carbon atom on each side of the equation. The balanced equation is shown schematically in Figure 3.2.

Now, let's look at a slightly more complicated example, analyzing stepwise what we are doing as we balance the equation. Combustion of octane (C_8H_{18}), a component of gasoline, produces CO_2 and H_2O. The balanced chemical equation for this reaction can be determined by using the following four steps.

First, the reactants and products are written in the unbalanced equation

$$C_8H_{18} + O_2 \longrightarrow CO_2 + H_2O \qquad [3.5]$$

Before a chemical equation can be written the identities of the reactants and products must be determined. In the present example this information was given to us in the verbal description of the reaction.

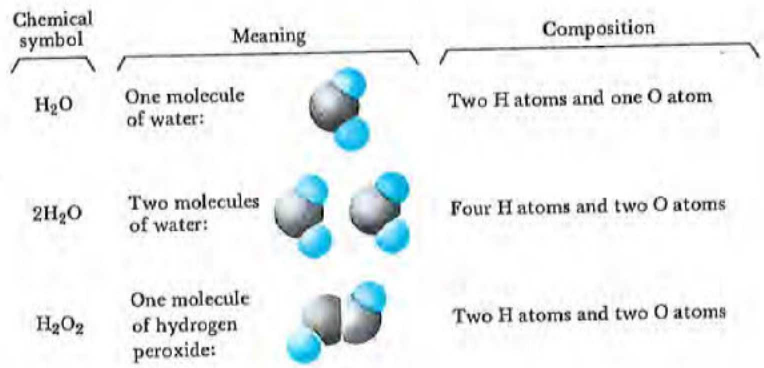
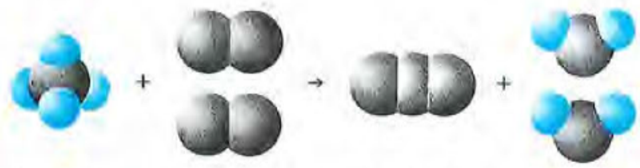


FIGURE 3.1 Illustration of the difference in meaning between a subscript in a chemical formula and a coefficient in front of the formula. Notice that the number of atoms of each type (listed under composition) is obtained by multiplying the coefficient and the subscript associated with each element in the formula.



One methane molecule	+	Two oxygen molecules	→	One carbon dioxide molecule	+	Two water molecules
CH_4	+	$2O_2$	→	CO_2	+	$2H_2O$
$\binom{1\,C}{4\,H}$		(4 O)		$\binom{1\,C}{2\,O}$		$\binom{2\,O}{4\,H}$

FIGURE 3.2 Balanced chemical equation for the combustion of CH_4. The drawings of the molecules involved call attention to the conservation of atoms through the reaction.

Second, the number of atoms of each type on each side of the equation is determined. In the reaction above there are 8C, 18H, and 2O among the reactants, and 1C, 2H, and 3O among the products; clearly, the equation is not balanced, because the number of atoms of each type differs from one side of the equation to the other.

Third, to balance the equation, coefficients are placed in front of the chemical formulas to indicate different quantities of reactants and products, so that the same number of atoms of each type appears on both sides of the equation. To decide what coefficients to try first, it is often convenient to focus attention on the molecule with the most atoms, in this case C_8H_{18}. This molecule contains 8C, all of which must end up in CO_2 molecules. Therefore, we place a coefficient 8 in front of CO_2. Similarly, the 18H end up as $9H_2O$. At this stage the equation reads

$$C_8H_{18} + O_2 \longrightarrow 8CO_2 + 9H_2O \qquad [3.6]$$

Although the C and H atoms are now balanced, the O atoms are not; there are 25O atoms among the products but only 2 among the reactants. It takes $12.5O_2$ to produce 25O atoms among the reactants:

$$C_8H_{18} + 12.5O_2 \longrightarrow 8CO_2 + 9H_2O \qquad [3.7]$$

However, this equation is not in its most conventional form, because it contains a fractional coefficient. Therefore, we must go on to the next step.

Fourth, for most purposes a balanced equation should contain the smallest possible whole-number coefficients. Therefore, we multiply each side of the equation above by 2, removing the fraction and achieving the following balanced equation:

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O \qquad [3.8]$$

16C, 36H, 50O	16C, 36H, 50O
Reactants	Products

The atoms are inventoried below the equation to show graphically that the equation is indeed balanced. You might note that although atoms are conserved, molecules are not—the reactants contain 27 molecules while the products contain 34. All in all, this approach to balancing equations is largely trial and error. It is much easier to verify that an equation is balanced than actually to balance one, so practice in balancing equations is essential.

It should also be noted that the physical state of each chemical in a chemical equation is often indicated parenthetically using the symbols (g), (l), (s), and (aq) to indicate gas, liquid, solid, and aqueous (water) solution, respectively. Thus the balanced equation above can be written

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(l) \qquad [3.9]$$

Sometimes an upward arrow (↑) is employed to indicate the escape of a gaseous product, whereas a downward arrow (↓) indicates a precipitating solid (that is, a solid that separates from solution during the reaction). Often the conditions under which the reaction proceeds are indicated above the arrow between the two sides of the equation. For example, the temperature or pressure at which the reaction occurs could be so indicated. The symbol Δ is often placed above the arrow to indicate the addition of heat.

SAMPLE EXERCISE 3.1

Balance the following equation:

$$Na(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$

Solution: A quick inventory of atoms reveals that there are equal numbers of Na and O atoms on both sides of the equation, but that there are two H atoms among reactants and three H atoms among products. To increase the number of H atoms among reactants, we might place a coefficient 2 in front of H_2O:

$$Na(s) + 2H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$

Now we have four H atoms among reactants but only three H atoms among the products. The H atoms can be balanced with a coefficient 2 in front of NaOH:

$$Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

If we again inventory the atoms on each side of the equation, we find that the H atoms and O atoms are balanced but not the Na atoms. However, a coefficient 2 in front of Na gives two Na atoms on each side of the equation:

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

If the atoms are inventoried once more we find two Na atoms, four H atoms, and two O atoms on each side of the equation. The equation is therefore balanced.

3.3 CHEMICAL REACTIONS

Our discussion in Section 3.2 focused on how to balance chemical equations given the reactants and products for the reactions. You were not asked to predict the products for a reaction. Students sometimes ask how the products are determined. For example, how do we know that sodium metal (Na) reacts with water (H_2O) to form H_2 and NaOH as shown in Sample Exercise 3.1? These products are identified by experiment. As the reaction proceeds, there is a fizzing or bubbling where the sodium is in contact with the water (if too much sodium is used the reaction is quite violent, so small quantities would be used in our experiment). If the gas is captured, it can be identified as H_2 from its chemical and physical properties. After the reaction is complete, a clear solution remains. If this is evaporated to dryness, a white solid will remain. From its properties this solid can be identified as NaOH. However, it is not necessary to perform an experiment every time we wish to write a reaction. We can predict what will happen if we have seen the reaction or a similar one before. So far we have seen too little chemistry to predict the products for many reactions. Nevertheless, even now you should be able to make some predictions. For example, what would you expect to happen when potassium metal is added to water? We have just discussed the reaction of sodium metal with water, for which the balanced chemical equation is

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g) \qquad [3.10]$$

Because sodium and potassium are in the same family of the periodic table (the alkali metal family, family 1A), we would expect them to behave similarly, producing the same types of products. Indeed, this prediction is correct, and the reaction of potassium metal with water is

$$2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g) \qquad [3.11]$$

You can readily see that it will be helpful in your study of chemistry if you are able to classify chemical reactions into certain types. We have just considered two examples of a type we might call reaction of an active metal with water. Let's briefly consider here a few of the more important and common types you will be encountering in your laboratory work and in the chapters ahead.

Combustion in Oxygen

We have already encountered three examples of combustion reactions: the combustion of carbon, Equation 3.1; of methane, Equation 3.4; and of octane (C_8H_{18}), Equation 3.8. Combustion is a rapid reaction that usually produces a flame. Most of the combustions we observe involve O_2 as a reactant. From the examples we have already seen it should be easy to predict the products of the combustion of propane C_3H_8. We expect that combustion of this compound would lead to carbon dioxide and water as products, by analogy with our previous examples. That expectation is correct; propane is the major ingredient in LP (liquid propane) gas, used for cooking and home heating. It burns in air as described by the balanced equation

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad [3.12]$$

If we looked at further examples, we would find that combustion of compounds containing oxygen atoms as well as carbon and hydrogen (for example, CH_3OH) also produces CO_2 and H_2O.

Acids, Bases, and Neutralization

Acids are substances that increase the H^+ ion concentration in aqueous solution. For example, hydrochloric acid, which we often represent as $HCl(aq)$, exists in water as $H^+(aq)$ and $Cl^-(aq)$ ions. Thus the process of dissolving hydrogen chloride in water to form hydrochloric acid can be represented as follows:

$$HCl(g) \xrightarrow{H_2O} HCl(aq)$$

or [3.13]

$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

The H_2O given above the arrows in these equations is to remind us that the reaction medium is water. Pure sulfuric acid is a liquid; when it dissolves in water it releases H^+ ions in two successive steps:

$$H_2SO_4(l) \xrightarrow{H_2O} H^+(aq) + HSO_4^-(aq) \quad [3.14]$$

$$HSO_4^-(aq) \xrightarrow{H_2O} H^+(aq) + SO_4^{2-}(aq) \quad [3.15]$$

Thus, although we frequently represent aqueous solutions of sulfuric acid as $H_2SO_4(aq)$, these solutions actually contain a mixture of $H^+(aq)$, $HSO_4^{2-}(aq)$, and $SO_4^{2-}(aq)$.

Bases are compounds that increase the hydroxide ion, OH^-, concentration in aqueous solution. A base such as sodium hydroxide does this because it is an ionic substance composed of Na^+ and OH^- ions. When NaOH dissolves in water, the cations and anions simply separate in the solution:

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq) \quad [3.16]$$

Thus, although aqueous solutions of sodium hydroxide might be written as $NaOH(aq)$, sodium hydroxide exists as $Na^+(aq)$ and $OH^-(aq)$ ions. Many other bases such as $Ca(OH)_2$ are also ionic hydroxide compounds. However, NH_3 (ammonia) is a base although it is not a compound of this sort.

It may seem odd at first glance that ammonia is a base, because it contains no hydroxide ions. However, we must remember that the definition of a base is that it *increases* the concentration of OH^- ions in water. Ammonia does this by a reaction with water. We can represent the dissolving of ammonia gas in water as follows:

$$NH_3(g) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq) \quad [3.17]$$

Solutions of ammonia in water are often labeled ammonium hydroxide, NH_4OH, to remind us that ammonia solutions are basic. (Ammonia is referred to as a weak base, which means that not all the NH_3 that dissolves in water goes on to form NH_4^+ and OH^- ions; but that is a matter for Chapter 15 and need not concern us here.)

Acids and bases are among the most important compounds in industry and in the chemical laboratory. Table 3.1 lists several acids and bases and the amount of each compound produced in the United States each year. You can see that these substances are produced in enormous quantities.

Solutions of acids and bases have very different properties. Acids have

TABLE 3.1 U.S. production of some acids and bases, 1982

Compound	Formula	Annual production (kg)
Acids:		
Sulfuric	H_2SO_4	3.0×10^{10}
Phosphoric	H_3PO_4	7.7×10^{9}
Nitric	HNO_3	6.9×10^{9}
Hydrochloric	HCl	2.3×10^{9}
Bases:		
Sodium hydroxide	NaOH	8.3×10^{9}
Calcium hydroxide	$Ca(OH)_2$	1.3×10^{10}
Ammonia	NH_3	1.4×10^{10}

a sour taste, whereas bases have a bitter taste.* Acids can change the colors of certain dyes in a specific way that differs from the effect of a base. For example, the dye known as litmus is changed from blue to red by an acid, and from red to blue by a base. In addition, acidic and basic solutions differ in chemical properties in several important ways. When a solution of an acid is mixed with a solution of a base, a **neutralization reaction** occurs. The products of the reaction have none of the characteristic properties of either the acid or base. For example, when a solution of hydrochloric acid is mixed with precisely the correct quantity of a sodium hydroxide solution, the result is a solution of sodium chloride, a simple ionic compound possessing neither acidic nor basic properties. (In general, such ionic products are referred to as **salts**.) The neutralization reaction can be written as follows:

$$HCl(aq) + NaOH(aq) \longrightarrow H_2O(l) + NaCl(aq) \qquad [3.18]$$

When we write the reaction as we have here, it is important to keep in mind that the substances shown as (aq) are present in the form of the separated ions, as discussed above. Notice that the acid and base in Equation 3.18 have combined to form water as a product. The general description of an acid-base neutralization reaction in aqueous solution, then, is that *an acid and base react to form a salt and water*. Using this general description we can predict the products formed in any acid-base neutralization reaction.

*Tasting chemical solutions is, of course, not a good practice. However, we have all had acids such as ascorbic acid (vitamin C), acetylsalicylic acid (aspirin), and citric acid (in citrus fruits) in our mouths, and we are familiar with the characteristic sour taste. It differs from the taste of soaps, which are mostly basic.

SAMPLE EXERCISE 3.2

Write a balanced equation for the reaction of hydrobromic acid, HBr, with barium hydroxide, $Ba(OH)_2$.

Solution: The products of any acid-base reaction are a salt and water. The salt is that formed from the cation of the base, $Ba(OH)_2$, and the anion of the acid, HBr. The charge on the barium ion is 2+ (see Table 2.5), and that on the bromide ion is 1−. Therefore, to maintain electrical neutrality, the formula for the salt must be $BaBr_2$. The unbalanced equation for the neutralization reaction is therefore

$$HBr(aq) + Ba(OH)_2(aq) \longrightarrow H_2O(l) + BaBr_2(aq)$$

To balance the equation we must provide two molecules of HBr to furnish the two Br^- ions and to supply the two H^+ ions needed to combine with the two OH^- ions of the base. The balanced equation is thus

$$2HBr(aq) + Ba(OH)_2(aq) \longrightarrow 2H_2O(l) + BaBr_2(aq)$$

Precipitation Reactions

One very important class of reactions occurring in solution is the precipitation reaction, in which one of the reaction products is insoluble. We will concern ourselves in this brief introduction with reactions between acids, bases, or salts in aqueous solution. As a simple example, consider the reaction between hydrochloric acid solution and a solution of the salt silver nitrate, $AgNO_3$. When the two solutions are mixed, a finely divided white solid forms. Upon analysis this solid proves to be silver chloride, AgCl, a salt that has a very low solubility* in water. The reaction as just described can be represented by the equation

$$HCl(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + HNO_3(aq) \qquad [3.19]$$

The formation of a precipitate in a chemical equation may be represented by a following (s), by a downward arrow following the formula for the solid, or by underlining the formula for the solid. You are reminded once again that substances indicated by (aq) may be present in the solution as separated ions.

The following equations provide further examples of precipitation reactions:

$$Pb(NO_3)_2(aq) + Na_2CrO_4(aq) \longrightarrow PbCrO_4(s) + 2NaNO_3(aq) \qquad [3.20]$$

$$CuCl_2(aq) + 2NaOH(aq) \longrightarrow Cu(OH)_2(s) + 2NaCl(aq) \qquad [3.21]$$

Notice that in each equation the positive ions (cations) and negative ions (anions) exchange partners. Reactions that fit this pattern of reactivity, whether they be precipitation reactions, neutralization reactions, or reactions of some other sort, are called **metathesis reactions** (muh-TATH-uh-sis; Greek, "to transpose").

*Solubility will be considered in some detail in Chapter 11. It is a measure of the amount of substance that can be dissolved in a given quantity of solvent (see Section 3.9).

SAMPLE EXERCISE 3.3

When solutions of sodium phosphate and barium nitrate are mixed, a precipitate of barium phosphate forms. Write a balanced equation to describe the reaction.

Solution: Our first task is to determine the formulas of the reactants. The sodium ion is Na^+ and the phosphate ion is PO_4^{3-}; thus sodium phosphate is Na_3PO_4. The barium ion is Ba^{2+} and the nitrate ion is NO_3^-; thus barium nitrate is $Ba(NO_3)_2$. The Ba^{2+} and PO_4^{3-} ions combine to form the barium phosphate precipitate, $Ba_3(PO_4)_2$. The other ions, Na^+ and NO_3^-, remain in solution and are represented as $NaNO_3(aq)$. The *unbalanced* equation for the reaction is thus

$$Na_3PO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow Ba_3(PO_4)_2(s) + NaNO_3(aq)$$

Because the NO_3^- and PO_4^{3-} ions maintain their identity through the reaction, we can treat them as units in balancing the equation. There are two (PO_4) units on the right, so we place a coefficient 2 in front of Na_3PO_4. This then gives six Na atoms on the left, necessitating a coefficient of 6 in front of $NaNO_3$. Finally, the presence of six (NO_3) units on the right requires a coefficient of 3 in front of $Ba(NO_3)_2$:

$$2Na_3PO_4(aq) + 3Ba(NO_3)_2(aq) \longrightarrow Ba_3(PO_4)_2(s) + 6NaNO_3(aq)$$

A balanced equation implies a quantitative relation between the reactants and the products involved in a chemical reaction. Thus complete combustion of a molecule of C_3H_8 requires exactly five molecules of O_2, no more and no less, as shown in Equation 3.12. Although it is not possible to count directly the number of molecules of each type in any reaction, this count can be made indirectly if the mass of each molecule is known. Indeed, this indirect approach is the one taken to obtain quantitative information about the amounts of substances involved in any chemical transformation. Therefore, before we can pursue the quantitative aspects of chemical reactions further, we must explore the concept of atomic and molecular weights.

3.4 ATOMIC AND MOLECULAR WEIGHTS

Dalton's atomic theory led him and other scientists of the time to a new problem. If it is true that atoms combine with one another in the ratios of small whole numbers to form compounds, what *are* the ratios with which they combine? Atoms are too small to be measured individually by any means available in the early nineteenth century. However, if one knew the *relative* masses of the atoms, then by measuring out convenient quantities in the laboratory, one could determine the relative numbers of atoms in a sample. Consider a simple analogy: Suppose that oranges are on the average four times heavier than plums; the number of oranges in 48 kg of oranges will then be the same as the number of plums in 12 kg of plums. Similarly, if you knew that oxygen atoms were on the average 16 times more massive than hydrogen atoms, then you would know that the number of oxygen atoms in 16 g of oxygen is the same as the number of hydrogen atoms in 1 g of hydrogen. Thus the problem of determining the combining ratios becomes one of determining the relative masses of the atoms of the elements.

This is all very well, but there was great difficulty in getting started. Since atoms and molecules can't be seen, there was no simple way to be sure about the relative numbers of atoms in *any* compound. Dalton thought that the formula for water was HO. However, the French scientist Gay-Lussac showed in a brilliant set of measurements that it required two volumes of hydrogen gas to react with one volume of oxygen to form two volumes of water vapor. This observation was inconsistent with Dalton's formula for water. Furthermore, if oxygen were assumed to be a monatomic gas, as Dalton did, one could obtain two volumes of water vapor only by splitting the oxygen atoms in half, which of course violates the concept of the atom as indivisible in chemical reactions.