# Chapter 1 The Early Experiments

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# 1.0 INTRODUCTION

Chemistry is the science of matter, its properties, and the changes it undergoes. Chemists seek to understand our material universe at a molecular level and to use this understanding to improve our interaction with it, often creating new products that enhance our lives. These products include pharmaceuticals, fuels, plastics, batteries, soaps, perfumes, foods, fertilizers and pesticides, to name just a few. Chemists often design these products by considering the properties of the desired substance and then proposing reactions of atoms or molecules that might yield the substances of choice. This design process involves particles and processes chemists can envision but cannot see. Chemists can observe the results of a reaction, such as a color change, the formation of a gas or a solid, or the formation of the substance with the desired properties. However, they cannot view directly the collisions of the atoms or molecules in a reaction or the changes these collisions produce. Yet, chemists are confident that these collisions and changes do occur. How did we get to the point where we can envision these invisible processes? How do we know the nature of these invisible atoms and molecules? We start our study of chemistry by beginning to answer these two questions.

## THE OBJECTIVES OF CHAPTER 1 ARE TO:

- define the scientific method and illustrate its importance in scientific discovery;
- introduce Coulomb's law and the electromagnetic force;
- introduce the early scientists and the experiments that eventually led to the description of the nuclear atom and its components;
- describe the subatomic particles and their characteristics; and
- explain the use of the Periodic Table in predicting an element's physical and chemical properties.

# 1.1 SCIENTIFIC METHOD

Chemistry is a science, which means that all chemical knowledge is gained by the application of a set of principles and procedures known as the scientific method. To understand how chemistry progressed to where it is today and how it will progress in the future, you must first understand how this method is applied. The *scientific method* involves the following steps:

- 1. observation and collection of quantitative or qualitative data;\*
- 2. formulation of a hypothesis to explain the observation;
- 3. prediction based on the hypothesis; and
- 4. testing the prediction.

If a test supports a hypothesis, another experiment is devised to further test the hypothesis. If a test does not support a hypothesis, then the hypothesis is changed or even discarded depending upon how badly it fails the test. After a hypothesis has been supported by many independent observers, it becomes a law or a theory. A **law** summarizes many observations, while a **theory** provides an explanation for them. Theories cannot be proven and are valid only as long as they are supported or, at least, not disproved by experiment. Our understanding is constantly evolving as the sophistication of our tools and instruments improves and our scientific knowledge increases. Many long held theories have eventually failed the test of experiment and have been modified or discarded entirely. Thus, chemistry is a dynamic science that continues to build upon past observations and theories by exploring new discoveries and hypotheses. The struggle of the earliest scientists to understand and explain the nature of things around them is an amazing journey of discovery. In this chapter, we examine some of the experiments that brought us from the birth of modern chemistry at the end of the 18<sup>th</sup> century to the discovery of subatomic particles near the end of the 19<sup>th</sup> century.

# 1.2 LAVOISIER AND THE BIRTH OF MODERN CHEMISTRY

Controlling fire was a major factor in the rise of humans, so it is not surprising that one of the first theories dealt with burning objects. We can make two obvious observations about fire: it is hot; and the flame leaps from the fuel. **Phlogiston theory** was born from little more than this kind of fireside observation. According to phlogiston theory, materials that burned contained a substance called phlogiston, and burning was thought to be the release

\* Quantitative observations involve numbers, while qualitative observations do not. For example, "the mass of the object is 3.2 g" is a quantitative observation, while "the object is black" is a qualitative observation.

of phlogiston (the flame leaping from the fuel). The residue that remained after burning was called calx. A phlogistonist would view the brilliant white light that is produced when magnesium burns as the escape of phlogiston and represented the burning as

#### Magnesium $\rightarrow$ 'calx of Magnesium' + Phlogiston

Thus, it was believed that the metal lost phlogiston when it burned. Early in the eighteenth century, however, Antoine Lavoisier, a French chemist, showed that the mass of the calx was greater than the mass of the metal. Scientists that supported the phlogiston theory reasoned that either mass was not relevant to chemistry or that phlogiston had negative mass, but most scientists realized that phlogiston theory had failed an important test, and it was eventually discarded.

Lavoisier measured the mass of many reactions and observed that the total mass does not change. He summarized his results in the law of conservation of mass.

Law of Conservation of Mass: during a chemical reaction, the total mass (reactants + products) remains constant; that is, mass is neither created nor destroyed during a chemical reaction.

After careful and repeated experiments, he realized that burning a metal was the combination of the metal with oxygen, not the release of phlogiston. Lavoisier introduced a new way of thinking about chemistry and is known as the father of modern chemistry. He viewed the calx of a metal as the metal oxide and the reaction as

## Magnesium + Oxygen $\rightarrow$ Magnesium oxide

Lavoisier was also the first to classify matter as elements or compounds. An **element** is a pure substance that cannot be broken down by chemical means to a simpler substance. Magnesium and oxygen are examples of elements. Today, there are over 100 known elements. A **compound** is a pure substance that consists of more than one element. Magnesium oxide is a compound that is formed by the combination of two elements (magnesium and oxygen).

The scientists of the early 19th century had a new system and a new way of thinking about matter as the field of chemistry was born. They began testing the concept that matter consisted of elements and compounds and that mass was indeed relevant to chemistry. After a great number of measurements of relative masses had been performed, two more laws that summarized the results were accepted. **Law of Definite Proportions:** the elements of a compound are present in definite (fixed) proportions by mass. For example, the mass of table salt (sodium chloride) is always 39% sodium and 61% chlorine and that of water is always 11% hydrogen and 89% oxygen.

**Law of Multiple Proportions:** when two different compounds are formed from the same two elements, the masses of one element that combine with a fixed mass of the other are in a ratio of small whole numbers. For example, water and hydrogen peroxide are both compounds that are composed only of the elements hydrogen and oxygen. There are eight grams of oxygen for each gram of hydrogen in water, but there are 16 g of oxygen for each gram of hydrogen peroxide. For a specified mass of hydrogen (one gram), the mass ratio of oxygen in the two compounds is 8:16 or 1:2, a ratio of small whole numbers.

## Example 1.1

Sodium (Na) and oxygen (O) form two different compounds that are 59% and 74% Na by mass. Show that these compounds obey the law of multiple proportions.

First, determine the mass of sodium that is combined with a specified mass of oxygen. Percents can be converted easily into grams by assuming a total mass of 100 g. For example, 59% of a 100 g sample is 59 g. The compounds consist only of Na and O, so the sum of the percents must be 100. Consequently, %O = 100 - %Na.

Next, specify a fixed mass of one of the substances, which is usually set at 1 g. In the following, it is the mass of oxygen that is fixed. The mass of Na combined with 1 g of O is obtained by dividing the mass of Na by the mass of O with which it is combined. The following table shows the results.

Compound	%Na	%O	grams Na/1 gram O
I	59	41	<u>59 g Na</u> = <mark>1.4 g Na</mark> 41 g O = <mark>1 g O</mark>
П	74	26	$\frac{74 \text{ g Na}}{100 \text{ m}} = \frac{2.8 \text{ g Na}}{100 \text{ m}}$
			26gO 1gO

Finally, determine the ratio of the masses of Na combined with 1 g O in the two compounds. The ratio of compound II to compound I is

ratio =  $\frac{\frac{2.8 \text{ g Na in cmpd II}}{\frac{\text{g O}^{\ast}}{1.4 \text{ g Na in cmpd I}}} = \frac{2.8 \text{ g Na in cmpd II}}{1.4 \text{ g Na in cmpd I}} = \frac{2.0 \text{ g Na in cmpd II}}{1.0 \text{ g Na in cmpd I}}$ 

The ratio is a ratio of small whole numbers (2:1), so these compounds obey the law of multiple proportions. The ratio implies that there is twice as much Na per gram of O in compound II as there is in compound I. In fact, compound I is  $Na_2O_2$  (sodium peroxide) and compound II is  $Na_2O$  (sodium oxide).

\* Note that the units "g O" are in the denominators, so they cancel in the ratio to yield the desired ratio of masses of Na. Units are very important and their use in solving problems will be examined in more detail later in the chapter.

# 1.3 JOHN DALTON AND ATOMIC THEORY (1804)

Laws hold the key to understanding nature's secrets, and theories are our attempt to unlock the secrets. The chemists of the early 19th century had three laws to explain: conservation of mass, definite proportions, and multiple proportions. Elements and compounds were the accepted forms of matter; but what were the mass relationships telling them? In 1804, John Dalton, an English chemist, suggested an answer: elements consisted of tiny spheres, called atoms, which he likened to billiard balls with hooks on them. He assigned the following properties to atoms to assure that they behaved in a manner consistent with the laws of conservation of mass, definite proportions, and multiple proportions:

- An element is composed of extremely small particles called **atoms**. The atoms of a given element all exhibit identical chemical properties,\* but atoms of different elements have different chemical properties.
- 2. In the course of a chemical reaction, no atom disappears or is changed into another atom. This property explains The *law of conservation of mass* and is the basis for writing *balanced chemical equations*. In a balanced chemical equation, the number of each kind of atom must be the same on both sides of the equation.
- 3. Compounds are formed when atoms of different elements combine. In a given pure compound, the relative numbers of atoms of each element present will be definite and constant, and their ratios can be expressed as integers or simple fractions. This property explains the *laws of definite proportions and multiple proportions*.

Atoms combine with one another to form **molecules**, which are the smallest units of a substance that have the chemical properties of the substance. Dalton assumed that the simplest form of an element was an atom, while the simplest form of a compound was a molecule; but we shall soon see that this assumption is not quite correct because some elements exist as molecules.

Dalton developed a list of symbols to represent the different atoms. Hydrogen was  $\odot$  and oxygen was O. Lacking any information to the contrary, he assumed water contained one hydrogen atom and one oxygen atom and was therefore represented as  $\odot O$ . Fortunately, his system was discarded for one in which the symbol of the element was formed from one or two letters of its name, usually the first one or two. Thus, a hydrogen atom is now represented by H and an oxygen atom by O. A water molecule would have been HO, but we now know that a water molecule contains two hydrogen atoms and one oxygen atom, so it is H<sub>2</sub>O. The story of how the formula of this simple molecule was determined is fascinating and instructive, and it is presented in the next section.

\* Chemical properties indicate how a substance can be changed into another substance. "Hydrogen reacts with oxygen to produce water" is a statement of a chemical property. Physical properties are independent of other substances and involve no change in the identity of the compound. Melting and boiling points, conductivity, hardness, and color are physical properties.

# 1.4 ATOMS AND MOLECULES

Dalton recognized that mass was an important property of atoms and molecules, so he introduced the concepts of atomic and molecular mass.\* Hydrogen is the lightest of the known atoms, so Dalton assigned it a relative mass of one (no units). He assumed that the atom ratio in water was 1:1, so the reaction of hydrogen with oxygen to produce water was thought to be  $H + O \rightarrow HO$ . He also knew that 8 g of oxygen reacted for each 1 g of hydrogen to produce 9 g of water. Therefore, he reasoned that the mass of one oxygen atom was eight times that of one hydrogen atom, which meant that oxygen had a relative mass of 8. Water, which he assumed was HO, had a relative mass of 1 + 8 = 9.

At about the same time that Dalton was formulating his atomic theory, the French chemist, Joseph Gay-Lussac, was measuring the volumes of reacting gases. In 1808, he published his results, now known as the law of combining volumes.

Law of Combining Volumes: Volumes of reacting gases are in simple whole number ratios.

Experiment showed that the volumes of hydrogen and oxygen that react are in a 2:1 ratio.

## 2 volumes of hydrogen + 1 volume of oxygen $\rightarrow$ water

The law of combining volumes was soon explained in terms of Dalton's atomic theory, but the explanation rested on the assumption that *equal volumes of gases measured at the same temperature and pressure must contain equal numbers of particles!* The volume of hydrogen is twice that of oxygen in the reaction, so it was concluded that a water molecule contained twice as many hydrogen atoms as oxygen atoms. The formula of water had to be  $H_2O$ . The reaction was then thought to be  $2H + O \rightarrow H_2O$ .

The change in the formula of water meant that the *relative* masses that Dalton had determined for hydrogen and oxygen were wrong. One oxygen atom was eight times more massive than *two* hydrogen atoms and the atomic mass scale was changed accordingly. In the new scale, H = 1, O = 16, and  $H_2O = 18$ . The new scale was still consistent with the observation that 1 gram of hydrogen reacted with 8 grams of oxygen to produce 9 grams of water. However, one gram of hydrogen contained twice as many atoms as did 8 grams of oxygen.

The formula of water and the relative masses of hydrogen and oxygen had finally been determined, but the reaction of hydrogen and oxygen still had something to teach us. Consider that the equation  $2H + O \rightarrow H_2O$  predicts that 2 volumes of hydrogen combine with 1 volume of oxygen to produce 1 volume of water vapor, but experiment was soon to show that the reaction produces 2 volumes of water!

\* The terms atomic and molecular weights are commonly used, but the numbers represent masses not weights.

#### 2 volumes of hydrogen + 1 volume of oxygen $\rightarrow$ 2 volumes of water

The apparent dilemma was explained in 1811 by Amadeo Avogadro. His hypothesis became known as Avogadro's law.

# **Avogadro's law:** Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

Avogadro reasoned that elements, like compounds, can also occur as molecules, and it was the reaction of hydrogen and oxygen molecules, not atoms, that produced water molecules. His suggestion was contrary to Dalton's assertion that the atom is the simplest form of an element. Thus, an **element** is a substance that consists of only one type of atom, and a **compound** is a substance that contains more than one type of atom.

The relative volume of water produced in the reaction of hydrogen and oxygen could be explained if elementary hydrogen and oxygen each existed as diatomic (two atom) molecules, which means that the balanced reaction should be written as follows:

 $2H_2 + O_2 \rightarrow 2H_2O$ 

The above chemical equation is consistent with the experimental observations of both mass and volume ratios, and it is the way the reaction is written today. Hydrogen and oxygen are not the only elements to exist as diatomic molecules.

Common diatomic elements:  $H_2$ ,  $N_2$ ,  $O_2$ ,  $F_2$ ,  $CI_2$ ,  $Br_2$ , and  $I_2$ .

Some elemental molecules, such as  $P_4$  and  $S_8$ , contain more than two atoms.

The atomic mass scale was constructed by measuring relative masses of combining substances and assuming or determining the formula of the compound they produced. However, the modern system of atomic masses is not based on the hydrogen atom; rather it is based on the most common form of carbon, called carbon-12, which is *assigned* an atomic mass of exactly 12. The mass of an oxygen atom is  $\frac{4}{3}$  that of a carbon-12 atom, so oxygen's atomic mass is  $\binom{4}{3}(12) = 16$ .

## Example 1.2

Classify the following as elements or compounds and as atoms or molecules.

#### a) S<sub>8</sub>

 $S_8$  contains only one type of atom and is therefore an *element*. However, it contains eight chemically bound atoms, so it is also a *molecule*.

#### b) Ar

Ar contains only one type of atom and is therefore an *element*. In addition, it contains no chemical bonds and is an *atom*.

#### c) N<sub>2</sub>O<sub>5</sub>

 $N_2O_5$  contains two types of atoms, so it is a *compound*. The nitrogen and oxygen atoms are bound together to form a *molecule*.

# Example 1.3

Balance the following chemical equations.

#### a) $N_2 + O_2 \rightarrow N_2O_5$

The number of atoms of each element in a balanced equation are made the same on both sides by placing coefficients in front of each species. Subscripts in the formula must not be changed as that would change the identity of the molecules. Note that N<sub>2</sub> and O<sub>2</sub> are both diatomic molecules, so the number of oxygen and nitrogen atoms will each be even on the left side if integer coefficients are used. We therefore start by placing a 2 in front of the N<sub>2</sub>O<sub>5</sub> to assure an even number of oxygen atoms on the right side.

## $N_2 + O_2 \rightarrow 2N_2O_5$

The right side now shows four nitrogen atoms, which means that two  $N_2$  molecules must appear on the left. The right side also indicates ten oxygen atoms, so five  $O_2$  molecules are required on the left. Thus, we write

#### $2\mathsf{N}_2 + \mathsf{5O}_2 \to \mathsf{2N}_2\mathsf{O}_5$

The above equation shows four nitrogen atoms and ten oxygen atoms on each side. The number of each atom is the same on both sides, so the equation is balanced.

## b) AI + CuSO<sub>4</sub> $\rightarrow$ AI<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + Cu

The S and O atoms remain bound to one another in SO<sub>4</sub>, so we can balance the SO<sub>4</sub> as a unit rather than individual sulfur and oxygen atoms. We start by placing a one in front of the molecule with the greatest number of atoms,  $Al_2(SO_4)_3$ . That fixes the number of Al atoms and SO<sub>4</sub> units on the right side, so we must balance them on the left as follows:

#### $2AI + 3CuSO_4 \rightarrow 1AI_2(SO_4)_3 + Cu$

The number of Cu atoms is now fixed on the left at 3, so we balance them on the right. Finally, coefficients of one are not usually shown, so the balanced equation is

 $2AI + 3CuSO_4 \rightarrow AI_2(SO_4)_3 + 3Cu$ 

# 1.5 THE MOLE AND MOLAR MASS

The last equation balanced in the preceding exercise shows that Al atoms react with  $CuSO_4$  molecules in a 2:3 ratio, so we would like to mix the reactants in a ratio that is close to that. Unfortunately, individual atoms and molecules are much too small to see, and the numbers of atoms and molecules in reactions carried out in the laboratory are far too large to count, so we must measure the ratio of reacting atoms and molecules indirectly from their relative masses and their atomic or molecular masses.

If the masses of two pure substances are in the same ratio as their atomic or molecular masses, then the substances contain the same number of atoms or molecules.

The number of atoms or molecules in 12.0 g C, 16.0 g O, and 18.0 g H<sub>2</sub>O is identical. While Dalton had no idea what that number was, it was still a very useful concept because chemists could mix ingredients in the desired atom or molecule ratios using masses. The number of atoms or molecules in each of the above examples is called the *mole*. We count atoms and molecules in moles just as we count our shoes in pairs and our eggs in dozens.

A **mole**, which is abbreviated *mol*, is the number of atoms or molecules present in a sample of an element or a compound with a mass equal to its atomic or molecular mass expressed in grams. The number of items in a mole is called **Avogadro's number (N<sub>A</sub>)**, which has been determined to be  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ .

Just as *dozen* means 12 items, *mole* means  $6.022 \times 10^{23}$  items. Avogadro's number is a huge number, and its size is an indication of just how small atoms and molecules are. Consider that a mole of dice, each die 1/2 inch on a side, would cover the 48 contiguous states of the United States to a height of 100 miles, while a mole of water has a volume of only 18 mL. Yet, a mole of dice and a mole of water contain the same number of items.

A mass of a pure substance equal to its atomic or molecular mass expressed in grams contains one mole of the substance, so it is referred to as the **molar mass** ( $\mathbf{M}_{\mathbf{m}}$ ) of the substance. Alternatively, *the molar mass equals the atomic or molecular mass expressed in g*·*mol*<sup>-1</sup>. The atomic mass of O is 16, so its molar mass is 16.0 g·mol<sup>-1</sup>, while the molecular mass of O<sub>2</sub> is 32.0, so its molar mass is 32.0 g·mol<sup>-1</sup>. The mass of an individual atom or molecule is its atomic or molecular mass expressed in **atomic mass units (amu**). Thus, the mass of a single oxygen atom is 16.0 amu, the mass of one oxygen molecule is 32.0 amu, and the mass of one water molecule is 18.0 amu. Consequently, there are Avogadro's number of amu in one gram: 1 g = N<sub>A</sub> amu = 6.022x10<sup>23</sup> amu, which means that 1 amu = (1/N<sub>A</sub>) g = 1.661x10<sup>-24</sup> g.

## Example 1.4

#### a) What is the mass of 0.137 mol CaCO<sub>3</sub>?

Mass  $\leftrightarrow$  mole conversions are very important in chemistry, and are most easily done by multiplying the given quantity by the appropriate **conversion factor** that converts the given quantity into the desired quantity. The molar mass is the conversion factor in this problem.

 $M_m(CaCO_3) = M_m(Ca) + M_m(C) + 3M_m(O) = 40 \text{ g/mol} + 12 \text{ g/mol} + 3(16 \text{ g/mol})$ 

#### M<sub>m</sub>(CaCO<sub>3</sub>) = 100 g/mol

We now multiply the given quantity by the conversion factor so that the given units are converted into the desired units (mol  $CaCO_3$  cancel). Using units and conversion factors to solve a problem is called the **factor label method**.

0.137 mot  $GaCO_3 \times \frac{100 \text{ g } CaCO_3}{1 \text{ mot } GaCO_3} = 13.7 \text{ g } CaCO_3$ 

#### b) How many moles of CaCO<sub>3</sub> are present in 5.36 g of CaCO<sub>3</sub>?

We determined the molar mass of  $CaCO_3$  in Part a, so we multiply the given mass (5.36 g) by the conversion factor (100 g  $CaCO_3$ /mol  $CaCO_3$ ) such that g  $CaCO_3$  cancel and the result is the desired quantity.

5.36 
$$\overline{g}$$
 CaCO<sub>3</sub> ×  $\frac{1 \text{ mol CaCO}_3}{100 \overline{g}}$  = 0.0536 mol CaCO<sub>3</sub>

#### c) How many moles of oxygen atoms are present in 2.69 g of CaCO<sub>3</sub>?

Two conversion factors must be used in this example: one to convert grams of  $CaCO_3$  to moles of  $CaCO_3$  and one to convert moles of  $CaCO_3$  to moles of oxygen atoms.

2.69 g CaCO<sub>3</sub> × 
$$\frac{1 \text{ mol CaCO}_3}{100 \text{ g CaCO}_3}$$
 ×  $\frac{3 \text{ mol O}}{1 \text{ mol CaCO}_3}$  = 0.0807 mol O

Note that the units of the denominator of the second conversion factor cancel the units of the numerator of the first conversion factor (mol CaCO<sub>3</sub>). Using the units of the conversion factors to decide the order and manner of multiplication of the factors in a problem is a powerful tool. Refer to Appendix A for a review of how to use conversion factors in mass  $\leftrightarrow$  mole conversions.

See Appendix A for more examples.

Ratios of atoms or molecules are equal to ratios of moles of atoms or molecules, and chemists usually use moles rather than numbers of individual particles in the laboratory. The reaction  $2H_2 + O_2 \rightarrow 2H_2O$  shows us that 2 mol H<sub>2</sub> react with every 1 mol O<sub>2</sub> and are required to produce every 2 mol H<sub>2</sub>O. The ratio of the coefficients is the conversion factor, called the **stoichiometric factor**, that allows us to convert from one substance to another in a balanced chemical equation. The following stoichiometric factors and their reciprocals relate to the reaction of hydrogen and oxygen:

 $\frac{2 \text{ mol } H_2}{1 \text{ mol } O_2}; \ \frac{2 \text{ mol } H_2}{2 \text{ mol } H_2 O}; \ \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2 O}$ 

## Example 1.5

How many moles of  $H_2$  are required to react with 8.0 g  $O_2$  to produce  $H_2O$ ?

First, write the balanced chemical equation for the reaction.

 $2H_2 + O_2 \rightarrow 2H_2O$ 

The first thing that must always be done when solving a stoichiometry problem is to covert the masses into moles by dividing by the molar mass, which is  $32.0 \text{ g} \cdot \text{mol}^{-1}$  for O<sub>2</sub>.

8.0 
$$g O_2 \times \frac{1 \text{ mol } O_2}{32.0 g O_2} = 0.25 \text{ mol } O_2$$

The given number of moles is then converted into the chemically equivalent number of desired moles with the stoichiometric factor that contains both substances. The balanced equation indicates that 2 mol  $H_2$  are required for every 1 mol  $O_2$ , so we write

0.25 
$$\frac{\text{mol } O_2}{\text{mol } O_2} \times \frac{2 \text{ mol } H_2}{1 \text{ mol } O_2} = 0.50 \text{ mol } H_2 \text{ required}$$

This is an example of *reaction stoichiometry*, the topic of Appendix D.

Chemists seldom add chemicals in the exact stoichiometric ratio, so the amount of product that forms depends upon the amount of the reactant, called the **limiting reactant**, that is consumed first. Consider the reaction of 5 mol S and 6 mol  $O_2$  to produce  $SO_3$ . There are 5 mol S, and each mole of  $SO_3$  requires one mole of S, so there is enough S to produce 5 mol  $SO_3$ . There are 12 mol O atoms in 6 mol  $O_2$ , and each mole of  $SO_3$  requires 3 mol of O, so there is enough O to make only 4 mol  $SO_3$ . After 4 mol  $SO_3$  are produced, all of the  $O_2$  is gone, and no more  $SO_3$  can be made. Making 4 mol  $SO_3$  requires only 4 mol S, so there is 1 mol S left over. Thus,  $O_2$  is the limiting reactant, while S is in excess.

## Example 1.6

#### How much Al<sub>2</sub>O<sub>3</sub> can be produced from 10.0 mol Al and 9.0 mol O<sub>2</sub>?

The balanced chemical equation is  $4AI + 3O_2 \rightarrow 2AI_2O_3$ .

To find the limiting reactant, we must determine how much  $AI_2O_3$  can be made from each reactant.

10.0 mol Al 
$$\times \frac{2 \text{ mol Al}_2 O_3}{4 \text{ mol Al}} = 5.0 \text{ mol Al}_2 O_3$$
  
9.0 mol  $O_2 \times \frac{2 \text{ mol Al}_2 O_3}{3 \text{ mol } O_2} = 6.0 \text{ mol Al}_2 O_3$ 

There is enough AI to make 5.0 mol  $AI_2O_3$ , and enough  $O_2$  to make 6.0 mol  $AI_2O_3$ . Therefore, AI is the limiting reactant and 5.0 mol  $AI_2O_3$  is produced.

#### How many moles of excess reactant remain?

The number of moles of O2 consumed in the reaction with 10.0 mol AI is

10.0 mol Al 
$$\times \frac{3 \text{ mol } O_2}{4 \text{ mol Al}} = 7.5 \text{ mol } O_2$$

7.5 of the 9.0 moles of  $O_2$  react, so there are  $9.0 - 7.5 = 1.5 \text{ mol } O_2$  left over.

Dalton's atomic theory proved successful in predicting the experimental results of his time and became the accepted way to think about matter. His ideas on atomic masses also proved to be very useful, although some of the atomic masses had to be changed as new data became available. All in all, chemists of the day were quite comfortable with the idea that the smallest unit of matter was the 'billiard ball' atom proposed by Dalton. Then, near the end of the 19th century, new and more sophisticated experiments were performed that caused scientists to change their view. However, before we examine these experiments, we need to understand the roles of energy and charge in the study of chemistry.

# 1.6 ENERGY

Energy plays an important role throughout chemistry. Indeed, there is hardly a chapter in this text in which energy considerations are not required. In simple terms, energy is the capacity to move something. The energy of a substance is the sum of its kinetic energy and its potential energy. **Kinetic energy (KE)** is energy of motion; an object that is moving has the capacity to make another object move simply by colliding with it. The kinetic energy of a particle of mass m moving with a velocity v is given in Equation 1.1.

# $KE = \frac{1}{2} mv^{2}$

If mass is expressed in kg and speed in m·s<sup>-1</sup>, then the kinetic energy is in joules (J).

**Potential energy** is energy due to position. Some examples of objects with potential energy are a truck at the top of a hill, a stretched rubber band, and a stick of dynamite. In each case, the potential energy can be converted into kinetic energy. For example, releasing the brake of the truck causes the truck to gain speed as it rolls down the hill; and, because it is moving, it has kinetic energy. The stretched rubber band flies (moves) across the room as soon as it is released. The potential energy stored in a stick of dynamite is the result of the relative positions of the atoms in the molecules; that is, the energy is stored in the chemical bonds. The potential energy stored in the chemical bonds of the molecules in the dynamite is transformed into kinetic energy during the explosion.

A change in energy is represented by  $\Delta E$ . The sign of the energy change is a significant consideration, so it is important to calculate it in the same manner each time. The convention used is that energy change equals the final energy,  $E_f$ , minus the initial energy,  $E_i$ , as shown in Equation 1.2.

#### $\Delta E = final energy - initial energy = E_f - E_i$ Eq. 1.2

 $\Delta E > 0$  means that the energy of the object increases, while  $\Delta E < 0$  means that the energy of the object decreases.

# Example 1.7

#### a) What is the kinetic energy of a 2200 lb car moving at 40 mph?

This example serves as a basis by which to compare other energies we determine throughout the text. Clearly, the typical car moving at 40 mph has the capacity to move many objects, so it is representative of an object with substantial kinetic energy. All other energy considerations in this text are in joules, so we will calculate this kinetic energy in joules as well. Consequently, the mass must be in kilograms, and the speed must be in meters per second. We use the following equalities 1 kg = 2.2 lb and 1 km = 0.62 mi and the conversion-factor method to obtain the desired units.

$$2200 \text{ lb} \times \frac{1 \text{ kg}}{2.2 \text{ lb}} = 1000 \text{ kg}$$
$$\frac{40 \text{ mi}}{\text{hr}} \times \frac{1 \text{ hr}}{3600 \text{ s}} \times \frac{1 \text{ km}}{0.62 \text{ mi}} \times \frac{1000 \text{ m}}{1 \text{ km}} = 18 \text{ m} \cdot \text{s}^{-1}$$

Equation 1.1 can now be applied to obtain the kinetic energy of n object with this mass and speed.

 $KE = \frac{1}{2}mv^{2} = \frac{1}{2}(1000 \text{ kg})(18 \text{ m} \cdot \text{s}^{-1})^{2} = 1.6 \times 10^{5} \text{ J} = 160 \text{ kJ}$ 

How does this energy compare to the energy released in chemical reactions? To obtain 160 kJ of energy, one would have to burn only about 3 g of gasoline or 10 g of sugar.

b) What energy change would the car undergo when it stops?

The final kinetic energy is zero, and the initial kinetic energy is 160 kJ.

 $\Delta E = E_f - E_i = 0 - 160 \text{ kJ} = -160 \text{ kJ}$ 

Thus,  $\Delta E$  indicates that the car loses 160 kJ of energy.

Why does the truck roll down hill, the rubber band fly, and the dynamite explode? All three processes occur because systems in nature seek the position of lowest energy; i.e., nature favors processes for which  $\Delta E < 0.*$  Chemical processes can be understood in terms of this fundamental tendency and the fact that energy changes in chemistry are the result of interactions between charged particles. The relationship between energy and the charge on interacting particles is the topic of the next section.

# 1.7 ELECTROMAGNETISM AND COULOMB'S LAW

A great deal of research in the 1800's was centered on electricity and magnetism. Scientists recognized that there was a force of interaction, called the **electromagnetic force**, between charged particles when they were brought close to one another. The force could be either attractive or repulsive. Charles Augustus Coulomb measured this force and stated his observations in what is now called Coulomb's law.

**Coulomb's Law:** Two particles of charge  $q_1$  and  $q_2$  separated by a distance r experience a force **F** as shown in Equation 1.3.

$$F = \frac{kq_1q_2}{\varepsilon r^2}$$
 Eq. 1.3

 $k = 8.9875 \times 10^9 \text{ N} \cdot \text{m}^2/\text{C}^2$  and is called **Coulomb's constant**.  $q_1$  and  $q_2$  are the charges in Coulombs, and  $\epsilon$  is the **dielectric constant** of the medium separating the charges. The dielectric constant is a measure of how well the medium insulates the two charges.  $\epsilon = 1$  in a vacuum, but it is 79 in water, which means that the interaction between charges in water is only about 1.3% of that in a vacuum for the same charges and separation. This decrease in the interaction results because the intervening water molecules have the ability to effectively shield the two charges from one another. When **F** is negative (**q**<sub>1</sub> and **q**<sub>2</sub> have

\* As we will see in Chapter 9, ∆E < 0 is indeed an important driving force, but it is not the only one.

opposite signs), the force is attractive. When **F** is positive ( $\mathbf{q}_1$  and  $\mathbf{q}_2$  have the same signs), the force is repulsive. This is summarized by the statement that *opposite charges attract while like charges repel*. The force of attraction or repulsion between two particles is very small at large separation but gets stronger as the distance between the particles decreases. The force also becomes stronger as the charges on the particles increase.

In Section 1.5, energy was defined as the capacity to move something, but in order for something to be moved, a force (push or pull) must be exerted. Energy is defined as a force exerted through a distance ( $\mathbf{E} = \mathbf{F} \times \mathbf{r}$ ). Consequently, the change in potential energy that results when two charged particles interact can be obtained by multiplying Equation 1.3 by r. The result is given by Equation 1.4:

$$\mathsf{E} = \frac{\mathsf{kq}_1\mathsf{q}_2}{\varepsilon \mathsf{r}}$$

E is the potential energy of the two particles separated by distance **r** relative to their potential energy when they are not interacting\* ( $\mathbf{r} = \infty$ ). E, which we will call the energy of interaction between the two particles, depends upon the charges on the particles (**q**), the distance between them (**r**), and the intervening medium ( $\boldsymbol{\epsilon}$ ). A graph of the energy of interaction of two charged particles as a function of the distance between them is shown in Figure 1.1. At large separations, the charged particles do not interact and E ~ 0. As their separation decreases, however, their energy of interaction changes. If the charges are of the same sign, their energy of interaction (green line) becomes increasingly negative. Thus, particles of opposite charge are attracted because their potential energy decreases as they get closer to one another, while particles with charges of the same sign are repelled because their potential energy decreases as they move apart.

Coulomb's law, in combination with the fact that systems seek the position of lowest energy, is exceedingly important in the study of chemistry because interactions in chemistry can be viewed as interactions between charged particles. *We conclude that particles of opposite charge move closer and particles of like charge move apart to minimize their energy.* If particles of like charge are forced together or particles of opposite charge apart, the potential energy of the system rises and the process is unfavorable.

#### Eq. 1.4

E is actually the difference between the energy of interaction at a separation r and the energy when the charges at infinite separation; *i.e.*,  $\Delta E = E(r) - E(\infty)$ , but  $E(\infty) = 0$ , so  $\Delta E = E(r) - 0 = E(r)$ . Hence, the  $\Delta$  is often dropped and the energy of interaction is simply expressed as E.



#### Figure 1.1 Electrostatic or Coulombic energy of interaction

Opposite charges are attracted because their energy decreases as they get closer to one another (green line). Like charges repel because moving apart lowers their energy (red line).