

2 Atoms, Molecules, and Ions

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A worker in Thailand piles up salt crystals.



Where does one start in learning chemistry? Clearly we must consider some essential vocabulary and something about the origins of the science before we can proceed very far. Thus, while Chapter 1 provided background on the fundamental ideas and procedures of science in general, Chapter 2 covers the specific chemical background necessary for understanding the material in the next few chapters. The coverage of these topics is necessarily brief at this point. We will develop these ideas more fully as it becomes appropriate to do so. A major goal of this chapter is to present the systems for naming chemical compounds to provide you with the vocabulary necessary to understand this book and to pursue your laboratory studies.

Because chemistry is concerned first and foremost with chemical changes, we will proceed as quickly as possible to a study of chemical reactions (Chapters 3 and 4). However, before we can discuss reactions, we must consider some fundamental ideas about atoms and how they combine.

2.1 The Early History of Chemistry

Chemistry has been important since ancient times. The processing of natural ores to produce metals for ornaments and weapons and the use of embalming fluids are just two applications of chemical phenomena that were utilized prior to 1000 B.C.

The Greeks were the first to try to explain why chemical changes occur. By about 400 B.C. they had proposed that all matter was composed of four fundamental substances: fire, earth, water, and air. The Greeks also considered the question of whether matter is continuous, and thus infinitely divisible into smaller pieces, or composed of small, indivisible particles. Supporters of the latter position were Demokritos* of Abdera (c. 460–c. 370 B.C.) and Leucippos, who used the term *atomos* (which later became *atoms*) to describe these ultimate particles. However, because the Greeks had no experiments to test their ideas, no definitive conclusion could be reached about the divisibility of matter.

The next 2000 years of chemical history were dominated by a pseudoscience called *alchemy*. Some alchemists were mystics and fakes who were obsessed with the idea of turning cheap metals into gold. However, many alchemists were serious scientists, and this period saw important advances: The alchemists discovered several elements and learned to prepare the mineral acids.

The foundations of modern chemistry were laid in the sixteenth century with the development of systematic metallurgy (extraction of metals from ores) by a German, Georg Bauer (1494–1555), and the medicinal application of minerals by a Swiss alchemist/physician known as Paracelsus (full name: Philippus Theophrastus Bombastus von Hohenheim [1493–1541]).

The first “chemist” to perform truly quantitative experiments was Robert Boyle (1627–1691), who carefully measured the relationship between the pressure and volume of air. When Boyle published his book *The Sceptical Chymist* in 1661, the quantitative sciences of physics and chemistry were born. In addition to his results on the quantitative behavior of gases, Boyle’s other major contribution to chemistry consisted of his ideas about the chemical elements. Boyle held no preconceived notion about the number of elements. In his view, a substance was an element unless it could be broken down into two or more simpler substances. As Boyle’s experimental definition of an element became generally accepted, the list of known elements began to grow, and the Greek system of

*Democritus is an alternate spelling.

CHEMICAL IMPACT

There's Gold in Them There Plants!

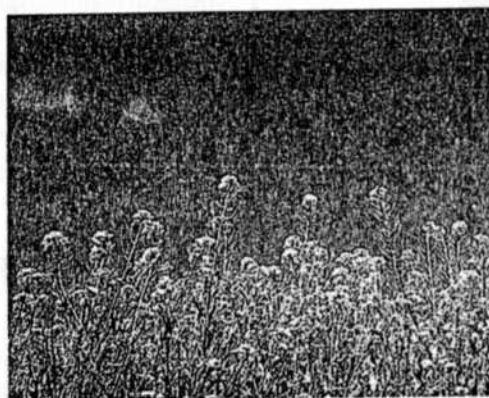
Gold has always held a strong allure. For example, the alchemists were obsessed with finding a way to transform cheap metals into gold. Also, when gold was discovered in California in 1849, a frantic rush occurred to that area and other areas in the west. Although gold is still valuable, most of the high-grade gold ores have been exhausted. This leaves the low-grade ores—ores with low concentrations of gold that are expensive to process relative to the amount of gold finally obtained.

Now two scientists have come across a novel way to concentrate the gold from low-grade ores. Christopher Anderson and Robert Brooks of Massey University in Palmerston North, New Zealand, have found plants that accumulate gold atoms as they grow in soil containing gold ore [*Nature* 395 (1998): 553]. The plants brassica (of the mustard family) and chicory seem especially effective as botanical “gold miners.” When these plants are dried and burned (after having grown in gold-rich soil), the resulting ash contains approximately 150 ppm (parts per million) of gold. (1 ppm gold represents 1 g of gold in 10^6 g of sample.)

The New Zealand scientists were able to double the amount of gold taken from the soil by the plants by treating

the soil with ammonium thiocyanate (NH_4SCN). The thiocyanate, which reacts with the gold, making it more available to the plants, subsequently breaks down in the soil and therefore poses no environmental hazard.

Thus plants seem to hold great promise as gold miners. They are efficient and reliable and will never go on strike.



This plant from the mustard family is a newly discovered source of gold.

four elements finally died. Although Boyle was an excellent scientist, he was not always right. For example, he clung to the alchemists' views that metals were not true elements and that a way would eventually be found to change one metal into another.

The phenomenon of combustion evoked intense interest in the seventeenth and eighteenth centuries. The German chemist Georg Stahl (1660–1734) suggested that a substance he called “phlogiston” flowed out of the burning material. Stahl postulated that a substance burning in a closed container eventually stopped burning because the air in the container became saturated with phlogiston. Oxygen gas, discovered by Joseph Priestley (1733–1804),* an English clergyman and scientist (Fig. 2.1), was found to support vigorous combustion and was thus supposed to be low in phlogiston. In fact, oxygen was originally called “dephlogisticated air.”



FIGURE 2.1

The Priestley Medal is the highest honor given by the American Chemical Society. It is named for Joseph Priestley, who was born in England on March 13, 1733. He performed many important scientific experiments, among them the discovery that a gas later identified as carbon dioxide could be dissolved in water to produce *seltzer*. Also, as a result of meeting Benjamin Franklin in London in 1766, Priestley became interested in electricity and was the first to observe that graphite was an electrical conductor. However, his greatest discovery occurred in 1774 when he isolated oxygen by heating mercuric oxide.

Because of his nonconformist political views, Priestley was forced to leave England. He died in the United States in 1804.

*Oxygen gas was actually first observed by the Swedish chemist Karl W. Scheele (1742–1786), but because his results were published after Priestley's, the latter is commonly credited with the discovery of oxygen.

2.2 Fundamental Chemical Laws

By the late eighteenth century, combustion had been studied extensively; the gases carbon dioxide, nitrogen, hydrogen, and oxygen had been discovered; and the list of elements continued to grow. However, it was Antoine Lavoisier (1743–1794), a French chemist (Fig. 2.2), who finally explained the true nature of combustion, thus clearing the way for the tremendous progress that was made near the end of the eighteenth century. Lavoisier, like Boyle, regarded measurement as the essential operation of chemistry. His experiments, in which he carefully weighed the reactants and products of various reactions, suggested that *mass is neither created nor destroyed*. Lavoisier's verification of this **law of conservation of mass** was the basis for the developments in chemistry in the nineteenth century.

Oxygen is from the French *oxygène*, meaning "generator of acid," because it was initially considered to be an integral part of all acids.

Lavoisier's quantitative experiments showed that combustion involved oxygen (which Lavoisier named), not phlogiston. He also discovered that life was supported by a process that also involved oxygen and was similar in many ways to combustion. In 1789 Lavoisier published the first modern chemistry textbook, *Elementary Treatise on Chemistry*, in which he presented a unified picture of the chemical knowledge assembled up to that time. Unfortunately, in the same year the text was published, the French Revolution broke out. Lavoisier, who had been associated with collecting taxes for the government, was executed on the guillotine as an enemy of the people in 1794.

After 1800, chemistry was dominated by scientists who, following Lavoisier's lead, performed careful weighing experiments to study the course of chemical reactions and to determine the composition of various chemical compounds. One of these chemists, a Frenchman, Joseph Proust (1754–1826), showed that *a given compound always contains exactly the same proportion of elements by mass*. For example, Proust found that the substance copper carbonate is always 5.3 parts copper to 4 parts oxygen to 1 part carbon (by mass). The principle of the constant composition of compounds, originally called "Proust's law," is now known as the **law of definite proportion**.

Proust's discovery stimulated John Dalton (1766–1844), an English schoolteacher (Fig. 2.3), to think about atoms as the particles that might compose elements. Dalton reasoned that if elements were composed of tiny individual particles, a given compound should always contain the same combination of these atoms. This concept explained why the same relative masses of elements were always found in a given compound.

FIGURE 2.2

Antoine Lavoisier was born in Paris on August 26, 1743. Although Lavoisier's father wanted his son to follow him into the legal profession, young Lavoisier was fascinated by science. From the beginning of his scientific career, Lavoisier recognized the importance of accurate measurements. His careful weighings showed that mass is conserved in chemical reactions and that combustion involves reaction with oxygen. Also, he wrote the first modern chemistry textbook. It is not surprising that Lavoisier is often called the father of modern chemistry.

To help support his scientific work, Lavoisier invested in a private tax-collecting firm and married the daughter of one of the company executives. His connection to the tax collectors proved fatal, for radical French revolutionaries demanded his execution, which occurred on the guillotine on May 8, 1794.



But Dalton discovered another principle that convinced him even more of the existence of atoms. He noted, for example, that carbon and oxygen form two different compounds that contain different relative amounts of carbon and oxygen, as shown by the following data:

Mass of Oxygen That Combines with 1 g of Carbon	
Compound I	1.33 g
Compound II	2.66 g

Dalton noted that compound II contains twice as much oxygen per gram of carbon as compound I, a fact that could easily be explained in terms of atoms. Compound I might be CO, and compound II might be CO₂.^{*} This principle, which was found to apply to compounds of other elements as well, became known as the **law of multiple proportions**: *When two elements form a series of compounds, the ratios of the masses of the second element that combine with 1 gram of the first element can always be reduced to small whole numbers.*

To make sure the significance of this observation is clear, in Sample Exercise 2.1 we will consider data for a series of compounds consisting of nitrogen and oxygen.

Sample Exercise 2.1

Illustrating the Law of Multiple Proportions

The following data were collected for several compounds of nitrogen and oxygen:

Mass of Nitrogen That Combines with 1 g of Oxygen	
Compound A	1.750 g
Compound B	0.8750 g
Compound C	0.4375 g

Show how these data illustrate the law of multiple proportions.

Solution

For the law of multiple proportions to hold, the ratios of the masses of nitrogen combining with 1 gram of oxygen in each pair of compounds should be small whole numbers. We therefore compute the ratios as follows:

$$\begin{aligned} \frac{A}{B} &= \frac{1.750}{0.875} = \frac{2}{1} \\ \frac{B}{C} &= \frac{0.875}{0.4375} = \frac{2}{1} \\ \frac{A}{C} &= \frac{1.750}{0.4375} = \frac{4}{1} \end{aligned}$$

These results support the law of multiple proportions.

See Exercises 2.27 and 2.28.

^{*}Subscripts are used to show the numbers of atoms present. The number 1 is understood (not written). The symbols for the elements and the writing of chemical formulas will be illustrated further in Sections 2.6 and 2.7.



FIGURE 2.3

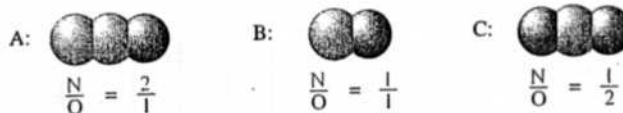
John Dalton (1766–1844), an Englishman, began teaching at a Quaker school when he was 12. His fascination with science included an intense interest in meteorology, which led to an interest in the gases of the air and their ultimate components, atoms. Dalton is best known for his atomic theory, in which he postulated that the fundamental differences among atoms are their masses. He was the first to prepare a table of relative atomic weights.

Dalton was a humble man with several apparent handicaps: He was not articulate and he was color-blind, a terrible problem for a chemist. Despite these disadvantages, he helped to revolutionize the science of chemistry.

These statements are a modern paraphrase of Dalton's ideas.

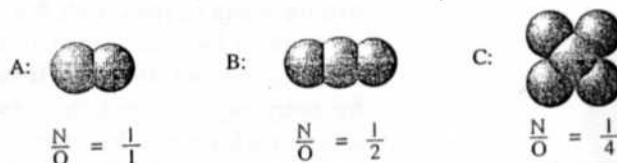
The significance of the data in Sample Exercise 2.1 is that compound A contains twice as much nitrogen (N) per gram of oxygen (O) as does compound B and that compound B contains twice as much nitrogen per gram of oxygen as does compound C.

These data can be explained readily if the substances are composed of molecules made up of nitrogen atoms and oxygen atoms. For example, one set of possibilities for compounds A, B, and C is



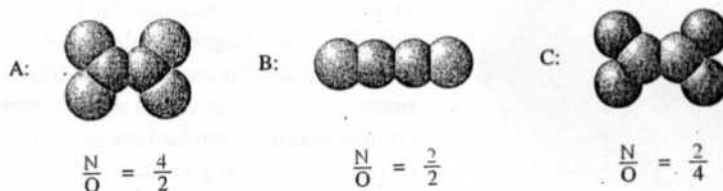
Now we can see that compound A contains two atoms of N for every atom of O, whereas compound B contains one atom of N per atom of O. That is, compound A contains twice as much nitrogen per given amount of oxygen as does compound B. Similarly, since compound B contains one N per O and compound C contains one N per two O's, the nitrogen content of compound C per given amount of oxygen is half that of compound B.

Another set of compounds that fits the data in Sample Exercise 2.1 is



Verify for yourself that these compounds satisfy the requirements.

Still another set that works is



See if you can come up with still another set of compounds that satisfies the data in Sample Exercise 2.1. How many more possibilities are there?

In fact, an infinite number of other possibilities exists. Dalton could not deduce absolute formulas from the available data on relative masses. However, the data on the composition of compounds in terms of the relative masses of the elements supported his hypothesis that each element consisted of a certain type of atom and that compounds were formed from specific combinations of atoms.

2.3 Dalton's Atomic Theory

In 1808 Dalton published *A New System of Chemical Philosophy*, in which he presented his theory of atoms:

1. Each element is made up of tiny particles called atoms.
2. The atoms of a given element are identical; the atoms of different elements are different in some fundamental way or ways.
3. Chemical compounds are formed when atoms of different elements combine with each other. A given compound always has the same relative numbers and types of atoms.
4. Chemical reactions involve reorganization of the atoms—changes in the way they are bound together. The atoms themselves are not changed in a chemical reaction.

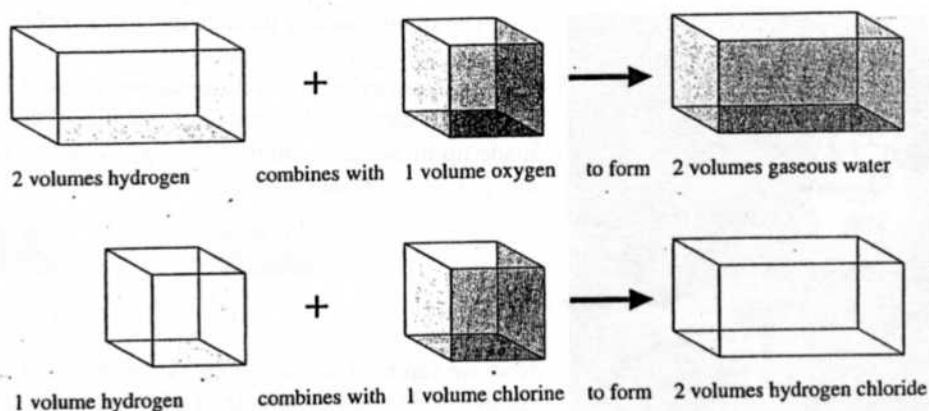


FIGURE 2.4
A representation of some of Gay-Lussac's experimental results on combining gas volumes.



Joseph Louis Gay-Lussac, a French physicist and chemist, was remarkably versatile. Although he is now known primarily for his studies on the combining of volumes of gases, Gay-Lussac was instrumental in the studies of many of the other properties of gases. Some of Gay-Lussac's motivation to learn about gases arose from his passion for ballooning. In fact, he made ascents to heights of over 4 miles to collect air samples, setting altitude records that stood for about 50 years. Gay-Lussac also was the codiscoverer of boron and the developer of a process for manufacturing sulfuric acid. As chief assayer of the French mint, Gay-Lussac developed many techniques for chemical analysis and invented many types of glassware now used routinely in labs. Gay-Lussac spent his last 20 years as a lawmaker in the French government.

It is instructive to consider Dalton's reasoning on the relative masses of the atoms of the various elements. In Dalton's time water was known to be composed of the elements hydrogen and oxygen, with 8 grams of oxygen present for every 1 gram of hydrogen. If the formula for water were OH, an oxygen atom would have to have 8 times the mass of a hydrogen atom. However, if the formula for water were H_2O (two atoms of hydrogen for every oxygen atom), this would mean that each atom of oxygen is 16 times as massive as *each* atom of hydrogen (since the ratio of the mass of one oxygen to that of *two* hydrogens is 8 to 1). Because the formula for water was not then known, Dalton could not specify the relative masses of oxygen and hydrogen unambiguously. To solve the problem, Dalton made a fundamental assumption: He decided that nature would be as simple as possible. This assumption led him to conclude that the formula for water should be OH. He thus assigned hydrogen a mass of 1 and oxygen a mass of 8.

Using similar reasoning for other compounds, Dalton prepared the first table of **atomic masses** (sometimes called **atomic weights** by chemists, since mass is often determined by comparison to a standard mass—a process called *weighing*). Many of the masses were later proved to be wrong because of Dalton's incorrect assumptions about the formulas of certain compounds, but the construction of a table of masses was an important step forward.

Although not recognized as such for many years, the keys to determining absolute formulas for compounds were provided in the experimental work of the French chemist Joseph Gay-Lussac (1778–1850) and by the hypothesis of an Italian chemist named Amadeo Avogadro (1776–1856). In 1809 Gay-Lussac performed experiments in which he measured (under the same conditions of temperature and pressure) the volumes of gases that reacted with each other. For example, Gay-Lussac found that 2 volumes of hydrogen react with 1 volume of oxygen to form 2 volumes of gaseous water and that 1 volume of hydrogen reacts with 1 volume of chlorine to form 2 volumes of hydrogen chloride. These results are represented schematically in Fig. 2.4.

In 1811 Avogadro interpreted these results by proposing that *at the same temperature and pressure, equal volumes of different gases contain the same number of particles*. This assumption (called **Avogadro's hypothesis**) makes sense if the distances between the particles in a gas are very great compared with the sizes of the particles. Under these conditions, the volume of a gas is determined by the number of molecules present, not by the size of the individual particles.

If Avogadro's hypothesis is correct, Gay-Lussac's result,

2 volumes of hydrogen react with 1 volume of oxygen \longrightarrow 2 volumes of water vapor
can be expressed as follows:

2 molecules* of hydrogen react with 1 molecule of oxygen \longrightarrow 2 molecules of water

*A *molecule* is a collection of atoms (see Section 2.6).

2.4 Early Experiments to Characterize the Atom

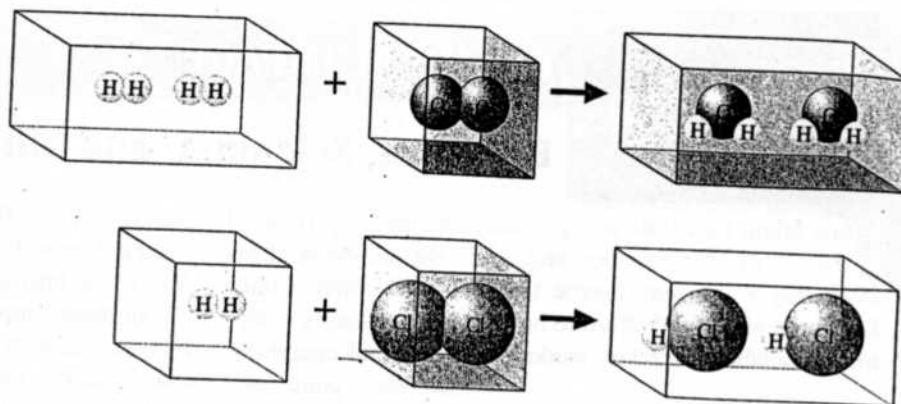


FIGURE 2.5

A representation of combining gases at the molecular level. The spheres represent atoms in the molecules.

The Italian chemist Stanislao Cannizzaro (1826–1910) cleared up the confusion in 1860 by doing a series of molar mass determinations that convinced the scientific community that the correct atomic mass of carbon is 12. For more information, see *From Caveman to Chemist* by Hugh Salzberg (American Chemical Society, 1991), p. 223.

These observations can best be explained by assuming that gaseous hydrogen, oxygen and chlorine are all composed of diatomic (two-atom) molecules: H_2 , O_2 , and Cl_2 respectively. Gay-Lussac's results can then be represented as shown in Fig. 2.5. (Note that this reasoning suggests that the formula for water is H_2O , not OH as Dalton believed)

Unfortunately, Avogadro's interpretations were not accepted by most chemists, and half-century of confusion followed, in which many different assumptions were made about formulas and atomic masses.

During the nineteenth century, painstaking measurements were made of the masses of various elements that combined to form compounds. From these experiments a list of relative atomic masses could be determined. One of the chemists involved in contributing to this list was a Swede named Jöns Jakob Berzelius (1779–1848), who discovered the elements cerium, selenium, silicon, and thorium and developed the modern symbols for the elements used in writing the formulas of compounds.

2.4 Early Experiments to Characterize the Atom

On the basis of the work of Dalton, Gay-Lussac, Avogadro, and others, chemistry was beginning to make sense. The concept of atoms was clearly a good idea. Inevitably, scientists began to wonder about the nature of the atom. What is an atom made of, and how do the atoms of the various elements differ?

The Electron

The first important experiments that led to an understanding of the composition of the atom were done by the English physicist J. J. Thomson (Fig. 2.6), who studied electrical discharges in partially evacuated tubes called **cathode-ray tubes** (Fig. 2.7) during the period from 1898 to 1903. Thomson found that when high voltage was applied to the tube, a "ray" he called a *cathode ray* (because it emanated from the negative electrode, or cathode) was produced. Because this ray was produced at the negative electrode and was repelled by the negative pole of an applied electric field (see Fig. 2.8), Thomson postulated that the ray was a stream of negatively charged particles, now called **electrons**. From experiments in which he measured the deflection of the beam of electrons in a magnetic field, Thomson determined the *charge-to-mass ratio* of an electron:

$$\frac{e}{m} = -1.76 \times 10^8 \text{ C/g}$$

where e represents the charge on the electron in coulombs (C) and m represents the electron mass in grams.

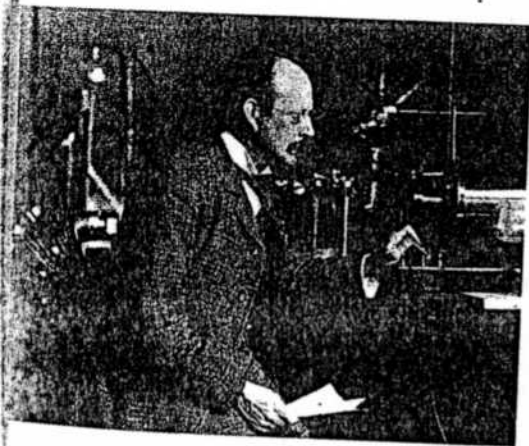


FIGURE 2.6

J. J. Thomson (1856–1940) was an English physicist at Cambridge University. He received the Nobel Prize in physics in 1906.

