CHAPTER 1

The Structure and Stability of Atoms

Where do atoms come from? Cosmologists believe that the atoms now found in all matter were formed billions of years ago by the gravitational collapse of massive stars. We'll learn more in the *FYI* at the end of this chapter.

People have always been fascinated by changes, particularly by changes that are dramatic or useful. In the ancient world, the change that occurred when a stick of wood burned, gave off heat, and turned into a small pile of ash was especially important. Similarly, the change that occurred when a reddish lump of rock (iron ore) was heated with charcoal (carbon) and produced a gray metal (iron) useful for making weapons, tools, and other implements was of enormous value. Observing such changes eventually caused people to think about what different materials might be composed of and led to the idea of fundamental substances that we today call *elements*.

At the same time people were pondering the question of elements, they were also thinking about related matters: What is an element made of? Is matter continuously divisible into ever smaller and smaller pieces, or is there an ultimate limit? Can you cut a piece of gold in two, take one of the pieces and cut *it* in two, and so on infinitely, or is there a point at which you must stop? Although most thinkers, including Plato and Aristotle, believed that matter is continuous, the Greek philosopher Democritus (460–370 BC) disagreed. Democritus proposed that elements are composed of tiny indestructible particles that we now call **atoms**, from the Greek word *atomos*, meaning "indivisible." Little else was learned about elements and atoms until the birth of modern experimental science some 2000 years later.

▲ Samples of mercury, silver, and sulfur (clockwise from top left).

1.1 CHEMISTRY AND THE ELEMENTS

Everything you see around you is formed from one or more of 118 presently known *elements*. An **element** is a fundamental substance that can't be chemically changed or broken down into anything simpler. Mercury, silver, and sulfur are common examples, as listed in **Table 1.1**.

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TABLE 1.1 Names and Symbols of Some Common Elements

Aluminum	**Al**	Chlorine	**Cl**	Manganese	**Mn**	Copper (*cuprum*)	**Cu**
Argon	**Ar**	Fluorine	**F**	Nitrogen	**N**	Iron (*ferrum*)	**Fe**
Barium	**Ba**	Helium	**He**	Oxygen	**O**	Lead (*plumbum*)	**Pb**
Boron	**B**	Hydrogen	**H**	Phosphorus	**P**	Mercury (*hydrargyrum*)	**Hg**
Bromine	**Br**	Iodine	**I**	Silicon	**Si**	Potassium (*kalium*)	**K**
Calcium	**Ca**	Lithium	**Li**	Sulfur	**S**	Silver (*argentum*)	**Ag**
Carbon	**C**	Magnesium	**Mg**	Zinc	**Zn**	Sodium (*natrium*)	**Na**

Actually, the previous statement about everything being made of one or more of 118 elements is an exaggeration because only about 90 of the 118 occur naturally. The remaining 28 have been produced artificially by nuclear chemists using high-energy particle accelerators.

Furthermore, only 83 of the 90 or so naturally occurring elements are found on Earth in any appreciable abundance. Hydrogen is thought to account for approximately 75% of the observed mass in the universe; oxygen and silicon together account for 75% of the mass of Earth's crust; and oxygen, carbon, and hydrogen make up more than 90% of the mass of the human body (**Figure 1.1**). By contrast, there are probably less than 20 grams of the element francium (Fr) dispersed over the entire Earth at any one time. Francium is an unstable radioactive element, atoms of which are continually being formed and destroyed. We'll discuss **radioactivity** briefly in Sections 1.10 and 1.11 and then again in more detail in Chapter 22.

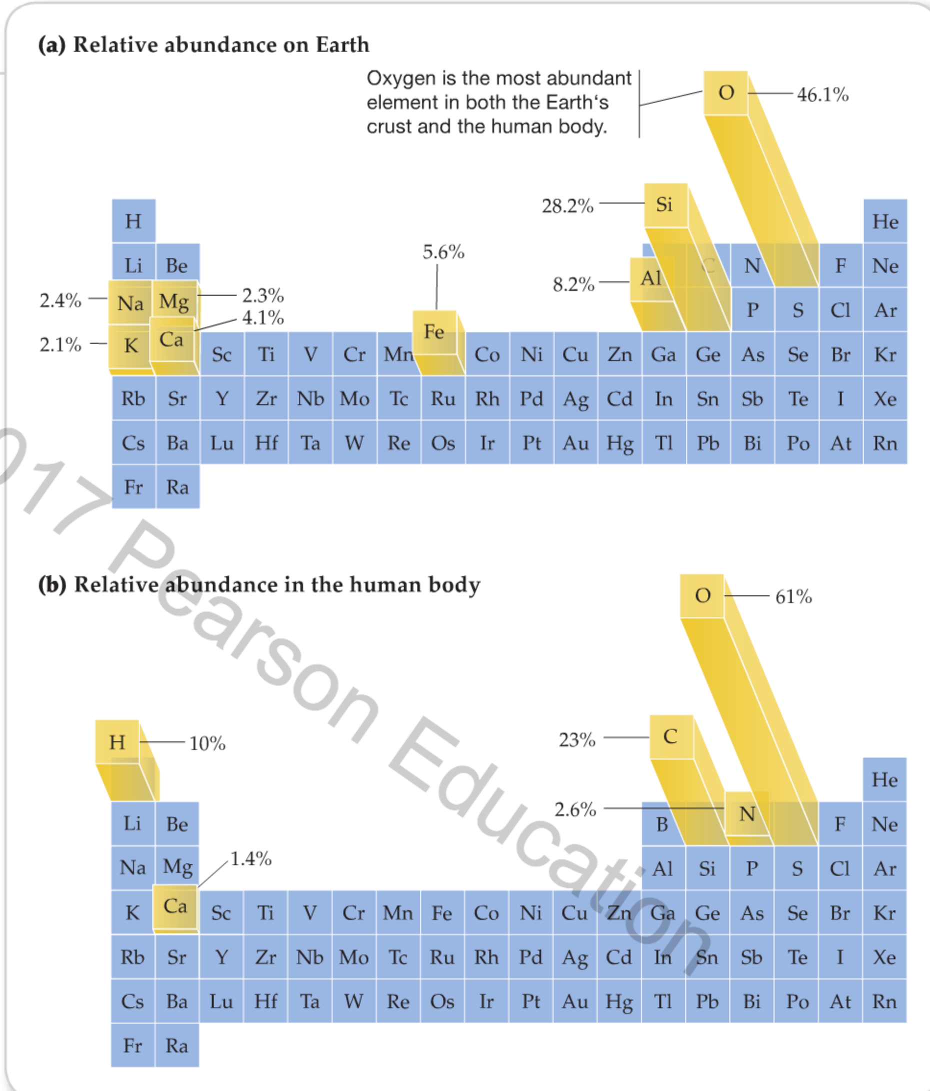
For simplicity, chemists refer to specific elements using one- or two-letter symbols. As shown by the examples in Table 1.1, the first letter of an element's symbol is always capitalized and the second letter, if any, is lowercase. Many of the symbols are just the first one or two letters of the element's English name: H = hydrogen, C = carbon, Al = aluminum, and so forth. Other symbols are derived from Latin or other languages: Na = sodium (Latin, *natrium*), Pb = lead (Latin, *plumbum*), W = tungsten (German, *Wolfram*). The names, symbols, and other information about all 118 known elements are given inside the front cover of this book, organized in a format you've undoubtedly seen before called the *periodic table*.

LOOKING AHEAD ...

As we'll see in Sections 1.10 and 1.11 and in Chapter 22, **radioactivity** is the spontaneous decay of certain unstable atoms with emission of some form of radiation.

FIGURE 1.1

Estimated elemental composition by mass percent of (a) Earth's crust and (b) the human body. Only the major constituents are shown in each case; small amounts of many other elements are also present.



PROBLEM 1.1 Look at the alphabetical list of elements inside the front cover, and find the symbols for the following elements:
(a) Cadmium (used in batteries)
(b) Antimony (used in alloys with other metals)
(c) Americium (used in smoke detectors)

PROBLEM 1.2 Look at the alphabetical list of elements inside the front cover, and tell what elements the following symbols represent:

(a) Ag	**(b)** Rh	**(c)** Re
(d) Cs	**(e)** Ar	**(f)** As

1.2 ELEMENTS AND THE PERIODIC TABLE

Ten elements have been known since the beginning of recorded history: antimony (Sb), carbon (C), copper (Cu), gold (Au), iron (Fe), lead (Pb), mercury (Hg), silver (Ag), sulfur (S), and tin (Sn). The first "new" element to be found in several thousand years was arsenic (As), discovered in about 1251. In fact, only 24 elements were known when the United States was founded in 1776.

As the pace of scientific discovery quickened in the late 1700s and early 1800s, chemists began to look for similarities among elements that might allow general conclusions to be drawn. Particularly important among the early successes was Johann Döbereiner's observation in 1829 that there were several *triads*, or groups of three elements, that appeared to behave similarly. Calcium (Ca), strontium (Sr), and barium (Ba) form one such triad; chlorine (Cl), bromine (Br), and iodine (I) form another; and lithium (Li), sodium (Na), and potassium (K) form a third. By 1843, 16 such triads were known, and chemists were searching for an explanation.

▲ Left to right, samples of **chlorine**, **bromine**, and **iodine**, one of Döbereiner's triads of elements with similar chemical properties.

Numerous attempts were made in the mid-1800s to account for the similarities among groups of elements, but the breakthrough came in 1869 when the Russian chemist Dmitri Mendeleev created the forerunner of the modern **periodic table**. Mendeleev's creation is an ideal example of how a scientific theory develops. At first there is only disconnected information—a large number of elements and many observations about their properties and behavior. As more and more facts become known, people try to organize the data in ways that make sense until ultimately a consistent theory emerges.

A good theory must do two things: It must explain known facts, and it must make predictions about phenomena yet unknown. If the predictions are tested and found true, then the theory is a good one and will stand until additional facts require that it be modified or discarded. Mendeleev's theory about how known chemical information could be organized passed all tests. Not only did the periodic table arrange data in a useful and consistent way to explain known facts about chemical reactivity, it also led to several remarkable predictions that were later found to be correct.

Using the experimentally observed chemistry of the elements as his primary organizing principle, Mendeleev arranged the known elements in order of the relative masses of their constituent particles (called their *atomic weights*, as we'll see in Section 1.9) and then grouped them according to their chemical reactivity. On so doing, he realized that there were several "holes" in the table, some of which are shown in **Figure 1.2**. The chemical behavior of aluminum (relative mass ≈ 27.3) is similar to that of boron (relative mass ≈ 11), but there was no element known at the time that fit into the slot below aluminum. In the same way, silicon (relative mass ≈ 28) is similar in many respects to carbon (relative mass ≈ 12), but there was no element known that fit below silicon.

FIGURE 1.2

A portion of Mendeleev's periodic table. The table shows the relative masses of atoms as known at the time and some of the holes representing unknown elements.

H = 1							
Li = 7	Be = 9.4		B = 11	C = 12	N = 14	O = 16	F = 19
Na = 23	Mg = 24		Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5
K = 39	Ca = 40	?, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn	? = 68	? = 72	As = 75	Se = 78	Br = 80

There is an unknown element, which turns out to be gallium (Ga), beneath aluminum (Al)…

…and another unknown element, which turns out to be germanium (Ge), beneath silicon (Si).

Looking at the holes in the table, Mendeleev predicted that two then-unknown elements existed and might be found at some future time. Furthermore, he predicted with remarkable accuracy what the properties of these unknown elements would be. The element immediately below aluminum, which he called *eka*-aluminum from a Sanskrit word meaning "first," should have a relative mass near 68 and should have a low melting point. Gallium, discovered in 1875, has exactly these properties. The element below silicon, which Mendeleev called *eka*-silicon, should have a relative mass near 72 and should be dark gray in color. Germanium, discovered in 1886, fits the description perfectly (**Table 1.2**).

▲ Gallium is a shiny, low-melting metal.

▲ Germanium is a hard, gray semimetal.

TABLE 1.2 A Comparison of Predicted and Observed Properties for Gallium (*eka*-Aluminum) and Germanium (*eka*-Silicon)

Element	Property	Mendeleev's Prediction	Observed Property
	Relative mass	68	69.7
Gallium	Density	5.9 g/cm^3	5.91 g/cm^3
	Melting point	Low	29.8 °C
	Relative mass	72	72.6
Germanium	Density	5.5 g/cm^3	5.35 g/cm^3
	Color	Dark gray	Light gray

In the modern periodic table, shown in **Figure 1.3**, elements are placed on a grid with 7 horizontal rows, called **periods,** and 18 vertical columns, called **groups**. When organized in this way, *the elements in a given group have similar chemical properties*. Lithium, sodium, potassium, and the other metallic elements on the left side of the periodic table in group 1A behave similarly. Beryllium, magnesium, calcium, and the other elements in group 2A behave similarly. Fluorine, chlorine, bromine, and the other elements in group 7A on the right side of the table behave similarly, and so on throughout. (Mendeleev, by the way, was completely unaware of the existence of the group 8A elements—He, Ne, Ar, Kr, Xe, and Rn—because none were known when he constructed his table. All are colorless, odorless gases with little or no chemical reactivity, and none were discovered until 1894, when argon was first isolated.)

The overall form of the periodic table is well accepted, but chemists in different countries have historically used different conventions for labeling the groups. To resolve these difficulties, an international standard calls for numbering the groups from 1 to 18 going left to right. This standard has not yet found complete acceptance, however, and we'll continue to use the U.S. system of numbers and capital letters—group 3B instead of group 3 and group 7A instead of group 17, for example. Labels for the newer system are shown in Figure 1.3, above those for the U.S. system.

One further comment: There are actually 32 groups in the periodic table rather than 18, but to make the table fit manageably on a page, the 14 elements beginning with lanthanum (the *lanthanides*) and the 14 beginning with actinium (the *actinides*) are pulled out and shown below the others. These groups are not numbered.

We'll see repeatedly throughout this book that the periodic table of the elements is the most important organizing principle in chemistry. The time you take now to familiarize yourself with the layout and organization of the periodic table will pay you back later on. Notice in Figure 1.3, for instance, that there is a regular progression in the size of the seven periods (rows). The first period has only 2 elements, hydrogen (H) and helium (He); the second and third periods have 8 elements each; the fourth and fifth periods have 18 elements each; and the sixth and seventh periods, which include the lanthanides and actinides, have 32 elements each. We'll see in **Section 2.13** that this regular progression in the periodic table reflects a similar regularity in the structure of atoms.

LOOKING AHEAD ...

We'll see in **Section 2.13** that the detailed structure of a given atom is related to its position in the periodic table.

Notice also that not all groups in the periodic table have the same number of elements. The two larger groups on the left and the six larger groups on the right, labeled A in the U.S. system, are called the **main groups**. Most of the elements on which life is based—carbon, hydrogen, nitrogen, oxygen, and phosphorus, for instance—are main-group elements. The 10 smaller groups in the middle of the table, labeled B in the U.S. system, are called the **transition metal groups**. Most of the metals you're probably familiar with—iron, copper, zinc, and gold, for instance—are transition metals. And the 14 groups shown separately at the bottom of the table are called the **inner transition metal groups**.

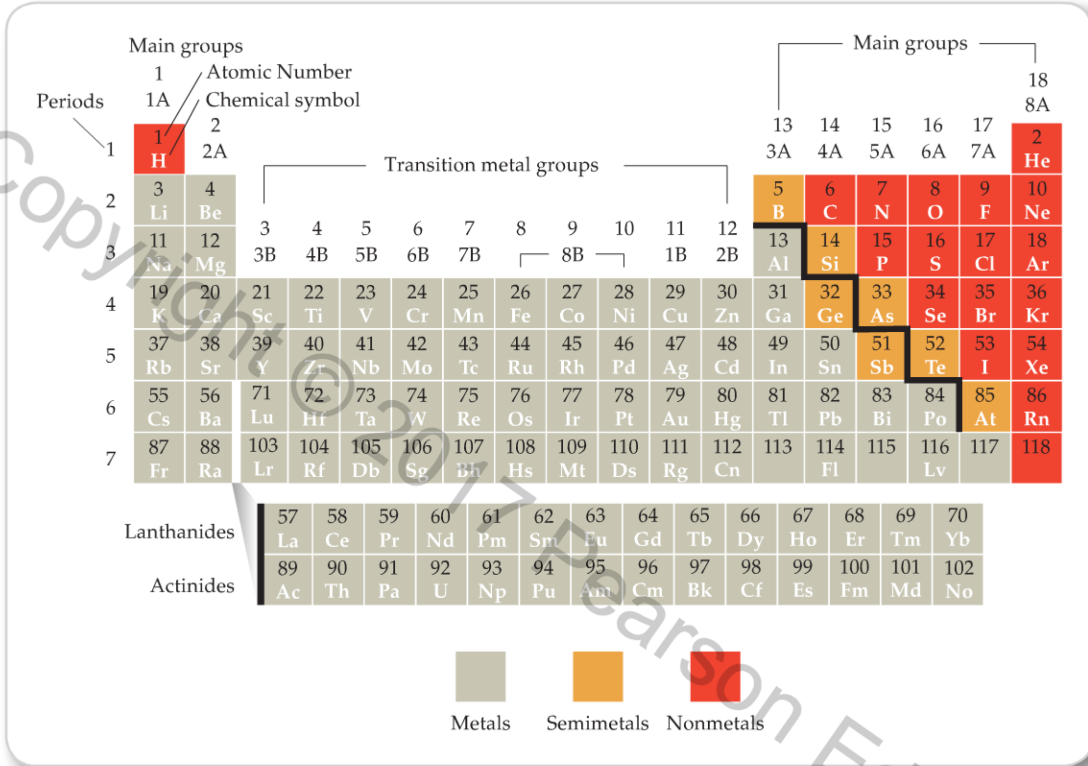


FIGURE 1.3

The periodic table. Each element is identified by a one- or two-letter symbol and is characterized by an atomic number. The table begins with hydrogen (H, atomic number 1) in the upper left-hand corner and continues to the yet unnamed element with atomic number 118. The 14 elements beginning with lanthanum (La, atomic number 57) and the 14 elements beginning with actinium (Ac, atomic number 89) are pulled out and shown below the others.

Elements are organized into 18 vertical columns, or *groups*, and 7 horizontal rows, or *periods*. The two groups on the left and the six on the right are the *main groups*; the ten in the middle are the *transition metal groups*. The 14 elements beginning with lanthanum are the *lanthanides*, and the 14 elements beginning with actinium are the *actinides*. Together, the lanthanides and actinides are known as the *inner transition metal groups*. Two systems for numbering the groups are shown above the top row and are explained in the text.

Those elements (except hydrogen) on the left side of the zigzag line running from boron (B) to astatine (At) are metals; those elements (plus hydrogen) to the right of the line are nonmetals; and seven of the nine elements abutting the line are metalloids, or semimetals.

1.3 SOME COMMON GROUPS OF ELEMENTS AND THEIR PROPERTIES

Any characteristic that can be used to describe or identify matter is called a **property**. Examples include volume, amount, odor, color, and temperature. Still other properties include such characteristics as melting point, solubility, and chemical behavior. For example, we might list some properties of sodium chloride (table salt) by saying it is a solid that melts at 1474 °F (or 801 °C), dissolves in water, and undergoes a chemical reaction to give an insoluble white precipitate when it comes into contact with a silver nitrate solution.

▲ Addition of a solution of silver nitrate to a solution of sodium chloride in water yields a white precipitate of solid silver chloride.

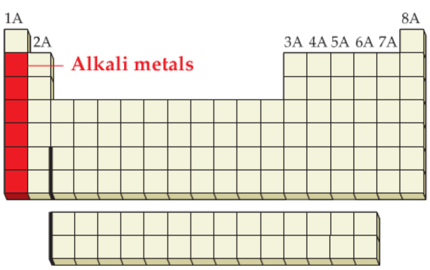
Properties can be classified as either *intensive* or *extensive*, depending on whether the value of the property changes with the amount of the sample. **Intensive properties**, like temperature and melting point, have values that don't depend on the amount of sample: A small ice cube might have the same temperature as a massive iceberg and melt at the same point. **Extensive properties,** like length and volume, have values that *do* depend on the sample size: An ice cube is much smaller than an iceberg.

Properties can also be classified as either *physical* or *chemical*, depending on whether the property involves a change in the chemical makeup of a substance. **Physical properties** are characteristics that don't involve a change in a sample's chemical makeup, whereas **chemical properties** are characteristics that do involve a change in chemical makeup. The melting point of ice, for instance, is a physical property because melting causes the water to change only in form, from solid to liquid, but not in chemical makeup. The rusting of an iron bicycle left in the rain is a chemical property, however, because iron combines with oxygen and moisture from the air to give the new chemical substance called rust. **Table 1.3** lists other examples of both physical and chemical properties.

TABLE 1.3 Some Examples of Physical and Chemical Properties

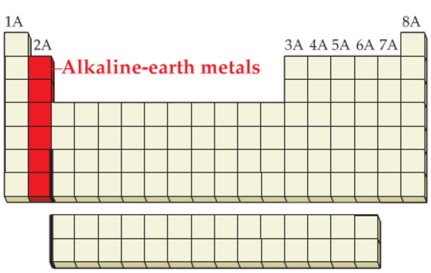
Physical Properties		Chemical Properties
Temperature	Amount	Rusting (of iron)
Color	Odor	Combustion (of gasoline)
Melting point	Solubility	Tarnishing (of silver)
Electrical conductivity	Hardness	Hardening (of cement)

As noted previously, the elements in a given group of the periodic table often show remarkable similarities in their chemical properties. Look at the following groups, for instance, to see some examples:



- **Group 1A—Alkali metals** Lithium (Li), sodium (Na), potassium (K), rubidium (Rb), and cesium (Cs) are soft, silvery metals. All react rapidly—often violently—with water to form products that are highly alkaline, or basic—hence the name *alkali metals*. Because of their high reactivity, the alkali metals are never found in the pure state but only in combination with other elements. Francium (Fr) is also an alkali metal but, as noted previously, it is so rare that little is known about it.

  Note that group 1A also contains hydrogen (H) even though, as a colorless gas, it is completely different in appearance and behavior from the alkali metals. We'll see the reason for this classification in Section 2.13.



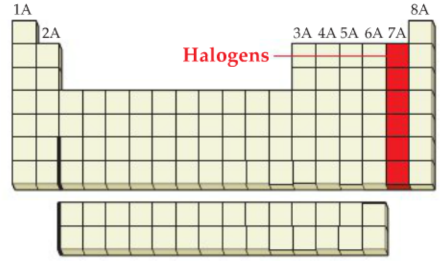
- **Group 2A—Alkaline-earth metals** Beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra) are also lustrous, silvery metals but are

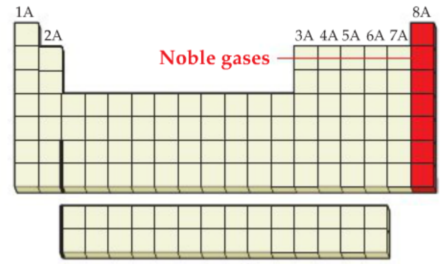
▲ Sodium, one of the alkali metals, reacts violently with water to yield hydrogen gas and an alkaline solution.

▲ Magnesium, one of the alkaline-earth metals, burns in air.

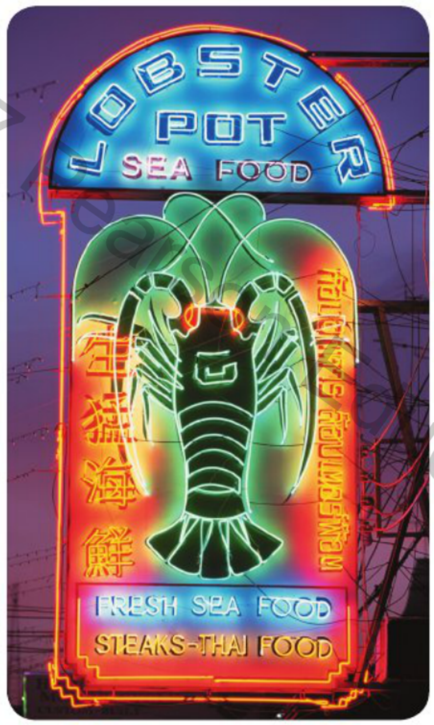
less reactive than their neighbors in group 1A. Like the alkali metals, the alkaline-earth metals are never found in nature in the pure state.

- **Group 7A—Halogens** Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) are colorful, corrosive nonmetals. They are found in nature only in combination with other elements, such as with sodium in table salt (sodium chloride, NaCl). In fact, the group name *halogen* is taken from the Greek word *hals*, meaning "salt." Astatine (At) is also a halogen, but it exists in such tiny amounts that little is known about it.
- **Group 8A—Noble gases** Helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn) are colorless gases with very low chemical reactivity. Helium and neon don't combine with any other element; argon, krypton, and xenon combine with very few.



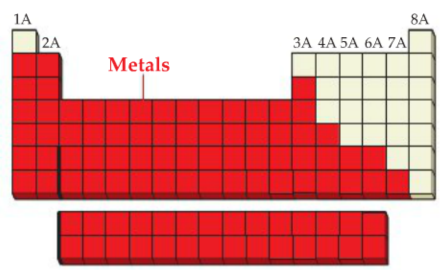


▲ Bromine, a halogen, is a corrosive dark red liquid at room temperature.

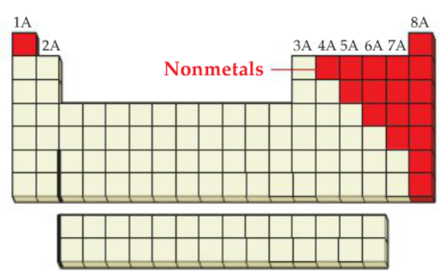


▲ Neon, one of the noble gases, is used in neon lights and signs.

As indicated previously in Figure 1.3, the elements of the periodic table are often divided into three major categories: metals, nonmetals, and semimetals.

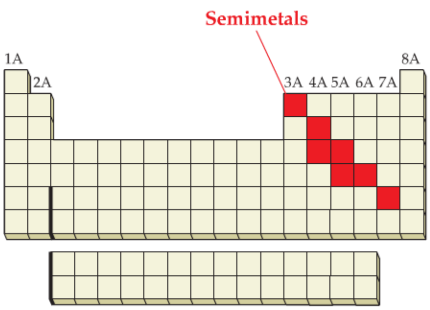


- **Metals** Metals, the largest category of elements, are found on the left side of the periodic table, bounded on the right by a zigzag line running from boron (B) at the top to astatine (At) at the bottom. The metals are easy to characterize by their appearance. All except mercury are solid at room temperature, and most have the silvery shine we normally associate with metals. In addition, metals are generally malleable rather than brittle, can be twisted and drawn into wires without breaking, and are good conductors of heat and electricity.
- **Nonmetals** Except for hydrogen, nonmetals are found on the right side of the periodic table and, like metals, are easy to characterize by their appearance. Eleven of the seventeen nonmetals are gases, one is a liquid (bromine), and only five are solids at room temperature (carbon, phosphorus, sulfur, selenium, and iodine). None are silvery in appearance, and several are brightly colored. The solid nonmetals are brittle rather than malleable and are poor conductors of heat and electricity.



▲ Lead, aluminum, copper, gold, iron, and silver (clockwise from left) are typical metals. All conduct electricity and can be formed into wires.

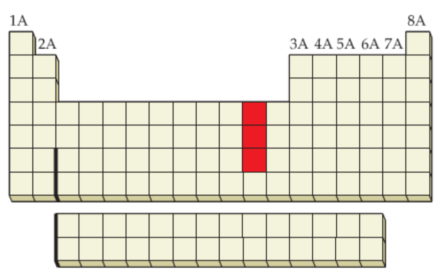
▲ Bromine, carbon, phosphorus, and sulfur (clockwise from top left) are typical nonmetals. None conduct electricity or can be made into wires.



- **Semimetals** Seven of the nine elements adjacent to the zigzag boundary between metals and nonmetals—boron, silicon, germanium, arsenic, antimony, tellurium, and astatine—are called semimetals because their properties are intermediate between those of their metallic and nonmetallic neighbors. Although most are silvery in appearance and all are solid at room temperature, semimetals are brittle rather than malleable and tend to be poor conductors of heat and electricity. Silicon, for example, is a widely used *semiconductor*, a substance whose electrical conductivity is intermediate between that of a metal and an insulator.

PROBLEM 1.3 Identify the following elements as metals, nonmetals, or semimetals:
(a) Ti **(b)** Te **(c)** Se **(d)** Sc **(e)** At **(f)** Ar

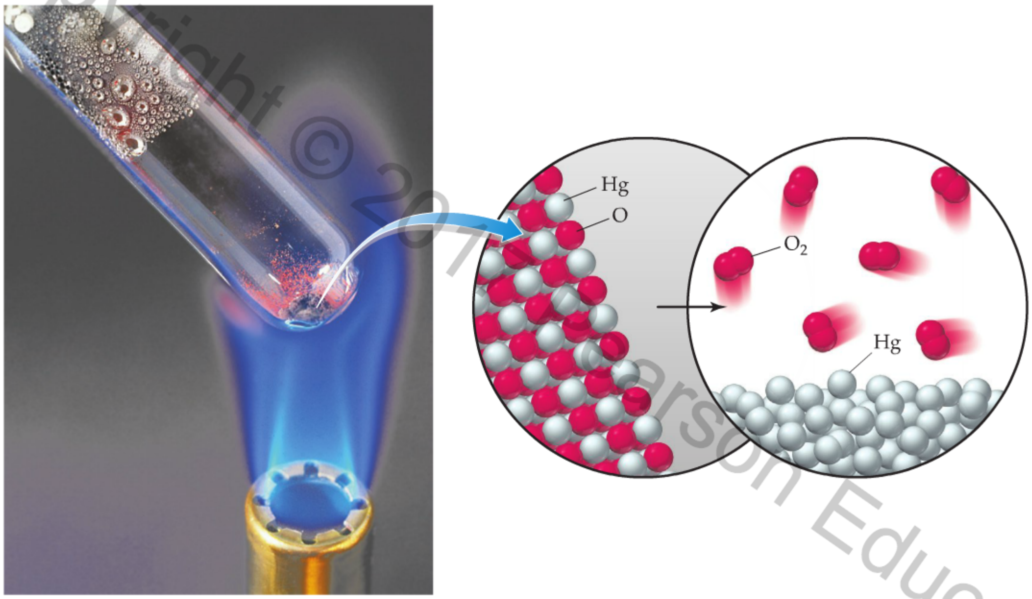
CONCEPTUAL PROBLEM 1.4 The three so-called coinage metals are located near the middle of the periodic table. Identify them.



1.4 A BIT OF HISTORY: THE CONSERVATION OF MASS AND THE LAW OF DEFINITE PROPORTIONS

The Englishman Robert Boyle (1627–1691) is generally credited with being the first to study chemistry as a separate intellectual discipline and the first to carry out rigorous chemical experiments. Through a careful series of researches into the nature and behavior of gases, Boyle provided clear evidence for the atomic makeup of matter. In addition, Boyle was the first to clearly define an element as a substance that cannot be chemically broken down further and to suggest that a substantial number of different elements might exist. Atoms of these different elements, in turn, can join together in different ways to yield a vast number of different substances we call **chemical compounds**.

Progress in chemistry was slow in the decades following Boyle, and it was not until the work of Joseph Priestley (1733–1804) that the next great leap was made. Priestley prepared and isolated the gas oxygen in 1774 by heating the compound mercury oxide (HgO) according to the chemical equation we would now write as $2\ HgO \rightarrow 2\ Hg + O_2$.



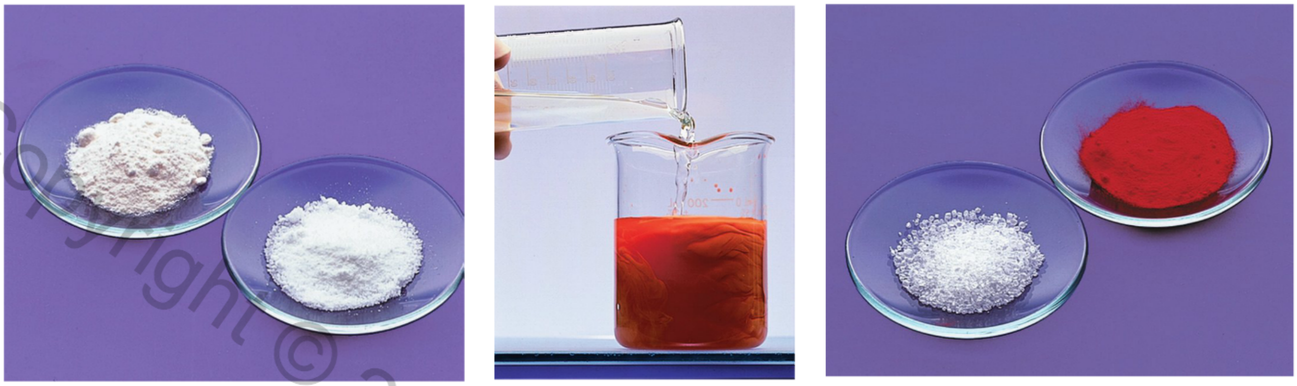
◀ Heating the red powder HgO causes it to decompose into the silvery liquid mercury and the colorless gas oxygen.

In this standard format for writing chemical transformations, each compound is described by its **chemical formula**, which lists the symbols of its constituent elements and uses subscripts to indicate the number of atoms of each. If no subscript is given, the number 1 is understood. Thus, sodium chloride (table salt) is written as NaCl, water as H_2O, and sucrose (table sugar) as $C_{12}H_{22}O_{11}$. A chemical reaction is written in a standard format called a **chemical equation**, in which the reactant substances undergoing change are written on the left, the product substances being formed are written on the right, and an arrow is drawn between them to indicate the direction of the chemical transformation.

Soon after Priestley's discovery, Antoine Lavoisier (1743–1794) showed that oxygen is the key substance involved in combustion. Furthermore, Lavoisier demonstrated with careful measurements that when combustion is carried out in a closed container, the mass of the combustion products exactly equals the mass of the starting reactants. When hydrogen gas burns and combines with oxygen to yield water (H_2O), for instance, the mass of the water formed is equal to the mass of the hydrogen and oxygen consumed. Called the **law of mass conservation**, this principle is a cornerstone of chemical science.

▶ **Law of mass conservation** Mass is neither created nor destroyed in chemical reactions.

It's easy to demonstrate the law of mass conservation by carrying out an experiment like that shown in **Figure 1.4**. If 3.25 g of mercury nitrate [$Hg(NO_3)_2$] and 3.32 g of potassium iodide (KI) are each dissolved in water and the solutions are mixed, an immediate chemical reaction occurs leading to formation of the insoluble orange solid mercury iodide (HgI_2).



Known amounts of solid KI and solid $Hg(NO_3)_2$ are weighed and then dissolved in water.

The solutions are mixed to give **solid HgI_2**, which is removed by filtration.

The solution that remains is evaporated to give solid KNO_3. On weighing, the combined masses of the products equal the combined masses of the reactants.

FIGURE 1.4

An illustration of the law of mass conservation. In any chemical reaction, the combined masses of the final products equal the combined masses of the starting reactants.

Filtering the reaction mixture gives 4.55 g of mercury iodide, and evaporation of the water from the remaining solution leaves 2.02 g of potassium nitrate (KNO_3). Thus, the combined mass of the reactants (3.25 g + 3.32 g = 6.57 g) is exactly equal to the combined mass of the products (4.55 g + 2.02 g = 6.57 g).

The combined masses of these two reactants . . .

. . . equals the combined masses of these two products.

$$\underset{\text{Mercury nitrate}}{Hg(NO_3)_2} + \underset{\text{Potassium iodide}}{2\,KI} \longrightarrow \underset{\text{Mercury iodide}}{HgI_2} + \underset{\text{Potassium nitrate}}{2\,KNO_3}$$

Further investigations in the decades following Lavoisier led the French chemist Joseph Proust (1754–1826) to formulate a second fundamental chemical principle that we now call the **law of definite proportions**.

> ▶ **Law of definite proportions** Different samples of a pure chemical compound always contain the same proportion of elements by mass.

Every sample of water (H_2O) contains 1 part hydrogen and 8 parts oxygen by mass; every sample of carbon dioxide (CO_2) contains 3 parts carbon and 8 parts oxygen by mass; and so on. *Elements combine in specific proportions, not in random proportions.*

1.5 MORE HISTORY: THE LAW OF MULTIPLE PROPORTIONS AND DALTON'S ATOMIC THEORY

At the same time that Proust was formulating the law of definite proportions, the English schoolteacher John Dalton (1766–1844) was exploring along similar lines. His work led him to propose what has come to be called the **law of multiple proportions**.

▶ **Law of multiple proportions** Elements can combine in different ways to form different chemical compounds, whose mass ratios are simple whole-number multiples of each other.

The key to Dalton's proposition was his realization that the *same* elements sometimes combine in different ratios to give *different* chemical compounds. For example, nitrogen and oxygen can combine either in a 7:8 = 0.875 mass ratio to make the compound we know today as nitric oxide (NO) or in a 7:16 = 0.4375 mass ratio to make the compound we know as nitrogen dioxide (NO_2). The first compound contains exactly twice as much nitrogen (or half as much oxygen) as the second:

▲ Copper metal reacts with nitric acid (HNO_3) to yield the brown gas NO_2.

NO contains 7 g nitrogen per 8 g oxygen	N:O mass ratio = 7:8 = 0.875
NO_2 contains 7 g nitrogen per 16 g oxygen	N:O mass ratio = 7:16 = 0.4375

$$\frac{\text{N:O mass ratio in NO}}{\text{N:O mass ratio in NO}_2} = \frac{0.875}{0.4375} = 2$$

This result makes sense only if we assume that matter is composed of discrete atoms that have characteristic masses and combine with one another in specific and well-defined ways (**Figure 1.5**).

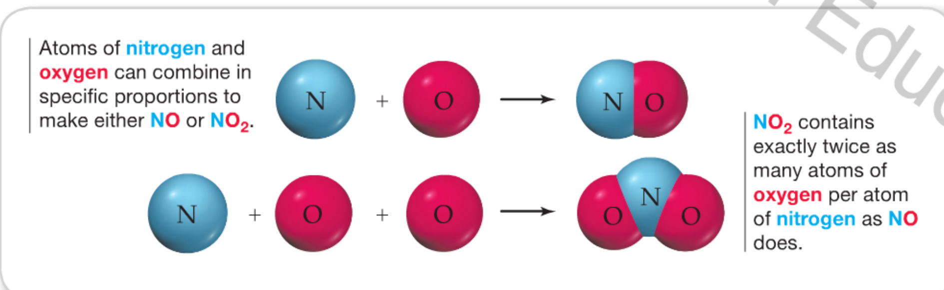


FIGURE 1.5

An illustration of Dalton's law of multiple proportions.

Taking all three laws together—the law of mass conservation, the law of definite proportions, and the law of multiple proportions—ultimately led Dalton to propose a new theory of matter that is still accepted today. He reasoned as follows:

- **Elements are made up of tiny particles called atoms.** Although Dalton didn't know what atoms were like, he nevertheless felt they were necessary to explain why there were so many different elements.
- **Each element is characterized by the mass of its atoms.** Dalton realized that there must be some feature that distinguishes the atoms of one element from those of another. Because Proust's law of definite proportions showed that elements always combine in specific mass ratios, Dalton reasoned that the distinguishing feature among atoms of different elements must be *mass*. Atoms of the same element have the same mass, but atoms of different elements have different masses.
- **The chemical combination of elements to make different chemical compounds occurs when atoms bond together in small whole-number ratios.** Only if whole numbers of atoms combine will different samples of a pure chemical compound always contain the same proportion of elements by mass (the law of definite proportions and the law of multiple proportions). Fractional parts of atoms are never involved in chemical reactions.

▲ These samples of sulfur and carbon have different masses but contain the same number of atoms.

- **Chemical reactions only rearrange how atoms are combined in chemical compounds; the atoms themselves don't change.** Dalton realized that atoms must be chemically indestructible for the law of mass conservation to be valid. If the same numbers and kinds of atoms are present in both reactants and products, then the masses of reactants and products must also be the same.

Not everything that Dalton proposed was correct. He thought, for instance, that water had the formula HO rather than H_2O. Nevertheless, his atomic theory of matter was ultimately accepted and came to form a cornerstone of modern chemical science.

Worked Example 1.1

Using the Law of Multiple Proportions

The two compounds methane and propane are both constituents of natural gas. A sample of methane contains 5.70 g of carbon atoms and 1.90 g of hydrogen atoms combined in a certain way, while a sample of propane contains 4.47 g of carbon atoms and 0.993 g of hydrogen atoms combined in a different way. Show that the two compounds obey the law of multiple proportions.

STRATEGY

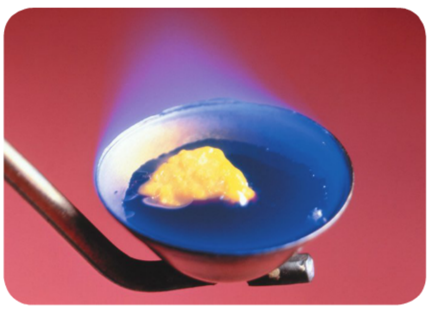
Find the C:H (or H:C) mass ratio in each compound, and then compare the two ratios to see whether they are small whole-number multiples of each other.

SOLUTION

$$\text{Methane:}\quad \text{C:H mass ratio} = \frac{5.70\text{ g C}}{1.90\text{ g H}} = 3.00$$

$$\text{Propane:}\quad \text{C:H mass ratio} = \frac{4.47\text{ g C}}{0.993\text{ g H}} = 4.50$$

$$\frac{\text{C:H mass ratio in methane}}{\text{C:H mass ratio in propane}} = \frac{3.00}{4.50} = \frac{2}{3}$$



▲ Sulfur burns with a bluish flame to yield colorless SO_2 gas.

PROBLEM 1.5 Compounds **A** and **B** are colorless gases obtained by combining sulfur with oxygen. Compound **A** results from combining 6.00 g of sulfur with 5.99 g of oxygen, and compound **B** results from combining 8.60 g of sulfur with 12.88 g of oxygen. Show that the mass ratios in the two compounds are simple multiples of each other.

1.6 THE STRUCTURE OF ATOMS: ELECTRONS

Dalton's atomic theory is fine as far as it goes, but it leaves unanswered the obvious question: What is an atom made of? Dalton himself had no way of answering this question, and it was not until nearly a century later that experiments by the English physicist J. J. Thomson (1856–1940) provided some clues. Thomson's experiments involved the use of *cathode-ray tubes* (CRTs), early predecessors of the tubes still found in older televisions and computer displays.

As shown in **Figure 1.6a**, a cathode-ray tube is a sealed glass vessel from which the air has been removed and in which two thin pieces of metal, called *electrodes*, have been sealed. When a sufficiently high voltage is applied across the electrodes, an electric current flows through the tube from the negatively charged electrode (the *cathode*) to the positively charged electrode (the *anode*). If the tube is not fully evacuated but still contains a small amount of air or other gas, the flowing current is visible as a glow called a *cathode ray*. Furthermore, if the anode has a hole in it and the end of the tube is coated with a phosphorescent substance such as zinc sulfide, some of the rays emanating from the cathode pass through the hole and strike the end of the tube, where they are visible as a bright spot of light—exactly what happens in a CRT television screen or computer monitor.

Experiments by a number of physicists in the 1890s had shown that cathode rays can be deflected by bringing either a magnet or an electrically charged plate near the tube (**Figure 1.6b**). Because the beam is produced at a negative electrode and is deflected toward a positive plate, Thomson proposed that cathode rays must consist of tiny, negatively charged particles, which we now call **electrons**. Furthermore, because electrons are emitted from electrodes made of many different elements, all these different elements must contain electrons.

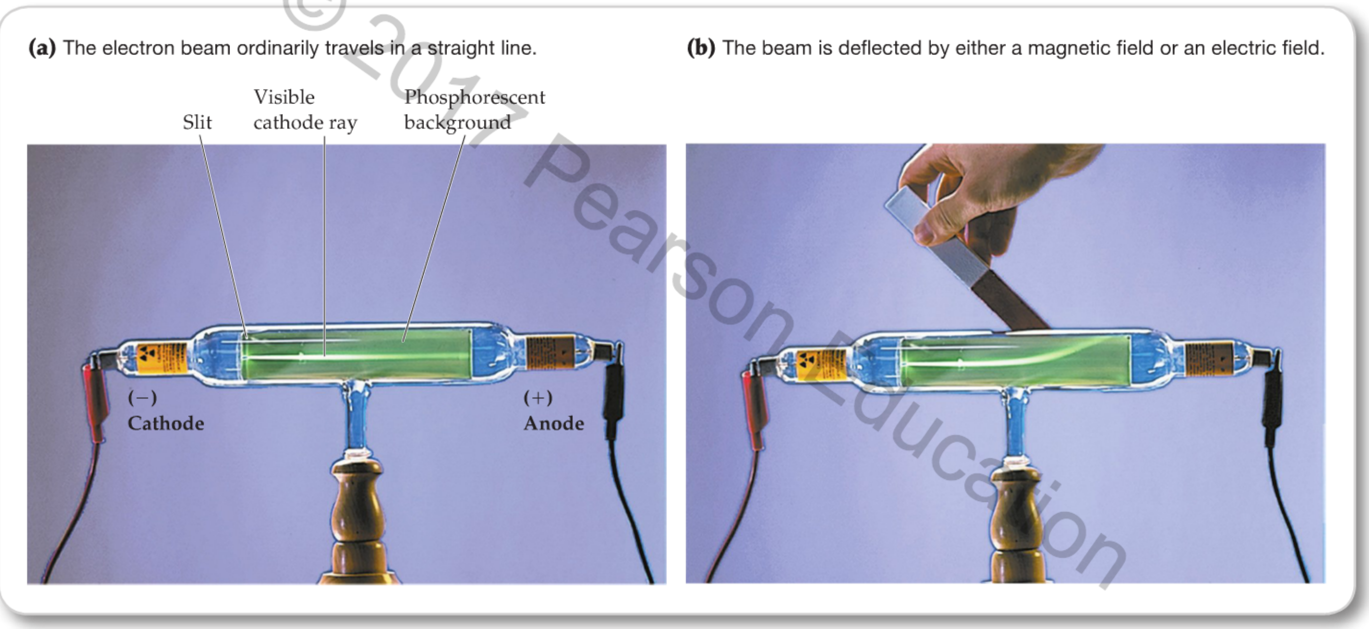


FIGURE 1.6

A cathode-ray tube. In a cathode-ray tube, a stream of electrons emitted from the cathode passes through a slit, moves toward the positively charged anode, and is visualized by a phosphorescent strip.

Thomson reasoned that the amount of deflection of the electron beam due to a nearby magnetic or electric field should depend on three factors:

1. **The strength of the deflecting magnetic or electric field.** The stronger the magnet or the higher the voltage on the charged plate, the greater the deflection.
2. **The size of the negative charge on the electron.** The larger the charge on the particle, the greater its interaction with the magnetic or electric field and the greater the deflection.
3. **The mass of the electron.** The lighter the particle, the greater its deflection (just as a table-tennis ball is more easily deflected than a bowling ball).

By carefully measuring the amount of deflection caused by electric and magnetic fields of known strength, Thomson was able to calculate the ratio of the electron's electric charge to its mass: its *charge-to-mass ratio, e/m*. The modern value is

$$\frac{e}{m} = 1.758\,821 \times 10^8 \text{ C/g}$$

where e is the magnitude of the charge on the electron in the derived SI unit coulombs (C) and m is the mass of the electron in grams. (We'll say more about **coulombs** and **electrical charge** in Sections 17.3 and 17.14.) Note that because e is defined as a positive quantity, the actual (negative) charge on the electron is $-e$.

LOOKING AHEAD ...

We'll see in Sections 17.3 and 17.14 that **coulombs** and **electrical charge** are fundamental to *electrochemistry*—the area of chemistry involving batteries, fuel cells, electroplating of metals, and the like.

Thomson was able to measure only the ratio of charge to mass, not charge or mass itself, and it was left to the American R. A. Millikan (1868–1953) to devise a method for measuring the mass of an electron (**Figure 1.7**). In Millikan's experiment, a fine mist of oil was sprayed into a chamber and the tiny oil droplets were allowed to fall between two horizontal plates. Observing the spherical droplets through a telescopic eyepiece made it possible to determine how rapidly they fell through the air, which in turn allowed their masses to be calculated. The droplets were then given a negative charge by irradiating them with X rays. By applying a voltage to the plates, with the upper plate positive, it was possible to counteract the downward fall of the charged droplets and keep them suspended.

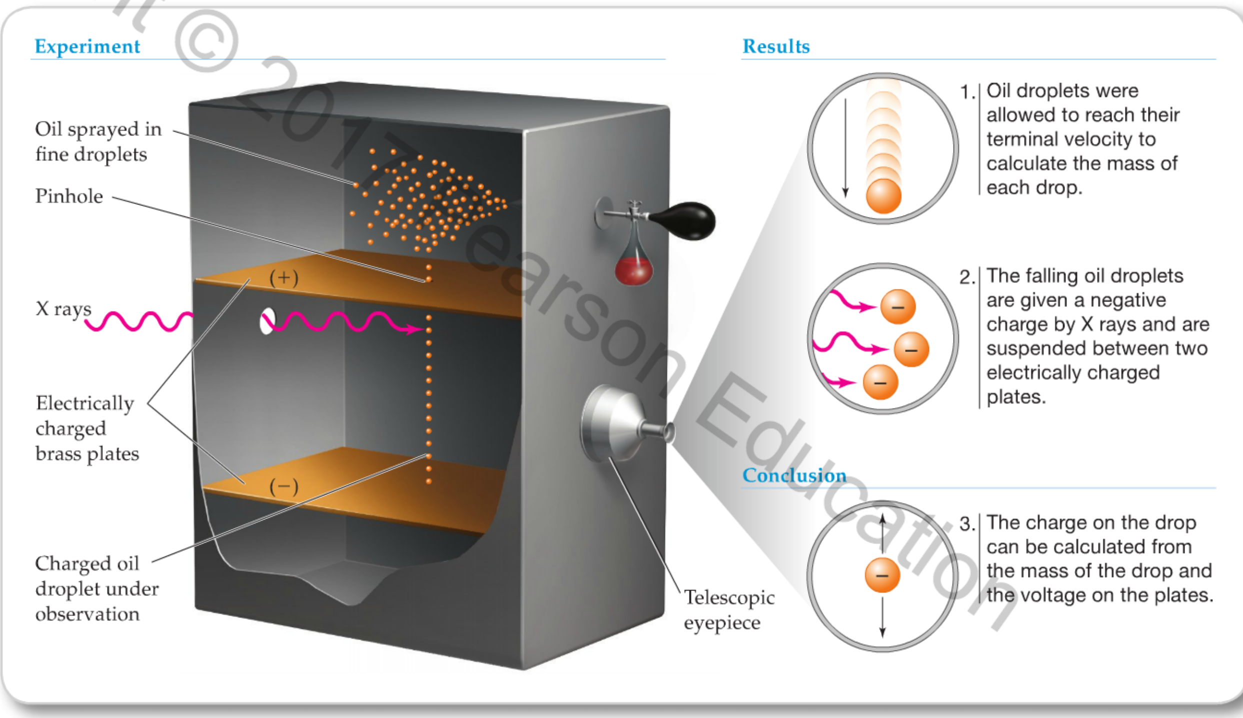


FIGURE 1.7

Millikan's oil drop experiment.

With the voltage on the plates and the mass of the droplets known, Millikan was able to show that the charge on a given droplet was always a small whole-number multiple of e, whose modern value is $1.602\,177 \times 10^{-19}$ C. Substituting the value of e into Thomson's charge-to-mass ratio then gives the mass m of the electron as $9.109\,383 \times 10^{-28}$ g:

$$\text{Because} \quad \frac{e}{m} = 1.758\,821 \times 10^{8}\ \text{C/g}$$

$$\text{then} \quad m = \frac{e}{1.758\,821 \times 10^{8}\ \text{C/g}} = \frac{1.602\,177 \times 10^{-19}\ \cancel{\text{C}}}{1.758\,821 \times 10^{8}\ \cancel{\text{C}}/\text{g}}$$

$$= 9.109\,383 \times 10^{-28}\ \text{g}$$

1.7 THE STRUCTURE OF ATOMS: PROTONS AND NEUTRONS

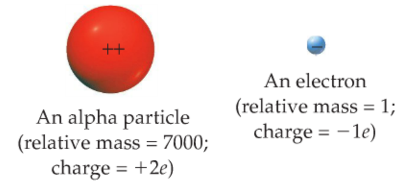
Think about the consequences of Thomson's cathode-ray experiments. Because matter is electrically neutral overall, the fact that the atoms in an electrode can give off *negatively* charged particles (electrons) must mean that those same atoms also contain *positively* charged particles for electrical balance. The search for those positively charged particles and for an overall picture of atomic structure led to a landmark experiment published in 1911 by the New Zealand physicist Ernest Rutherford (1871–1937).

Rutherford's work involved the use of ***alpha (α) particles***, a type of emission previously found to be given off by a number of naturally occurring radioactive elements, including radium, polonium, and radon. Rutherford knew that alpha particles are about 7000 times more massive than electrons and that they have a positive charge that is twice the magnitude of the charge on an electron, but opposite in sign.

When Rutherford directed a beam of alpha particles at a thin gold foil, he found that almost all the particles passed through the foil undeflected. A very small number, however (about 1 of every 20,000), were deflected at an angle, and a few actually bounced back toward the particle source (**Figure 1.8**).

LOOKING AHEAD ...

We'll see in Section 1.11 that **alpha (α) particles** are helium nuclei, He^{2+}, and are emitted by certain radioactive atoms.



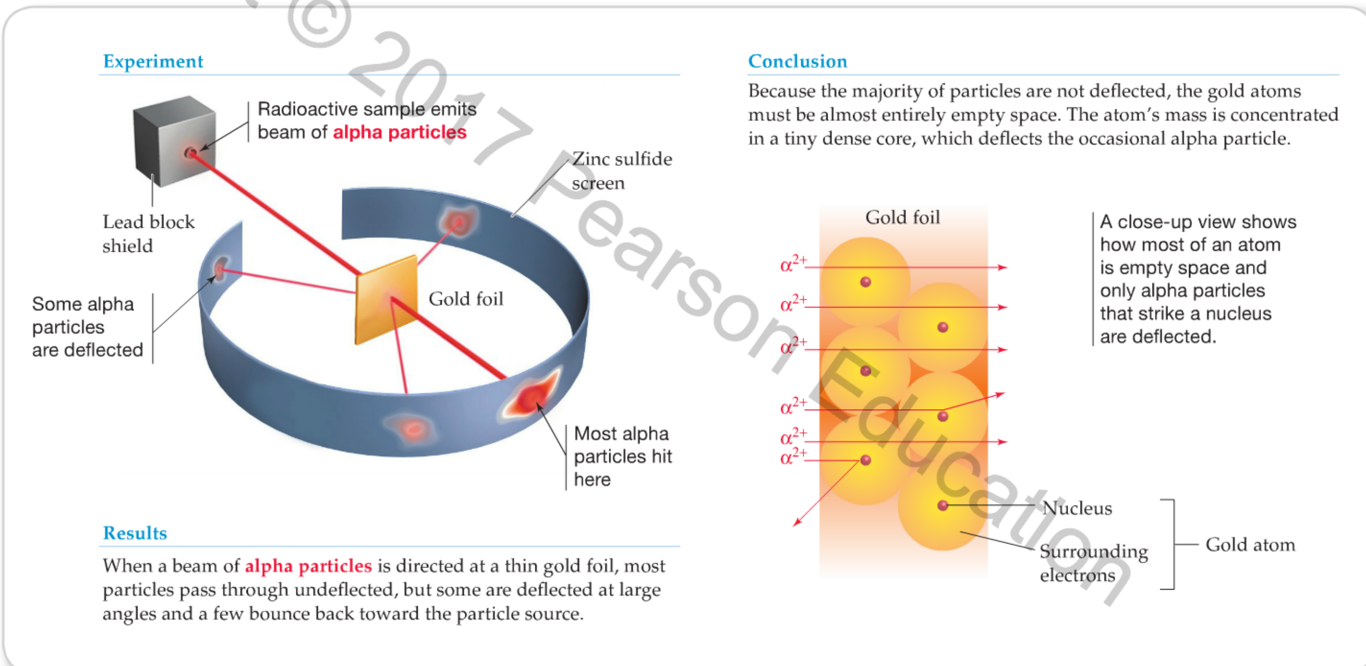


FIGURE 1.8

Rutherford's scattering experiment.

Rutherford explained his results by proposing that a metal atom must be almost entirely empty space and have its mass concentrated in a tiny central core that he called the **nucleus**. If the nucleus contains the atom's positive charges and most of its mass, and if the electrons are a relatively large distance away, then it is clear why the observed scattering results are obtained: Most alpha particles encounter empty space as they fly through the foil. Only when a positive alpha particle chances to come near a small but massive positive nucleus is it repelled strongly enough to make it bounce backward.

Modern measurements show that an atom has a diameter of roughly 10^{-10} m and that a nucleus has a diameter of about 10^{-15} m. It's difficult to imagine from these numbers alone, though, just how small a nucleus really is. For comparison purposes, if an atom were the size of a large domed stadium, the nucleus would be approximately the size of a small pea in the center of the playing field.

Further experiments by Rutherford and others between 1910 and 1930 showed that a nucleus is composed of two kinds of particles, called *protons* and *neutrons*. **Protons** have a mass of $1.672\,622 \times 10^{-24}$ g (about 1836 times that of an electron) and are positively charged. Because the charge on a proton is opposite in sign but equal in size to that on an electron, the numbers of protons and electrons in a neutral atom are equal. **Neutrons** ($1.674\,927 \times 10^{-24}$ g) are almost identical in mass to protons but carry no charge, and the number of neutrons in a nucleus is not directly related to the numbers of protons

▲ The relative size of the nucleus in an atom is roughly the same as that of a pea in the middle of this huge stadium.

and electrons. **Table 1.4** compares the three fundamental particles that make up an atom, and **Figure 1.9** gives an overall view of the atom.

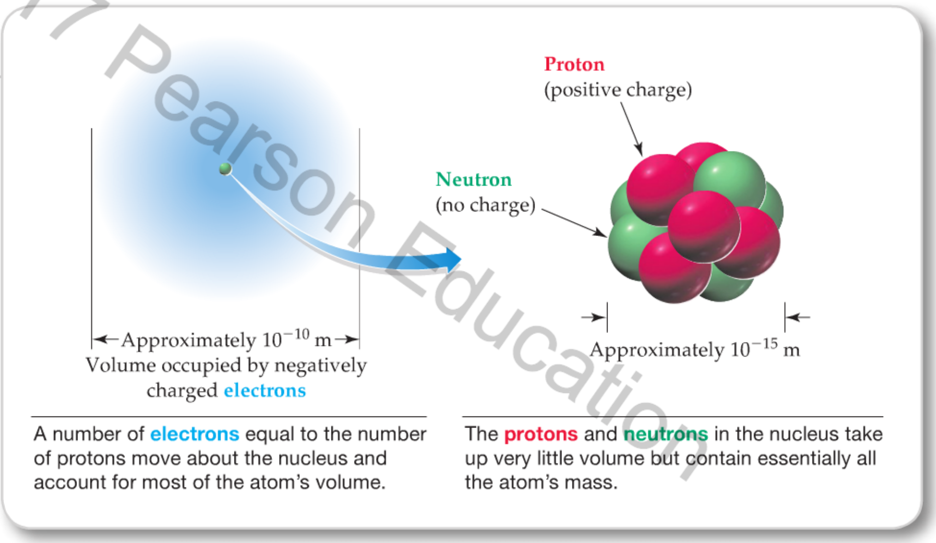
TABLE 1.4 A Comparison of Subatomic Particles

	Mass		Charge	
Particle	grams	u*	coulombs	*e*
Electron	$9.109\,383 \times 10^{-28}$	$5.485\,798 \times 10^{-4}$	$-1.602\,177 \times 10^{-19}$	-1
Proton	$1.672\,622 \times 10^{-24}$	$1.007\,276$	$+1.602\,177 \times 10^{-19}$	$+1$
Neutron	$1.674\,927 \times 10^{-24}$	$1.008\,665$	0	0

* The unified atomic mass unit (u) is defined in Section 1.9.

FIGURE 1.9

A view of the atom.



Worked Example 1.2

Calculations Using Atomic Size

Ordinary "lead" pencils contain no lead but instead are made of a form of carbon called graphite. If a pencil line is 0.35 mm wide and the diameter of a carbon atom is 1.5×10^{-10} m, how many atoms wide is the line?

STRATEGY

Begin with the known information, and set up an equation using appropriate conversion factors so that the unwanted units cancel. In this example, let's begin with the width of the pencil line in millimeters, convert to meters, and then divide the line width in meters by the diameter of a single atom in meters.

SOLUTION

$$\text{Atoms} = 0.35\ \cancel{\text{mm}} \times \frac{1\ \cancel{\text{m}}}{1000\ \cancel{\text{mm}}} \times \frac{1\ \text{atom}}{1.5 \times 10^{-10}\ \cancel{\text{m}}} = 2.3 \times 10^{6}\ \text{atoms}$$

✔ BALLPARK CHECK

A single carbon atom is about 10^{-10} m across, so it takes 10^{10} carbon atoms placed side by side to stretch 1 m, 10^{7} carbon atoms to stretch 1 mm, and about 0.3×10^{7} (or 3×10^{6}; 3 *million*) carbon atoms to stretch 0.35 mm. The estimate agrees with the solution.

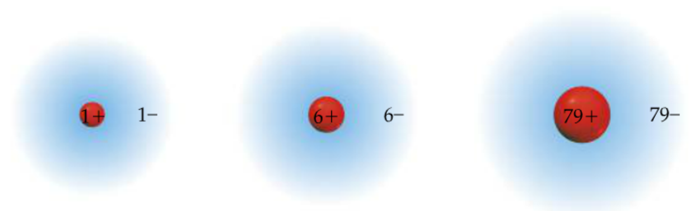
PROBLEM 1.6 The gold foil Rutherford used in his scattering experiment had a thickness of approximately 0.005 mm. If a single gold atom has a diameter of 2.9×10^{-8} cm and the atoms are arranged so as to touch each other in a straight line, how many atoms thick was Rutherford's foil?

PROBLEM 1.7 A small speck of carbon the size of a pinhead contains about 10^{19} atoms, the diameter of a carbon atom is 1.5×10^{-10} m, and the circumference of the Earth at the equator is 40,075 km. How many times around the Earth would the atoms from this speck of carbon extend if they were laid side by side?

1.8 ATOMIC NUMBERS

Thus far, we've described atoms only in general terms and have not yet answered the most important question: What is it that makes one atom different from another? How, for example, does an atom of gold differ from an atom of carbon? The answer turns out to be quite simple: *Elements differ from one another according to the number of protons in their atoms' nuclei*, a value called the element's **atomic number (*Z*)**. That is, all atoms of a given element contain the same number of protons in their nuclei. All hydrogen atoms, atomic number 1, have 1 proton; all helium atoms, atomic number 2, have 2 protons; all carbon atoms, atomic number 6, have 6 protons; and so on. Of course, every neutral atom also contains a number of electrons equal to its number of protons.

Atomic number (*Z*) = Number of protons in an atom's nucleus
= Number of electrons around an atom's nucleus



A hydrogen atom (1 proton; 1 electron)

A carbon atom (6 protons; 6 electrons)

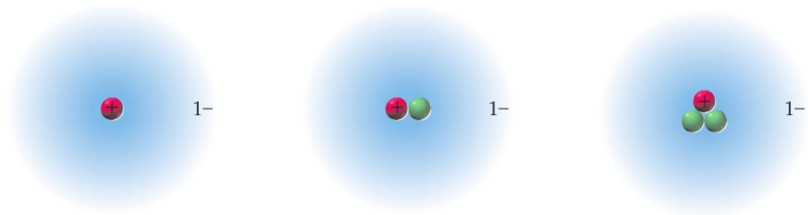
A gold atom (79 protons; 79 electrons)

In addition to protons, the nuclei of all atoms other than hydrogen also contain neutrons. The sum of the numbers of protons (Z) and neutrons (N) in an atom is called the atom's **mass number (*A*)**. That is, $A = Z + N$.

Mass number (*A*) = Number of protons (Z) + number of neutrons (N)

Most hydrogen atoms have 1 proton and no neutrons, so their mass number $A = 1 + 0 = 1$. Most helium atoms have 2 protons and 2 neutrons, so their mass number $A = 2 + 2 = 4$. Most carbon atoms have 6 protons and 6 neutrons, so their mass number $A = 6 + 6 = 12$; and so on. Except for hydrogen, atoms always contain at least as many neutrons as protons, although there is no simple way to predict how many neutrons a given atom will have.

Notice that we said *most* hydrogen atoms have mass number 1, most helium atoms have mass number 4, and most carbon atoms have mass number 12. In fact, different atoms of the same element can have different mass numbers depending on how many neutrons they have. Atoms with identical atomic numbers but different mass numbers are called **isotopes**. Hydrogen, for example, has three isotopes.



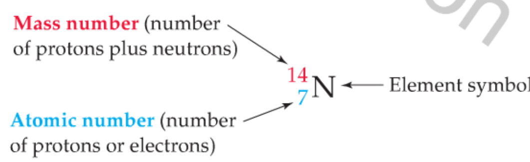
Protium—one proton (●) and no neutrons; mass number = 1

Deuterium—one proton (●) and one neutron (●); mass number = 2

Tritium—one proton (●) and two neutrons (●); mass number = 3

All hydrogen atoms have 1 proton in their nucleus (otherwise they wouldn't be hydrogen), but 99.985% of them have no neutrons. These hydrogen atoms, called *protium*, have mass number 1. In addition, 0.015% of hydrogen atoms, called *deuterium*, have 1 neutron and mass number 2. Still other hydrogen atoms, called *tritium*, have 2 neutrons and mass number 3. An unstable, radioactive isotope, tritium occurs only in trace amounts on Earth but is made artificially in nuclear reactors. As other examples, there are 15 known isotopes of nitrogen, only 2 of which occur naturally on Earth, and 25 known isotopes of uranium, only 3 of which occur naturally. In total, more than 3600 isotopes of the 118 known elements have been identified.

A specific isotope is represented by showing its element symbol, with its mass number as a left superscript and its atomic number as a left subscript. Thus, protium is represented as ${}^{1}_{1}H$, deuterium as ${}^{2}_{1}H$, and tritium as ${}^{3}_{1}H$. Similarly, the two naturally occurring isotopes of nitrogen are represented as ${}^{14}_{7}N$ (spoken as "nitrogen-14") and ${}^{15}_{7}N$ (nitrogen-15). The number of neutrons in an isotope is not given explicitly but can be calculated by subtracting the atomic number (subscript) from the mass number (superscript). For example, subtracting the atomic number 7 from the mass number 14 indicates that a ${}^{14}_{7}N$ atom has 7 neutrons.



The number of neutrons in an atom has relatively little effect on the atom's chemical properties. The chemical behavior of an element is determined almost entirely by the number of electrons it has, which in turn is determined by the number of protons in its nucleus. All three isotopes of hydrogen therefore behave similarly (although not identically) in their chemical reactions.

▲ Uranium-235 is used as fuel in this nuclear-powered icebreaker.

Worked Example 1.3

Interpreting an Isotope Symbol

The isotope of uranium used to generate nuclear power is ${}^{235}_{92}U$. How many protons, neutrons, and electrons does an atom of ${}^{235}_{92}U$ have?

STRATEGY

The atomic number (subscript 92) in the symbol ${}^{235}_{92}U$ indicates the number of protons and electrons in the atom. The number of neutrons is the difference between the mass number (superscript 235) and the atomic number (92).

SOLUTION

An atom of ${}^{235}_{92}U$ has 92 protons, 92 electrons, and $235 - 92 = 143$ neutrons.

Worked Example 1.4

Writing an Isotope Symbol

Element **X** is toxic to humans in high concentration but is essential to life in low concentrations. Identify element **X**, whose atoms contain 24 protons, and write the symbol for the isotope of **X** that has 28 neutrons.

STRATEGY

The number of protons in an atom's nucleus is the element's atomic number *Z*, given in the periodic table. The mass number *A* is the sum of the atomic number and the number of neutrons.

SOLUTION

According to the periodic table, the element with atomic number 24 is chromium (Cr). The particular isotope of chromium in this instance has a mass number of $24 + 28 = 52$ and is written $^{52}_{24}\text{Cr}$.

PROBLEM 1.8 The isotope $^{75}_{34}\text{Se}$ is used medically for the diagnosis of pancreatic disorders. How many protons, neutrons, and electrons does an atom of $^{75}_{34}\text{Se}$ have?

PROBLEM 1.9 Chlorine, one of the elements in common table salt (sodium chloride), has two main isotopes, with mass numbers 35 and 37. Look up the atomic number of chlorine, tell how many neutrons each isotope contains, and give the standard symbol for each.

PROBLEM 1.10 An atom of element **X** contains 47 protons and 62 neutrons. Identify the element, and write the symbol for the isotope in the standard format.

1.9 ATOMIC MASSES, ATOMIC WEIGHTS, AND THE MOLE

Pick up a pencil, and look at the small amount of tip visible. How many atoms (pencil lead is made of carbon) do you think are in the tip? One thing is certain: Atoms are so tiny that the number needed to make a visible sample is enormous. In fact, even the smallest speck of dust visible to the naked eye contains at least 10^{17} atoms. Thus, the mass in grams of a single atom is much too small a number for convenience and chemists therefore use a unit called either the *atomic mass unit (amu)* or, more correctly, the **unified atomic mass unit (u)**. Also known as a *dalton* (Da) in biological work, one unified atomic mass unit is defined as exactly 1/12 the mass of an atom of $^{12}_{6}\text{C}$ and is equal to $1.660\,538\,783 \times 10^{-24}$ g.

$$1\ \text{u} = \frac{\text{Mass of one } ^{12}_{6}\text{C atom}}{12} = 1.660\,538\,783 \times 10^{-24}\ \text{g}$$

Because the mass of an atom's electrons is negligible compared to the mass of its protons and neutrons, defining 1 u as 1/12 the mass of a $^{12}_{6}\text{C}$ atom means that protons and neutrons both have a mass of almost exactly 1 u (Table 1.4 on page 42). Thus, the mass of a specific atom—called the atom's **atomic mass**—is numerically close to the atom's mass number. A $^{1}_{1}\text{H}$ atom, for instance, has an atomic mass of **1**.007 825; a $^{235}_{92}\text{U}$ atom has an atomic mass of **235**.043 930; and so forth. In practice, atomic masses are taken to be dimensionless and the unit u is understood rather than specified.

Most elements occur naturally as a mixture of different isotopes. Thus, if you look at the periodic table inside the front cover, you'll see listed below the symbol for each element a value called the element's *atomic weight*. Again, the unit u is understood but not specified.