3

PERIODIC PROPERTIES OF THE ELEMENTS

The periodic table is a powerful tool for understanding and predicting the physical and chemical properties of elements. Typically, elements share common characteristics with neighbors that occupy the same column of the periodic table. Sodium, potassium, and rubidium are soft metals that react violently when they come in contact with water. Neon, argon, and krypton are colorless, chemically inert gases. Copper, silver, and gold are highly conductive metals that react slowly, if at all, with air and water.

As we saw in Chapter 6, this behavior arises from repeating patterns of electron configuration. Elements in the same column contain the same number of electrons in their **valence orbitals**—the occupied orbitals that hold the electrons involved in bonding. While elements from the same column tend to have similar properties, every element has its own identity. Nowhere are the differences between elements belonging to the same column more apparent than amongst the group 14 elements: carbon (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb). Carbon is a nonmetal that comes in many different forms, including diamond, one of the hardest known substances. Moving to the bottom of group 14, we find lead, which is a relatively soft metal. Our bodies and those of nearly every living thing on planet Earth are made from molecules that contain carbon, while the toxicity of lead is well documented. In between we find silicon and germanium, both of which have the same arrangement of atoms as diamond and are semiconductors used extensively in integrated circuits and computers. Tin has a split personality in the sense that it behaves as a metal at temperatures above 13 °C (β-Sn or white tin) and as a semiconductor below 13 °C (α-Sn or gray tin).

In this chapter, we explore several fundamental characteristics of elements. We see how these characteristics change as we move across a row or down a column of the periodic table, which in turn helps us rationalize and predict the physical and chemical properties of the elements.

◀ **THE LIGHTEST ELEMENT** in group 14, carbon, comes in many different forms including charcoal, whose rough texture, ability to draw light or intensely dark lines, and easy removability gives it a wide range of applications.

WHAT'S AHEAD

7.1 ▶ Development of the Periodic Table
Learn about the discovery and key moments in the development of the periodic table.

7.2 ▶ Effective Nuclear Charge
Understand the concept of *effective nuclear charge*, the force between the outer or valence electrons and the nucleus, and how it varies throughout the periodic table.

7.3 ▶ Sizes of Atoms and Ions Explore the relative sizes of atoms and ions, both of which follow trends that are related to their placement in the periodic table and the trends in effective nuclear charge.

7.4 ▶ Ionization Energy Learn that *ionization energy* is the energy required to remove one or more electrons from an atom. The periodic trends in ionization energy depend on variations in effective nuclear charge and atomic radii.

7.5 ▶ Electron Affinity Learn that *electron affinity* is the energy released when an electron is added to an atom and understand its periodic trends.

7.6 ▶ Metals, Nonmetals, and Metalloids
Differentiate the physical and chemical properties of metals from those of nonmetals. The differences in properties arise from the fundamental characteristics of atoms, particularly ionization energy. Metalloids display properties that are intermediate between those of metals and those of nonmetals.

7.7 ▶ Trends for Group 1 and Group 2 Metals Examine some periodic trends in the chemical and physical properties of metals belonging to groups 1 and 2.

7.8 ▶ Trends for Selected Nonmetals
Investigate some of the periodic trends in the chemical and physical properties of hydrogen and the elements in groups 16, 17, and 18.

7.1 | Development of the Periodic Table

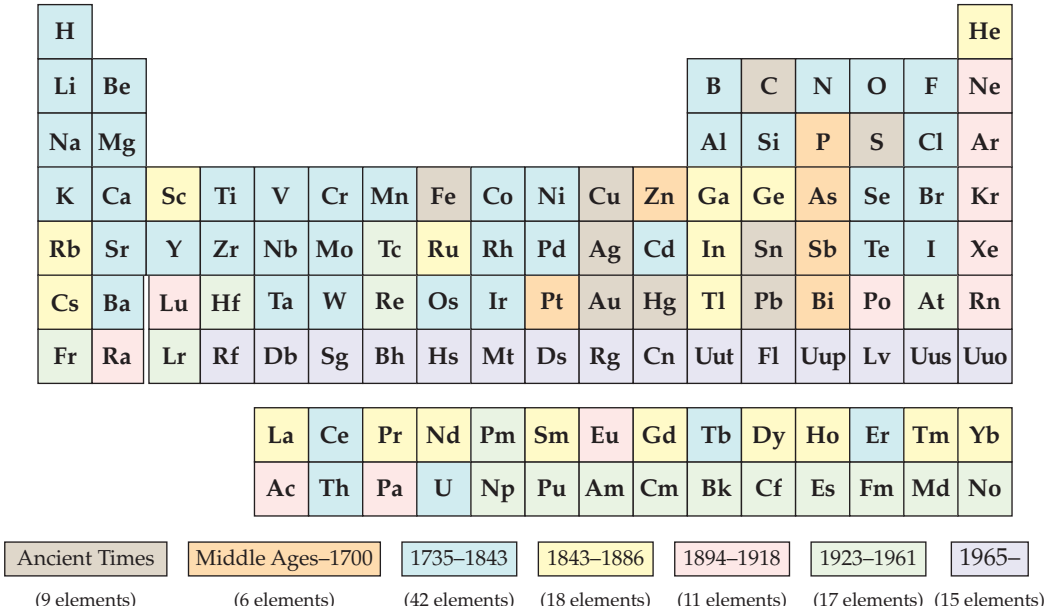
The discovery of chemical elements has been ongoing since ancient times (**Figure 7.1**). Certain elements, such as gold (Au), appear in nature in elemental form and were thus discovered thousands of years ago. In contrast, some elements, such as technetium (Tc), are radioactive and intrinsically unstable. We know about them only because of technology developed during the twentieth century.

The majority of elements readily form compounds and, consequently, are not found in nature in their elemental form. For centuries, therefore, scientists were unaware of their existence. During the early nineteenth century, advances in chemistry made it easier to isolate elements from their compounds. As a result, the number of known elements more than doubled from 31 in 1800 to 63 by 1865.

As the number of known elements increased, scientists began classifying them. In 1869, Dmitri Mendeleev (1834–1907) in Russia and Lothar Meyer (1830–1895) in Germany published nearly identical classification schemes. Both noted that similar chemical and physical properties recur periodically when the elements are arranged in order of increasing atomic weight. Scientists at that time had no knowledge of atomic numbers. Atomic weights, however, generally increase with increasing atomic number, so both Mendeleev and Meyer fortuitously arranged the elements in nearly the proper sequence.

Although Mendeleev and Meyer came to essentially the same conclusion about the periodicity of elemental properties, Mendeleev is given credit for advancing his ideas more vigorously and stimulating new work. His insistence that elements with similar characteristics be listed in the same column forced him to leave blank spaces in his table.

Go Figure Copper, silver, and gold have all been known since ancient times, whereas most of the other metals were not isolated until much later. Can you suggest an explanation?



▲ **Figure 7.1** Discovering the elements.

TABLE 7.1 Comparison of the Properties of Eka-Silicon Predicted by Mendeleev with the Observed Properties of Germanium

Property	Mendeleev's Predictions for Eka-Silicon (made in 1871)	Observed Properties of Germanium (discovered in 1886)
Atomic weight	72	72.59
Density (g/cm^3)	5.5	5.35
Specific heat (J/g-K)	0.305	0.309
Melting point (°C)	High	947
Color	Dark gray	Grayish white
Formula of oxide	XO_2	GeO_2
Density of oxide (g/cm^3)	4.7	4.70
Formula of chloride	XCl_4	$GeCl_4$
Boiling point of chloride (°C)	A little under 100	84

For example, both gallium (Ga) and germanium (Ge) were unknown to Mendeleev. He boldly predicted their existence and properties, referring to them as *eka-aluminum* ("under" aluminum) and *eka-silicon* ("under" silicon), respectively, after the elements under which they appeared in his table. When these elements were discovered, their properties closely matched those predicted by Mendeleev, as shown in **Table 7.1**.

In 1913, two years after Rutherford proposed the nuclear model of the atom (Section 2.2), English physicist Henry Moseley (1887–1915) developed the concept of atomic numbers. Bombarding different elements with high-energy electrons, Moseley found that each element produced X rays of a unique frequency and that the frequency generally increased as the atomic mass increased. He arranged the X-ray frequencies in order by assigning a unique whole number, called an *atomic number*, to each element. Moseley correctly identified the atomic number as the number of protons in the nucleus of the atom. (Section 2.3)

The concept of atomic number clarified some problems in the periodic table of Moseley's day, which was based on atomic weights. For example, the atomic weight of Ar (atomic number 18) is greater than that of K (atomic number 19), yet the chemical and physical properties of Ar are much more like those of Ne and Kr than like those of Na and Rb. When the elements are arranged in order of increasing atomic number, Ar and K appear in their correct places in the table. Moseley's studies also made it possible to identify "holes" in the periodic table, which led to the discovery of new elements.

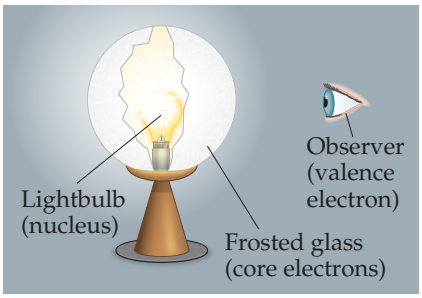
Give It Some Thought

Looking at the periodic table on the front inside cover, can you find an example other than Ar and K where the order of the elements would be different if the elements were arranged in order of increasing atomic weight?

7.2 Effective Nuclear Charge

Many properties of atoms depend on electron configuration and on how strongly the outer electrons in the atoms are attracted to the nucleus. Coulomb's law tells us that the strength of the interaction between two electrical charges depends on the magnitudes of the charges and on the distance between them. (Section 2.3) Thus, the attractive force between an electron and the nucleus depends on the magnitude of the nuclear charge and on the average distance between the nucleus and the electron. The force increases as the nuclear charge increases and decreases as the electron moves farther from the nucleus.

Understanding the attraction between the electron and the nucleus in a hydrogen atom is straightforward because we have only one electron and one proton. In a many-electron atom, however, the situation is more complicated. In addition to the



▲ **Figure 7.2 An analogy for effective nuclear charge.** We envision the nucleus as a light bulb, the core electrons as a frosted glass lampshade, and a valence electron as an observer. The amount of light seen by the observer depends on the intensity of the light bulb and the screening by the frosted glass lampshade.

attraction of each electron to the nucleus, each electron experiences the repulsion due to other electrons. These electron–electron repulsions cancel some of the attraction of the electron to the nucleus so that the electron experiences less attraction than it would if the other electrons weren't there. In essence, each electron in a many-electron atom is *screened* from the nucleus by the other electrons. It therefore experiences a net attraction that is smaller than it would experience in the absence of other electrons.

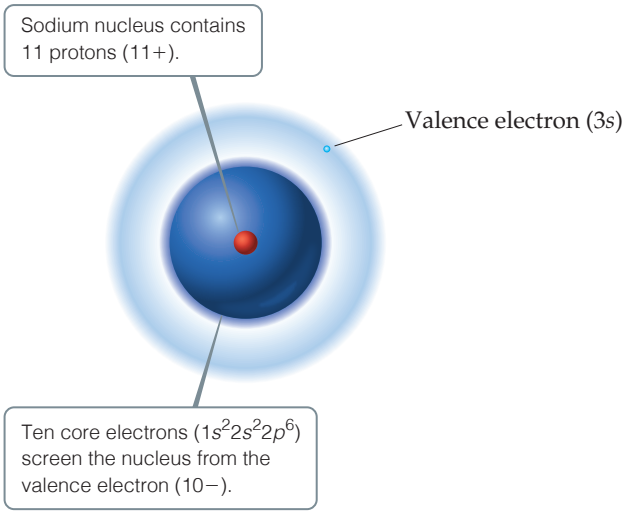
How can we account for the combination of nuclear attraction and electron repulsions for our electron of interest? The simplest way to do so is to imagine that the electron experiences a net attraction that is the result of the nuclear attraction decreased by the electron–electron repulsions. We call this partially screened nuclear charge the **effective nuclear charge**, Z_{eff}. Because the full attractive force of the nucleus has been decreased by the electron repulsions, we see that the effective nuclear charge is always less than the *actual* nuclear charge ($Z_{\text{eff}} < Z$). We can define the amount of screening of the nuclear charge quantitatively by using a *screening constant*, S, such that

$$Z_{\text{eff}} = Z - S \qquad [7.1]$$

where S is a positive number. For a valence electron, most of the shielding is due to the core electrons, which are much closer to the nucleus. As a result, for the valence electrons in an atom *the value of S is usually close to the number of core electrons in the atom*. (Electrons in the same valence shell do not screen one another very effectively, but they do affect the value of S slightly; see "A Closer Look: Effective Nuclear Charge.")

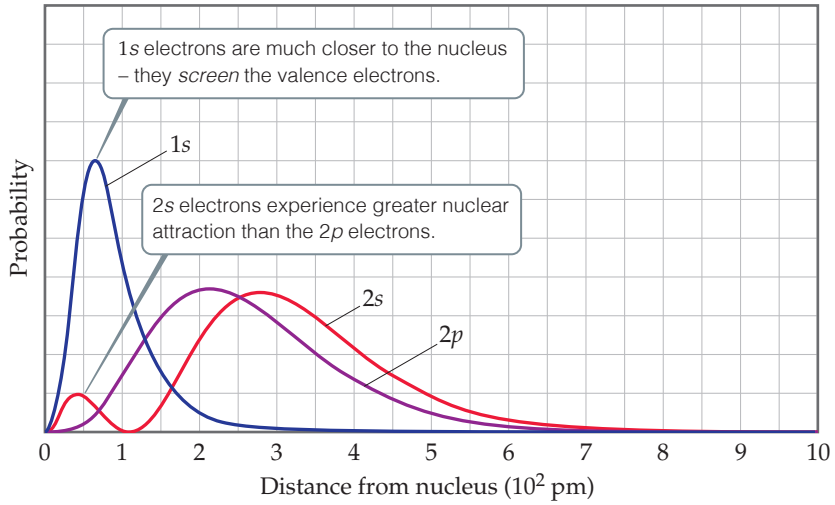
To understand better the notion of effective nuclear charge, we can use an analogy of a light bulb with a frosted glass shade (**Figure 7.2**). The light bulb represents the nucleus, and the observer is the electron of interest, which is usually a valence electron. The amount of light that the electron "sees" is analogous to the amount of net nuclear attraction experienced by the electron. The other electrons in the atom, especially the core electrons, act like a frosted glass lampshade, decreasing the amount of light that gets to the observer. If the light bulb gets brighter while the lampshade stays the same (Z increases), more light is observed. Likewise, if the lampshade gets thicker (S increases), less light is observed. We will find it helpful to keep this analogy in mind as we discuss trends in effective nuclear charge.

Let's consider what we would expect for the magnitude of Z_{eff} for the sodium atom. Sodium has the electron configuration $[\text{Ne}]3s^1$. The nuclear charge is $Z = 11+$, and there are 10 core electrons ($1s^2 2s^2 2p^6$), which serve as a "lampshade" to screen the nuclear charge "seen" by the $3s$ electron. Therefore, in the simplest approach, we expect S to equal 10 and the $3s$ electron to experience an effective nuclear charge of $Z_{\text{eff}} = 11 - 10 = 1+$ (**Figure 7.3**). The situation is more complicated, however, because the $3s$ electron has a small probability of being very close to the nucleus, in the region occupied by the core electrons. (Section 6.6) Thus, this electron experiences a greater net attraction than our simple $S = 10$ model suggests: The actual value of Z_{eff} for the $3s$ electron in Na is $Z_{\text{eff}} = 2.5+$. In other words, because there is a small



▶ **Figure 7.3 Effective nuclear charge.** The effective nuclear charge experienced by the $3s$ electron in a sodium atom depends on the 11+ charge of the nucleus and the 10− charge of the core electrons.

Go Figure Which electron has a higher probability of being found within 50 pm of the nucleus, one in a 2*s* orbital or one in a 2*p* orbital? Which orbital, 2*s* or 2*p*, will be lower in energy in a multielectron atom?



▲ **Figure 7.4 Comparison of 1*s*, 2*s*, and 2*p* radial probability functions.**

probability that the 3*s* electron is close to the nucleus, the value of S in Equation 7.1 changes from 10 to 8.5.

The notion of effective nuclear charge also explains an important effect we noted in Section 6.7: For a many-electron atom, the energies of orbitals with the same n value increase with increasing l value. For example, in the carbon atom, whose electron configuration is $1s^2 2s^2 2p^2$, the energy of the 2*p* orbital ($l = 1$) is higher than that of the 2*s* orbital ($l = 0$), even though both orbitals are in the $n = 2$ shell (Figure 6.25). This difference in energies is due to the radial probability functions for the orbitals (**Figure 7.4**). We see first that the 1*s* electrons are much closer to the nucleus—they serve as an effective "lampshade" for the 2*s* and 2*p* electrons. Notice next that the 2*s* probability function has a small peak fairly close to the nucleus, whereas the 2*p* probability function does not. As a result, a 2*s* electron is not screened as much by the core orbitals as is a 2*p* electron. The greater attraction between the 2*s* electron and the nucleus leads to a lower energy for the 2*s* orbital than for the 2*p* orbital. The same reasoning explains the general trend in orbital energies ($ns < np < nd$) in many-electron atoms.

Finally, let's examine trends in valence-electron Z_{eff} values.

The effective nuclear charge increases from left to right across any period of the periodic table.

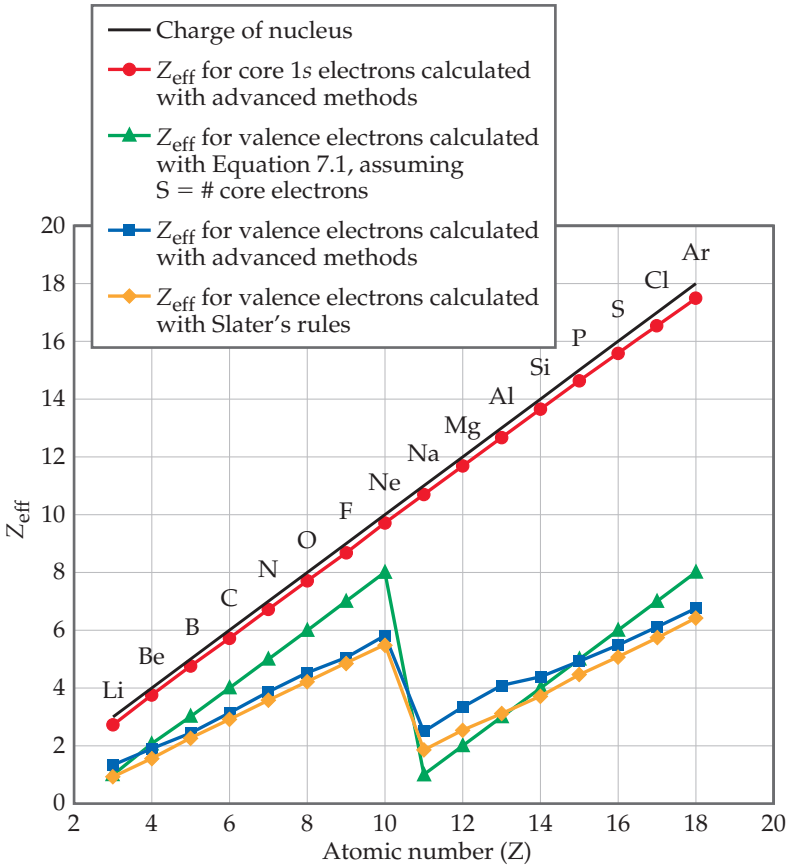
Although the number of core electrons stays the same across the period, the number of protons increases—in our analogy, we are increasing the brightness of the light bulb while keeping the shade the same. The valence electrons added to counterbalance the increasing nuclear charge screen one another ineffectively. Thus, Z_{eff} increases steadily. For example, the two core electrons of lithium ($1s^2 2s^1$) screen the 2*s* valence electron from the 3+ nucleus fairly efficiently. Consequently, the valence electron experiences an effective nuclear charge of roughly $3 - 2 = 1+$. For beryllium ($1s^2 2s^2$) the effective nuclear charge experienced by each valence electron is larger because here the two core 1*s* electrons screen a 4+ nucleus, and each 2*s* electron only partially screens the other. Consequently, the effective nuclear charge experienced by each 2*s* electron is about $4 - 2 = 2+$.

Going down a column, the effective nuclear charge experienced by valence electrons changes far less than it does across a period. For example, using our simple estimate for S, we would expect the effective nuclear charge experienced by the valence electrons in lithium and sodium to be about the same, roughly $3 - 2 = 1+$ for lithium and $11 - 10 = 1+$ for sodium. In fact, however, *effective nuclear charge increases slightly as we go down a column*

A CLOSER LOOK Effective Nuclear Charge

To get a sense of how effective nuclear charge varies as both nuclear charge and number of electrons increase, consider Figure 7.5. Although the details of how the Z_{eff} values in the graph were calculated are beyond the scope of our discussion, the trends are instructive.

The effective nuclear charge felt by the outermost electrons is smaller than that felt by inner electrons because of screening by the inner electrons. In addition, the effective nuclear charge felt by the outermost electrons does not increase as steeply with increasing atomic number because the valence electrons make a small but nonnegligible contribution to the screening constant *S*. The most striking feature associated with the Z_{eff} value for the outermost electrons is the sharp drop between the last period 2 element (Ne) and the first period 3 element (Na). This drop reflects the fact that the core electrons are much more effective than the valence electrons at screening the nuclear charge.



▲ **Figure 7.5 Variations in effective nuclear charge for period 2 and period 3 elements.** Moving from one element to the next in the periodic table, the increase in Z_{eff} felt by the innermost (1*s*) electrons (red circles) closely tracks the increase in nuclear charge *Z* (black line) because these electrons are not screened much. The results of several methods to calculate Z_{eff} for valence electrons are shown in other colors.

Because Z_{eff} can be used to understand many physically measurable quantities, it is desirable to have a simple method for estimating it. The value of *Z* in Equation 7.1 is known exactly, so the challenge boils down to estimating the value of *S*. In the text, we estimated *S* very simply by assuming that each core electron contributes 1.00 to *S* and the outer electrons contribute nothing. A more accurate approach was developed by John Slater (1900–1976), however, and we can use his approach if we limit ourselves to elements that do not have electrons in *d* or *f* subshells.

Electrons for which the principal quantum number *n* is larger than the value of *n* for the electron of interest contribute 0 to the value of *S*. Electrons with the same value of *n* as the electron of interest contribute 0.35 to the value of *S*. Electrons that have principal quantum number $n - 1$ contribute 0.85, while those with even smaller values of *n* contribute 1.00. For example, consider fluorine, which has the ground-state electron configuration $1s^2 2s^2 2p^5$. For a valence electron in fluorine, Slater's rules tell us that $S = (0.35 \times 6) + (0.85 \times 2) = 3.8$. (Slater's rules ignore the contribution of an electron to itself in screening; therefore, we consider only six $n = 2$ electrons, not all seven). Thus, $Z_{eff} = Z - S = 9 - 3.8 = 5.2+$, a little lower than the simple estimate of $9 - 2 = 7+$.

Values of Z_{eff} estimated using the simple method outlined in the text, as well as those estimated with Slater's rules, are plotted in Figure 7.5. While neither of these methods exactly replicates the values of Z_{eff} obtained from more sophisticated calculations, both methods effectively capture the periodic variation in Z_{eff}. While Slater's approach is more accurate, the method outlined in the text does a reasonably good job of estimating Z_{eff} despite its simplicity. For our purposes, therefore, we can assume that the screening constant *S* in Equation 7.1 is roughly equal to the number of core electrons.

Related Exercises: 7.15, 7.16, 7.31, 7.32, 7.80, 7.81, 7.110

because the more diffuse core electron cloud is less able to screen the valence electrons from the nuclear charge. In the case of the alkali metals, Z_{eff} increases from 1.3+ for lithium, to 2.5+ for sodium, to 3.5+ for potassium.

Give It Some Thought

Which would you expect to experience a greater effective nuclear charge, a 3*p* electron of an Ar atom or a 4*s* electron of a Ca atom?

7.3 Sizes of Atoms and Ions

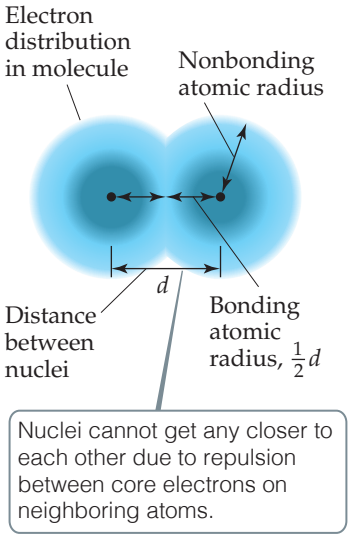
It is tempting to think of atoms as hard, spherical objects. According to the quantum-mechanical model, however, atoms do not have sharply defined boundaries at which the electron distribution becomes zero. (Section 6.5) Nevertheless, we can define atomic size in several ways, based on the distances between atoms in various situations.

Imagine a collection of argon atoms in the gas phase. When two of these atoms collide, they ricochet apart like colliding billiard balls. This ricocheting happens because the electron clouds of the colliding atoms cannot penetrate each other to any significant extent. The shortest distance separating the two nuclei during such collisions is twice the radii of the atoms. We call this radius the *nonbonding atomic radius* or the *van der Waals* radius (**Figure 7.6**).

In molecules, the attractive interaction between any two adjacent atoms is what we recognize as a chemical bond. We discuss bonding in Chapters 8 and 9. For now, we need to realize that two bonded atoms are closer together than they would be in a nonbonding collision where the atoms ricochet apart. We can therefore define an atomic radius based on the distance between the nuclei when two atoms are bonded to each other, shown as distance d in Figure 7.6. The **bonding atomic radius** for any atom in a molecule is equal to half of the bond distance d. Note from Figure 7.6 that the bonding atomic radius (also known as the *covalent radius*) is smaller than the nonbonding atomic radius. Unless otherwise noted, we mean the bonding atomic radius when we speak of the "size" of an atom.

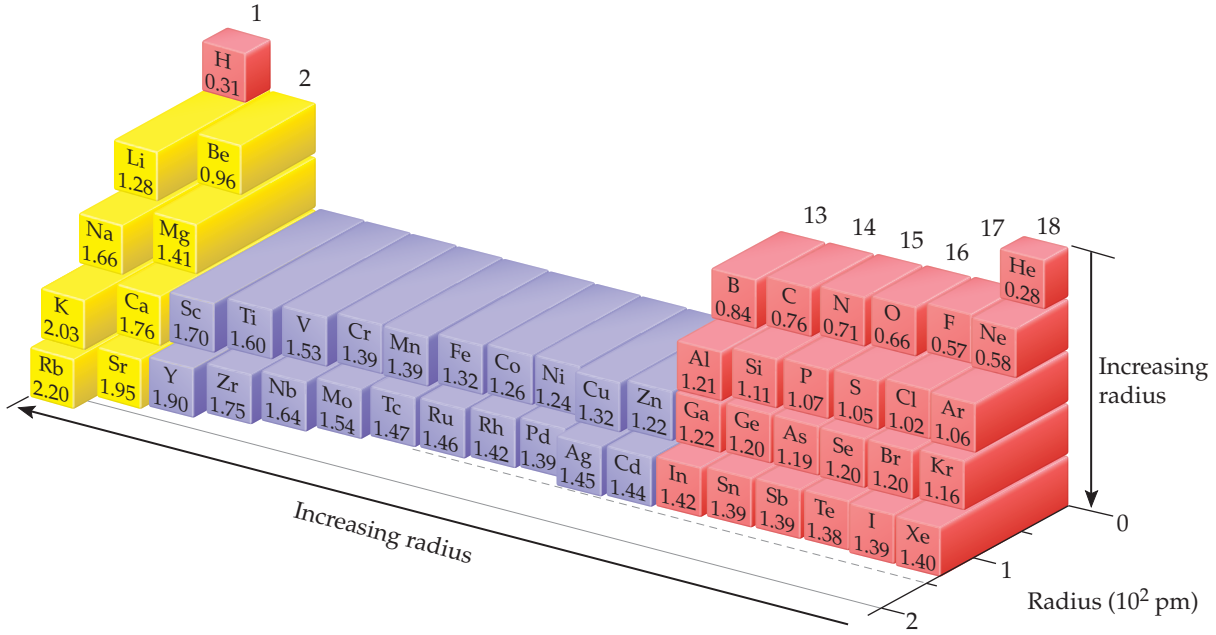
Although it is very difficult to measure the nonbonding atomic radius of an atom, scientists have developed a variety of techniques for measuring the distances separating nuclei in molecules. From observations of these distances in many molecules, each element can be assigned a bonding atomic radius. For example, in the I_2 molecule, the distance separating the nuclei is observed to be 266 pm, which means the bonding atomic radius of an iodine atom in I_2 is $(266\text{ pm})/2 = 133\text{ pm}$. Similarly, the distance separating adjacent carbon nuclei in diamond (a three-dimensional solid network of carbon atoms) is 154 pm; thus, the bonding atomic radius of carbon in diamond is 77 pm. By using structural information on more than 30,000 substances, a consistent set of bonding atomic radii of the elements can be defined (**Figure 7.7**). Note that for the lighter noble gases, the bonding atomic radii must be estimated because there are no known compounds of these elements.

The atomic radii in Figure 7.7 allows us to estimate bond lengths in molecules. For example, the bonding atomic radii for C and Cl are 76 pm and 102 pm, respectively. In CCl_4 the measured length of the C—Cl bond is 177 pm, very close to the sum $(76 + 102\text{ pm})$ of the bonding atomic radii of Cl and C.



▲ **Figure 7.6** **Distinction between nonbonding and bonding atomic radii within a molecule.**

Go Figure Which part of the periodic table (top/bottom, left/right) has the elements with the largest atoms?

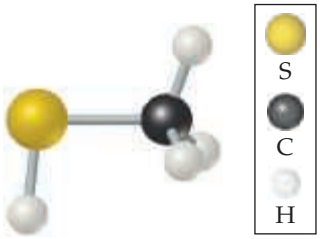


▲ **Figure 7.7** **Trends in bonding atomic radii for periods 1 through 5.**

Sample Exercise 7.1

Bond Lengths in a Molecule

Natural gas used in home heating and cooking is odorless. Because natural gas leaks pose the danger of explosion or suffocation, various smelly substances are added to the gas to allow detection of a leak. One such substance is methyl mercaptan, CH_3SH. Use Figure 7.7 to predict the lengths of the C—S, C—H, and S—H bonds in this molecule.



Methyl mercaptan

SOLUTION

Analyze and Plan We are given three bonds and told to use Figure 7.7 for bonding atomic radii. We will assume that each bond length is the sum of the bonding atomic radii of the two atoms involved.

Solve

$$\begin{aligned} \text{C—S bond length} &= \text{bonding atomic radius of C} \\ &\quad + \text{bonding atomic radius of S} \\ &= 76\ \text{pm} + 105\ \text{pm} = 181\ \text{pm} \\ \text{C—H bond length} &= 76\ \text{pm} + 31\ \text{pm} = 107\ \text{pm} \\ \text{S—H bond length} &= 105\ \text{pm} + 31\ \text{pm} = 136\ \text{pm} \end{aligned}$$

Check The experimentally determined bond lengths are C—S = 182 pm, C—H = 110 pm, and S—H = 133 pm. (In general, the lengths of bonds involving hydrogen show larger deviations from the values predicted from bonding atomic radii than do bonds involving larger atoms.)

Comment Notice that our estimated bond lengths are close but not exact matches to the measured bond lengths. Bonding atomic radii must be used with some caution in estimating bond lengths.

Practice Exercise 1

Hypothetical elements X and Y form a molecule XY_2, in which both Y atoms are bonded to atom X (and not to one another). The X—X distance in the elemental form of X is 204 pm, and the Y—Y distance in elemental Y is 168 pm. What would you predict for the X—Y distance in the XY_2 molecule?
(**a**) 84 pm (**b**) 102 pm (**c**) 186 pm (**d**) 270 pm (**e**) 372 pm

Practice Exercise 2

Using Figure 7.7, predict which is longer, the P—Br bond in PBr_3 or the As—Cl bond in $AsCl_3$.

Periodic Trends in Atomic Radii

Figure 7.7 shows two interesting trends:

1. *Within each group, bonding atomic radius tends to increase from top to bottom*. This trend results primarily from the increase in the principal quantum number (n) of the outer electrons. As we go down a column, the outer electrons have a greater probability of being farther from the nucleus, causing the atomic radius to increase.
2. *Within each period, bonding atomic radius tends to decrease from left to right* (although there are some minor exceptions, such as for Cl to Ar or As to Se). The major factor influencing this trend is the increase in effective nuclear charge Z_{eff} across a period. The increasing effective nuclear charge steadily draws the valence electrons closer to the nucleus, causing the bonding atomic radius to decrease.

Periodic Trends in Ionic Radii

Just as bonding atomic radii can be determined from interatomic distances in molecules, ionic radii can be determined from interatomic distances in ionic compounds. Like the

Give It Some Thought

In Section 7.2 we said that Z_{eff} generally increases when you move down a column of the periodic table, whereas in Chapter 6 we saw that the "size" of an orbital increases as the principal quantum number n increases. With respect to atomic radii, do these trends work together or against each other? Which effect is larger?

Sample Exercise 7.2

Predicting Relative Sizes of Atomic Radii

Referring to the periodic table, arrange (as much as possible) the atoms B, C, Al, and Si in order of increasing size.

SOLUTION

Analyze and Plan We are given the chemical symbols for four elements and told to use their relative positions in the periodic table to predict the relative size of their atomic radii. We can use the two periodic trends described in the text to help with this problem.

Solve

B and C are in the same period, with C to the right of B. Therefore, we expect the radius of C to be smaller than that of B because radii usually decrease as we move across a period.	radius C $<$ radius B
Al and Si are in the same period, with Si to the right of Al.	radius Si $<$ radius Al
The radius increases as we move down a group with Al and B belonging to the same group, as do C and Si.	radius B $<$ radius Al radius C $<$ radius Si
Combining these comparisons, we can conclude that C has the smallest radius and Al the largest. Unfortunately, the two periodic trends available to us do not supply enough information to determine the relative sizes of B and Si.	radius C $<$ radius B $\sim$ radius Si $<$ radius Al

Check Referring back to Figure 7.7, we can obtain numerical values for each atomic radius that allow us to say that the radius of Si is greater than that of B.

$$\text{C}(76\text{ pm}) < \text{B}\,(84\text{ pm}) < \text{Si}\,(111\text{ pm}) < \text{Al}\,(121\text{ pm})$$

If you examine Figure 7.7 carefully, you will discover that for the *s*- and *p*-block elements the increase in radius moving one element down a column tends to be greater than the increase moving one element left across a row. There are exceptions, however.

Comment Note that the trends we have just discussed are for the *s*- and *p*-block elements. As seen in Figure 7.7, the transition elements do not show a regular decrease moving across a period.

Practice Exercise 1

By referring to the periodic table, but not to Figure 7.7, place the following atoms in order of increasing bonding atomic radius: N, O, P, Ge.

(**a**) N $<$ O $<$ P $<$ Ge
(**b**) P $<$ N $<$ O $<$ Ge
(**c**) O $<$ N $<$ Ge $<$ P
(**d**) O $<$ N $<$ P $<$ Ge
(**e**) N $<$ P $<$ Ge $<$ O

Practice Exercise 2

Arrange Be, C, K, and Ca in order of increasing atomic radius.

size of an atom, the size of an ion depends on its nuclear charge, the number of electrons it possesses, and the orbitals in which the valence electrons reside. When a cation is formed from a neutral atom, electrons are removed from the occupied atomic orbitals that are the most spatially extended from the nucleus. Also, when a cation is formed the number of electron–electron repulsions is reduced. Therefore, *cations are smaller than their parent atoms* (**Figure 7.8**). The opposite is true of anions. When electrons are added to an atom to form an anion, the increased electron–electron repulsions cause the electrons to spread out more in space. Thus, *anions are larger than their parent atoms.*

Sample Exercise 7.3

Predicting Relative Sizes of Atomic and Ionic Radii

Arrange Mg^{2+}, Ca^{2+}, and Ca in order of decreasing radius.

SOLUTION

Cations are smaller than their parent atoms, and so $Ca^{2+} < Ca$. Because Ca is below Mg in group 2A, Ca^{2+} is larger than Mg^{2+}. Consequently, $Ca > Ca^{2+} > Mg^{2+}$.

Practice Exercise 1

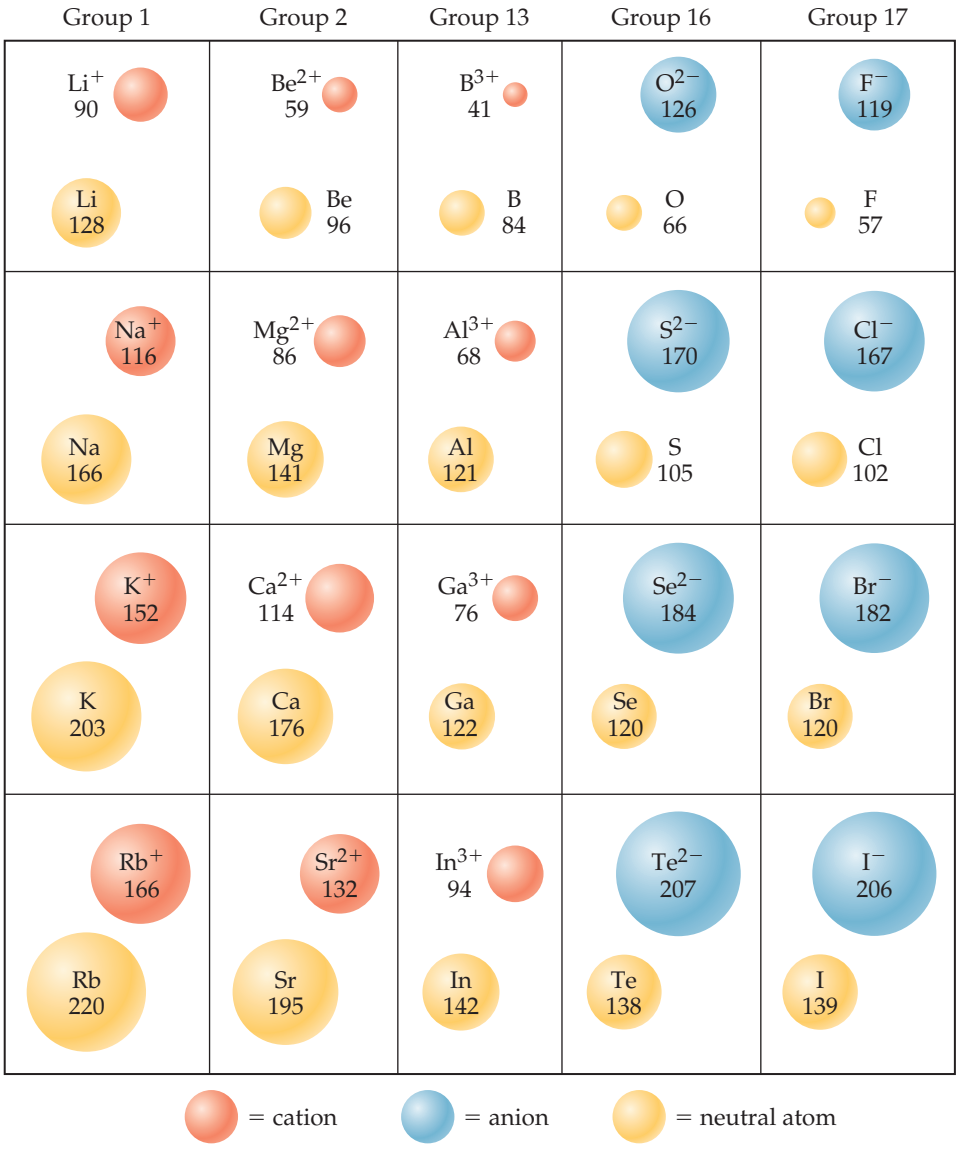
Arrange the following atoms and ions in order of increasing ionic radius: F, S^{2-}, Cl, and Se^{2-}.

(**a**) F $<$ S^{2-} $<$ Cl $<$ Se^{2-}
(**b**) F $<$ Cl $<$ S^{2-} $<$ Se^{2-}
(**c**) F $<$ S^{2-} $<$ Se^{2-} $<$ Cl
(**d**) Cl $<$ F $<$ Se^{2-} $<$ S^{2-}
(**e**) S^{2-} $<$ F $<$ Se^{2-} $<$ Cl

Practice Exercise 2

Which of the following atoms and ions is largest: S^{2-}, S, O^{2-}?

Go Figure How do cations of the same charge change in radius as you move down a column in the periodic table?



▲ **Figure 7.8 Cation and anion size.** Radii, in picometers, of atoms and their ions for five groups of representative elements.

For ions carrying the same charge, ionic radius increases as we move down a column in the periodic table (Figure 7.8). In other words, as the principal quantum number of the outermost occupied orbital of an ion increases, the radius of the ion increases.

An **isoelectronic series** is a group of ions all containing the same number of electrons. For example, each ion in the isoelectronic series O^{2-}, F^-, Na^+, Mg^{2+}, and Al^{3+} has 10 electrons. In any isoelectronic series, we can list the members in order of increasing atomic number; therefore, the nuclear charge increases as we move through the series. Because the number of electrons remains constant, ionic radius decreases with increasing nuclear charge as the electrons are more strongly attracted to the nucleus:

Increasing nuclear charge ⟶

8 protons	9 protons	11 protons	12 protons	13 protons
10 electrons	10 electrons	10 electrons	10 electrons	10 electrons
O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
126 pm	119 pm	116 pm	86 pm	68 pm

Decreasing ionic radius ⟶

Notice the positions and atomic numbers of these elements in the periodic table. The nonmetal anions precede the noble gas Ne in the table. The metal cations follow Ne. Oxygen, the largest ion in this isoelectronic series, has the lowest atomic number, 8. Aluminum, the smallest of these ions, has the highest atomic number, 13.

Sample Exercise 7.4

Ionic Radii in an Isoelectronic Series

Arrange the ions K^+, Cl^-, Ca^{2+}, and S^{2-} in order of decreasing size.

SOLUTION

This is an isoelectronic series, with all ions having 18 electrons. In such a series, size decreases as nuclear charge (atomic number) increases. The atomic numbers of the ions are S 16, Cl 17, K 19, Ca 20. Thus, the ions decrease in size in the order $S^{2-} > Cl^- > K^+ > Ca^{2+}$.

Practice Exercise 1

Arrange the following ions in order of increasing ionic radius: Br^-, Rb^+, Se^{2-}, Sr^{2+}, Te^{2-}.

(**a**) $Sr^{2+} < Rb^+ < Br^- < Se^{2-} < Te^{2-}$
(**b**) $Br^- < Sr^{2+} < Se^{2-} < Te^{2-} < Rb^+$
(**c**) $Rb^+ < Sr^{2+} < Se^{2-} < Te^{2-} < Br^-$
(**d**) $Rb^+ < Br^- < Sr^{2+} < Se^{2-} < Te^{2-}$
(**e**) $Sr^{2+} < Rb^+ < Br^- < Te^{2-} < Se^{2-}$

Practice Exercise 2

In the isoelectronic series Ca^{2+}, Cs^+, Y^{3+}, which ion is largest?

CHEMISTRY PUT TO WORK Ionic Size and Lithium-Ion Batteries

Ionic size plays a major role in determining the properties of devices that rely on movement of ions, such as batteries. "Lithium-ion" batteries, which have become common energy sources for electronic devices such as cell phones, iPads, laptop computers, and electric vehicles rely in part on the small size of the lithium ion for their operation.

A fully charged battery spontaneously produces an electric current and, therefore, power when its positive and negative electrodes are connected to an electrical load, such as a device to be powered. The positive electrode is called the anode, and the negative electrode is called the cathode. The materials used for the electrodes in lithium-ion batteries are under intense development. Currently, the anode material is graphite, a form of carbon, and the cathode is a transition metal oxide, often lithium cobalt oxide, $LiCoO_2$ (**Figure 7.9**). Between anode and cathode is a *separator,* a porous solid material that allows the passage of lithium ions but not electrons.

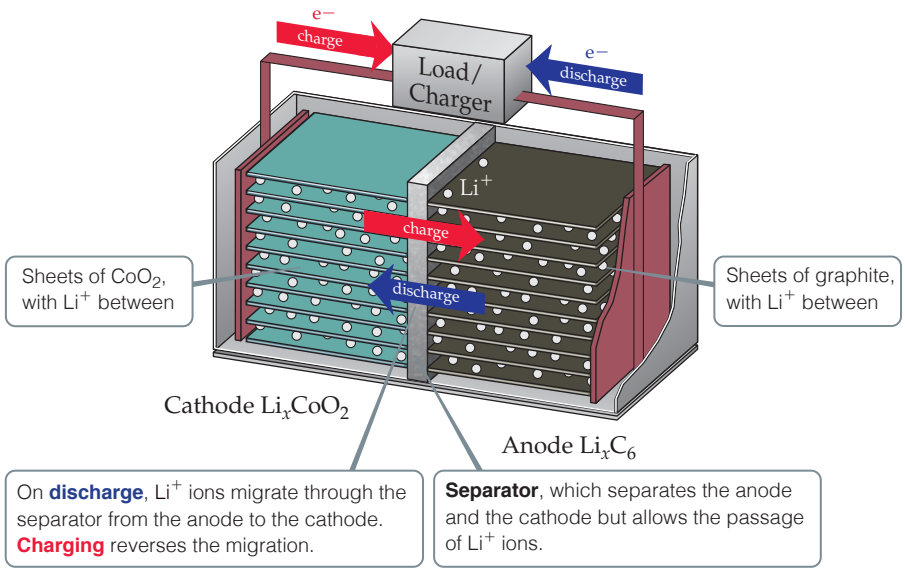
When the battery is being charged by an external source, lithium ions migrate through the separator from the cathode to the anode where they insert between the layers of carbon atoms. The ability of an ion to move through a solid increases as the size of the ion decreases and as the charge on the ion decreases. Lithium ions are smaller than most other cations, and they carry only a 1+ charge, which allows them to migrate more readily than other ions can. As an added bonus, lithium is one of the lightest elements, which is attractive for use in electric vehicles. When the battery discharges, the lithium ions move from anode to cathode. To maintain charge balance, electrons simultaneously migrate from anode to cathode through an external circuit, thereby producing electricity.

At the cathode, lithium ions then insert in the oxide material. Again, the small size of lithium ions is an advantage. For every lithium ion that inserts into the lithium cobalt oxide cathode, a Co^{4+} ion is reduced to a Co^{3+} ion by an electron that has traveled through the external circuit.

The ion migration and the changes in structure that result when lithium ions enter and leave the electrode materials are complicated. Furthermore, the operation of all batteries generate heat because they are not perfectly efficient. In the case of Li-ion batteries, the heating of the separator material (typically a polymer) has led to problems as the size of the batteries has been scaled larger to increase energy capacity. In a very small number of cases, overheating of Li-ion batteries has caused the batteries to catch fire.

Teams worldwide are trying to discover new cathode and anode materials that will easily accept and release lithium ions without falling apart over many repeated cycles. New separator materials that allow for faster passage of lithium ions with less heat generation are also under development. Some research groups are looking at using sodium ions instead of lithium ions because sodium is far more abundant than lithium, although the larger size of sodium ions poses additional challenges. In the coming years, look for continued advances in battery technology based on alkali metal ions.

Related Exercise: 7.89



▲ **Figure 7.9** Schematic of a lithium-ion battery.

7.4 | Ionization Energy

The ease with which electrons can be removed from an atom or ion has a major impact on chemical behavior. The **ionization energy** of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion. We first encountered ionization in our discussion of the Bohr model of the hydrogen atom. (Section 6.3) If the electron in an H atom is excited from $n = 1$ (the ground state) to $n = \infty$, the electron is completely removed from the atom; the atom is *ionized*.

In general, the *first ionization energy*, I_1, is the energy needed to remove the first electron from a neutral atom. For example, the first ionization energy for the sodium atom is the energy required for the process

$$Na(g) \longrightarrow Na^+(g) + e^- \qquad [7.2]$$

The *second ionization energy*, I_2, is the energy needed to remove the second electron, and so forth, for successive removals of additional electrons. Thus, I_2 for the sodium atom is the energy associated with the process

$$Na^+(g) \longrightarrow Na^{2+}(g) + e^- \qquad [7.3]$$

Variations in Successive Ionization Energies

The magnitude of the ionization energy tells us how much energy is required to remove an electron; the greater the ionization energy, the more difficult it is to remove an electron. Notice in **Table 7.2** that ionization energies for a given element increase as successive electrons are removed: $I_1 < I_2 < I_3$, and so forth. This trend makes sense because with each successive removal, an electron is being pulled away from an increasingly positive ion, requiring increasingly more energy.

Give It Some Thought

Light can be used to ionize atoms and ions. Which of the two processes shown in Equations 7.2 and 7.3 requires shorter-wavelength radiation?

A second important feature shown in Table 7.2 is the sharp increase in ionization energy that occurs when an inner-shell electron is removed. For example, consider silicon, $1s^2 2s^2 2p^6 3s^2 3p^2$. The ionization energies increase steadily from 786 to 4356 kJ/mol for the four electrons in the $3s$ and $3p$ subshells. Removal of the fifth electron, which comes from the $2p$ subshell, requires a great deal more energy: 16,091 kJ/mol. The large increase occurs because the $2p$ electron is much more likely to be found close to the nucleus than are the four $n = 3$ electrons, and, therefore, the $2p$ electron experiences a much greater effective nuclear charge than do the $3s$ and $3p$ electrons.

Give It Some Thought

Which would you expect to be greater, I_1 for a sulphur atom or I_2 for an aluminium atom?

TABLE 7.2 Successive Values of Ionization Energies, *I*, for the Elements Sodium through Argon (kJ/mol)

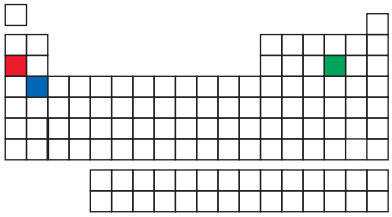
Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4562					
Mg	738	1451	7733		(inner-shell electrons)		
Al	578	1817	2745	11,577			
Si	786	1577	3232	4356	16,091		
P	1012	1907	2914	4964	6274	21,267	
S	1000	2252	3357	4556	7004	8496	27,107
Cl	1251	2298	3822	5159	6542	9362	11,018
Ar	1521	2666	3931	5771	7238	8781	11,995

Every element exhibits a large increase in ionization energy when the first of its inner-shell electrons is removed. This observation supports the idea that only the outermost electrons are involved in the sharing and transfer of electrons that give rise to chemical bonding and reactions. As we will see when we talk about chemical bonds in Chapters 8 and 9, the inner electrons are too tightly bound to the nucleus to be lost from the atom or even shared with another atom.

Sample Exercise 7.5

Trends in Ionization Energy

Three elements are indicated in the periodic table in the margin. Which one has the largest second ionization energy?



SOLUTION

Analyze and Plan The locations of the elements in the periodic table allow us to predict the electron configurations. The greatest ionization energies involve removal of core electrons. Thus, we should look first for an element with only one electron in the outermost occupied shell.

Solve The red box represents Na, which has one valence electron. The second ionization energy of this element is associated, therefore, with the removal of a core electron. The other elements indicated, S (green) and Ca (blue), have two or more valence electrons. Thus, Na should have the largest second ionization energy.

Check A chemistry handbook gives these I_2 values: Ca, 1145 kJ/mol; S, 2252 kJ/mol; Na, 4562 kJ/mol.

Practice Exercise 1

The third ionization energy of bromine is the energy required for which of the following processes?

(**a**) $Br(g) \longrightarrow Br^+(g) + e^-$ (**b**) $Br^+(g) \longrightarrow Br^{2+}(g) + e^-$
(**c**) $Br(g) \longrightarrow Br^{2+}(g) + 2\,e^-$ (**d**) $Br(g) \longrightarrow Br^{3+}(g) + 3\,e^-$
(**e**) $Br^{2+}(g) \longrightarrow Br^{3+}(g) + e^-$

Practice Exercise 2

Which has the greater third ionization energy, Ca or S?

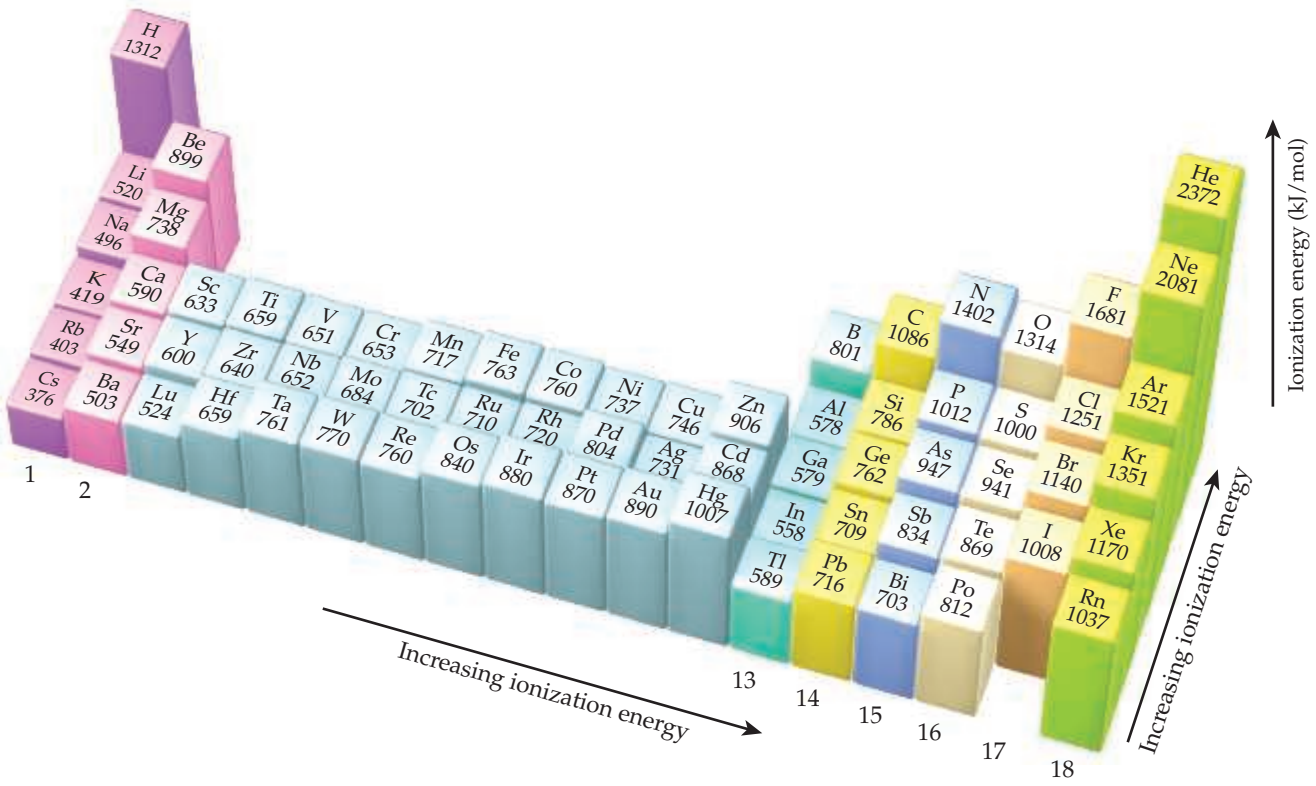
Periodic Trends in First Ionization Energies

Figure 7.10 shows, for the first 54 elements, the trends we observe in first ionization energies as we move from one element to another in the periodic table. The important trends are as follows:

1. I_1 *generally increases as we move left to right across a period.* The alkali metals show the lowest ionization energy in each period, and the noble gases show the highest. There are slight irregularities in this trend that we will discuss shortly.
2. I_1 *generally decreases as we move down any column in the periodic table*. For example, the ionization energies of the noble gases follow the order He > Ne > Ar > Kr > Xe.
3. *The* s- *and* p-*block elements show a larger range of* I_1 *values than do the transition-metal elements*. Generally, the ionization energies of the transition metals increase slowly from left to right in a period. The *f*-block metals (not shown in Figure 7.10) also show only a small variation in the values of I_1.

In general, smaller atoms have higher ionization energies. The same factors that influence atomic size also influence ionization energies. The energy needed to remove an electron from the outermost occupied shell depends on both the effective nuclear charge and the average distance of the electron from the nucleus. Either increasing the effective nuclear charge or decreasing the distance from the nucleus increases the attraction between the electron and the nucleus. As this attraction increases, it becomes more difficult to remove the electron, and, thus, the ionization energy increases. As we move across a period, there is both an increase in effective nuclear charge and a decrease in atomic radius, causing the ionization energy to increase. As we move down a column, the atomic radius increases, while the effective nuclear charge increases only gradually. The increase in radius dominates, so the attraction between the nucleus and the electron decreases, causing the ionization energy to decrease.

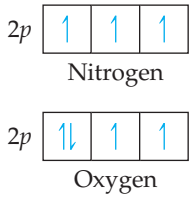
Go Figure The value for astatine, At, is missing in this figure. To the nearest 100 kJ/mol, what estimate would you make for the first ionization energy of At?



▲ **Figure 7.10** **The first ionization energies of the elements in kJ/mol.**

Go Figure

Why is it easier to remove a 2*p* electron from an oxygen atom than from a nitrogen atom?



▲ **Figure 7.11** **2*p* orbital filling in nitrogen and oxygen.**

The irregularities in a given period are subtle but still readily explained. For example, the decrease in ionization energy from beryllium ($[He]2s^2$) to boron ($[He]2s^22p^1$), shown in Figure 7.10, occurs because the third valence electron of B must occupy the 2*p* subshell, which is empty for Be. Recall that the 2*p* subshell is at a higher energy than the 2*s* subshell (Figure 6.25). The slight decrease in ionization energy when moving from nitrogen ($[He]2s^22p^3$) to oxygen ($[He]2s^22p^4$) is the result of the repulsion of paired electrons in the p^4 configuration (**Figure 7.11**). Remember that according to Hund's rule, each electron in the p^3 configuration resides in a different *p* orbital, which minimizes the electron–electron repulsion among the three 2*p* electrons. (Section 6.8)

Electron Configurations of Ions

When electrons are removed from an atom to form a cation, they are always removed first from the occupied orbitals having the largest principal quantum number, *n*. For example, when one electron is removed from a lithium atom ($1s^22s^1$), it is the $2s^1$ electron:

$$Li(1s^22s^1) \Rightarrow Li^+(1s^2) + e^-$$

Likewise, when two electrons are removed from Fe ($[Ar]4s^23d^6$), the $4s^2$ electrons are the ones removed:

$$Fe([Ar]4s^23d^6) \Rightarrow Fe^{2+}([Ar]3d^6) + 2\,e^-$$

If an additional electron is removed, forming Fe^{3+}, it comes from a 3*d* orbital because all the orbitals with $n = 4$ are empty:

$$Fe^{2+}([Ar]3d^6) \Rightarrow Fe^{3+}([Ar]3d^5) + e^-$$

Sample Exercise 7.6

Periodic Trends in Ionization Energy

Referring to the periodic table, arrange the atoms Ne, Na, P, Ar, K in order of increasing first ionization energy.

SOLUTION

Analyze and Plan We are given the chemical symbols for five elements. To rank them according to increasing first ionization energy, we need to locate each element in the periodic table. We can then use their relative positions and the trends in first ionization energies to predict their order.

Solve Ionization energy increases as we move left to right across a period and decreases as we move down a group. Because Na, P, and Ar are in the same period, we expect I_1 to vary in the order Na $<$ P $<$ Ar. Because Ne is above Ar in group 18, we expect Ar $<$ Ne. Similarly, K is directly below Na in group 1, and so we expect K $<$ Na.

From these observations, we conclude that the ionization energies follow the order

$$\text{K} < \text{Na} < \text{P} < \text{Ar} < \text{Ne}$$

Check The values shown in Figure 7.10 confirm this prediction.

Practice Exercise 1

Consider the following statements about first ionization energies:

(i) Because the effective nuclear charge for Mg is greater than that for Be, the first ionization energy of Mg is greater than that of Be.

(ii) The first ionization energy of O is less than that of N because in O we must pair electrons in one of the 2*p* orbitals.

(iii) The first ionization energy of Ar is less than that of Ne because a 3*p* electron in Ar is farther from the nucleus than a 2*p* electron in Ne.

Which of the statements (i), (ii), and (iii) is or are true?

(**a**) Only one of the statements is true.
(**b**) Statements (i) and (ii) are true.
(**c**) Statements (i) and (iii) are true.
(**d**) Statements (ii) and (iii) are true.
(**e**) All three statements are true.

Practice Exercise 2

Which has the lowest first ionization energy, B, Al, C, or Si? Which has the highest?

It may seem odd that 4*s* electrons are removed before 3*d* electrons in forming transition-metal cations. After all, in writing electron configurations, we added the 4*s* electrons before the 3*d* ones. In writing electron configurations for atoms, however, we are going through an imaginary process in which we move through the periodic table from one element to another. In doing so, we are adding both an electron to an orbital and a proton to the nucleus to change the identity of the element. In ionization, we *do not* reverse this process because no protons are being removed. For example, both Ca and Ti^{2+} have 20 electrons, but a Ti^{2+} ion has more protons than a Ca atom (22 vs. 20). That changes the relative energy levels of the orbitals enough that the two species have different electron configurations: Ca($[Ar]4s^2$) and Ti^{2+} ($[Ar]3d^2$).

If there is more than one occupied subshell for a given value of *n*, the electrons are first removed from the orbital with the highest value of *l*. For example, a tin atom loses its 5*p* electrons before it loses its 5*s* electrons:

$$\text{Sn}([\text{Kr}]5s^2 4d^{10} 5p^2) \Rightarrow \text{Sn}^{2+}([\text{Kr}]5s^2 4d^{10}) + 2\,\text{e}^- \Rightarrow \text{Sn}^{4+}([\text{Kr}]4d^{10}) + 4\,\text{e}^-$$

Electrons added to an atom to form an anion are added to the empty or partially filled orbital having the lowest value of *n*. For example, an electron added to a fluorine atom to form the F^- ion goes into the one remaining vacancy in the 2*p* subshell:

$$\text{F}(1s^2 2s^2 2p^5) + \text{e}^- \Rightarrow \text{F}^-(1s^2 2s^2 2p^6)$$

Give It Some Thought

Do Co^{3+} and Fe^{2+} have the same or different electron configurations?

Sample Exercise 7.7

Electron Configurations of Ions

Write the electron configurations for (**a**) Ca^{2+}, (**b**) Co^{3+}, and (**c**) S^{2-}.

SOLUTION

Analyze and Plan We are asked to write electron configurations for three ions. To do so, we first write the electron configuration of each parent atom and then remove or add electrons to form the ions. Electrons are first removed from the orbitals having the highest value of n. They are added to the empty or partially filled orbitals having the lowest value of n.

Solve

(**a**) Calcium (atomic number 20) has the electron configuration $[Ar]4s^2$. To form a 2+ ion, the two outer 4*s* electrons must be removed, giving an ion that is isoelectronic with Ar:

$$Ca^{2+}: [Ar]$$

(**b**) Cobalt (atomic number 27) has the electron configuration $[Ar]4s^23d^7$. To form a 3+ ion, three electrons must be removed. As discussed in the text, the 4*s* electrons are removed before the 3*d* electrons. Consequently, we remove the two 4*s* electrons and one of the 3*d* electrons, and the electron configuration for Co^{3+} is

$$Co^{3+}: [Ar]3d^6$$

(**c**) Sulfur (atomic number 16) has the electron configuration $[Ne]3s^23p^4$. To form a 2− ion, two electrons must be added. There is room for two additional electrons in the 3*p* orbitals. Thus, the S^{2-} electron configuration is

$$S^{2-}: [Ne]3s^23p^6 = [Ar]$$

Comment Remember that many of the common ions of the *s*- and *p*-block elements, such as Ca^{2+} and S^{2-}, have the same number of electrons as the closest noble gas. (Section 2.7)

Practice Exercise 1

The ground-state electron configuration of a Tc atom is $[Kr]5s^24d^5$. What is the electron configuration of a Tc^{3+} ion? (**a**) $[Kr]4d^4$ (**b**) $[Kr]5s^24d^2$ (**c**) $[Kr]5s^14d^3$ (**d**) $[Kr]5s^24d^8$ (**e**) $[Kr]4d^{10}$

Practice Exercise 2

Write the electron configurations for (**a**) Ga^{3+}, (**b**) Cr^{3+}, and (**c**) Br^-.

7.5 | Electron Affinity

The first ionization energy of an atom is a measure of the energy change associated with removing an electron from the atom to form a cation. For example, the first ionization energy of Cl(*g*), 1251 kJ/mol, is the energy change associated with the process

$$\textit{Ionization energy}: \quad Cl(g) \longrightarrow Cl^+(g) + e^- \qquad \Delta E = 1251 \text{ kJ/mol} \qquad [7.4]$$

$$[Ne]3s^23p^5 \qquad [Ne]3s^23p^4$$

The positive value of the ionization energy means that energy must be put into the atom to remove the electron. *All ionization energies for atoms are positive: Energy must be absorbed to remove an electron.*

Most atoms can also gain electrons to form anions. The energy change that occurs when an electron is added to a gaseous atom is called the **electron affinity** because it measures the attraction, or *affinity,* of the atom for the added electron. For most atoms, energy is *released* when an electron is added. For example, the addition of an electron to a chlorine atom is accompanied by an energy change of −349 kJ/mol, the negative sign indicating that energy is released during the process. We therefore say that the electron affinity of Cl is −349 kJ/mol.*

$$\textit{Electron affinity}: \quad Cl(g) + e^- \longrightarrow Cl^-(g) \qquad EA = -349 \text{ kJ/mol} \qquad [7.5]$$

$$[Ne]3s^23p^5 \qquad [Ne]3s^23p^6$$

It is important to understand the difference between ionization energy and electron affinity:

- Ionization energy measures the energy change when an atom *loses* an electron.
- Electron affinity measures the energy change when an atom *gains* an electron.

*Two sign conventions are used for electron affinity. In most introductory texts, including this one, the thermodynamic sign convention is used: A negative sign indicates that addition of an electron is an exothermic process, as in the electron affinity for chlorine, −349 kJ/mol. Historically, however, electron affinity has been defined as the energy released when an electron is added to a gaseous atom or ion. Because 349 kJ/mol is released when an electron is added to Cl(*g*), the electron affinity by this convention would be +349 kJ/mol.

The greater the attraction between an atom and an added electron, the more negative the atom's electron affinity. For some elements, such as the noble gases, the electron affinity has a positive value, meaning that the anion is higher in energy than are the separated atom and electron:

$$\underset{[Ne]3s^23p^6}{Ar(g)} + e^- \longrightarrow \underset{[Ne]3s^23p^64s^1}{Ar^-(g)} \qquad EA > 0 \qquad [7.6]$$

The fact that the electron affinity is positive means that an electron will not attach itself to an Ar atom; in other words the Ar^- ion is unstable and does not form.

Periodic Trends in Electron Affinity

The electron affinities for the *s*- and *p*-block elements of the first five periods are shown in **Figure 7.12**. Notice that the trends are not as evident as they are for ionization energy. The halogens, which are one electron shy of a filled *p* subshell, have the most negative electron affinities. By gaining an electron, a halogen atom forms a stable anion that has a noble-gas configuration (Equation 7.5). The addition of an electron to a noble gas, however, requires that the electron reside in a higher-energy subshell that is empty in the atom (Equation 7.6). Because occupying a higher-energy subshell is energetically unfavorable, the electron affinity is highly positive. The electron affinities of Be and Mg are positive for the same reason; the added electron would reside in a previously empty *p* subshell that is higher in energy.

The electron affinities of the group 15 elements are also interesting. Because these elements have half-filled *p* subshells, the added electron must be put in an orbital that is already occupied, resulting in larger electron–electron repulsions. Consequently, these elements have electron affinities that are either positive (N) or less negative than those of their neighbors to the left (P, As, Sb). Recall that in Section 7.4 we saw a discontinuity in the trends in first ionization energy for the same reason.

Electron affinities do not change greatly as we move down a group (Figure 7.12). With F, for instance, the added electron goes into a 2*p* orbital, for Cl a 3*p* orbital, for Br a 4*p* orbital, and so forth. As we proceed from F to I, therefore, the average distance between the added electron and the nucleus steadily increases, causing the electron–nucleus attraction to decrease. However, the orbital that holds the outermost electron is increasingly spread out, so that as we proceed from F to I, the electron–electron repulsions are also reduced. As a result, the reduction in the electron–nucleus attraction is counterbalanced by the reduction in electron–electron repulsions.

Go Figure

Why are the electron affinities of the Group 14 elements more negative than those of the Group 15 elements?

1												18
H −73	2											He > 0
Li −60	Be > 0					13	14	15	16	17		Ne > 0
Na −53	Mg > 0					B −27	C −122	N > 0	O −141	F −328		Ar > 0
K −48	Ca −2					Al −43	Si −134	P −72	S −200	Cl −349		Kr > 0
Rb −7	Sr −5					Ga −30	Ge −119	As −78	Se −195	Br −325		Xe > 0
						In −30	Sn −107	Sb −103	Te −190	I −295		

▲ **Figure 7.12** Electron affinity in kJ/mol for selected *s*- and *p*-block elements.

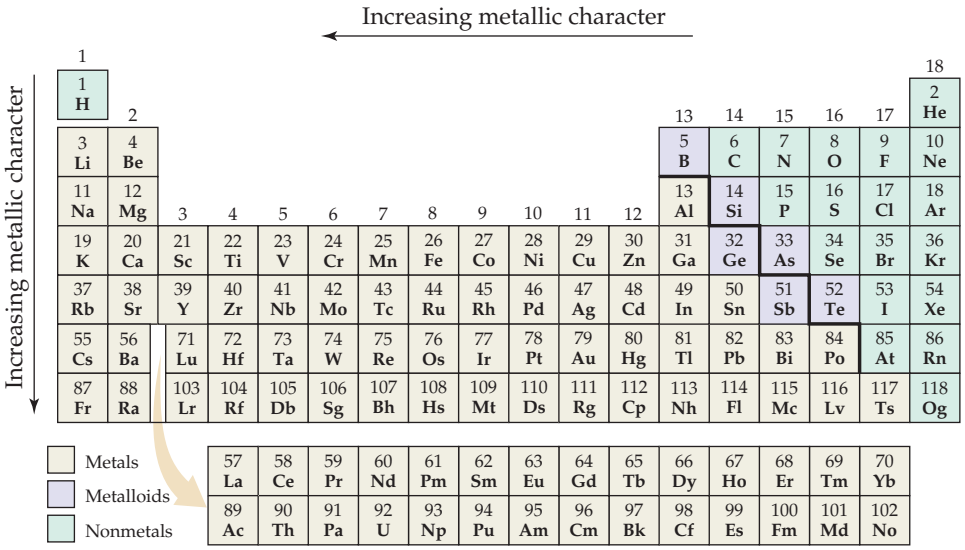
Give It Some Thought

What is the relationship between the value for the first ionization energy of a $Cl^-(g)$ ion and the electron affinity of $Cl(g)$?

7.6 Metals, Nonmetals, and Metalloids

Atomic radii, ionization energies, and electron affinities are properties of individual atoms. With the exception of the noble gases, however, none of the elements exist in nature as individual atoms. To get a broader understanding of the properties of elements, we must also examine periodic trends in properties of samples that involve large collections of atoms.

Go Figure How do the periodic trends in metallic character compare to those for ionization energy?



▲ **Figure 7.13** Metals, metalloids, and nonmetals.

TABLE 7.3 Characteristic Properties of Metals and Nonmetals

Metals	Nonmetals
Have a shiny luster; various colors, although most are silvery	Do not have a luster; various colors
Solids are malleable and ductile	Solids are usually brittle; some are hard, and some are soft
Good conductors of heat and electricity	Poor conductors of heat and electricity
Most metal oxides are ionic solids that are basic	Most nonmetal oxides are molecular substances that form acidic solutions
Tend to form cations in aqueous solution	Tend to form anions or oxyanions in aqueous solution

The elements can be broadly grouped as metals, nonmetals, and metalloids (**Figure 7.13**). (Section 2.5) Some of the distinguishing properties of metals and nonmetals are summarized in **Table 7.3**.

In the following sections, we explore some common patterns of reactivity across the periodic table. We will examine reactivity for selected nonmetals and metals in more depth in later chapters.

The more an element exhibits the physical and chemical properties of metals, the greater its **metallic character**. As indicated in Figure 7.13, metallic character generally increases as we proceed down a group of the periodic table and decreases as we proceed right across a period. Let's now examine the close relationships that exist between electron configurations and the properties of metals, nonmetals, and metalloids.

▲ **Figure 7.14** Metals are shiny, malleable, and ductile.

Metals

Most metallic elements exhibit the shiny luster we associate with metals (**Figure 7.14**). Metals conduct heat and electricity. In general, they are malleable (can be pounded into thin sheets) and ductile (can be drawn into wires). All are solids at room temperature except mercury (melting point = −39 °C), which is a liquid at room temperature. Two metals melt at slightly above room temperature, cesium at 28.4 °C and gallium at 29.8 °C. At the other extreme, many metals melt at very high temperatures. For example, tungsten, which is used for the filaments of incandescent light bulbs, melts at 3400 °C.

Metals tend to have low ionization energies (Figure 7.10) *and therefore tend to form cations relatively easily.* As a result, metals are oxidized (lose electrons) when they undergo

Go Figure The red stepped line divides metals from nonmetals. How are common oxidation states divided by this line?

1	2											13	14	15	16	17	18
H^+																H^-	NOBLE GASES
Li^+														N^{3-}	O^{2-}	F^-	
Na^+	Mg^{2+}	Transition metals										Al^{3+}		P^{3-}	S^{2-}	Cl^-	
K^+	Ca^{2+}	Sc^{3+}	Ti^{4+}	V^{5+} V^{4+}	Cr^{3+}	Mn^{2+} Mn^{4+}	Fe^{2+} Fe^{3+}	Co^{2+} Co^{3+}	Ni^{2+}	Cu^+ Cu^{2+}	Zn^{2+}				Se^{2-}	Br^-	
Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}						Pd^{2+}	Ag^+	Cd^{2+}		Sn^{2+} Sn^{4+}	Sb^{3+} Sb^{5+}	Te^{2-}	I^-	
Cs^+	Ba^{2+}	Lu^{3+}	Hf^{4+}						Pt^{2+}	Au^+ Au^{3+}	Hg_2^{2+} Hg^{2+}		Pb^{2+} Pb^{4+}	Bi^{3+} Bi^{5+}			

▲ **Figure 7.15 Representative oxidation states of the elements.** Note that hydrogen exhibits both positive and negative oxidation numbers, +1 and −1.

chemical reactions. Among the fundamental atomic properties (radius, electron configuration, electron affinity, and so forth), first ionization energy is the best indicator of whether an element behaves as a metal or a nonmetal.

Figure 7.15 shows the oxidation states of representative ions of metals and nonmetals. As noted in Section 2.7, the charge on any alkali metal ion in a compound is always 1+, and that on any alkaline earth metal is always 2+. For atoms belonging to either of these groups, the outer *s* electrons are easily lost, yielding a noble-gas electron configuration. For metals belonging to groups with partially occupied *p* orbitals (groups 13–17), cations are formed either by losing only the outer *p* electrons (such as Sn^{2+}) or the outer *s* and *p* electrons (such as Sn^{4+}). The charge on transition-metal ions does not follow an obvious pattern. One characteristic of the transition metals is their ability to form more than one cation. For example, compounds of Fe^{2+} and Fe^{3+} are both very common.

Give It Some Thought

Arsenic forms binary compounds with Cl and with Mg. Will it be in the same oxidation state in these two compounds?

Compounds made up of a metal and a nonmetal tend to be ionic substances. For example, most metal oxides and halides are ionic solids. To illustrate, the reaction between nickel metal and oxygen produces nickel oxide, an ionic solid containing Ni^{2+} and O^{2-} ions:

$$2\,Ni(s) + O_2(g) \longrightarrow 2\,NiO(s) \qquad [7.7]$$

The oxides are particularly important because of the great abundance of oxygen in our environment.

Most metal oxides are basic. Those that dissolve in water react to form metal hydroxides, as in the following examples:

$$\text{Metal oxide} + \text{water} \longrightarrow \text{metal hydroxide}$$

$$Na_2O(s) + H_2O(l) \longrightarrow 2\,NaOH(aq) \qquad [7.8]$$

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq) \qquad [7.9]$$

The basicity of metal oxides is due to the oxide ion, which reacts with water:

$$O^{2-}(aq) + H_2O(l) \longrightarrow 2\,OH^-(aq) \qquad [7.10]$$

Sample Exercise 7.8

Properties of Metal Oxides

(**a**) Would you expect scandium oxide to be a solid, liquid, or gas at room temperature?
(**b**) Write the balanced chemical equation for the reaction of scandium oxide with nitric acid.

SOLUTION

Analyze and Plan We are asked about one physical property of scandium oxide—its state at room temperature—and one chemical property—how it reacts with nitric acid.

Solve

(**a**) Because scandium oxide is the oxide of a metal, we expect it to be an ionic solid. Indeed it is, with the very high melting point of 2485 °C.

(**b**) In compounds, scandium has a 3+ charge, Sc^{3+}, and the oxide ion is O^{2-}. Consequently, the formula of scandium oxide is Sc_2O_3. Metal oxides tend to be basic and, therefore, to react with acids to form a salt plus water. In this case, the salt is scandium nitrate, $Sc(NO_3)_3$:

$$Sc_2O_3(s) + 6\,HNO_3(aq) \longrightarrow 2\,Sc(NO_3)_3(aq) + 3\,H_2O(l)$$

Practice Exercise 1

Suppose that a metal oxide of formula M_2O_3 were soluble in water. What would be the major product or products of dissolving the substance in water?
(**a**) $MH_3(aq) + O_2(g)$
(**b**) $M(s) + H_2(g) + O_2(g)$
(**c**) $M^{3+}(aq) + H_2O_2(aq)$
(**d**) $M(OH)_2(aq)$
(**e**) $M(OH)_3(aq)$

Practice Exercise 2

Write the balanced chemical equation for the reaction between copper(II) oxide and sulfuric acid.

Go Figure Would you expect NiO to dissolve in an aqueous solution of $NaNO_3$?

Nickel oxide (NiO), nitric acid (HNO_3), and water

NiO is insoluble in water but reacts with HNO_3 to give a green solution of the salt $Ni(NO_3)_2$.

▲ **Figure 7.16 Metal oxides react with acids.** NiO does not dissolve in water but does react with nitric acid (HNO_3) to give a green solution of $Ni(NO_3)_2$.

Go Figure

Do you think sulfur is malleable?

▲ **Figure 7.17 Sulfur, known to the medieval world as "brimstone," is a nonmetal.**

Even metal oxides that are insoluble in water demonstrate their basicity by reacting with acids to form a salt plus water, as illustrated in **Figure 7.16**:

$$\text{Metal oxide} + \text{acid} \longrightarrow \text{salt} + \text{water}$$
$$NiO(s) + 2\,HNO_3(aq) \longrightarrow Ni(NO_3)_2(aq) + H_2O(l) \qquad [7.11]$$

Nonmetals

Nonmetals can be solid, liquid, or gas. They are not lustrous and generally are poor conductors of heat and electricity. Their melting points are generally lower than those of metals (although diamond, a form of carbon, is an exception and melts at 3570 °C). Under ordinary conditions, seven nonmetals exist as diatomic molecules. Five of these are gases (H_2, N_2, O_2, F_2, and Cl_2), one is a liquid (Br_2), and one is a volatile solid (I_2). Excluding the noble gases, the remaining nonmetals are solids that can be either hard, such as diamond, or soft, such as sulfur (**Figure 7.17**).