

7

PERIODIC PROPERTIES OF THE ELEMENTS

7.1 | Development of the Periodic Table



The discovery of chemical elements has been ongoing since ancient times. 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.

WHAT'S AHEAD

- 7.1 ► Development of the Periodic Table
- 7.2 ► Effective Nuclear Charge
- 7.3 ► Sizes of Atoms and Ions
- 7.4 ► Ionization Energy
- 7.5 ► Electron Affinity
- 7.6 ► Metals, Nonmetals, and Metalloids
- 7.7 ► Trends for Group 1 and Group 2 Metals
- 7.8 ► Trends for Selected Nonmetals

By the end of this section, you should

- Have an appreciation for the historical context of the periodic table

As the number of known elements increased ([Figure 7.1](#)), 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. 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.

Table 7.1.

In 1913, two years after Rutherford proposed the nuclear model of the atom, 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.

 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

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.

Self-Assessment Exercise

- 7.1** Around the start of the twentieth century, improvements in refrigeration techniques allowed Sir William Ramsay to discover which elements?
- (a) Copper, silver, and gold
 - (b) Sodium, potassium, and rubidium
 - (c) Neon, argon, and krypton

Exercises

- 7.2** The prefix *eka-* comes from the Sanskrit word for "one." Mendeleev used this prefix to indicate that the unknown element was one place away from the known element that followed the prefix. For example, *eka-silicon*, which we now call germanium, is one element below silicon. Mendeleev also predicted the existence of *eka-manganese*, which was not experimentally confirmed until 1937 because this element is radioactive and does not occur in nature. Based on

the periodic table shown in Figure 7.1, what do we now call the element Mendeleev called *eka-manganese*?

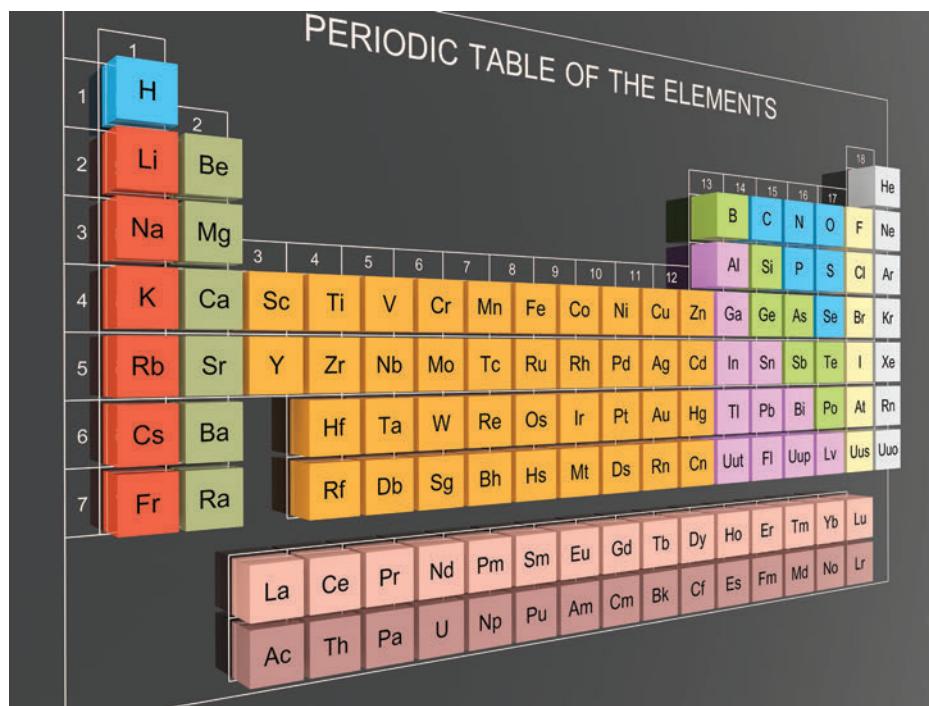
- 7.3** (a) The five most abundant elements in the Earth's crust are O, Si, Al, Fe, and Ca. Referring to Figure 7.1, are any of these elements among those known before 1700? If so which ones? (b) Seven of the nine elements known since ancient times are metals. Referring to Table 4.5, are these metals mostly found at the bottom or top of the activity series?

7.1 (c)

Answers to Self-Assessment Exercises



7.2 | Effective Nuclear Charge



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. It is also possible to understand trends observed across a period, all of which are based on the attraction between the nuclear charge and the surrounding electrons.

By the end of this section, you should be able to

- Understand the factors that contribute to 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. 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 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

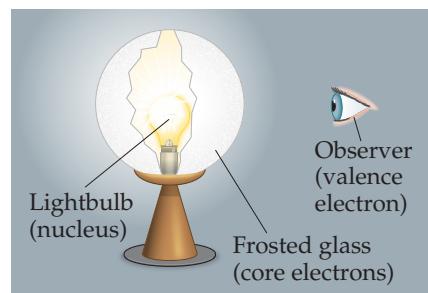
$$Z_{\text{eff}} = Z - S \quad [7.1]$$

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.”)

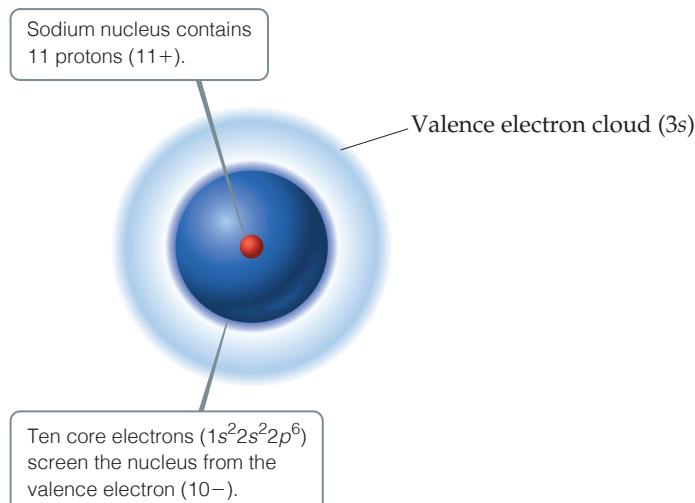
To understand better the notion of effective nuclear charge, we can use an analogy of a light bulb with a frosted glass shade (Figure 7.2). The light bulb represents the nucleus, and the observer is the electron of interest, which is usually a valence electron. The amount of light that the electron “sees” 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 ($1s^22s^22p^6$), 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. 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 probability that the $3s$ 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



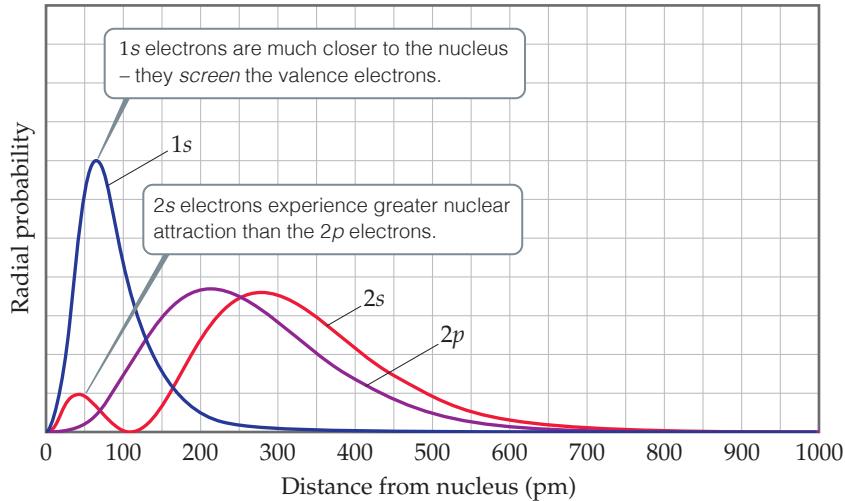
▲ Figure 7.2 An analogy for effective nuclear charge. We envision the nucleus as a light bulb, the core electrons as a frosted glass lampshade, and a valence electron as an observer. The amount of light seen by the observer depends on the intensity of the light bulb and the screening by the frosted glass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



▲ 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 2s orbital or one in a 2p orbital? Which orbital, 2s or 2p, will be lower in energy in a multielectron atom?



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

configuration is $1s^2 2s^2 2p^2$, the energy of the 2p orbital ($l = 1$) is higher than that of the 2s orbital ($l = 0$), even though both orbitals are in the $n = 2$ shell (Figure 6.24). This difference in energies is due to the radial probability functions for the orbitals (Figure 7.4). We see first that the 1s electrons are much closer to the nucleus—they serve as an effective “lampshade” for the 2s and 2p electrons. Notice next that the 2s probability function has a small peak fairly close to the nucleus, whereas the 2p probability function does not. As a result, a 2s electron is not screened as much by the core orbitals as is a 2p electron. The greater attraction between the 2s electron and the nucleus leads to a lower energy for the 2s orbital than for the 2p 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 2s 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 1s electrons screen a $4+$ nucleus, and each 2s electron only partially screens the other. Consequently, the effective nuclear charge experienced by each 2s electron is about $4 - 2 = 2+$.

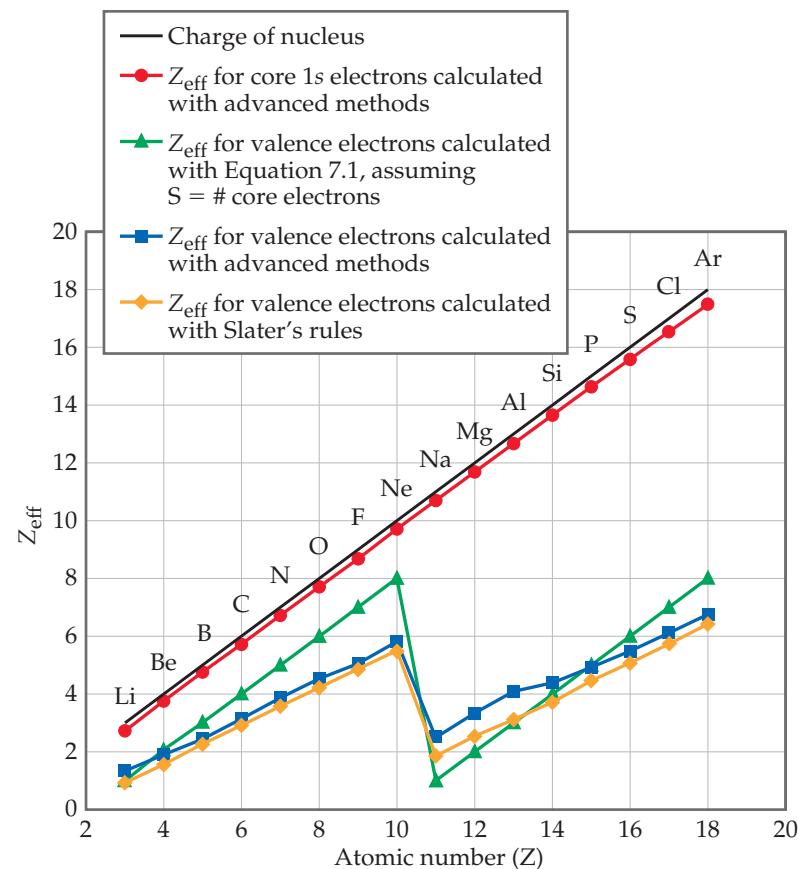
Going down a column, the effective nuclear charge experienced by valence electrons changes far less than it does across a period. For example, using our simple estimate for S , we would expect the effective nuclear charge experienced by the valence electrons in lithium and sodium to be about the same, 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* 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.

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 (1s) 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 $1s^22s^22p^5$. 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, $Z_{\text{eff}} = Z - S = 9 - 3.8 = 5.2+$, 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: 7.6, 7.16, 7.54, 7.62, 7.89, 7.90, 7.119

Self-Assessment Exercise

- 7.4** Which would you expect to experience a greater effective nuclear charge?
 (a) A $3p$ electron of an Ar atom
 (b) A $4s$ electron of a Ca atom

Exercises

- 7.5** Among the elements N, O, P, and S, which element or elements have the smallest effect nuclear charge if we use Equation 7.1 to calculate Z_{eff} ? Which element or elements have the largest effective nuclear charge?
- 7.6** Detailed calculations show that the value of Z_{eff} for the outermost electrons in Na and K atoms is 2.51+ and 3.49+, respectively. (a) What value do you estimate for Z_{eff} experienced by the outermost electron in both Na and K by

assuming core electrons contribute 1.00 and valence electrons contribute 0.00 to the screening constant? (b) What values do you estimate for Z_{eff} using Slater's rules? (c) Which approach gives a more accurate estimate of Z_{eff} ? (d) Does either method of approximation account for the gradual increase in Z_{eff} that occurs upon moving down a group?

(e) Predict Z_{eff} for the outermost electrons in the Rb atom based on the calculations for Na and K.

- 7.7 Which will experience the greater effect nuclear charge, the electrons in the $n = 2$ shell in F or the $n = 2$ shell in B? Which will be closer to the nucleus?

7.4 (a)

Answers to Self-Assessment Exercises



7.3 | Sizes of Atoms and Ions



Hydrogen offers considerable promise as a clean fuel to power vehicles. However, finding an effective means of storage is currently a barrier to its widespread adoption. The very low boiling point (-253°C) makes cryogenic storage expensive, and compressing hydrogen in tanks adds an unacceptable amount of weight to any vehicle. The very small size of the hydrogen molecule could be the key to its storage. A class of new materials called MOFs (metal organic frameworks) have been engineered by chemists to have a porous structure with cavities large enough to accommodate hydrogen molecules. Rather like water in a sponge, the absorption of hydrogen into the MOF structure is reversible and storage capacities greater than that in a compressed gas tank can be achieved.

By the end of this section, you should be able to

- Use the periodic table to predict the trends in atomic radii
- Explain how the radius of an atom changes upon losing electrons to form a cation or gaining electrons to form an anion

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. Nevertheless, we can define atomic size in several ways, based on the distances between atoms in various situations.

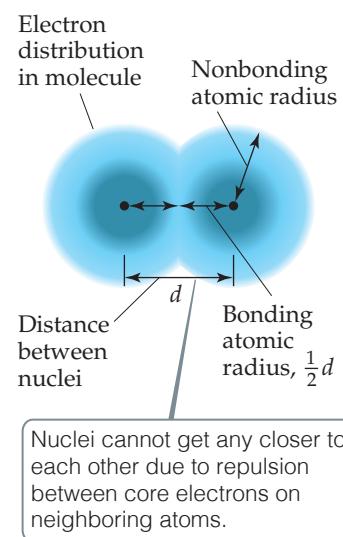
Imagine a collection of argon atoms in the gas phase. When two of these atoms collide, they ricochet apart like colliding billiard balls. This ricocheting happens because

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).

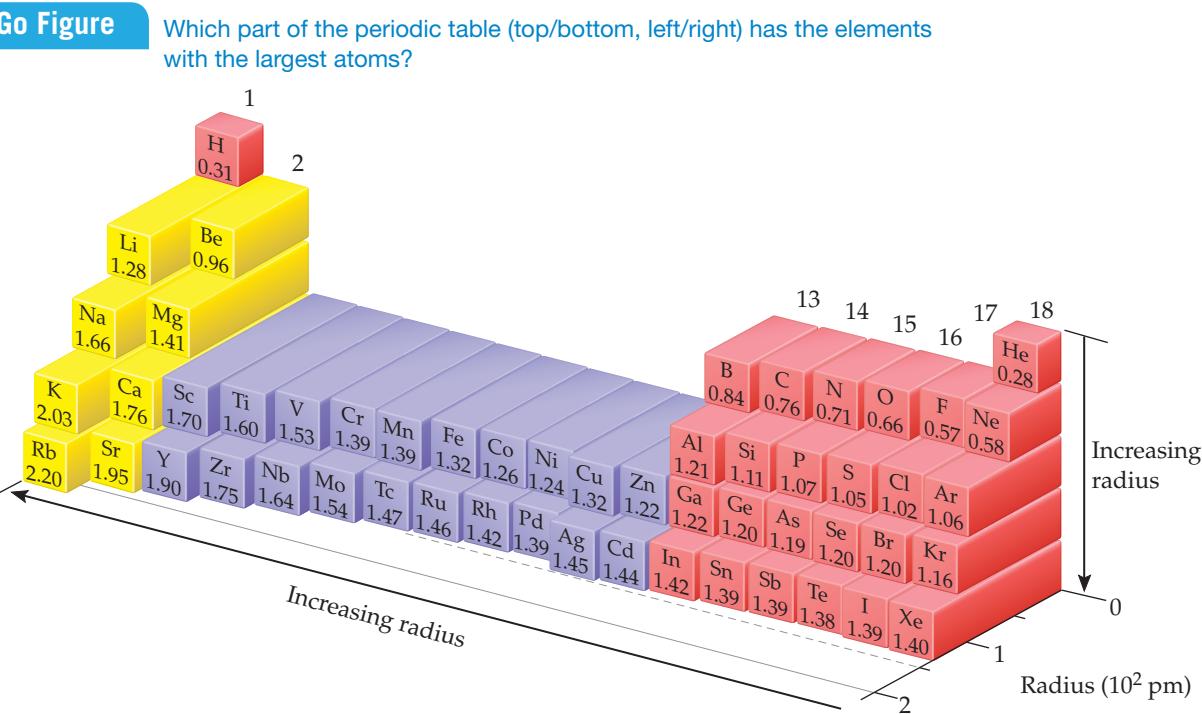
In molecules, the attractive interaction between any two adjacent atoms is what we recognize as a chemical bond. We discuss bonding in Chapters 8 and 9. For now, we need to realize that two bonded atoms are closer together than they would be in a nonbonding collision where the atoms ricochet apart. We 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.



▲ 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.

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.

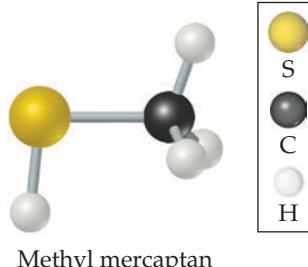
Solve

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

$$\text{C—H bond length} = 76 \text{ pm} + 31 \text{ pm} = 107 \text{ pm}$$

$$\text{S—H bond length} = 105 \text{ pm} + 31 \text{ pm} = 136 \text{ pm}$$

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



Methyl mercaptan

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

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 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*.

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



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.

$$\text{radius C} < \text{radius B}$$

Al and Si are in the same period, with Si to the right of Al.

$$\text{radius Si} < \text{radius Al}$$

The radius increases as we move down a group with Al and B belonging to the same group, as do C and Si.

$$\text{radius B} < \text{radius Al}$$

$$\text{radius C} < \text{radius Si}$$

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.

$$\text{radius C} < \text{radius B} \sim \text{radius Si} < \text{radius Al}$$

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

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



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 $\text{Ca}^{2+} < \text{Ca}$. Because Ca is below Mg in Group 2, Ca^{2+} is larger than Mg^{2+} . Consequently, $\text{Ca} > \text{Ca}^{2+} > \text{Mg}^{2+}$.

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

► Practice Exercise

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

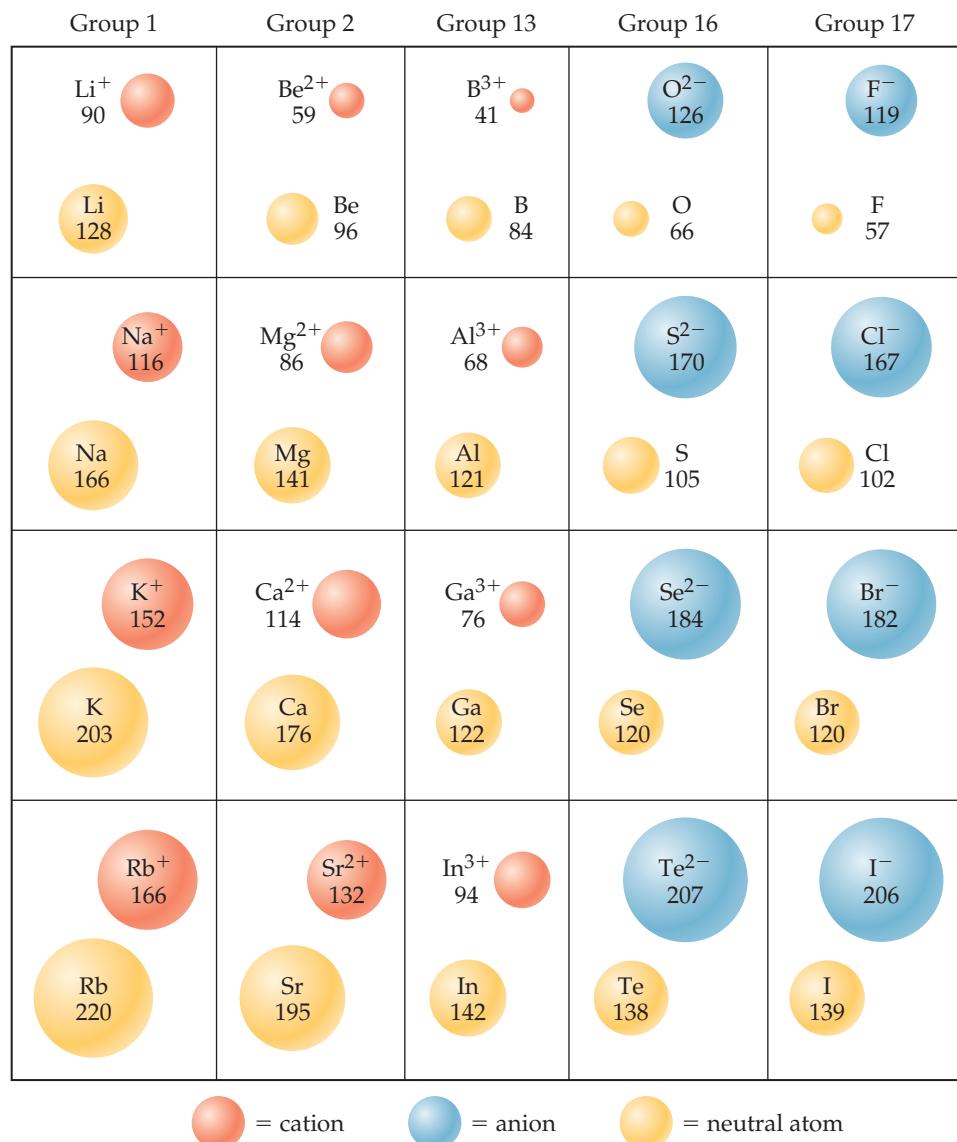
10 electrons. In any isoelectronic series, we can list the members in order of increasing atomic number; therefore, the nuclear charge increases as we move through the series. Because the number of electrons remains constant, ionic radius decreases with increasing nuclear charge as the electrons are more strongly attracted to the nucleus:

Increasing nuclear charge →

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

**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.

**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 $\text{S}^{2-} > \text{Cl}^- > \text{K}^+ > \text{Ca}^{2+}$.

► Practice Exercise

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

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

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.

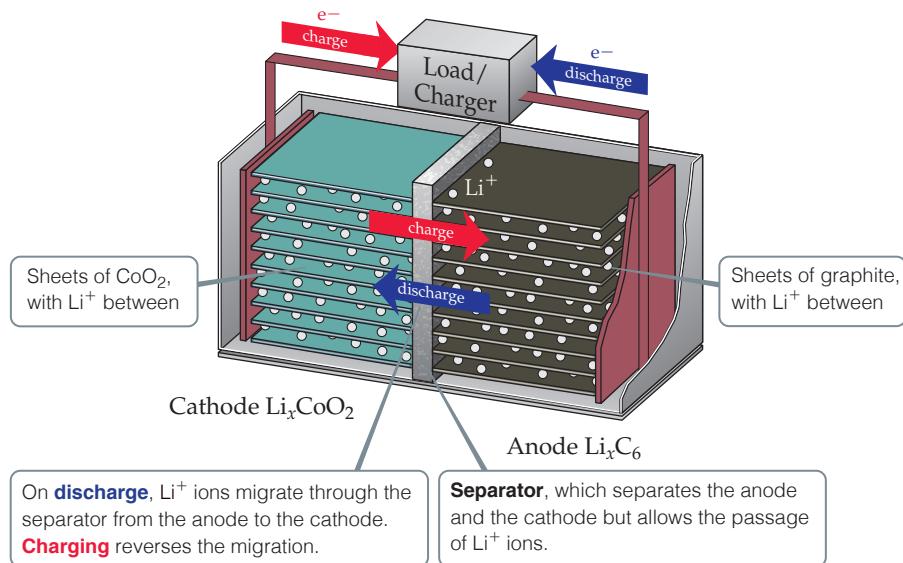
At the cathode, lithium ions then insert in the oxide material. Again, the small size of lithium ions is an advantage. For every lithium ion that inserts into the lithium cobalt oxide cathode, a Co^{4+} ion is reduced to a Co^{3+} ion by an electron that has traveled through the external circuit.

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: 7.98



▲ Figure 7.9 Schematic of a lithium-ion battery.

Self-Assessment Exercise

- 7.8** The decrease in atomic size left to right across a period is due to:
- Atoms of higher atomic number having more electrons
 - An increase in Z_{eff} across a period
 - An increase in the principle quantum number of the outer electrons across a period
- 7.9** When an atom forms a cation, does the radius of the species increase or decrease?
- Increase
 - Decrease

Exercises

- 7.10** Which quantity must be determined experimentally in order to determine the bonding atomic radius of an atom?
- The distance from the nucleus where the probability of finding an electron goes to zero.
 - The distance between the nuclei of two atoms that are bonded together.
 - The effective nuclear charge of an atom.
- 7.11** Tungsten has the highest melting point of any metal in the periodic table: 3422°C . The distance between W atoms in tungsten metal is 274 pm. (a) What is the atomic radius of a tungsten atom in this environment? (This radius is called the *metallic radius*.) (b) If you put tungsten metal under high pressure, predict what would happen to the distance between W atoms.

- 7.12** Estimate the P—Cl bond length from the data in Figure 7.7 and compare your value to the experimental P—Cl bond length in phosphorus tetrachloride PCl_3 , 204 pm.
- 7.13** Using only the periodic table, arrange each set of atoms in order from largest to smallest: **(a)** Ar, As, Kr; **(b)** Cd, Rb, Te; **(c)** C, Cl, Cu.
- 7.14** Identify each statement as true or false: **(a)** Cations are larger than their corresponding neutral atoms. **(b)** Li^+ is smaller than Li. **(c)** Cl^- is bigger than I^- .

- 7.15** Which neutral atom is isoelectronic with each of the following ions? H^- , Ca^{2+} , In^{3+} , Ge^{2+} .
- 7.16** Consider the isoelectronic ions F^- and Na^+ . **(a)** Which ion is smaller? **(b)** Using Equation 7.1 and assuming that core electrons contribute 1.00 and valence electrons contribute 0.00 to the screening constant, S , calculate Z_{eff} for the $2p$ electrons in both ions. **(c)** Repeat this calculation using Slater's rules to estimate the screening constant, S . **(d)** For isoelectronic ions, how are effective nuclear charge and ionic radius related?

7.8 (b) 7.9 (b)

Answers to Self-Assessment Exercises



7.4 | Ionization Energy



Solar wind is a stream of charged particles, mostly electrons, protons, and alpha particles, that is constantly emitted by the sun. The magnetosphere of the earth protects us from this radiation. However, there are times when the magnetic shield and solar wind do interact and give rise to excited atoms, molecules, and ions, which are observed as a beautiful play of lights, the aurora, in the sky near the poles.

By the end of this section, you should be able to

- Predict the trends in ionization energy as successive electrons are removed from an atom.

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. 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



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



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.

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, $1s^22s^22p^63s^23p^2$. 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.

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.

TABLE 7.2 Successive Values of Ionization Energies, I , for the Elements Sodium to 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	11577			
Si	786	1577	3232	4356	16091		
P	1012	1907	2914	4964	6274	21267	
S	1000	2252	3357	4556	7004	8496	27107
Cl	1251	2298	3822	5159	6542	9362	11018
Ar	1521	2666	3931	5771	7238	8781	11995



Sample Exercise 7.5

Trends in Ionization Energy

Three elements are indicated in the periodic table in the margin.

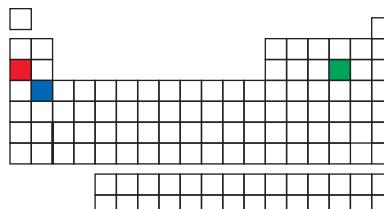
Which one has the largest second ionization energy?

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

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

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

Periodic Trends in First Ionization Energies

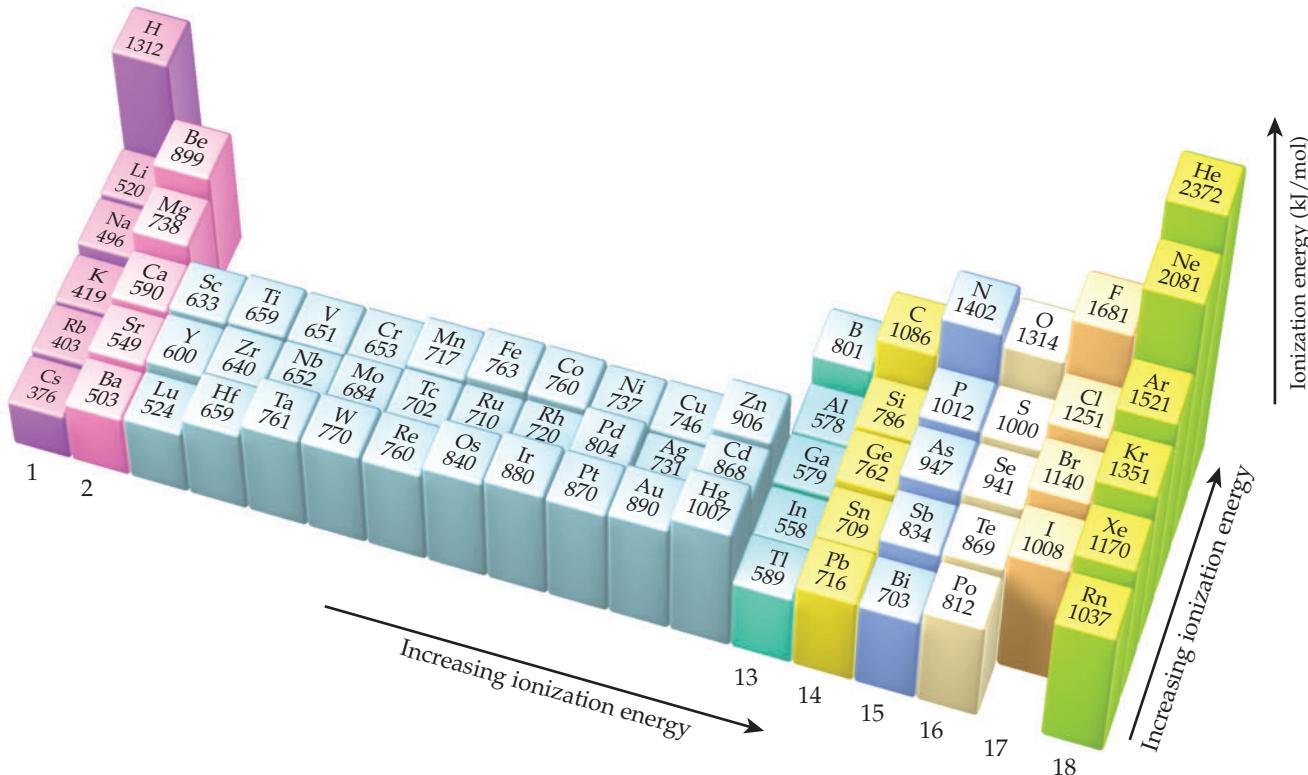
Figure 7.10 shows, for the first 54 elements, the trends we observe in first ionization energies as we move from one element to another in the periodic table. The important trends are as follows:

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 $\text{He} > \text{Ne} > \text{Ar} > \text{Kr} > \text{Xe}$.
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?

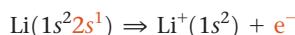


▲ **Figure 7.10** The first ionization energies of the elements in kJ/mol.

The irregularities in a given period are subtle but still readily explained. For example, the decrease in ionization energy from beryllium ($[\text{He}]2s^2$) to boron ($[\text{He}]2s^22p^1$), shown in Figure 7.10, occurs because the third valence electron of B must occupy the $2p$ subshell, which is empty for Be. Recall that the $2p$ subshell is at a higher energy than the $2s$ subshell (Figure 6.24). The slight decrease in ionization energy when moving from nitrogen ($[\text{He}]2s^22p^3$) to oxygen ($[\text{He}]2s^22p^4$) 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 $2p$ electrons.

Electron Configurations of Ions

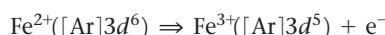
When electrons are removed from an atom to form a cation, they are always removed first from the occupied orbitals having the largest principal quantum number, n . For example, when one electron is removed from a lithium atom ($1s^22s^1$), it is the $2s^1$ electron:



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



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



Go Figure

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

$2p$	1	1	1
Nitrogen			

$2p$	1	1	1
Oxygen			

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



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 $\text{Na} < \text{P} < \text{Ar}$. Because Ne is above Ar in Group 18, we expect $\text{Ar} < \text{Ne}$. Similarly, K is directly below Na in Group 1, and so we expect $\text{K} < \text{Na}$.

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



Check The values shown in Figure 7.10 confirm this prediction.

► Practice Exercise

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

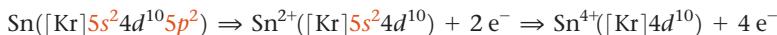
Which of the statements (i), (ii), and (iii) is or are true?

- (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.

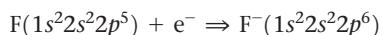
It may seem odd that $4s$ electrons are removed before $3d$ electrons in forming transition-metal cations. After all, in writing electron configurations, we added the $4s$ electrons before the $3d$ ones. In writing electron configurations for atoms, however, we are going through an imaginary process 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]4s²) and Ti²⁺ ([Ar]3d²).

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 5p electrons before it loses its 5s electrons:



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 2p subshell:



Sample Exercise 7.7

Electron Configurations of Ions

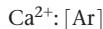
Write the electron configurations for (a) Ca²⁺, (b) Co³⁺, and (c) S²⁻.

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]4s². To form a 2+ ion, the two outer 4s electrons must be removed, giving an ion that is isoelectronic with Ar:

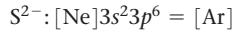


(b) Cobalt (atomic number 27) has the electron configuration [Ar]4s²3d⁷. To form a 3+ ion, three electrons must be removed. As discussed in the text, the 4s electrons are removed before the 3d electrons. Consequently, we remove

the two 4s electrons and one of the 3d electrons, and the electron configuration for Co³⁺ is



(c) Sulfur (atomic number 16) has the electron configuration [Ne]3s²3p⁴. To form a 2- ion, two electrons must be added. There is room for two additional electrons in the 3p orbitals. Thus, the S²⁻ electron configuration is



Comment Remember that many of the common ions of the s- and p-block elements, such as Ca²⁺ and S²⁻, have the same number of electrons as the closest noble gas. (Section 2.7)

► Practice Exercise

The ground-state electron configuration of a Tc atom is [Kr]5s²4d⁵. What is the electron configuration of a Tc³⁺ ion?

- (a) [Kr]4d⁴ (b) [Kr]5s²4d² (c) [Kr]5s¹4d³ (d) [Kr]5s²4d⁸
(e) [Kr]4d¹⁰

Self-Assessment Exercise

7.17 Which would you expect to be greater: I_1 for a sulfur atom or I_2 for an aluminum atom?

(a) I_1 for a sulfur atom

(b) I_2 for an aluminum atom

Exercises

7.18 Write equations that show the processes that describe the first, second, and third ionization energies of a chlorine atom. Which process would require the least amount of energy?

7.19 Which element has the highest second ionization energy: Li, K, or Be?

7.20 (a) What is the general relationship between the size of an atom and its first ionization energy? (b) Which element in the periodic table has the largest ionization energy? Which has the smallest?

7.21 Based on their positions in the periodic table, predict which atom of the following pairs will have the smaller first ionization energy: (a) Br, Kr; (b) C, Ca; (c) Li, Rb; (d) Pb, Si; (e) Al, B.

7.22 Write the electron configurations for the following ions, and determine which have noble-gas configurations: (a) Cu²⁺, (b) Ca²⁺, (c) N³⁻, (d) Ru²⁺, (e) H⁻.

7.23 Give three examples of +2 ions that have an electron configuration of nd^{10} ($n = 3, 4, 5 \dots$).

7.17 (b)

7.5 | Electron Affinity

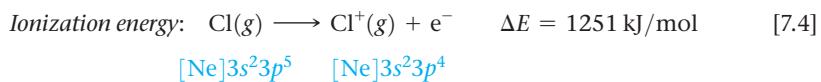


Plastic food wrap has a low permeability to oxygen and water vapor. It may be used to keep food fresh and is a convenient means to cover plates, bowls, and jugs of different shapes and sizes. Its stretchiness allows it to wrap easily around objects and static electricity helps it stick. When the food wrap is pulled off its roll, electrons can be removed from the molecules on one surface and added to another. This builds up a small charge that helps it stick to the object you are covering.

We have looked at the ionization of atoms in the previous section. Here, we look at the addition of electrons to atoms to form anions, a process called electron affinity. By the end of this section, you should be able to

- Explain how electron affinity and ionization energy are related and how irregularities in the periodic trends for electron affinity can be related to electron configuration.

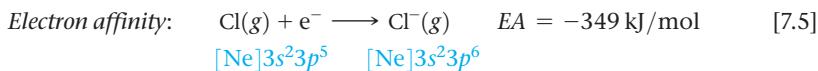
The first ionization energy of an atom is a measure of the energy change associated with removing an electron from the atom to form a cation. For example, the first ionization energy of Cl(g), 1251 kJ/mol, is the energy change associated with the process



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 .*

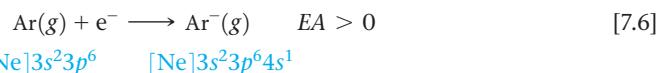
*Two sign conventions are used for electron affinity. In most introductory texts, including this one, the thermodynamic sign convention is used: A negative sign indicates that addition of an electron is an exothermic process, as in the electron affinity for chlorine, -349 kJ/mol . Historically, however, 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 $+349 \text{ kJ/mol}$.



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.

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:



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 $2p$ orbital, for Cl a $3p$ orbital, for Br a $4p$ 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	B -27	C -122	N > 0	O -141	F -328	Ne > 0
Na -53	Mg > 0	Al -43	Si -134	P -72	S -200	Cl -349	Ar > 0
K -48	Ca -2	Ga -30	Ge -119	As -78	Se -195	Br -325	Kr > 0
Rb -7	Sr -5	In -30	Sn -107	Sb -103	Te -190	I -295	Xe > 0

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

Self-Assessment Exercise

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

- (a) The values are the same magnitude but of opposite sign
 (b) EA for $\text{Cl}(g) > I_1$ for $\text{Cl}^-(g)$

Exercises

- 7.25** Write an equation for the first electron affinity of helium. Would you predict a positive or a negative energy value for this process? Is it possible to directly measure the first electron affinity of helium?
- 7.26** Which of the following, I or I^- , will have a negative electron affinity?

- 7.27** Consider the first ionization energy of neon and the electron affinity of fluorine. (a) Write equations, including electron configurations, for each process. (b) These two quantities have opposite signs. Which will be positive, and which will be negative? (c) Would you expect the magnitudes of these two quantities to be equal? If not, which one would you expect to be larger?

7.24 (a)

Answers to Self-Assessment Exercises



7.6 | Metals, Nonmetals, and Metalloids

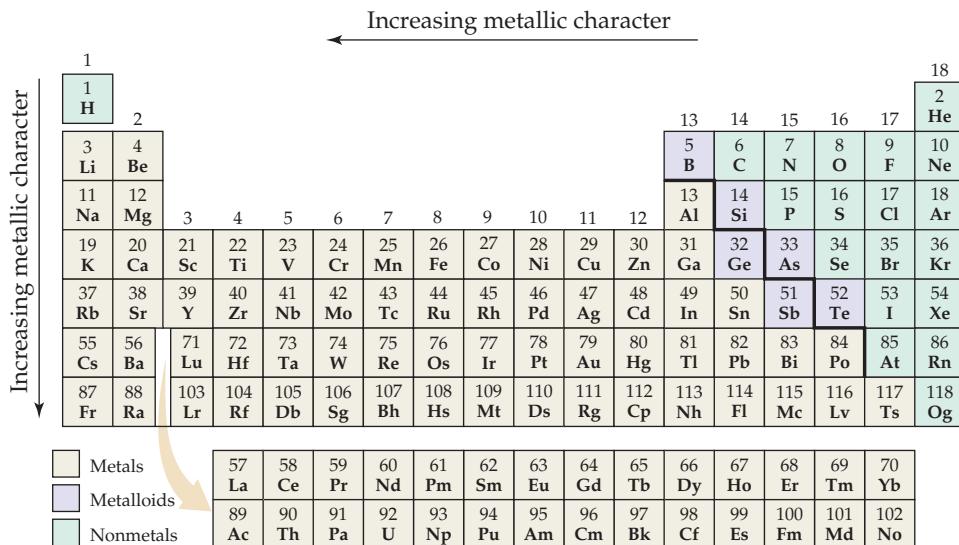


Atomic radii, ionization energies, and electron affinities are properties of individual atoms. With the exception of the noble gases, however, none of the elements exist in nature as individual atoms. To get a broader understanding of the properties of elements, we must also examine periodic trends in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

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). The lightest element in Group 14, carbon, comes in many different forms from the very hard diamond to charcoal, whose rough texture, ability to draw light or intensely dark lines, and easy removability give it a wide range of applications. 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

 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

and are semiconductors used extensively in integrated circuits and computers. Tin shows dual behavior 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).

By the end of this section, you should be able to

- Recognize the general properties of the elements and their oxides

The elements can be broadly grouped as metals, nonmetals, and metalloids (**Figure 7.13**). 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


Go Figure

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

1	H^+	2	Transition metals										13	14	15	16	H^-	17	18	
Li^+													Al^{+3}		P^{-3}	S^{-2}	Cl^-	N O B L E	G A S E S	
Na^+	Mg^{+2}																Se^{-2}	Br^-		
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}						Sn^{+2} Sn^{+4}	Sb^{+3} Sb^{+5}	Te^{-2}	I^-
Rb^+	Sr^{+2}	Y^{+3}	Zr^{+4}							Pd^{+2}	Ag^+	Cd^{+2}					Pb^{+2} Pb^{+4}	Bi^{+3} Bi^{+5}		
Cs^+	Ba^{+2}	Lu^{+3}	Hf^{+4}							Pt^{+2}	Au^+ Au^{+3}	Hg_2^{+2} Hg^{+2}								

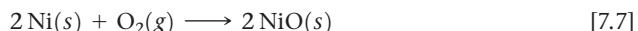
▲ **Figure 7.15 Representative oxidation states of the elements.** Note that hydrogen exhibits both positive and negative oxidation numbers, +1 and -1.

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 3422°C .

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

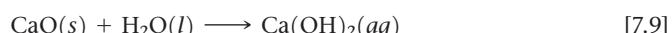
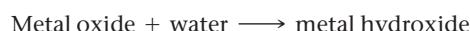
Figure 7.15 shows the oxidation states of representative ions of metals and nonmetals. As noted in Section 2.7, the charge on any alkali metal ion in a compound is always $1+$, and that on any alkaline earth metal is always $2+$. For atoms belonging to either of these groups, the outer s electrons are 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.

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:

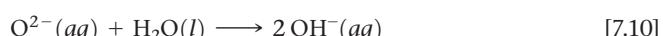


The oxides are particularly important because of the great abundance of oxygen in our environment.

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



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





Sample Exercise 7.8

Properties of Metal Oxides

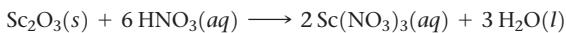
- (a) Would you expect scandium oxide to be a solid, liquid, or gas at room temperature?
 (b) Write the balanced chemical equation for the reaction of scandium oxide with nitric acid.

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, $\text{Sc}(\text{NO}_3)_3$:



► Practice Exercise

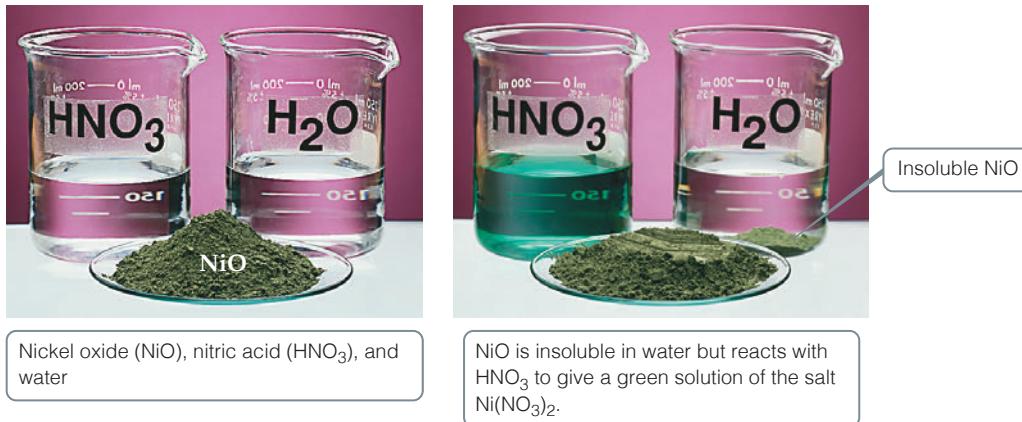
Suppose that a metal oxide of formula M_2O_3 were soluble in water. What would be the major product or products of dissolving the substance in water?

- (a) $\text{MH}_3(aq) + \text{O}_2(g)$
- (b) $\text{M}(s) + \text{H}_2(g) + \text{O}_2(g)$
- (c) $\text{M}^{3+}(aq) + \text{H}_2\text{O}_2(aq)$
- (d) $\text{M}(\text{OH})_2(aq)$
- (e) $\text{M}(\text{OH})_3(aq)$



Go Figure

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



▲ **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 $\text{Ni}(\text{NO}_3)_2$.



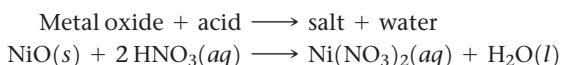
Go Figure

Do you think sulfur is malleable?



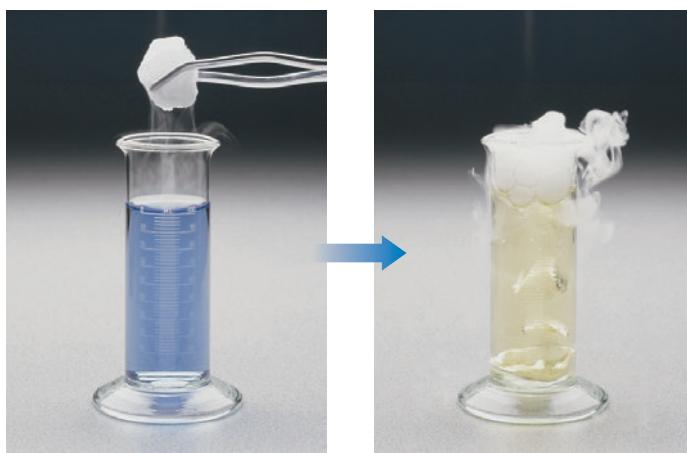
▲ **Figure 7.17** Sulfur, known to the medieval world as “brimstone,” is a nonmetal.

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**:



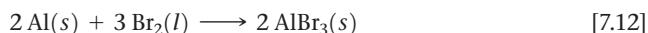
Nonmetals

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**).

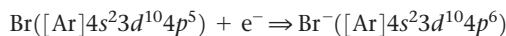


▲ **Figure 7.18** The reaction of CO_2 with water containing a bromothymol blue indicator. Initially, the blue color tells us the water is slightly basic. When a piece of solid carbon dioxide (“dry ice”) is added, the color changes to yellow, indicating an acidic solution. The mist is water droplets condensed from the air by cold CO_2 gas that sublimes off before reacting.

Because of their relatively large, negative electron affinities, nonmetals tend to gain electrons when they react with metals. For example, the reaction of aluminum with bromine produces the ionic compound aluminum bromide:

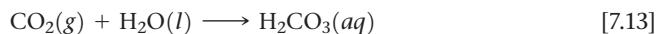
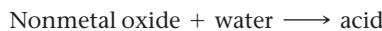


A nonmetal will typically gain enough electrons to fill its outermost occupied p subshell, giving a noble-gas electron configuration. For example, the bromine atom gains one electron to fill its $4p$ subshell:

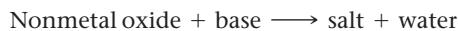


Compounds composed entirely of nonmetals are typically molecular substances that tend to be gases, liquids, or low melting point solids at room temperature. Examples include the common hydrocarbons we use for fuel (methane, CH_4 ; propane, C_3H_8 ; octane, C_8H_{18}) and the gases HCl , NH_3 , and H_2S . Many pharmaceuticals are molecules composed of C, H, N, O, and other nonmetals. For example, the molecular formula for the drug Celebrex® is $\text{C}_{17}\text{H}_{14}\text{F}_3\text{N}_3\text{O}_2\text{S}$.

Most nonmetal oxides are acidic, which means that those that dissolve in water form acids:



The reaction of carbon dioxide with water (**Figure 7.18**) accounts for the acidity of carbonated water and, to some extent, rainwater. Because sulfur is present in oil and coal, combustion of these common fuels produces sulfur dioxide and sulfur trioxide. These substances dissolve in water to produce *acid rain*, a major pollutant in many parts of the world. Like acids, most nonmetal oxides dissolve in basic solutions to form a salt plus water:



Metalloids

Metalloids have properties intermediate between those of metals and those of nonmetals. They may have some characteristic metallic properties but lack others. For example, the metalloid silicon *looks* like a metal (**Figure 7.19**), but it is brittle rather than malleable and does not conduct heat or electricity nearly as well as metals do.



▲ **Figure 7.19** Elemental silicon.



Sample Exercise 7.9

Reactions of Nonmetal Oxides

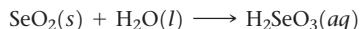
Write a balanced chemical equation for the reaction of solid selenium dioxide, $\text{SeO}_2(s)$, with (a) water, (b) aqueous sodium hydroxide.

SOLUTION

Analyze and Plan We note that selenium is a nonmetal. We therefore need to write chemical equations for the reaction of a nonmetal oxide with water and with a base, NaOH . Nonmetal oxides are acidic, reacting with water to form an acid and with bases to form a salt and water.

Solve

- (a) The reaction between selenium dioxide and water is like that between carbon dioxide and water (Equation 7.13):



(It does not matter that SeO_2 is a solid and CO_2 is a gas under ambient conditions; the point is that both are water-soluble nonmetal oxides.)

The reaction with sodium hydroxide is like that in Equation 7.15:



► Practice Exercise

Consider the following oxides: SO_2 , Y_2O_3 , MgO , Cl_2O , N_2O_5 . How many are expected to form acidic solutions in water?

- (a) 1 (b) 2 (c) 3 (d) 4 (e) 5

Several metalloids, most notably silicon, are electrical semiconductors and are the principal elements used in integrated circuits and computer chips. One of the reasons metalloids can be used for integrated circuits is that their electrical conductivity is intermediate between that of metals and that of nonmetals. Very pure silicon is an electrical insulator, but its conductivity can be dramatically increased with the addition of specific impurities called *dopants*. This modification provides a mechanism for controlling the electrical conductivity by controlling the chemical composition. We will return to this point in Chapter 12.

Self-Assessment Exercise

- 7.28** A compound XCl_2 , where X is an element, has a melting point of -121°C . Would you expect the compound to be ionic or molecular?

- (a) Ionic
(b) Molecular

Exercises

- 7.29** (a) Does metallic character increase, decrease, or remain unchanged as one goes from left to right across a row of the periodic table? (b) Does metallic character increase, decrease, or remain unchanged as one goes down a column of the periodic table? (c) Are the periodic trends in (a) and (b) the same as or different from those for first ionization energy?

- 7.30** Discussing this chapter, a classmate says, “An element that commonly forms a cation is a metal.” Do you agree or disagree?

- 7.31** Predict whether each of the following oxides is ionic or molecular: ZnO , K_2O , SO_2 , OF_2 , TiO_2 .

- 7.32** Would you expect zirconium(II) oxide, ZrO , to react more readily with $\text{HCl}(aq)$ or $\text{NaOH}(aq)$?

- 7.33** Chlorine reacts with oxygen to form Cl_2O_7 . (a) What is the name of this product (see Table 2.6)? (b) Write a balanced equation for the formation of $\text{Cl}_2\text{O}_7(l)$ from the elements. (c) Would you expect Cl_2O_7 to be more reactive toward $\text{H}^+(aq)$ or $\text{OH}^-(aq)$? (d) If the oxygen in Cl_2O_7 is considered to have the -2 oxidation state, what is the oxidation state of the Cl? What is the electron configuration of Cl in this oxidation state?

- 7.34** Write balanced equations for the following reactions: (a) boron trichloride with water, (b) cobalt (II) oxide with nitric acid, (c) phosphorus pentoxide with water, (d) carbon dioxide with aqueous barium hydroxide.

7.28 (b)



7.7 | Trends for Group 1 and Group 2 Metals



▲ Figure 7.20 Sodium, like the other alkali metals, is soft enough to be cut with a knife.

In the 1820's, Goldsworthy Gurney found that a sample of calcium oxide heated with a hydrogen-oxygen blowpipe glowed with an intense white light. This was adopted by theatres in the 1830's and 1840's, and the expression 'in the limelight' was born. While effective, the lights needed constant attention and were a fire hazard. Consequently, they were replaced by electric lighting soon after its invention by Thomas Edison in 1789.

By the end of this section, you should have

- Acquired an overview of the chemistry of Group 1 and 2 metals

As we have seen, elements in a given group possess general similarities. However, trends also exist within each group. In this section, we use the periodic table and our knowledge of electron configurations to examine the chemistry of the **alkali metals** and **alkaline earth metals**.

Group 1: The Alkali Metals

The alkali metals are soft metallic solids (Figure 7.20). All have characteristic metallic properties, such as a silvery, metallic luster, and high thermal and electrical conductivity. The name *alkali* comes from an Arabic word meaning "ashes." Many compounds of sodium and potassium, two alkali metals, were isolated from wood ashes by early chemists.

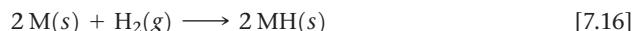
As Table 7.4 shows, the alkali metals have low densities and melting points, and these properties vary in a fairly regular way with increasing atomic number. We see

TABLE 7.4 Some Properties of the Alkali Metals

Element	Electron Configuration	Melting Point (°C)	Density (g/cm ³)	Atomic Radius (pm)	I ₁ (kJ/mol)
Lithium	[He]2s ¹	181	0.53	128	520
Sodium	[Ne]3s ¹	98	0.97	166	496
Potassium	[Ar]4s ¹	63	0.86	203	419
Rubidium	[Kr]5s ¹	39	1.53	220	403
Cesium	[Xe]6s ¹	28	1.88	244	376

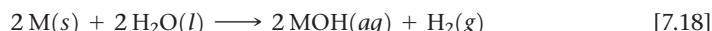
the usual trends as we move down the group, such as increasing atomic radius and decreasing first ionization energy. The alkali metal of any given period has the lowest I_1 value in the period (Figure 7.10), which reflects the relative ease with which its outer s electron can be removed. As a result, the alkali metals are all very reactive, losing one electron to form ions carrying a $1+$ charge.

The alkali metals exist in nature only as compounds. Sodium and potassium are relatively abundant in Earth's crust, in seawater, and in biological systems, always as the cations of ionic compounds. All alkali metals combine directly with most nonmetals. For example, they react with hydrogen to form hydrides and with sulfur to form sulfides:



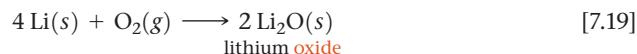
where M represents any alkali metal. In hydrides of the alkali metals (LiH , NaH , and so forth), hydrogen is present as H^- , the **hydride ion**. A hydrogen atom that has gained an electron, this ion is distinct from the hydrogen ion, H^+ , formed when a hydrogen atom loses its electron.

The alkali metals react vigorously with water, producing hydrogen gas and a solution of an alkali metal hydroxide:



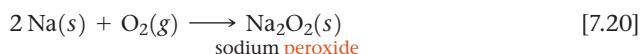
These reactions are very exothermic (Figure 7.21). In many cases, enough heat is generated to ignite the H_2 , producing a fire or sometimes even an explosion, as in the case of K reacting with water. The reaction is even more violent for Rb and, especially, Cs, because their ionization energies are even lower than that of K.

Recall that the most common ion of oxygen is the oxide ion, O^{2-} . We would therefore expect that the reaction of an alkali metal with oxygen would produce the corresponding metal oxide. Indeed, reaction of Li metal with oxygen does form lithium oxide:



When dissolved in water, Li_2O and other soluble metal oxides form hydroxide ions from the reaction of O^{2-} ions with H_2O (Equation 7.10).

The reactions of the other alkali metals with oxygen are more complex than we would anticipate. For example, when sodium reacts with oxygen, the main product is sodium *peroxide*, which contains the O_2^{2-} ion:



Go Figure

Would you expect rubidium metal to be more or less reactive with water than potassium metal?

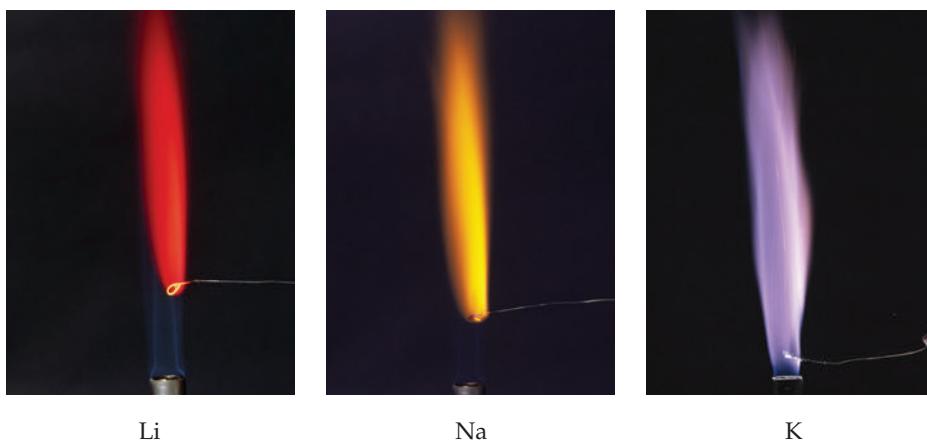


Li

Na

K

▲ Figure 7.21 The alkali metals react vigorously with water.



▲ Figure 7.22 Placed in a flame, ions of each alkali metal emit light of a characteristic wavelength.

Potassium, rubidium, and cesium react with oxygen to form compounds that contain the O_2^- ion, which we call the *superoxide ion*. For example, potassium forms potassium superoxide, KO_2 :



Be aware that the reactions in Equations 7.20 and 7.21 are somewhat unexpected; in most cases, the reaction of oxygen with a metal forms the metal oxide.

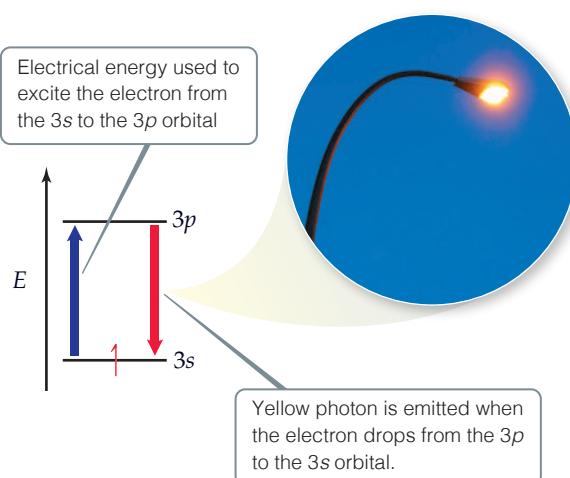
As seen from Equations 7.18 through 7.21, the alkali metals are extremely reactive toward water and oxygen. Because of this reactivity, the metals are usually stored submerged in a liquid hydrocarbon, such as mineral oil or kerosene.

Although alkali metal ions are colorless, each emits a characteristic color when placed in a flame (Figure 7.22). The ions are reduced to gaseous metal atoms in the flame. The high temperature excites the valence electron from the ground state to a higher-energy orbital, causing the atom to be in an excited state. The atom then emits energy in the form of visible light as the electron falls back into the lower-energy orbital and the atom returns to its ground state. The light emitted is at a specific wavelength for each element, just as we saw earlier for line spectra of hydrogen and sodium. The characteristic yellow emission of sodium at 589 nm is the basis for sodium vapor lamps (Figure 7.23).



Go Figure

If we had potassium vapor lamps, what color would they be?



▲ Figure 7.23 The characteristic yellow light in a sodium lamp results from excited electrons in the high-energy 3p orbital falling back to the lower-energy 3s orbital.



Sample Exercise 7.10

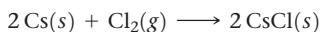
Reactions of an Alkali Metal

Write a balanced equation for the reaction of cesium metal with (a) $\text{Cl}_2(g)$, (b) $\text{H}_2\text{O}(l)$, (c) $\text{H}_2(g)$.

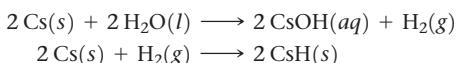
SOLUTION

Analyze and Plan Because cesium is an alkali metal, we expect its chemistry to be dominated by oxidation of the metal to Cs^+ ions. Further, we recognize that Cs is far down the periodic table, which means it is among the most active of all metals and probably reacts with all three substances.

Solve The reaction between Cs and Cl_2 is a simple combination reaction between a metal and a nonmetal, forming the ionic compound CsCl :



From Equations 7.18 and 7.16, we predict the reactions of cesium with water and hydrogen to proceed as follows:



All three reactions are redox reactions where cesium forms a Cs^+ ion. The Cl^- , OH^- , and H^- are all $1-$ ions, which means the products have 1:1 stoichiometry with Cs^+ .

► Practice Exercise

Consider the following three statements about the reactivity of an alkali metal M with oxygen gas:

- (i) Based on their positions in the periodic table, the expected product is the ionic oxide M_2O .
- (ii) Some of the alkali metals produce metal peroxides or metal superoxides when they react with oxygen.
- (iii) When dissolved in water, an alkali metal oxide produces a basic solution.

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.

CHEMISTRY AND LIFE The Improbable Development of Lithium Drugs

Alkali metal ions tend to play an unexciting role in most chemical reactions. As noted in Section 4.2, all salts of the alkali metal ions are soluble in water, and the ions are spectators in most aqueous reactions (except for those involving the alkali metals in their elemental form, such as those in Equations 7.16 through 7.21). However, these ions play an important role in human physiology. Sodium and potassium ions, for example, are major components of blood plasma and intracellular fluid, respectively, with average concentrations of 0.1 M. These electrolytes serve as vital charge carriers in normal cellular function. In contrast, the lithium ion has no known function in normal human physiology. Since the discovery of lithium in 1817, however, people have believed that salts of the element possessed almost mystical healing powers. There were even claims that lithium ions were an ingredient in ancient “fountain of youth” formulas. In 1927, C. L. Grigg began marketing a soft drink that contained lithium. The original unwieldy name of the beverage was “Bib-Label Lithiated Lemon-Lime Soda,” which was soon changed to the simpler and more familiar name 7UP® (Figure 7.24).

Because of concerns of the US Food and Drug Administration, lithium was removed from 7UP® during the early 1950s. At nearly the same time, psychiatrists discovered that lithium ions have a remarkable therapeutic effect on the mental condition called *bipolar disorder*. Individuals that suffer from this psychosis, undergo severe mood swings from deep depression to a manic euphoria. The lithium ion smoothes these mood swings, allowing the bipolar patient to function more effectively in daily life.

The antipsychotic action of Li^+ was discovered by accident in the 1940s by Australian psychiatrist John Cade (1912–1980) as he was researching the use of uric acid—a component of urine—to treat manic-depressive illness. He administered the acid to manic laboratory animals in the form of its most soluble salt, lithium urate, and found that many of the manic symptoms seemed to disappear. Later studies showed that uric acid has no role in the therapeutic effects observed; rather, the Li^+ ions were responsible. Because lithium overdose can cause severe side effects in humans, including kidney failure and death, lithium salts were not approved as antipsychotic drugs for humans until 1970. Today Li^+ is usually administered orally in the form of Li_2CO_3 , which is the active ingredient in prescription drugs such as Eskalith®. Lithium drugs are effective for about 70% of bipolar patients who take it.



▲ **Figure 7.24** **Lithium no more.** The soft drink 7UP® originally contained a lithium salt that was claimed to give the beverage healthful benefits, including “an abundance of energy, enthusiasm, a clear complexion, lustrous hair, and shining eyes!” The lithium was removed from the beverage in the early 1950s, about the time that the antipsychotic action of Li^+ was discovered.

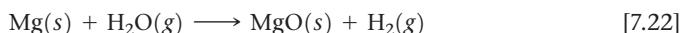
In this age of sophisticated drug design and biotechnology, the simple lithium ion is still the most effective treatment of this destructive psychiatric disorder. Remarkably, despite intensive research, scientists still do not fully understand the biochemical action of lithium that leads to its therapeutic effects. Because of its similarity to Na^+ , Li^+ is incorporated into blood plasma, where it can affect the behavior of nerve and muscle cells. Because Li^+ has a smaller radius than Na^+ (Figure 7.8), the way Li^+ interacts with molecules in human cells is different from the way Na^+ interacts with the molecules. Other studies indicate that Li^+ alters the function of certain neurotransmitters, which might lead to its effectiveness as an antipsychotic drug.

Group 2: The Alkaline Earth Metals

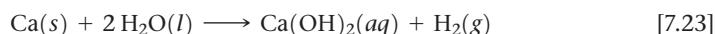
Like the alkali metals, the alkaline earth metals are all solids at room temperature and have typical metallic properties (Table 7.5). Compared with the alkali metals, the alkaline earth metals are harder and denser, and melt at higher temperatures.

The first ionization energies of the alkaline earth metals are low but not as low as those of the alkali metals. Consequently, the alkaline earth metals are less reactive than their alkali metal neighbors. As noted in Section 7.4, the ease with which the elements lose electrons decreases as we move across a period and increases as we move down a group. Thus, beryllium and magnesium, the lightest alkaline earth metals, are the least reactive.

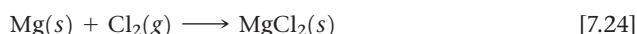
The trend of increasing reactivity within the group is shown by the way the alkaline earth metals behave in the presence of water. Beryllium does not react with either water or steam, even when heated red-hot. Magnesium reacts slowly with liquid water and more readily with steam:



Calcium and the elements below it react readily with water at room temperature (although more slowly than the alkali metals adjacent to them in the periodic table). The reaction between calcium and water (Figure 7.25), for example, is



Equations 7.22 and 7.23 illustrate the dominant pattern in the reactivity of the alkaline earth elements: They tend to lose their two outer s electrons and form $2+$ ions. For example, magnesium reacts with chlorine at room temperature to form MgCl_2 and burns with dazzling brilliance in air to give MgO :



In the presence of O_2 , magnesium metal is protected by a thin coating of water-insoluble MgO . Thus, even though Mg is high in the activity series, it can be incorporated into lightweight structural alloys used in, for example, automobile wheels. The heavier alkaline earth metals (Ca, Sr, and Ba) are even more reactive toward nonmetals than is magnesium.

The heavier alkaline earth ions give off characteristic colors when heated in a hot flame. Strontium salts produce the brilliant red color in fireworks, and barium salts produce the green color.

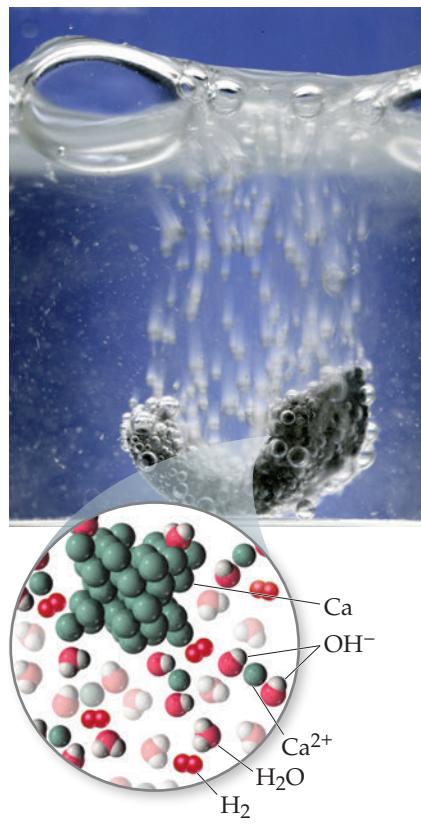
Like their neighbors sodium and potassium, magnesium and calcium are relatively abundant on Earth and in seawater and are essential for living organisms as cations in ionic compounds. Calcium is particularly important for growth and maintenance of bones and teeth.

TABLE 7.5 Some Properties of the Alkaline Earth Metals

Element	Electron Configuration	Melting Point (°C)	Density (g/cm ³)	Atomic Radius (pm)	I_1 (kJ/mol)
Beryllium	[He]2s ²	1287	1.85	96	899
Magnesium	[Ne]3s ²	650	1.74	141	738
Calcium	[Ar]4s ²	842	1.55	176	590
Strontium	[Kr]5s ²	777	2.63	195	549
Barium	[Xe]6s ²	727	3.51	215	503

Go Figure

What is the cause of the bubbles that are formed? How could you test your answer?



▲ Figure 7.25 Elemental calcium reacts with water.

Self-Assessment Exercise

7.35 Which ion do you expect to have the smallest radius?

- (a) K⁺
- (b) Ca²⁺

Exercises

7.36 (a) Why is calcium generally more reactive than beryllium?
(b) Why is calcium generally less reactive than rubidium?

7.37 Write a balanced equation for the reaction that occurs in each of the following cases: (a) Potassium metal is exposed to an atmosphere of chlorine gas. (b) Strontium oxide is added to water. (c) A fresh surface of lithium metal is exposed to oxygen gas. (d) Sodium metal reacts with molten sulfur.

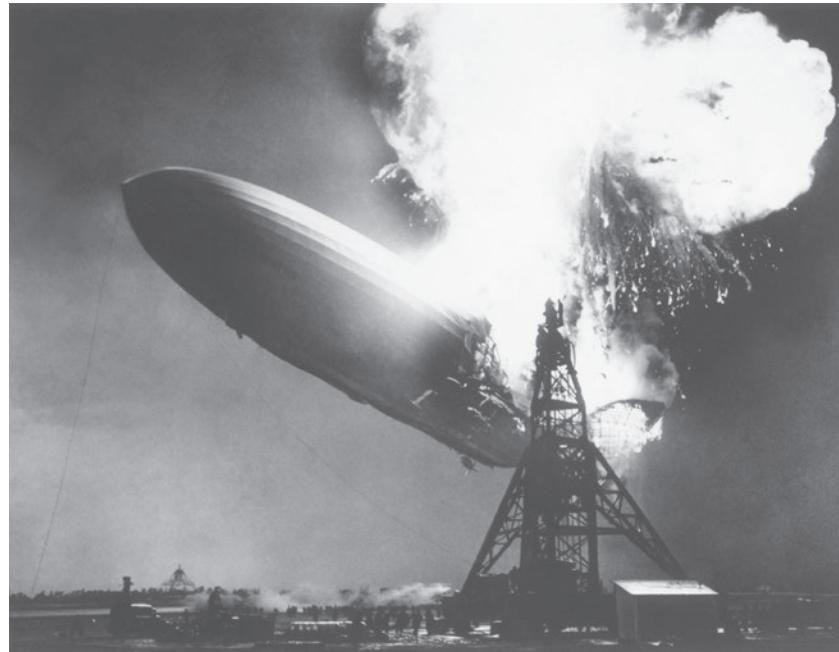
7.38 (a) As described in Section 7.7, the alkali metals react with hydrogen to form hydrides and react with halogens to form halides. Compare the roles of hydrogen and halogens in these reactions. Write balanced equations for the reaction of fluorine with calcium and for the reaction of hydrogen with calcium. (b) What is the oxidation number and electron configuration of calcium in each product?

7.35 (b)

Answers to Self-Assessment Exercises



7.8 | Trends for Selected Nonmetals



Hydrogen, generated from the reaction of dilute acid on iron filings, was first reported by Robert Boyle in 1671. The gas was recognized as a new substance ninety years later by Henry Cavendish who called it ‘flammable air’ but this was changed to hydrogen by Antoine Lavoisier in 1783 upon observing that the gas burnt in air to give water. The name is derived from the Greek *hydro* for water and *genes* for creator.

As the lightest element, it was the obvious choice of gas for the early airships that appeared around 1900. However, the highly flammable nature of hydrogen lead to the disaster of the Hindenburg on 6th May 1937, when the airship burst into flames while attempting to dock at Lakehurst, New Jersey. Air travel was still in its infancy, and there were journalists on hand to report on the arrival of the airship’s maiden flight from Europe to the USA. It took just 90 seconds for the hydrogen to burn out and spelt the end to commercial travel by airship.

By the end of this section, you should have

- Acquired an overview of the chemistry of selected non-metals

Hydrogen

We have seen that the chemistry of the alkali metals is dominated by the loss of their outer ns^1 electron to form cations. The $1s^1$ electron configuration of hydrogen suggests that its chemistry should have some resemblance to that of the alkali metals. The chemistry of hydrogen is much richer and more complex than that of the alkali metals,

however, mainly because the ionization energy of hydrogen, 1312 kJ/mol, is higher than any metal and comparable to that of oxygen. As a result, hydrogen is a nonmetal that occurs as a colorless diatomic gas, $\text{H}_2(g)$, under most conditions.

The reactivity of hydrogen with nonmetals reflects its much greater tendency to hold on to its electron relative to the alkali metals. Unlike the alkali metals, hydrogen reacts with most nonmetals to form molecular compounds in which its electron is shared with, rather than completely transferred to, the other nonmetal. For example, we have seen that sodium metal reacts vigorously with chlorine gas to produce the ionic compound sodium chloride, in which the outermost sodium electron is completely transferred to a chlorine atom (Figure 2.19):



By contrast, molecular hydrogen reacts with chlorine gas to form hydrogen chloride gas, which consists of HCl molecules:



Hydrogen readily forms molecular compounds with other nonmetals, such as the formation of water, $\text{H}_2\text{O}(l)$; ammonia, $\text{NH}_3(g)$; and methane, $\text{CH}_4(g)$. The ability of hydrogen to form bonds with carbon is one of the most important aspects of organic chemistry, as will see in later chapters.

We have seen that, particularly in the presence of water, hydrogen does readily form H^+ ions in which the hydrogen atom has lost its electron. For example, $\text{HCl}(g)$ dissolves in H_2O to form a solution of hydrochloric acid, $\text{HCl}(aq)$, in which the electron of the hydrogen atom is transferred to the chlorine atom—a solution of hydrochloric acid consists largely of $\text{H}^+(aq)$ and $\text{Cl}^-(aq)$ ions stabilized by the H_2O solvent.* Indeed, the ability of molecular compounds of hydrogen with nonmetals to form acids in water is one of the most important aspects of aqueous chemistry. We will discuss the chemistry of acids and bases in detail later in the text, particularly in Chapter 16.

Finally, as is typical for nonmetals, hydrogen also has the ability to gain an electron from a metal with a low ionization energy. For example, we saw in Equation 7.16 that hydrogen reacts with active metals to form solid metal hydrides that contain the hydride ion, H^- . The fact that hydrogen can gain an electron further illustrates that it behaves much more like a nonmetal than an alkali metal.

Group 16: The Oxygen Group

As we proceed down Group 16, there is a change from nonmetallic to metallic character (Figure 7.13). Oxygen, sulfur, and selenium are typical nonmetals. Tellurium is a metalloid, and polonium, which is radioactive and quite rare, is a metal. Oxygen is a colorless gas at room temperature; all of the other members of Group 16 are solids. Some of the physical properties of the Group 16 elements are given in **Table 7.6**.

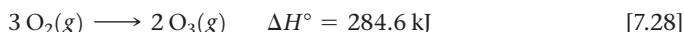
As we saw in Section 2.6, oxygen exists in two molecular forms, O_2 and O_3 . Because O_2 is the more common form, people generally mean it when they say “oxygen,”

TABLE 7.6 Some Properties of the Group 16 Elements

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (pm)	I_1 (kJ/mol)
Oxygen	[He] $2s^22p^4$	-218	1.43 g/L	66	1314
Sulfur	[Ne] $3s^23p^4$	115	1.96 g/cm ³	105	1000
Selenium	[Ar] $3d^{10}4s^24p^4$	221	4.82 g/cm ³	120	941
Tellurium	[Kr] $4d^{10}5s^25p^4$	450	6.24 g/cm ³	138	869
Polonium	[Xe] $4f^{14}5d^{10}6s^26p^4$	254	9.20 g/cm ³	140	812

*A more realistic description is one where an H^+ ion is transferred from HCl to H_2O forming Cl^- and H_3O^+ . We will explore this chemistry in detail in Chapter 16.

although the name *dioxygen* is more descriptive. The O₃ form is **ozone**. The two forms of oxygen are examples of *allotropes*, defined as different forms of the same element. About 21% of dry air consists of O₂ molecules. Ozone is present in very small amounts in the upper atmosphere and in polluted air. It is also formed from O₂ in electrical discharges, such as in lightning storms:

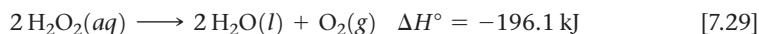


This reaction is strongly endothermic, telling us that O₃ is less stable than O₂.

Although both O₂ and O₃ are colorless and therefore do not absorb visible light, O₃ absorbs certain wavelengths of ultraviolet light that O₂ does not. Because of this difference, the presence of ozone in the upper atmosphere is beneficial, filtering out harmful UV light. Ozone and oxygen also have different chemical properties. Ozone, which has a pungent odor, is a powerful oxidizing agent. Because of this property, ozone is sometimes added to water to kill bacteria or used in low levels to help to purify air. However, the reactivity of ozone also makes its presence in polluted air near Earth's surface detrimental to human health.

Oxygen has a great tendency to attract electrons from other elements (to *oxidize* them). Oxygen in combination with a metal is almost always present as the oxide ion, O²⁻. This ion has a noble-gas configuration and is particularly stable. As shown in Figure 5.14, the formation of nonmetal oxides is also often very exothermic and thus energetically favorable.

In our discussion of the alkali metals, we noted two less common oxygen anions—the peroxide (O₂²⁻) ion and the superoxide (O₂⁻) ion. Compounds of these ions often react to produce an oxide and O₂:



After oxygen, the most important member of Group 16 is sulfur. This element exists in several allotrophic forms, the most common and stable of which is the yellow solid having the molecular formula S₈. This molecule consists of an eight-membered ring of sulfur atoms (Figure 7.26). Even though solid sulfur consists of S₈ rings, we usually write it simply as S(s) in chemical equations to simplify the stoichiometric coefficients.

Like oxygen, sulfur has a tendency to gain electrons from other elements to form sulfides, which contain the S²⁻ ion. In fact, most sulfur in nature is present as metal sulfides. Sulfur is below oxygen in the periodic table, and the tendency of sulfur to form sulfide anions is not as great as that of oxygen to form oxide ions. As a result, the chemistry of sulfur is more complex than that of oxygen. In fact, sulfur and its compounds (including those in coal and petroleum) can be burned in oxygen. The main product is sulfur dioxide, a major air pollutant:



Below sulfur in Group 16 is selenium, Se. This relatively rare element is essential for life in trace quantities, although it is toxic at high doses. There are many allotropes of Se, including several eight-membered ring structures that resemble the S₈ ring.

The next element in the group is tellurium, Te. Its elemental structure is even more complex than that of Se, consisting of long, twisted chains of Te—Te bonds. Both Se and Te favor the –2 oxidation state, as do O and S.

From O to S to Se to Te, the elements form larger and larger molecules and become increasingly metallic. The thermal stability of Group 16 compounds with hydrogen decreases down the column: H₂O > H₂S > H₂Se > H₂Te, with H₂O, water, being the most stable of the series.

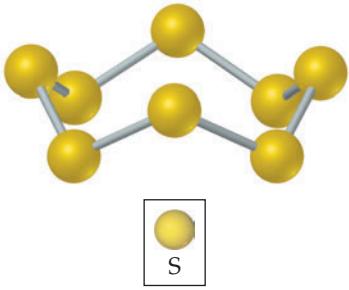
Group 17: The Halogens

Some of the properties of the Group 17 elements, the **halogens**, are given in Table 7.7. Astatine, which is both extremely rare and radioactive, is omitted because many of its properties are not yet known. Even less is known about the recently discovered Tennessine.

Unlike the Group 16 elements, all of the halogens that have been characterized are nonmetals. Their melting and boiling points increase with increasing atomic number. Fluorine and chlorine are gases at room temperature, bromine is a liquid, and iodine is a solid. Each element consists of diatomic molecules: F₂, Cl₂, Br₂, and I₂ (Figure 7.27).

Go Figure

Suppose it were possible to flatten the S₈ ring. What shape would you expect the flattened ring to have?



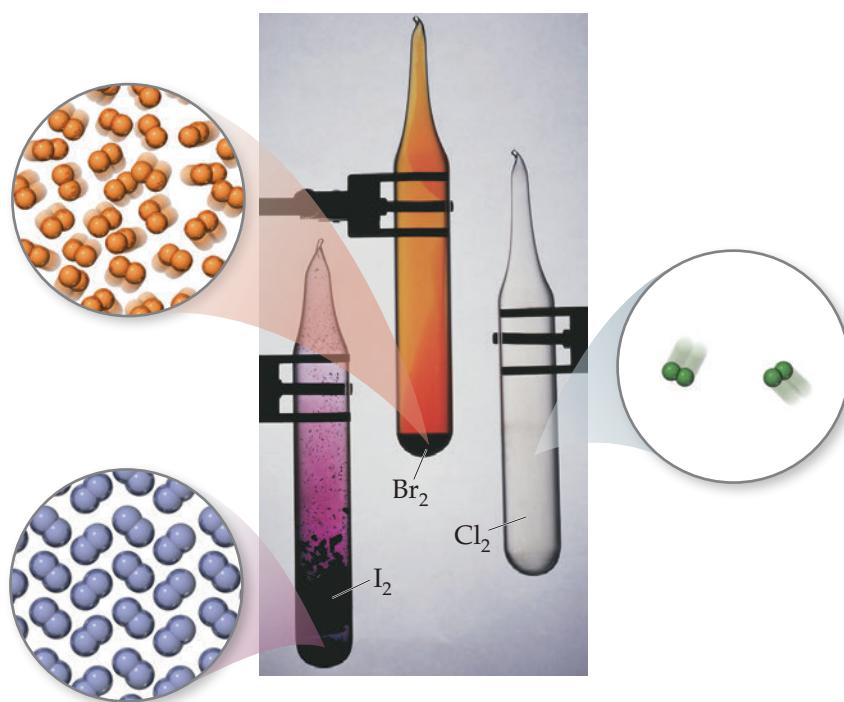
▲ Figure 7.26 Elemental sulfur exists as the S₈ molecule. At room temperature, this is the most common allotropic form of sulfur.

TABLE 7.7 Some Properties of the Halogens

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (pm)	I_1 (kJ/mol)
Fluorine	[He]2s ² 2p ⁵	-220	1.69 g/L	57	1681
Chlorine	[Ne]3s ² 3p ⁵	-102	3.12 g/L	102	1251
Bromine	[Ar]4s ² 3d ¹⁰ 4p ⁵	-7.3	3.12 g/cm ³	120	1140
Iodine	[Kr]5s ² 4d ¹⁰ 5p ⁵	114	4.94 g/cm ³	139	1008

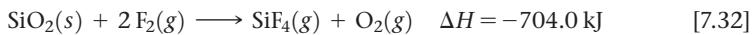
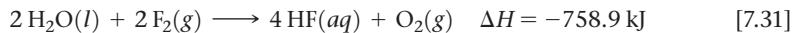

Go Figure

Why are more molecules of I_2 seen in the molecular view relative to the number of Cl_2 molecules?



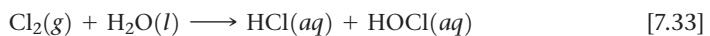
▲ **Figure 7.27** The elemental halogens exist as diatomic molecules.

The halogens have highly negative electron affinities (Figure 7.12). Thus, it is not surprising that the chemistry of the halogens is dominated by their tendency to gain electrons from other elements to form halide ions, X^- . (In many equations, X is used to indicate any one of the halogen elements.) Fluorine and chlorine are more reactive than bromine and iodine. In fact, fluorine removes electrons from almost any substance with which it comes into contact, including water, and usually does so very exothermically, as in the following examples:



As a result, fluorine gas is difficult and dangerous to use in the laboratory, requiring specialized equipment.

Chlorine is the most industrially useful of the halogens. It is produced by a process called electrolysis, where an electrical current is used to oxidize chloride anions to molecular chlorine, Cl_2 . Unlike fluorine, chlorine reacts slowly with water to form relatively stable aqueous solutions of HCl and $HOCl$ (hypochlorous acid):



Chlorine is often added to drinking water and swimming pools because the HOCl(*aq*) that is generated serves as a disinfectant.

The halogens react directly with most metals to form ionic halides. The halogens also react with hydrogen to form gaseous hydrogen halide compounds:



These compounds are all very soluble in water and dissolve to form the hydrohalic acids. As we discussed in Section 4.3, HCl(*aq*), HBr(*aq*), and HI(*aq*) are strong acids, whereas HF(*aq*) is a weak acid.

Group 18: The Noble Gases

The Group 18 elements, known as the **noble gases**, are all nonmetals that are gases at room temperature. They are all *monatomic* (that is, they consist of single atoms rather than molecules). Some physical properties of the noble-gas elements are listed in **Table 7.8**. The high radioactivity of radon (Rn, atomic number 86) has limited the study of its reaction chemistry and some of its properties.

The noble gases have completely filled *s* and *p* subshells. All elements of Group 18 have large first ionization energies, and we see the expected decrease as we move down the column. Because the noble gases possess such stable electron configurations, they are exceptionally unreactive. In fact, until the early 1960s the elements were called the *inert gases* because they were thought to be incapable of forming chemical compounds. In 1962, Neil Bartlett (1932–2008) at the University of British Columbia reasoned that the ionization energy of Xe might be low enough to allow it to form compounds. For this to happen, Xe would have to react with a substance with an extremely high ability to remove electrons from other substances, such as fluorine. Bartlett synthesized the first noble-gas compound by combining Xe with the fluorine-containing compound PtF₆. Xenon also reacts directly with F₂(*g*) to form the molecular compounds XeF₂, XeF₄, and XeF₆. Krypton has a higher *I*₁ value than xenon and is therefore less reactive. In fact, only a single stable compound of krypton is known, KrF₂. In 2000, Finnish scientists reported the first neutral molecule that contains argon, the HArF molecule, which is stable only at low temperatures.

TABLE 7.8 Some Properties of the Noble Gases

Element	Electron Configuration	Boiling Point (K)	Density (g/L)	Atomic Radius* (pm)	<i>I</i> ₁ (kJ/mol)
Helium	1s ²	4.2	0.18	28	2372
Neon	[He]2s ² 2p ⁶	27.1	0.90	58	2081
Argon	[Ne]3s ² 3p ⁶	87.3	1.78	106	1521
Krypton	[Ar]4s ² 3d ¹⁰ 4p ⁶	120	3.75	116	1351
Xenon	[Kr]5s ² 4d ¹⁰ 5p ⁶	165	5.90	140	1170
Radon	[Xe]6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶	211	9.73	150	1037

*Only the heaviest of the noble-gas elements form chemical compounds. Thus, the atomic radii for the lighter noble-gas elements are estimated values.

Self-Assessment Exercise

- 7.39** The density of bromine is 1000 times larger than chlorine. What factor do you think plays the biggest role in this dramatic change?

- (a) The increased mass of a bromine atom.
- (b) The fact that bromine is a liquid and chlorine a gas.
- (c) The larger atomic radius of bromine.

Exercises

- 7.40** Compare the elements bromine and chlorine with respect to the following properties: (a) electron configuration, (b) most common ionic charge, (c) first ionization energy, (d) reactivity toward water, (e) electron affinity, (f) atomic radius. Account for the differences between the two elements.
- 7.41** Until the early 1960s, the Group 18 elements were called the inert gases. (a) Why was the term *inert gases* dropped?
- (b) What discovery triggered this change in name? (c) What name is applied to the group now?
- 7.42** Write a balanced equation for the reaction that occurs in each of the following cases: (a) White phosphorous, $P_4(s)$, reacts with chlorine gas. (b) Sodium metal reacts with water. (c) Hydrogen bromide gas reacts with chlorine gas. (d) Aluminum trichloride reacts with aqueous sodium hydroxide.

7.39 (a)

Answers to Self-Assessment Exercises



Sample Integrative Exercise

Putting Concepts Together

The element bismuth (Bi, atomic number 83) is the heaviest member of Group 15. A salt of the element, bismuth subsalicylate, is the active ingredient in Pepto-Bismol®, an over-the-counter medication for gastric distress.

- (a) Based on values presented in Figure 7.7 and Tables 7.5 and 7.6, what might you expect for the bonding atomic radius of bismuth?
- (b) What accounts for the general increase in atomic radius going down the Group 15 elements?
- (c) Another major use of bismuth has been as an ingredient in low-melting metal alloys, such as those used in fire sprinkler systems and in typesetting. The element itself is a brittle white crystalline solid. How do these characteristics fit with the fact that bismuth is in the same periodic group with such nonmetallic elements as nitrogen and phosphorus?
- (d) Bi_2O_3 is a basic oxide. Write a balanced chemical equation for its reaction with dilute nitric acid. If 6.77 g of Bi_2O_3 is dissolved in dilute acidic solution to make 0.500 L of solution, what is the molarity of the solution of Bi^{3+} ion?
- (e) ^{209}Bi is the heaviest stable isotope of any element. How many protons and neutrons are present in this nucleus?
- (f) The density of Bi at 25 °C is 9.808 g/cm³. How many Bi atoms are present in a cube of the element that is 5.00 cm on each edge? How many moles of the element are present?

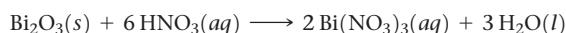
SOLUTION

- (a) Bismuth is directly below antimony, Sb, in Group 15. Based on the observation that atomic radii increase as we go down a column, we would expect the radius of Bi to be greater than that of Sb, which is 139 pm. We also know that atomic radii generally decrease as we proceed from left to right in a period. Tables 7.5 and 7.6 each give an element in the same period, namely, Ba and Po. We would therefore expect that the radius of Bi is smaller than that of Ba (215 pm) and larger than that of Po (140 pm). We also see that in other periods, the difference in radius between the neighboring Group 15 and Group 16 elements is relatively small. We might therefore expect that the radius of Bi is slightly larger than that of Po—much closer to the radius of Po than to the radius of Ba. The tabulated value for the atomic radius on Bi is 148 pm, in accord with our expectations.
- (b) The general increase in radius with increasing atomic number in the Group 15 elements occurs because additional shells of electrons are being added, with corresponding increases in nuclear charge. The core electrons in each case largely screen the outermost electrons from the nucleus, so the effective nuclear charge does not vary

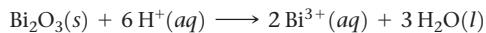
greatly as we go to higher atomic numbers. However, the principal quantum number, n , of the outermost electrons steadily increases, with a corresponding increase in orbital radius.

- (c) The contrast between the properties of bismuth and those of nitrogen and phosphorus illustrates the general rule that there is a trend toward increased metallic character as we move down in a given group. Bismuth, in fact, is a metal. The increased metallic character occurs because the outermost electrons are more readily lost in bonding, a trend that is consistent with its lower ionization energy.
- (d) Following the procedures described in Section 4.2 for writing molecular and net ionic equations, we have the following:

Molecular equation:



Net ionic equation:



In the net ionic equation, nitric acid is a strong acid and $Bi(NO_3)_3$ is a soluble salt, so we need to show only the reaction of the solid with the hydrogen ion forming the $Bi^{3+}(aq)$ ion

Continued

and water. To calculate the concentration of the solution, we proceed as follows (Section 4.5):

$$\frac{6.77 \text{ g Bi}_2\text{O}_3}{0.500 \text{ L soln}} \times \frac{1 \text{ mol Bi}_2\text{O}_3}{466.0 \text{ g Bi}_2\text{O}_3} \times \frac{2 \text{ mol Bi}^{3+}}{1 \text{ mol Bi}_2\text{O}_3}$$

$$= \frac{0.0581 \text{ mol Bi}^{3+}}{1 \text{ L soln}} = 0.0581 \text{ M}$$

- (e) Recall that the atomic number of any element is the number of protons and electrons in a neutral atom of the element. Bismuth is element 83; there are therefore 83 protons in the nucleus. Because the atomic mass number is 209, there are $209 - 83 = 126$ neutrons in the nucleus.

- (f) We can use the density and the atomic weight to determine the number of moles of Bi, and then use Avogadro's number to convert the result to the number of atoms. The volume of the cube is $(5.00)^3 \text{ cm}^3 = 125 \text{ cm}^3$. Then we have

$$125 \text{ cm}^3 \text{ Bi} \times \frac{9.808 \text{ g Bi}}{1 \text{ cm}^3} \times \frac{1 \text{ mol Bi}}{209.0 \text{ g Bi}} = 5.87 \text{ mol Bi}$$

$$5.87 \text{ mol Bi} \times \frac{6.022 \times 10^{23} \text{ atom Bi}}{1 \text{ mol Bi}} = 3.53 \times 10^{24} \text{ atoms Bi}$$

Chapter Summary and Key Terms

DEVELOPMENT OF THE PERIODIC TABLE (INTRODUCTION AND SECTION 7.1) The periodic table was first developed by Mendeleev and Meyer on the basis of the similarity in chemical and physical properties exhibited by certain elements. Moseley established that each element has a unique atomic number, which added more order to the periodic table.

We now know that elements in the same column of the periodic table have the same number of electrons in their **valence orbitals**. This similarity in valence electronic structure leads to the similarities among elements in the same group. Differences among elements in the same group arise because their valence orbitals are in different shells.

EFFECTIVE NUCLEAR CHARGE (SECTION 7.2) Many properties of atoms depend on the **effective nuclear charge**, which is the portion of the nuclear charge that an outer electron experiences after accounting for repulsions by other electrons in the atom. The core electrons are very effective in screening the outer electrons from the full charge of the nucleus, whereas electrons in the same shell do not screen each other very effectively. Because the actual nuclear charge increases as we progress through a period, the effective nuclear charge experienced by valence electrons increases as we move left to right across a period.

SIZES OF ATOMS AND IONS (SECTION 7.3) The size of an atom can be gauged by its **bonding atomic radius**, which is based on measurements of the distances separating atoms in their chemical compounds. In general, atomic radii increase down a column in the periodic table and decrease left to right across a row.

Cations are smaller than their parent atoms; anions are larger than their parent atoms. For ions of the same charge, size increases going down a column of the periodic table. An **isoelectronic series** is a series of ions that has the same number of electrons. For such a series, size decreases with increasing atomic number as the electrons are attracted more strongly to the nucleus as its positive charge increases.

IONIZATION ENERGY (SECTION 7.4) The first **ionization energy** of an atom is the minimum energy needed to remove an electron from the atom in the gas phase, forming a cation. The second ionization energy is the energy needed to remove a second electron, and so forth. Ionization energies show a sharp increase after all the valence electrons have been removed because of the much higher effective nuclear charge experienced by the core electrons. The first ionization energies of the elements show periodic trends that are opposite those seen for atomic radii, with smaller atoms having higher first ionization energies. Thus, first ionization energies decrease as we go down a column and increase as we proceed left to right across a row.

We can write electron configurations for ions by first writing the electron configuration of the neutral atom and then removing or adding the appropriate number of electrons. For cations, electrons

are removed first from the orbitals of the neutral atom with the largest value of n . If there are two valence orbitals with the same value of n (such as $4s$ and $4p$), then the electrons are lost first from the orbital with a higher value of l (in this case, $4p$). For anions, electrons are added to orbitals in the reverse order.

ELECTRON AFFINITY (SECTION 7.5) The **electron affinity** of an element is the energy change upon adding an electron to an atom in the gas phase, forming an anion. A negative electron affinity means that energy is released when the electron is added; hence, when the electron affinity is negative the anion is stable. By contrast, a positive electron affinity means that the anion is not stable relative to the separated atom and electron. In general, electron affinities become more negative as we proceed from left to right across the periodic table. The halogens have the most negative electron affinities. The electron affinities of the noble gases are positive because the added electron would have to occupy a new, higher-energy subshell.

METALS, NONMETALS, AND METALLOIDS (SECTION 7.6) The elements can be categorized as metals, nonmetals, and metalloids. Most elements are metals; they occupy the left side and the middle of the periodic table. Nonmetals appear in the upper-right section of the table. Metalloids occupy a narrow band between the metals and nonmetals. The tendency of an element to exhibit the properties of metals, called the **metallic character**, increases as we proceed down a column and decreases as we proceed from left to right across a row.

Metals have a characteristic luster, and they are good conductors of heat and electricity. When metals react with nonmetals, the metal atoms are oxidized to cations and ionic substances are generally formed. Most metal oxides are basic; they react with acids to form salts and water.

Nonmetals lack metallic luster and are generally poor conductors of heat and electricity. Several are gases at room temperature. Compounds composed entirely of nonmetals are generally molecular. Nonmetals usually form anions in their reactions with metals. Nonmetal oxides are acidic; they react with bases to form salts and water. Metalloids have properties that are intermediate between those of metals and nonmetals.

TRENDS FOR GROUP 1 AND 2 METALS (SECTION 7.7) The periodic properties of the elements can help us understand the properties of groups of the representative elements. The **alkali metals** (Group 1) are soft metals with low densities and low melting points. They have the lowest ionization energies of the elements. As a result, they are very reactive toward nonmetals, easily losing their outer s electron to form $1+$ ions.

The **alkaline earth metals** (Group 2) are harder and denser, and have higher melting points than the alkali metals. They are also very

reactive toward nonmetals, although not as reactive as the alkali metals. The alkaline earth metals readily lose their two outer s electrons to form $2+$ ions. Both alkali and alkaline earth metals react with hydrogen to form ionic substances that contain the **hydride ion**, H^- .

TRENDS FOR SELECTED NONMETALS (SECTION 7.8) Hydrogen is a nonmetal with properties that are distinct from any of the groups of the periodic table. It forms molecular compounds with other nonmetals, such as oxygen and the halogens.

Oxygen and sulfur are the most important elements in Group 16. Oxygen is usually found as a diatomic molecule, O_2 . **Ozone**, O_3 , is an important allotrope of oxygen. Oxygen has a strong tendency to gain electrons from other elements, thus oxidizing them. In combination

with metals, oxygen is usually found as the oxide ion, O^{2-} , although salts of the peroxide ion, O_2^{2-} , and superoxide ion, O_2^- , are sometimes formed. Elemental sulfur is most commonly found as S_8 molecules. In combination with metals, it is most often found as the sulfide ion, S^{2-} .

The **halogens** (Group 17) exist as diatomic molecules. The halogens have the most negative electron affinities of the elements. Thus, their chemistry is dominated by a tendency to form $1-$ ions, especially in reactions with metals.

The **noble gases** (Group 18) exist as monatomic gases. They are very unreactive because they have completely filled s and p subshells. Only the heaviest noble gases are known to form compounds, and they do so only with very active nonmetals, such as fluorine.

Learning Outcomes After studying this chapter, you should be able to:

- Explain the meaning of effective nuclear charge, Z_{eff} , and how Z_{eff} depends on nuclear charge and electron configuration. (Section 7.2) *Related Exercises: 7.5–7.7, 7.53*
 - Use the periodic table to predict the trends in atomic radii, ionic radii, ionization energy, and electron affinity. (Sections 7.2, 7.3, 7.4, and 7.5) *Related Exercises: 7.27, 7.59, 7.69, 7.70*
 - Explain how the radius of an atom changes upon losing electrons to form a cation or gaining electrons to form an anion. (Section 7.3) *Related Exercises: 7.60, 7.63–7.65*
 - Use the periodic table to determine the electron configurations of ions. (Section 7.3) *Related Exercises: 7.15, 7.22, 7.61, 7.71*
 - Predict the trends in ionization energy as successive electrons are removed, including the discontinuous increase that occurs when the ionization corresponds to removing a core electron. (Section 7.4) *Related Exercises: 7.18, 7.19, 7.67, 7.69*
 - Explain how electron affinity and ionization energy are related, and how irregularities in the periodic trends for electron affinity can be related to electron configuration. (Section 7.5)
- Related Exercises: 7.27, 7.75, 7.101, 7.104*
- Explain the differences in chemical and physical properties of metals and nonmetals, including the basicity of metal oxides and the acidity of nonmetal oxides. (Section 7.6) *Related Exercises: 7.31, 7.76, 7.78, 7.79*
 - Explain how atomic properties, such as ionization energy and electron affinity, relate to the chemical reactivity and physical properties of the alkali and alkaline earth metals (Groups 1 and 2). (Section 7.7) *Related Exercises: 7.36, 7.82*
 - Write balanced equations for the reactions of the Group 1 and 2 metals with water, oxygen, hydrogen, and the halogens. (Sections 7.7 and 7.8) *Related Exercises: 7.37, 7.83*
 - List and explain the unique characteristics of hydrogen. (Section 7.8) *Related Exercises: 7.38, 7.84, 7.108*
 - Explain how the atomic properties, such as ionization energy and electron affinity, of Group 16, 17, and 18 elements relate to their chemical reactivity and physical properties. (Section 7.8) *Related Exercises: 7.40, 7.85, 7.86*

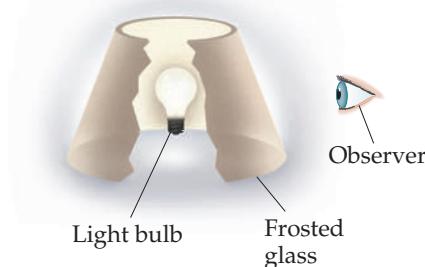
Key Equations

$$\bullet \quad Z_{\text{eff}} = Z - S \quad [7.1] \quad \text{Estimating effective nuclear charge}$$

Exercises

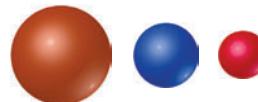
Visualizing Concepts

- 7.43** As discussed in the text, we can draw an analogy between the attraction of an electron to a nucleus and the act of perceiving light from a light bulb through a frosted glass shade, as shown in the illustration.



Using the simple method of estimating effective nuclear charge, Equation 7.1, how does the intensity of the light bulb and/or the thickness of the frosting change in the following cases: (a) Moving from boron to carbon? (b) Moving from boron to aluminum? [Section 7.2]

- 7.44** Which of these spheres represents F, which represents Br, and which represents Br^- ? [Section 7.3]

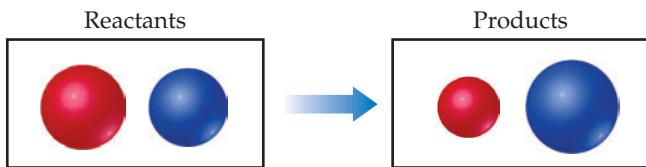


- 7.45** Consider the Mg^{2+} , Cl^- , K^+ , and Se^{2-} ions. The four spheres below represent these four ions, scaled according to ionic size. (a) Without referring to Figure 7.8, match each ion to its

appropriate sphere. (b) In terms of size, between which of the spheres would you find the (i) Ca^{2+} and (ii) S^{2-} ions? [Section 7.3]

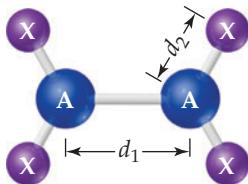


7.46 In the following reaction

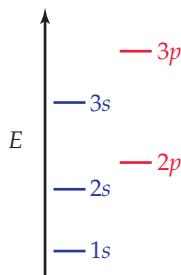


which sphere represents a metal and which represents a nonmetal? [Section 7.3]

7.47 Consider the A_2X_4 molecule depicted here, where A and X are elements. The A—A bond length in this molecule is d_1 , and the four A—X bond lengths are each d_2 . (a) In terms of d_1 and d_2 , how could you define the bonding atomic radii of atoms A and X? (b) In terms of d_1 and d_2 , what would you predict for the X—X bond length of an X_2 molecule? [Section 7.3]



7.48 A qualitative diagram of the atomic orbital energies for an Na atom is shown here. The number of orbitals in each subshell is not shown.



- (a) Are all of the subshells for $n = 1$, $n = 2$, and $n = 3$ shown? If not, what is missing?
 - (b) The 2s and 2p energy levels are different. Which of the following is the best explanation for why this is the case?
 (i) The 2s and 2p energy levels have different energies in the hydrogen atom, so of course they will have different energies in the sodium atom, (ii) The energy of the 2p orbital is higher than that of the 2s in all many-electron atoms. (iii) The 2s level in Na has electrons in it, whereas the 2p does not.
 - (c) Which of the energy levels holds the highest-energy electron in a sodium atom?
 - (d) A sodium vapor lamp (Figure 7.23) operates by using electricity to excite the highest-energy electron to the next highest-energy level. Light is produced when the excited electron drops back to the lower level. Which two energy levels are involved in this process for the Na atom? [Section 7.7]
- 7.49** Which of the following charts shows the general periodic trends for each of the following properties of the main-group elements (you can neglect small deviations going

either across a row or down a column of the periodic table)?

- (1) Bonding atomic radius, (2) first ionization energy, (3) effective nuclear charge. [Sections 7.2–7.6]

increase →

(i)

H	Main Group Elements							He
Li	Be							Ne
Na	Mg							Ar
K	Ca							Kr
Rb	Sr							Xe
Cs	Ba							

↓ increase ↓

(ii)

H	Main Group Elements							He
Li	Be							Ne
Na	Mg							Ar
K	Ca							Kr
Rb	Sr							Xe
Cs	Ba							

↑ increase ↑

(iii)

H	Main Group Elements							He
Li	Be							Ne
Na	Mg							Ar
K	Ca							Kr
Rb	Sr							Xe
Cs	Ba							

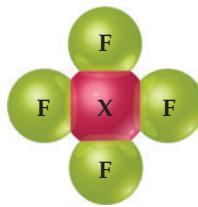
← increase ←

(iv)

H	Main Group Elements							He
Li	Be							Ne
Na	Mg							Ar
K	Ca							Kr
Rb	Sr							Xe
Cs	Ba							

← increase ←

- 7.50** An element X reacts with $\text{F}_2(g)$ to form the molecular product shown here. (a) Write a balanced equation for this reaction (do not worry about the phases for X and the product). (b) Do you think that X is a metal or nonmetal? [Section 7.6]

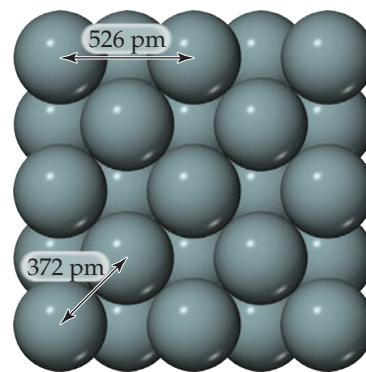


Periodic Table; Effective Nuclear Charge (Sections 7.1 and 7.2)

- 7.51** (a) Evaluate the expressions 2×1 , $2 \times (1 + 3)$, $2 \times (1 + 3 + 5)$, and $2 \times (1 + 3 + 5 + 7)$. (b) How do the atomic numbers of the noble gases relate to the numbers from part (a)? (c) What topic discussed in Chapter 6 is the source of the number “2” in the expressions in part (a)?
- 7.52** Moseley’s experiments on X rays emitted from atoms led to the concept of atomic numbers. (a) If arranged in order of increasing atomic mass, which element would come after chlorine? (b) Describe two ways in which the properties of this element differ from the other elements in Group 18.
- 7.53** Which of the following statements about effective nuclear charge for the outermost valence electron of an atom is *incorrect*? (i) The effective nuclear charge can be thought of as the true nuclear charge minus a screening constant due to the other electrons in the atom. (ii) Effective nuclear charge increases going left to right across a row of the periodic table. (iii) Valence electrons screen the nuclear charge more effectively than do core electrons. (iv) The effective nuclear charge shows a sudden decrease when we go from the end of one row to the beginning of the next row of the periodic table. (v) The change in effective nuclear charge going down a column of the periodic table is generally less than that going across a row of the periodic table.
- 7.54** Detailed calculations show that the value of Z_{eff} for the outermost electrons in Si and Cl atoms is 4.29+ and 6.12+, respectively. (a) What value do you estimate for Z_{eff} experienced by the outermost electron in both Si and Cl by assuming core electrons contribute 1.00 and valence electrons contribute 0.00 to the screening constant? (b) What values do you estimate for Z_{eff} using Slater’s rules? (c) Which approach gives a more accurate estimate of Z_{eff} ? (d) Which method of approximation more accurately accounts for the steady increase in Z_{eff} that occurs upon moving left to right across a period? (e) Predict Z_{eff} for a valence electron in P, phosphorus, based on the calculations for Si and Cl.
- 7.55** Arrange the following atoms in order of increasing effective nuclear charge experienced by the electrons in the $n = 2$ shell: Be, Br, Na, P, Se.

Atomic and Ionic Radii (Section 7.3)

- 7.56** With the exception of helium, the noble gases condense to form solids when they are cooled sufficiently. At temperatures below 83 K, argon forms a close-packed solid whose structure is shown here. (a) What is the apparent radius of an argon atom in solid argon, assuming the atoms touch as shown in this figure? (b) Is this value larger or smaller than the bonding atomic radius estimated for argon in Figure 7.7? (c) Based on this comparison would you say that the atoms are held together by chemical bonds in solid argon?

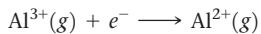


- 7.57** Which of the following statements about the bonding atomic radii in Figure 7.7 is *incorrect*? (i) For a given period, the radii of the representative elements generally decrease from left to right across a period. (ii) The radii of the representative elements for the $n = 3$ period are all larger than those of the corresponding elements in the $n = 2$ period. (iii) For most of the representative elements, the change in radius from the $n = 2$ to the $n = 3$ period is greater than the change in radius from $n = 3$ to $n = 4$. (iv) The radii of the transition elements generally increase moving from left to right within a period. (v) The large radii of the Group 1 elements are due to their relatively small effective nuclear charges.
- 7.58** The experimental Pb—Cl bond length in lead(II)chloride, PbCl_2 , is 244 pm. Based on this value and data in Figure 7.7, predict the atomic radius of Pb.
- 7.59** Using only the periodic table, arrange each set of atoms in order of increasing radius: (a) Cs, Se, Te; (b) S, Si, Sr; (c) P, Po, Pb.
- 7.60** Explain the following variations in atomic or ionic radii:
- (a) $\text{I}^- > \text{I} > \text{I}^+$
 - (b) $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Be}^{2+}$
 - (c) $\text{Fe} > \text{Fe}^{2+} > \text{Fe}^{3+}$
- 7.61** Some ions do not have a corresponding neutral atom that has the same electron configuration. For each of the following ions, identify the neutral atom that has the same number of electrons and determine if this atom has the same electron configuration. (a) Cl^- , (b) Sc^{3+} , (c) Fe^{2+} , (d) Zn^{2+} , (e) Sn^{4+} .
- 7.62** Consider the isoelectronic ions Cl^- and K^+ . (a) Which ion is smaller? (b) Using Equation 7.1 and assuming that core electrons contribute 1.00 and valence electrons contribute nothing to the screening constant, S , calculate Z_{eff} for these two ions. (c) Repeat this calculation using Slater’s rules to estimate the screening constant, S . (d) For isoelectronic ions, how are effective nuclear charge and ionic radius related?
- 7.63** Consider S, Cl, and K and their most common ions. (a) List the atoms in order of increasing size. (b) List the ions in order of increasing size. (c) Explain any differences in the orders of the atomic and ionic sizes.
- 7.64** Arrange each of the following sets of atoms and ions, in order of increasing size: (a) Pb, Pb^{2+} , Pb^{4+} ; (b) V $^{3+}$, Co^{2+} , Co^{3+} ; (c) Se^{2-} , S^{2-} , Sn^{2+} ; (d) K^+ , Rb^+ , Br^- .
- 7.65** Provide a brief explanation for each of the following: (a) Cl^- is larger than Ar. (b) P^{3-} is larger than S^{2-} . (c) K^+ is larger than Na^+ . (d) F^- is larger than F.
- 7.66** In the ionic compounds LiF, NaCl, KBr, and RbI, the measured cation–anion distances are 201 pm (Li–F), 282 pm (Na–Cl), 330 pm (K–Br), and 367 pm (Rb–I), respectively. (a) Predict the cation–anion distance using the values of ionic radii given in Figure 7.8. (b) Calculate the difference between the experimentally measured ion–ion distances and the ones predicted from Figure 7.8. (c) What estimates of the cation–anion

distance would you obtain for these four compounds using neutral atom *bonding atomic radii*? Are these estimates as accurate as the estimates using ionic radii?

Ionization Energies; Electron Affinities (Sections 7.4 and 7.5)

- 7.67** Write equations that show the process for (a) the first two ionization energies of zinc and (b) the fourth ionization energy of calcium.
- 7.68** Identify each statement as true or false: (a) Ionization energies are always endothermic. (b) Potassium has a larger first ionization energy than lithium. (c) The second ionization energy of the sodium atom is larger than the second ionization energy of the magnesium atom. (d) The third ionization energy is three times the first ionization energy of an atom.
- 7.69** (a) What is the trend in first ionization energies as one proceeds down the Group 17 elements? Explain how this trend relates to the variation in atomic radii. (b) What is the trend in first ionization energies as one moves across the fourth period from K to Kr? How does this trend compare with the trend in atomic radii?
- 7.70** For each of the following pairs, indicate which element has the smaller first ionization energy: (a) Cs, Cl; (b) Fe, Zn; (c) I, Cl; (d) Se, Sn.
- 7.71** Write the electron configurations for the following ions, and determine which have noble-gas configurations: (a) Ti^{2+} , (b) Br^- , (c) Mg^{2+} , (d) Po^{2-} , (e) Pt^{2+} , (f) V^{3+} .
- 7.72** Give examples of transition metal ions with +3 charge that have an electron configuration of nd^5 ($n = 3, 4, 5 \dots$).
- 7.73** If the electron affinity for an element is a negative number, does it mean that the anion of the element is more stable than the neutral atom? Explain.
- 7.74** What is the relationship between the ionization energy of an anion with a 1– charge such as F^- and the electron affinity of the neutral atom, F?
- 7.75** Consider the following equation:



Which of the following statements are true? (i) The energy change for this process is the second electron affinity of Al atom since $\text{Al}^{2+}(g)$ is formed. (ii) The energy change for this process is the negative of the third ionization energy of the Al atom. (iii) The energy change for this process is the electron affinity of the Al^{2+} ion.

Properties of Metals and Nonmetals (Section 7.6)

- 7.76** You read the following statement about two elements X and Y: One of the elements is a good conductor of electricity, and the other is a semiconductor. Experiments show that the first ionization energy of X is twice as great as that of Y. Which element has the greater metallic character?
- 7.77** Discussing this chapter, a classmate says, “Since elements that form cations are metals and elements that form anions are nonmetals, elements that do not form ions are metalloids.” Do you agree or disagree?
- 7.78** Some metal oxides, such as Sc_2O_3 , do not react with pure water, but they do react when the solution becomes either

acidic or basic. Do you expect Sc_2O_3 to react when the solution becomes acidic or when it becomes basic? Write a balanced chemical equation to support your answer.

- 7.79** Arrange the following oxides in order of increasing acidity: K_2O , BaO , ZnO , H_2O , CO_2 , SO_2 .
- 7.80** An element X reacts with oxygen to form XO_2 and with chlorine to form XCl_4 . XO_2 is a white solid that melts at high temperatures (above 1000 °C). Under usual conditions, XCl_4 is a colorless liquid with a boiling point of 58 °C. (a) XCl_4 reacts with water to form XO_2 and another product. What is the likely identity of the other product? (b) Do you think that element X is a metal, nonmetal, or metalloid? (c) By using a sourcebook such as the *CRC Handbook of Chemistry and Physics*, try to determine the identity of element X.
- 7.81** Write balanced equations for the following reactions: (a) sulfur dioxide with water, (b) lithium oxide in water, (c) zinc oxide with dilute hydrochloric acid, (d) arsenic trioxide with aqueous potassium hydroxide.

Group Trends in Metals and Nonmetals (Sections 7.7 and 7.8)

- 7.82** Copper and calcium both form +2 ions, but copper is far less reactive. Suggest an explanation, taking into account the ground-state electron configurations of these elements and their atomic radii.
- 7.83** Write a balanced equation for the reaction that occurs in each of the following cases: (a) Lithium is added to water. (b) Calcium is added to water. (c) Potassium reacts with chlorine gas. (d) Rubidium reacts with oxygen.
- 7.84** Potassium and hydrogen react to form the ionic compound potassium hydride. (a) Write a balanced equation for this reaction. (b) Use data in Figures 7.10 and 7.12 to determine the energy change in kJ/mol for the following two reactions:
- $$\text{K}(g) + \text{H}(g) \longrightarrow \text{K}^+(g) + \text{H}^-(g)$$
- $$\text{K}(g) + \text{H}(g) \longrightarrow \text{K}^-(g) + \text{H}^+(g)$$
- (c) Based on your calculated energy changes in (b), which of these reactions is energetically more favorable (or less unfavorable)? (d) Is your answer to (c) consistent with the description of potassium hydride as containing hydride ions?
- 7.85** Little is known about the properties of astatine, At, because of its rarity and high radioactivity. Nevertheless, it is possible for us to make many predictions about its properties. (a) Do you expect the element to be a gas, liquid, or solid at room temperature? Explain. (b) Would you expect At to be a metal, nonmetal, or metalloid? Explain. (c) What is the chemical formula of the compound it forms with Na?
- 7.86** (a) Why does xenon react with fluorine, whereas neon does not? (b) Using appropriate reference sources, look up the bond lengths of Xe–F bonds in several molecules. How do these numbers compare to the bond lengths calculated from the atomic radii of the elements?
- 7.87** Write a balanced equation for the reaction that occurs in each of the following cases: (a) Calcium metal is heated in an atmosphere of oxygen gas. (b) Copper oxide is heated in an atmosphere of hydrogen gas. (c) Chlorine reacts with nitrogen gas. (d) Boron tribromide reacts with water.

Additional Exercises

7.88 Consider the stable elements through lead ($Z = 82$). In how many instances are the atomic weights of the elements out of order relative to the atomic numbers of the elements?

7.89 Figure 7.4 shows the radial probability distribution functions for the $2s$ orbitals and $2p$ orbitals. **(a)** Which orbital, $2s$ or $2p$, has more electron density close to the nucleus? **(b)** How would you modify Slater's rules to adjust for the difference in electronic penetration of the nucleus for the $2s$ and $2p$ orbitals?

7.90 **(a)** If the core electrons were totally effective at screening the valence electrons and the valence electrons provided no screening for each other, what would be the effective nuclear charge acting on the $3s$ and $3p$ valence electrons in P? **(b)** Repeat these calculations using Slater's rules. **(c)** Detailed calculations indicate that the effective nuclear charge is $5.6+$ for the $3s$ electrons and $4.9+$ for the $3p$ electrons. Why are the values for the $3s$ and $3p$ electrons different? **(d)** If you remove a single electron from a P atom, which orbital will it come from?

7.91 As we move across a period of the periodic table, why do the sizes of the transition elements change more gradually than those of the representative elements?

7.92 In the series of Group 16 hydrides, of general formula MH_2 , the measured bond distances are O—H, 96 pm; S—H, 134 pm; Se—H, 146 pm. **(a)** Compare these values with those estimated by use of the atomic radii in Figure 7.7. **(b)** Explain the steady increase in M—H bond distance in this series in terms of the electron configurations of the M atoms.

7.93 In Table 7.8, the bonding atomic radius of neon is listed as 58 pm, whereas that for xenon is listed as 140 pm. A classmate of yours states that the value for Xe is more realistic than the one for Ne. Is she correct? If so, what is the basis for her statement?

7.94 The P—P bond length in white phosphorus is 189 pm. The Cl—Cl bond length in Cl_2 is 199 pm. **(a)** Based on these data, what is the predicted P—Cl bond length in phosphorus trichloride, PCl_3 , in which each of the three Cl atoms is bonded to the P atom? **(b)** What bond length is predicted for PCl_3 , using the atomic radii in Figure 7.7?

7.95 The following observations are made about two hypothetical elements A and B: The A—A and B—B bond lengths in the elemental forms of A and B are 236 and 194 pm, respectively. A and B react to form the binary compound AB_2 , which has a linear structure (that is $\angle B-A-B = 180^\circ$). Based on these statements, predict the separation between the two B nuclei in a molecule of AB_2 .

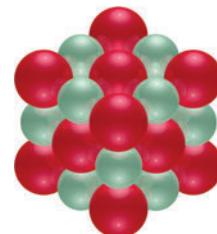
7.96 Elements in Group 17 in the periodic table are called the halogens; elements in Group 16 are called the chalcogens. **(a)** What is the most common oxidation state of the chalcogens compared to the halogens? **(b)** For each of the following periodic properties, state whether the halogens or the chalcogens have larger values: atomic radii, ionic radii of the most common oxidation state, first ionization energy, second ionization energy.

7.97 Note from the following table that there is a significant increase in atomic radius upon moving from Y to La, whereas the radii of Zr to Hf are the same. Suggest an explanation for this effect.

Atomic Radii (pm)			
Sc	170	Ti	160
Y	190	Zr	175
La	207	Hf	175

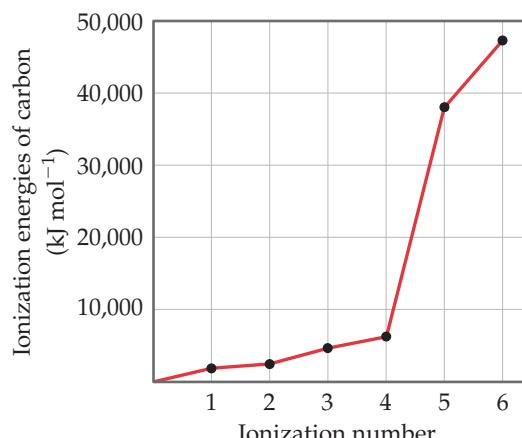
7.98 **(a)** Which ion is smaller, Co^{3+} or Co^{4+} ? **(b)** In a lithium-ion battery that is discharging to power a device, for every Li^+ that inserts into the lithium cobalt oxide electrode, a Co^{4+} ion must be reduced to a Co^{3+} ion to balance charge. Using the CRC Handbook of Chemistry and Physics or other standard reference, find the ionic radii of Li^+ , Co^{3+} , and Co^{4+} . Order these ions from smallest to largest. **(c)** Will the lithium cobalt oxide cathode expand or contract as lithium ions are inserted? **(d)** Lithium is not nearly as abundant as sodium. If sodium ion batteries were developed that function in the same manner as lithium ion batteries, do you think “sodium cobalt oxide” would still work as the electrode material? Explain. **(e)** If you don’t think cobalt would work as the redox-active partner ion in the sodium version of the electrode, suggest an alternative metal ion and explain your reasoning.

7.99 The ionic substance strontium oxide, SrO , forms from the reaction of strontium metal with molecular oxygen. The arrangement of the ions in solid SrO is analogous to that in solid $NaCl$:



(a) Write a balanced equation for the formation of $SrO(s)$ from its elements. **(b)** Based on the ionic radii in Figure 7.8, predict the length of the side of the cube in the figure (the distance from the center of an atom at one corner to the center of an atom at a neighboring corner). **(c)** The density of SrO is 5.10 g/cm^3 . Given your answer to part (b), how many formula units of SrO are contained in the cube shown here?

7.100 Explain the variation in the ionization energies of carbon, as displayed in this graph:



7.101 Group 14 elements have much more negative electron affinities than their neighbors in Groups 13 and 15 (see Figure 7.12). Which of the following statements best explains this observation? **(i)** The Group 14 elements have much higher first ionization energies than their neighbors in Groups 13 and 15. **(ii)** The addition of an electron to a Group 14 element leads to a half-filled np^3 outer electron configuration. **(iii)** The Group 14 elements have unusually large atomic radii. **(iv)** The Group 14 elements are easier to vaporize than are the Group 13 and 15 elements.

7.102 In the chemical process called *electron transfer*, an electron is transferred from one atom or molecule to another. (We will talk about electron transfer extensively in Chapter 20.) A simple electron transfer reaction is



In terms of the ionization energy and electron affinity of atom A, what is the energy change for this reaction? For a representative nonmetal such as chlorine, is this process exothermic? For a representative metal such as sodium, is this process exothermic?

7.103 **(a)** Use orbital diagrams to illustrate what happens when an oxygen atom gains two electrons. **(b)** Why does O^{3-} not exist?

7.104 Use electron configurations to explain the following observations: **(a)** The first ionization energy of phosphorus is greater than that of sulfur. **(b)** The electron affinity of nitrogen is lower (less negative) than those of both carbon and oxygen. **(c)** The second ionization energy of oxygen is greater than the first ionization energy of fluorine. **(d)** The third ionization energy of manganese is greater than those of both chromium and iron.

7.105 Identify a $+2$ cation that has the following ground state electron configurations: **(a)** [Ne] **(b)** [Ar] $3d^9$ **(c)** [Xe] $4f^{14}5d^{10}6s^2$.

7.106 Which of the following chemical equations is connected to the definitions of **(a)** the first ionization energy of oxygen, **(b)** the second ionization energy of oxygen, and **(c)** the electron affinity of oxygen?

- (i)** $O(g) + e^- \longrightarrow O^-(g)$ **(ii)** $O(g) \longrightarrow O^+(g) + e^-$
(iii) $O(g) + 2e^- \longrightarrow O^{2-}(g)$ **(iv)** $O(g) \longrightarrow O^{2+}(g) + 2e^-$
(v) $O^+(g) \longrightarrow O^{2+}(g) + e^-$

7.107 The electron affinities, in kJ/mol, for the Group 11 and Group 12 metals are as follows:

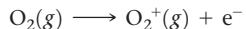
Cu -119	Zn > 0
Ag -126	Cd > 0
Au -223	Hg > 0

(a) Why are the electron affinities of the Group 12 elements greater than zero? **(b)** Why do the electron affinities of the Group 11 elements become more negative as we move down the group? [Hint: Examine the trends in the electron affinities of other groups as we proceed down the periodic table.]

7.108 Hydrogen is an unusual element because it behaves in some ways like the alkali metal elements and in other ways like nonmetals. Its properties can be explained in part by its electron configuration and by the values for its ionization energy and electron affinity. **(a)** Explain why the electron affinity of hydrogen is much closer to the values for the alkali elements than for the halogens. **(b)** Is the following statement true? “Hydrogen has the smallest bonding atomic radius of any element that forms chemical compounds.” If not, correct it. If it is, explain in terms of electron configurations. **(c)** Explain

why the ionization energy of hydrogen is closer to the values for the halogens than for the alkali metals. **(d)** The hydride ion is H^- . Write out the process corresponding to the first ionization energy of the hydride ion. **(e)** How does the process in part (d) compare to the process for the electron affinity of a neutral hydrogen atom?

7.109 The first ionization energy of the oxygen molecule is the energy required for the following process:



The energy needed for this process is 1175 kJ/mol, very similar to the first ionization energy of Xe. Would you expect O_2 to react with F_2 ? If so, suggest a product or products of this reaction.

7.110 It is possible to define *metallic character* as we do in this book and base it on the reactivity of the element and the ease with which it loses electrons. Alternatively, one could measure how well electricity is conducted by each of the elements to determine how “metallic” the elements are. On the basis of conductivity, there is not much of a trend in the periodic table: Silver is the most conductive metal, and manganese the least. Look up the first ionization energies of silver and manganese; which of these two elements would you call more metallic based on the way we define it in this book?

7.111 Which of the following is the expected product of the reaction of $Mg(s)$ and $N_2(g)$ under heat? **(i)** $Mg_3N(s)$, **(ii)** $MgN_2(s)$, **(iii)** $Mg_3N_2(s)$, **(iv)** $Mg(s)$ and $N_2(g)$ will not react with one another.

7.112 Elemental barium reacts more violently with water than does elemental calcium. Which of the following best explains this difference in reactivity? **(i)** Calcium has greater metallic character than does barium. **(ii)** The electron affinity of calcium is smaller than that of barium. **(iii)** The first and second ionization energies of barium are less than those of calcium. **(iv)** The atomic radius of barium is smaller than that of calcium. **(v)** The ionic radius of the barium ion is larger than that of the calcium ion.

7.113 **(a)** One of the alkali metals reacts with oxygen to form a solid white substance. When this substance is dissolved in water, the solution gives a positive test for hydrogen peroxide, H_2O_2 . When the solution is tested in a burner flame, a lilac-purple flame is produced. What is the likely identity of the metal? **(b)** Write a balanced chemical equation for the reaction of the white substance with water.

7.114 Zinc in its $2+$ oxidation state is an essential metal ion for life. Zn^{2+} is found bound to many proteins that are involved in biological processes, but unfortunately Zn^{2+} is hard to detect by common chemical methods. Therefore, scientists who are interested in studying Zn^{2+} -containing proteins frequently substitute Cd^{2+} for Zn^{2+} , since Cd^{2+} is easier to detect. **(a)** On the basis of the properties of the elements and ions discussed in this chapter and their positions in the periodic table, describe the pros and cons of using Cd^{2+} as a Zn^{2+} substitute. **(b)** Proteins that speed up (catalyze) chemical reactions are called *enzymes*. Many enzymes are required for proper metabolic reactions in the body. One problem with using Cd^{2+} to replace Zn^{2+} in enzymes is that Cd^{2+} substitution can decrease or even eliminate enzymatic activity. Can you suggest a different metal ion that might replace Zn^{2+} in enzymes instead of Cd^{2+} ? Justify your answer.

7.115 A historian discovers a nineteenth-century notebook in which some observations, dated 1822, were recorded on a substance thought to be a new element. Here are some of the data recorded in the notebook: “Ductile, silver-white, metallic looking. Softer than lead. Unaffected by water. Stable in air. Melting point: 153 °C. Density: 7.3 g/cm³. Electrical conductivity: 20% that of copper. Hardness: About 1% as hard as iron. When 4.20 g of the unknown is heated in an excess of oxygen, 5.08 g of a white solid is formed. The solid could be

sublimed by heating to over 800 °C.” (a) Using information in the text and the *CRC Handbook of Chemistry and Physics*, and making allowances for possible variations in numbers from current values, identify the element reported. (b) Write a balanced chemical equation for the reaction with oxygen. (c) Judging from Figure 7.1, might this nineteenth-century investigator have been the first to discover a new element?

- 7.116** In April 2010, a research team reported that it had made Element 117. This discovery was confirmed in 2012 by additional experiments. Write the ground-state electron configuration for Element 117 and estimate values for its first ionization energy, electron affinity, atomic size, and common oxidation state based on its position in the periodic table.
- 7.117** We will see in Chapter 12 that semiconductors are materials that conduct electricity better than nonmetals but not as well

as metals. The only two elements in the periodic table that are technologically useful semiconductors are silicon and germanium. Integrated circuits in computer chips today are based on silicon. Compound semiconductors are also used in the electronics industry. Examples are gallium arsenide, GaAs; gallium phosphide, GaP; cadmium sulfide, CdS; and cadmium selenide, CdSe. (a) What is the relationship between the compound semiconductors’ compositions and the positions of their elements on the periodic table relative to Si and Ge? (b) Workers in the semiconductor industry refer to “II–VI” and “III–V” materials, using Roman numerals. Can you identify which compound semiconductors are II–VI and which are III–V? (c) Suggest other compositions of compound semiconductors based on the positions of their elements in the periodic table.

Integrative Exercises

- 7.118** Moseley established the concept of atomic number by studying X rays emitted by the elements. The X rays emitted by some of the elements have the following wavelengths:

Element	Wavelength (pm)
Ne	1461
Ca	335.8
Zn	143.5
Zr	78.6
Sn	49.1

- (a) Calculate the frequency, ν , of the X rays emitted by each of the elements, in Hz. (b) Plot the square root of versus the atomic number of the element. What do you observe about the plot? (c) Explain how the plot in part (b) allowed Moseley to predict the existence of undiscovered elements. (d) Use the result from part (b) to predict the X-ray wavelength emitted by iron. (e) A particular element emits X rays with a wavelength of 98.0 pm. What element do you think it is?
- 7.119** (a) Write the electron configuration for Li and estimate the effective nuclear charge experienced by the valence electron. (b) The energy of an electron in a one-electron atom or ion equals $(-2.18 \times 10^{-18} \text{ J}) \left(\frac{Z^2}{n^2} \right)$, where Z is the nuclear charge and n is the principal quantum number of the electron. Estimate the first ionization energy of Li. (c) Compare the result of your calculation with the value reported in Table 7.4 and explain the difference. (d) What value of the effective nuclear charge gives the proper value for the ionization energy? Does this agree with your explanation in part (c)?

- 7.120** One way to measure ionization energies is ultraviolet photoelectron spectroscopy (PES), a technique based on the photoelectric effect. In PES, monochromatic light is directed onto a sample, causing electrons to be emitted. The kinetic energy of the emitted electrons is measured. The difference between the energy of the photons and the kinetic energy of the electrons corresponds to the energy needed to remove the electrons (that is, the ionization energy). Suppose that a PES experiment is performed in which mercury vapor is irradiated with ultraviolet light of wavelength 58.4 nm. (a) What is the energy of a photon of this light, in joules? (b) Write an equation that shows the process corresponding to the first ionization energy of Hg. (c) The kinetic energy of the emitted electrons is measured to be $1.72 \times 10^{-18} \text{ J}$. What is the first ionization energy of Hg, in

kJ/mol? (d) Using Figure 7.10, determine which of the halogen elements has a first ionization energy closest to that of mercury.

- 7.121** Mercury in the environment can exist in oxidation states 0, +1, and +2. One major question in environmental chemistry research is how to best measure the oxidation state of mercury in natural systems; this is made more complicated by the fact that mercury can be reduced or oxidized on surfaces differently than it would be if it were free in solution. XPS, X-ray photoelectron spectroscopy, is a technique related to PES (see Exercise 7.120), but instead of using ultraviolet light to eject valence electrons, X rays are used to eject core electrons. The energies of the core electrons are different for different oxidation states of the element. In one set of experiments, researchers examined mercury contamination of minerals in water. They measured the XPS signals that corresponded to electrons ejected from mercury’s $4f$ orbitals at 105 eV, from an X-ray source that provided 1253.6 eV of energy ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$). The oxygen on the mineral surface gave emitted electron energies at 531 eV, corresponding to the $1s$ orbital of oxygen. Overall the researchers concluded that oxidation states were +2 for Hg and -2 for O. (a) Calculate the wavelength of the X rays used in this experiment. (b) Compare the energies of the $4f$ electrons in mercury and the $1s$ electrons in oxygen from these data to the first ionization energies of mercury and oxygen from the data in this chapter. (c) Write out the ground-state electron configurations for Hg^{2+} and O^{2-} ; which electrons are the valence electrons in each case?

- 7.122** When magnesium metal is burned in air (Figure 3.5), two products are produced. One is magnesium oxide, MgO . The other is the product of the reaction of Mg with molecular nitrogen, magnesium nitride. When water is added to magnesium nitride, it reacts to form magnesium oxide and ammonia gas. (a) Based on the charge of the nitride ion (Table 2.5), predict the formula of magnesium nitride. (b) Write a balanced equation for the reaction of magnesium nitride with water. What is the driving force for this reaction? (c) In an experiment, a piece of magnesium ribbon is burned in air in a crucible. The mass of the mixture of MgO and magnesium nitride after burning is 0.470 g. Water is added to the crucible, further reaction occurs, and the crucible is heated to dryness until the final product is 0.486 g of MgO . What was the mass percentage of magnesium nitride in the mixture obtained after the initial burning? (d) Magnesium nitride can also be formed by reaction of the metal with ammonia at high temperature. Write a balanced equation for this reaction. If a 6.3 g Mg ribbon reacts with 2.57 g $\text{NH}_3(g)$ and the reaction goes to completion, which component

is the limiting reactant? What mass of $\text{H}_2(g)$ is formed in the reaction? (e) The standard enthalpy of formation of solid magnesium nitride is -461.08 kJ/mol . Calculate the standard enthalpy change for the reaction between magnesium metal and ammonia gas.

- 7.123** (a) The measured Bi—Br bond length in bismuth tribromide, BiBr_3 , is 263 pm. Based on this value and the data in Figure 7.8, predict the atomic radius of Bi. (b) Bismuth tribromide is soluble in acidic solution. It is formed by treating solid bismuth(III) oxide with aqueous hydrobromic acid. Write a balanced chemical equation for this reaction. (c) While bismuth(III) oxide is soluble in acidic solutions, it is insoluble in basic solutions such as $\text{NaOH}(aq)$. Based on these properties, is bismuth characterized as a metallic, metalloid, or nonmetallic element? (d) Treating bismuth with fluorine gas forms BiF_5 . Use the electron configuration of Bi to explain the formation of a

compound with this formulation. (e) While it is possible to form BiF_5 in the manner just described, pentahalides of bismuth are not known for the other halogens. Explain why the pentahalide might form with fluorine but not with the other halogens. How does the behavior of bismuth relate to the fact that xenon reacts with fluorine to form compounds but not with the other halogens?

- 7.124** Potassium superoxide, KO_2 , is often used in oxygen masks (such as those used by firefighters) because KO_2 reacts with CO_2 to release molecular oxygen. Experiments indicate that 2 mol of $\text{KO}_2(s)$ react with each mole of $\text{CO}_2(g)$. (a) The products of the reaction are $\text{K}_2\text{CO}_3(s)$ and $\text{O}_2(g)$. Write a balanced equation for the reaction between $\text{KO}_2(s)$ and $\text{CO}_2(g)$. (b) Indicate the oxidation number for each atom involved in the reaction in part (a). What elements are being oxidized and reduced? (c) What mass of $\text{KO}_2(s)$ is needed to consume 18.0 g $\text{CO}_2(g)$? What mass of $\text{O}_2(g)$ is produced during this reaction?

Design an Experiment

In this chapter we have seen that the reaction of potassium metal with oxygen leads to a product that we might not expect, namely, potassium superoxide, $\text{KO}_2(s)$. Let's design some experiments to learn more about this unusual product.

- (a) One of your team members proposes that the capacity to form a superoxide such as KO_2 is related to a low value for the first ionization energy. How would you go about testing this hypothesis for the metals of Group 1? What other periodic property of the alkali metals might be considered as a factor favoring superoxide formation?
- (b) $\text{KO}_2(s)$ is the active ingredient in many breathing masks used by firefighters because it can be used as a source of $\text{O}_2(g)$. In principle, $\text{KO}_2(s)$ can react with both major components of human

breath, $\text{H}_2\text{O}(g)$ and $\text{CO}_2(g)$, to produce $\text{O}_2(g)$ and other products (all of which follow the expected patterns of reactivity we have seen). Predict the other products in these reactions and design experiments to determine whether $\text{KO}_2(s)$ does actually react with both $\text{H}_2\text{O}(g)$ and $\text{CO}_2(g)$.

- (c) Propose an experiment to determine whether either of the reactions in part (b) is more important in the operation of a firefighter's breathing mask.
- (d) The reaction of $\text{K}(s)$ and $\text{O}_2(g)$ leads to a mixture of $\text{KO}_2(s)$ and $\text{K}_2\text{O}(s)$. Use ideas presented in this exercise to design an experiment to determine the percentages of $\text{KO}_2(s)$ and $\text{K}_2\text{O}(s)$ in the product mixture that results from the reaction of $\text{K}(s)$ with excess $\text{O}_2(g)$.