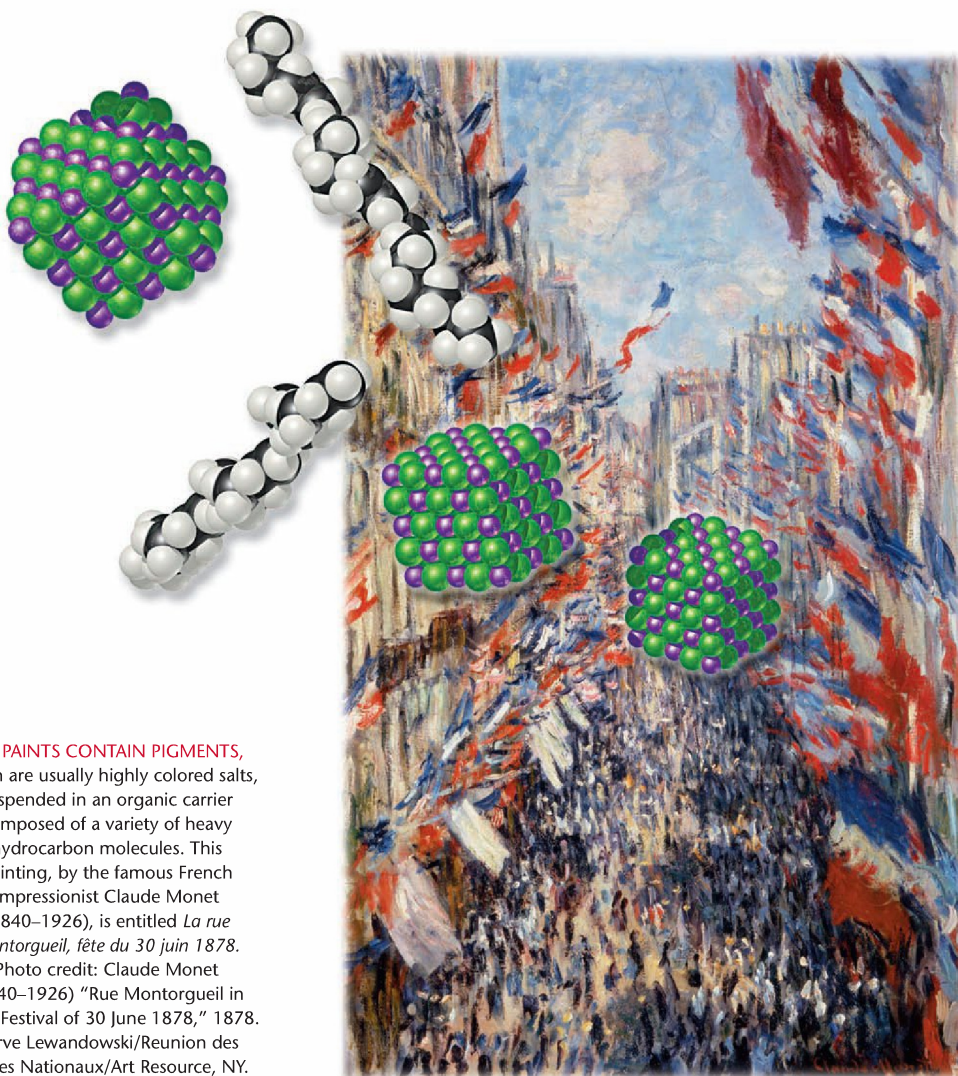


CHAPTER
7

PERIODIC PROPERTIES OF THE ELEMENTS



OIL PAINTS CONTAIN PIGMENTS, which are usually highly colored salts, suspended in an organic carrier composed of a variety of heavy hydrocarbon molecules. This painting, by the famous French Impressionist Claude Monet (1840–1926), is entitled *La rue Montorgueil, fête du 30 juin 1878*.
Photo credit: Claude Monet (1840–1926) “Rue Montorgueil in Paris, Festival of 30 June 1878,” 1878.
Herve Lewandowski/Reunion des Muses Nationaux/Art Resource, NY.

WHAT'S AHEAD

7.1 Development of the Periodic Table

We begin our discussion with a brief history of the periodic table.

7.2 Effective Nuclear Charge

We next explore the many properties of atoms that depend both on the net attraction of the outer electrons to the nucleus and on the average distance of those electrons from the nucleus. The net positive charge of the nucleus experienced by the outer electrons is called the *effective nuclear charge*.

7.3 Sizes of Atoms and Ions

We explore the relative sizes (or radii) of atoms and ions, both of which follow trends that are related to their placement in the periodic table.

7.4 Ionization Energy

We next encounter the energy—called ionization energy—required to remove one or more electrons from an atom. The periodic trends in ionization energy depend upon variations in effective nuclear charge and atomic radii.

7.5 Electron Affinities

Next we will examine periodic trends in the energy released when an electron is added to an atom.

7.6 Metals, Nonmetals, and Metalloids

We recognize that the physical and chemical properties of metals and nonmetals are distinctly different and can be understood from the fundamental characteristics of atoms discussed earlier in the chapter, particularly ionization energy. Metalloids display properties that are intermediate between metals and nonmetals.

7.7 Group Trends for the Active Metals

We examine some periodic trends in the chemistry of the active metals (groups 1A and 2A).

7.8 Group Trends for Selected Nonmetals

We examine some periodic trends in the chemistry of hydrogen, as well as groups 6A, 7A, and 8A.

THE BEAUTY OF AN IMPRESSIONIST OIL PAINTING, such as the Monet masterpiece shown here, begins with chemistry. Colorful inorganic salts are suspended in various organic media that contain hydrocarbons and other molecular substances. Indeed, the great painters

had a gift for using compounds of elements that span nearly the entire periodic table.

Today the periodic table is still the most significant tool chemists have for organizing and remembering chemical facts. As we saw in Chapter 6, the periodic nature of the table arises from the repeating patterns in the electron configurations of the elements. Elements in the same column of the table contain the same number of electrons in their **valence orbitals**, the occupied orbitals that hold the electrons involved in bonding. For example, O ($[\text{He}]2s^2 2p^4$) and S ($[\text{Ne}]3s^2 3p^4$) are both members of group 6A. The similarity of the electron distribution in their valence *s* and *p* orbitals leads to similarities in the properties of these two elements.

When we compare O and S, however, it is apparent that they exhibit differences as well, not the least of which is that oxygen is a colorless gas at room



▲ **Figure 7.1 Oxygen and sulfur.** Because they are both group 6A elements, oxygen and sulfur have many chemical similarities. They also have many differences, however, including the forms they take at room temperature. Oxygen consists of O_2 molecules that appear as a colorless gas (shown here enclosed in a glass container on the left). In contrast, sulfur consists of S_8 molecules that form a yellow solid.

temperature, whereas sulfur is a yellow solid (Figure 7.1 ◀)! One of the major differences between atoms of these two elements is their electron configurations: the outermost electrons of O are in the second shell, whereas those of S are in the third shell. We will see that electron configurations can be used to explain differences as well as similarities in the properties of elements.

In this chapter we explore how some of the important properties of elements change as we move across a row or down a column of the periodic table. In many cases the trends within a row or column allow us to make predictions about the physical and chemical properties of the elements.

7.1 DEVELOPMENT OF THE PERIODIC TABLE

The discovery of the chemical elements has been an ongoing process since ancient times (Figure 7.2 ▼). Certain elements, such as gold, appear in nature in elemental form and were thus discovered thousands of years ago. In contrast, some elements, such as technetium, are radioactive and intrinsically unstable. We know about them only because of technology developed during the twentieth century.

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

As the number of known elements increased, scientists began to investigate the possibilities of classifying them in useful ways. In 1869, Dmitri Mendeleev in Russia and Lothar Meyer in Germany published nearly identical classification schemes. Both scientists 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 proper sequence. The tables of elements advanced by Mendeleev and Meyer were the forerunners of the modern periodic table.

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 much new work in chemistry.

► **Figure 7.2 Discovering the elements.** Periodic table showing the dates of discovery of the elements.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No		

■ Ancient Times	■ 1735–1843	■ 1894–1918
■ Middle Ages–1700	■ 1843–1886	■ 1923–1961
		■ 1965–

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

His insistence that elements with similar characteristics be listed in the same family forced him to leave several blank spaces in his table. For example, both gallium (Ga) and germanium (Ge) were unknown at that time. Mendeleev 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 appear in the periodic table. When these elements were discovered, their properties closely matched those predicted by Mendeleev, as shown in Table 7.1 ▲.

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

The concept of atomic number clarified some problems in the periodic table of Moseley’s day, which was based on atomic weights. For example, the atomic weight of Ar (atomic number 18) is greater than that of K (atomic number 19), yet the chemical and physical properties of Ar are much more like that of Ne and Kr than they are like Na and Rb. However, when the elements are arranged in order of increasing atomic number, rather than increasing atomic weight, 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 other previously unknown elements.

GIVE IT SOME THOUGHT

Arranging the elements by atomic weight leads to a slightly different order than arranging them by atomic number. Why does this happen? Can you find an example, other than the case of Ar and K discussed above, where the order of the elements would be different if the elements were arranged in order of increasing atomic weight?

7.2 EFFECTIVE NUCLEAR CHARGE

Because electrons are negatively charged, they are attracted to nuclei, which are positively charged. Many of the properties of atoms depend on their electron configurations and on how strongly their outer electrons are attracted to the nucleus. Coulomb’s law tells us that the strength of the interaction

between two electrical charges depends on the magnitudes of the charges and on the distance between them. ∞ (Section 2.3) Thus, the force of attraction between an electron and the nucleus depends on the magnitude of the net nuclear charge acting on the electron and on the average distance between the nucleus and the electron. The force of attraction increases as the nuclear charge increases, and it decreases as the electron moves farther from the nucleus.

In a many-electron atom, each electron is simultaneously attracted to the nucleus and repelled by the other electrons. In general, there are so many electron–electron repulsions that we cannot analyze the situation exactly. We can, however, estimate the net attraction of each electron to the nucleus by considering how it interacts with the *average* environment created by the nucleus and the other electrons in the atom. This approach allows us to treat each electron individually as though it were moving in the net electric field created by the nucleus and the electron density of the other electrons. We can view this net electric field as if it results from a single positive charge located at the nucleus, called the **effective nuclear charge**, Z_{eff} .

It is important to realize that the effective nuclear charge acting on an electron in an atom is smaller than the *actual* nuclear charge because the effective nuclear charge also accounts for the repulsion of the electron by the other electrons in the atom—in other words, $Z_{\text{eff}} < Z$. Let's consider how we can get a sense of the magnitude of Z_{eff} for an electron in an atom.

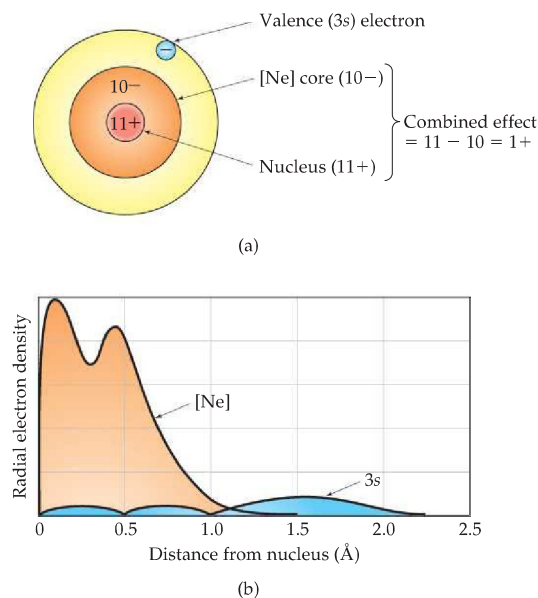
A valence electron in an atom is attracted to the nucleus of the atom and is repelled by the other electrons in the atom. In particular, the electron density that is due to the inner (core) electrons is particularly effective at partially canceling the attraction of the valence electron to the nucleus. We say that the inner electrons partially *shield* or *screen* the outer electrons from the attraction of the nucleus. We can therefore write a simple relationship between the effective nuclear charge, Z_{eff} , and the number of protons in the nucleus, Z :

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

The factor S is a positive number called the *screening constant*. It represents the portion of the nuclear charge that is screened from the valence electron by

the other electrons in the atom. Because the core electrons are most effective at screening a valence electron from the nucleus, *the value of S is usually close to the number of core electrons in an 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” on Effective Nuclear Charge). Let's take a look at a Na atom to see what we would expect for the magnitude of Z_{eff} . Sodium (atomic number 11) has a condensed electron configuration of $[\text{Ne}]3s^1$. The nuclear charge of the atom is $11+$, and the Ne inner core consists of ten electrons ($1s^2 2s^2 2p^6$). Very roughly then, we would expect the $3s$ valence electron of the Na atom to experience an effective nuclear charge of about $11 - 10 = 1+$, as pictured in a simplified way in Figure 7.3(a) \blacktriangleleft . The situation is a bit more complicated because of the electron distributions of atomic orbitals. ∞ (Section 6.6) Recall that a $3s$ electron has a small probability of being found close to the nucleus and inside the core electrons, as shown in Figure 7.3(b). Thus, there is a probability that the $3s$ electron will experience a greater attraction than our simple model suggests, which will increase the value of Z_{eff} somewhat. Indeed, the value of Z_{eff} obtained from detailed calculations indicate that the effective nuclear charge acting on the $3s$ electron in Na is $2.5+$.

▼ Figure 7.3 Effective nuclear charge. (a) The effective nuclear charge experienced by the valence electron in sodium depends mostly on the $11+$ charge of the nucleus and the $10-$ charge of the neon core. If the neon core were totally effective in shielding the valence electron from the nucleus, then the valence electron would experience an effective nuclear charge of $1+$. (b) The $3s$ electron has some probability of being inside the Ne core. Because of this “penetration,” the core is not completely effective in screening the $3s$ electron from the nucleus. Thus, the effective nuclear charge experienced by the $3s$ electron is somewhat greater than $1+$.



The notion of effective nuclear charge also explains an important effect we noted in Section 6.7, namely, that for a many-electron atom the energies of orbitals with the same n value increase with increasing l value. For example, consider a carbon atom, for which the electron configuration is $1s^2 2s^2 2p^2$. The energy of the $2p$ orbital ($l = 1$) is somewhat higher than that of the $2s$ orbital ($l = 0$) even though both of these orbitals are in the $n = 2$ shell (Figure 6.25). The reason that these orbitals have different energy in a many-electron atom is due to the radial probability functions for the orbitals, shown in Figure 7.4. Notice that the $2s$ probability function has a small peak fairly close to the nucleus, whereas the $2p$ probability function does not. As a result, an electron in the $2s$ orbital is less effectively screened by the core orbitals than is an electron in the $2p$ orbital. In other words, the electron in the $2s$ orbital experiences a higher effective nuclear charge than one in the $2p$ orbital. 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 the trends in Z_{eff} for valence electrons as we move from one element to another in the periodic table. The effective nuclear charge increases as we move across any row (period) of the table. Although the number of core electrons stays the same as we move across the row, the actual nuclear charge increases. The valence electrons added to counterbalance the increasing nuclear charge shield one another very ineffectively. Thus, the effective nuclear charge, Z_{eff} , increases steadily. For example, the $1s^2$ core electrons of lithium ($1s^2 2s^1$) shield the $2s$ valence electron from the $3+$ nucleus fairly efficiently. Consequently, the outer electron experiences an effective nuclear charge of roughly $3 - 2 = 1+$. For beryllium ($1s^2 2s^2$) the effective nuclear charge experienced by each $2s$ valence electron is larger; in this case, the inner $1s$ electrons are shielding a $4+$ nucleus, and each $2s$ electron only partially shields the other from the nucleus. Consequently, the effective nuclear charge experienced by each $2s$ electron is about $4 - 2 = 2+$.

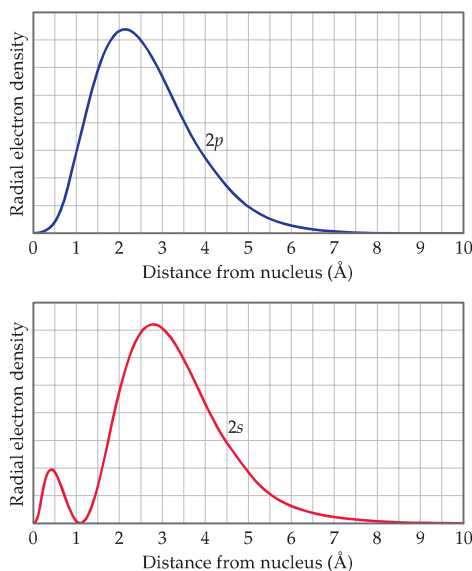
Going down a column, the effective nuclear charge experienced by valence electrons changes far less than it does across a row. For example, we would expect the effective nuclear charge for the outer electrons in lithium and sodium to be about the same, roughly $3 - 2 = 1+$ for lithium and $11 - 10 = 1+$ for sodium. In fact, however, the effective nuclear charge increases slightly as we go down a family because larger electron cores are less able to screen the outer electrons from the nuclear charge. In the case of the alkali metals, the value of Z_{eff} increases from $1.3+$ for lithium, to $2.5+$ for sodium, to $3.5+$ for potassium. Nevertheless, the increase in effective nuclear charge that occurs moving down a column is smaller than the change that occurs when moving horizontally from one side of the periodic table to the other.

GIVE IT SOME THOUGHT

Which would you expect to experience a greater effective nuclear charge, a $2p$ electron of a Ne atom or a $3s$ electron of a Na atom?

7.3 SIZES OF ATOMS AND IONS

Size is one of the important properties of an atom or an ion. We often think of atoms and ions as hard, spherical objects. According to the quantum mechanical model, however, atoms and ions do not have sharply defined boundaries at which the electron distribution becomes zero. ∞ (Section 6.5) Nevertheless,



▲ **Figure 7.4 2s and 2p radial functions.** The radial probability function for the $2s$ orbital of the hydrogen atom (red curve) shows a “bump” of probability close to the nucleus, whereas that for the $2p$ orbital (blue curve) does not. As a result, an electron in the $2s$ orbital for a many-electron atom “sees” more of the nuclear charge than does an electron in the $2p$ orbital. Hence, the effective nuclear charge experienced by the $2s$ electron is greater than that for the $2p$ electron.

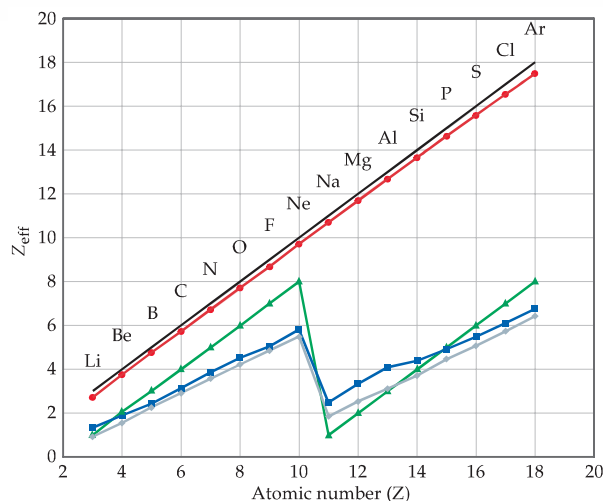
A Closer Look

EFFECTIVE NUCLEAR CHARGE

To get a better sense of how the effective nuclear charge varies as both the charge of the nucleus and the number of electrons increase, consider Figure 7.5. This figure shows the variation in Z_{eff} for elements in the second (Li – Ne) and third (Na – Ar) periods. The effective nuclear charge is plotted for electrons in the 1s subshell (in red) and for the outermost valence electrons (in blue). These values are considered the most accurate estimate of Z_{eff} . Although the details of how they are calculated are beyond the scope of our discussion, the trends are instructive. The effective nuclear charge as felt by electrons in the 1s subshell closely track the increasing charge of the nucleus, Z , (in black) because the other electrons do little to shield these innermost electrons from the charge of the nucleus.

Compare the values of Z_{eff} experienced by the inner core electron (in red) with those experienced by the outermost electrons (in blue). The values of Z_{eff} as felt by the outermost electrons are smaller 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 non-negligible contribution to the screening constant, S . However, the most striking feature associated with the Z_{eff} for the outermost electrons is the sharp drop between the last element of the second period (Ne) and the first element of the third period (Na). This drop reflects the fact that the core electrons are much more effective than the valence electrons at screening the charge of the nucleus.

Effective nuclear charge is a tool that can be used to understand many physically measurable quantities, such as ionization energy, atomic radii, and electron affinity. Therefore, it is desirable to have a simple method for estimating Z_{eff} without resorting to sophisticated calculations or memorization. The charge of the nucleus, Z , is known exactly, so the challenge boils down to estimating accurately the value of the screening constant, S . The approach outlined in the text was to estimate S by assuming that the core electrons contribute a value of 1.00 to the screening constant, and the outer electrons contribute nothing to S . A more accurate approach is to use an empirical set of rules developed by John Slater. If we limit ourselves to elements that do not have electrons in d or f subshells (the rules become somewhat more complicated for such elements), Slater's rules are straightforward to apply. Electrons with larger values of n , the principal quantum number, than the electron of interest contribute 0 to the value of the screening constant, S . Electrons with the same value of n , as the electron of interest contribute 0.35 to the value of S . Electrons with a



▲ **Figure 7.5 Variations in effective nuclear charge.**

This figure shows the variation in effective nuclear charge, Z_{eff} , as felt by the innermost electrons, those in the 1s subshell (red circles), which closely tracks the increase in nuclear charge, Z (black line). The Z_{eff} felt by the outermost valence electrons (blue squares) not only is significantly smaller than Z , it does not evolve linearly with increasing atomic number. It is also possible to estimate Z_{eff} using certain rules. The values shown as green triangles were obtained by assuming the core electrons are completely effective at screening and the valence electrons do not screen the nuclear charge at all. The values shown as gray diamonds were estimated using Slater's rules.

principal quantum number one less than the electron of interest contribute 0.85 to the value of S , while those with even smaller values of n contribute 1.00 to the value of S . Values of Z_{eff} as estimated using the simple method outlined in the text (in green), as well as those estimated with Slater's rules (in grey), are plotted in Figure 7.5. While neither of these methods exactly replicate the values of Z_{eff} obtained from more sophisticated calculations, we see that 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 the effective nuclear charge, despite its simplicity. For our purposes, we can assume that the screening constant, S , in Equation 7.1 is roughly equal to the number of core electrons.

Related Exercises: 7.13, 7.14, 7.33, 7.34, 7.85, 7.87

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 atoms collide with each other in the course of their motions, they ricochet apart—somewhat like billiard balls. This movement happens because the electron clouds of

the colliding atoms cannot penetrate each other to any significant extent. The closest distances separating the nuclei during such collisions determine the *apparent radii* of the argon atoms. We might call this radius the *nonbonding atomic radius* of an atom.

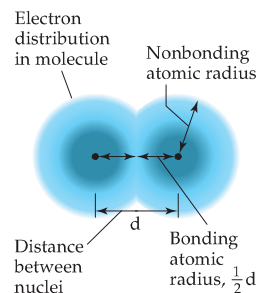
When two atoms are chemically bonded to each other, as in the Cl_2 molecule, an attractive interaction exists between the two atoms leading to a chemical bond. We will discuss the nature of such bonding in Chapter 8. For now, the only thing we need to realize is that this attractive interaction brings the two atoms closer together than they would be in a nonbonding collision. We can define an atomic radius based on the distances separating the nuclei of atoms when they are chemically bonded to each other. This distance, called the **bonding atomic radius**, is shorter than the nonbonding atomic radius, as illustrated in Figure 7.6. Unless otherwise noted, we will refer to the bonding atomic radius when we speak of the size of an atom.

Scientists have developed a variety of experimental 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 iodine nuclei is observed to be 2.66 \AA .^{*} We can define the bonding atomic radius of iodine on this basis to be one-half of the bond distance, namely 1.33 \AA . Similarly, the distance separating two adjacent carbon nuclei in diamond, which is a three-dimensional solid network, is 1.54 \AA ; thus, the bonding atomic radius of carbon is assigned the value 0.77 \AA . The radii of other elements can be similarly defined (Figure 7.7).

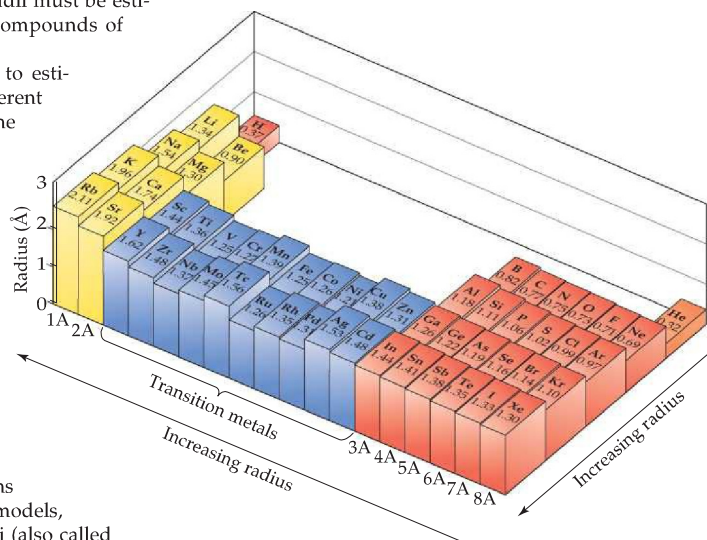
(For helium and neon, the bonding radii must be estimated because there are no known compounds of these elements.)

Knowing atomic radii allows us to estimate the bond lengths between different elements in molecules. For example, the Cl—Cl bond length in Cl_2 is 1.99 \AA , so a radius of 0.99 \AA is assigned to Cl. In the compound CCl_4 the measured length of the C—Cl bond is 1.77 \AA , very close to the sum ($0.77 + 0.99 \text{ \AA}$) of the atomic radius of C and Cl.

If we consider the radius of an atom as one-half the distance between the nuclei of atoms that are held together by a bond, you may wonder why the spheres representing atoms seem to overlap in some drawings, such as those in Figures 1.1 and 2.20. These depictions of molecules are called space-filling models, and they use nonbonding atomic radii (also called *van der Waals radii*) to represent the sizes of different elements. Even in these representations the distance between the centers of two adjacent atoms in the molecule is determined from bonding atomic radii (also called *covalent radii*).

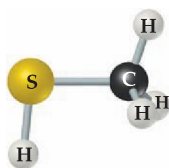


▲ **Figure 7.6 Distinction between nonbonding and bonding atomic radii.** The nonbonding atomic radius is the effective radius of an atom when it is not involved in bonding to another atom. Values of bonding atomic radii are obtained from measurements of interatomic distances in chemical compounds.



▲ **Figure 7.7 Trends in atomic radii.** Bonding atomic radii for the first 54 elements of the periodic table. The height of the bar for each element is proportional to its radius, giving a “relief map” view of the radii.

^{*}Remember: The angstrom ($1 \text{ \AA} = 10^{-10} \text{ m}$) is a convenient metric unit for atomic measurements of length. The angstrom is not an SI unit. The most commonly used SI unit for such measurements is the picometer ($1 \text{ pm} = 10^{-12} \text{ m}$; $1 \text{ \AA} = 100 \text{ pm}$).



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 , whose structure is shown in the margin. 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 the list of bonding atomic radii. We will assume that each bond length is the sum of the radii of the two atoms involved.

Solve: Using radii for C, S, and H from Figure 7.7, we predict

$$\begin{aligned}\text{C—S bond length} &= \text{radius of C} + \text{radius of S} \\ &= 0.77 \text{ \AA} + 1.02 \text{ \AA} = 1.79 \text{ \AA}\end{aligned}$$

$$\text{C—H bond length} = 0.77 \text{ \AA} + 0.37 \text{ \AA} = 1.14 \text{ \AA}$$

$$\text{S—H bond length} = 1.02 \text{ \AA} + 0.37 \text{ \AA} = 1.39 \text{ \AA}$$

Check: The experimentally determined bond lengths in methyl mercaptan (taken from the chemical literature) are C—S = 1.82 Å, C—H = 1.10 Å, and S—H = 1.33 Å. (In general, the lengths of bonds involving hydrogen show larger deviations from the values predicted by the sum of the atomic radii than do those bonds involving larger atoms.)

Comment: Notice that the estimated bond lengths using bonding atomic radii are close, but not exact matches, to the experimental bond lengths. Atomic radii must be used with some caution in estimating bond lengths. In Chapter 8 we will examine some of the average lengths of common types of bonds.

PRACTICE EXERCISE

Using Figure 7.7, predict which will be greater, the P—Br bond length in PBr_3 or the As—Cl bond length in AsCl_3 .

Answer: P—Br

Periodic Trends in Atomic Radii

If we examine the “relief map” of atomic radii shown in Figure 7.7, we observe two interesting trends in the data:

1. Within each column (group), 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 atom to increase in size.
2. Within each row (period), atomic radius tends to decrease from left to right. The major factor influencing this trend is the increase in the effective nuclear charge (Z_{eff}) as we move across a row. The increasing effective nuclear charge steadily draws the valence electrons closer to the nucleus, causing the atomic radius to decrease.

GIVE IT SOME THOUGHT

In section 7.2 we said that the effective nuclear charge generally increases when you move down a column of the periodic table, whereas in Chapter 6 we saw that the “size” of an orbital increases as the principal quantum number increases. With respect to atomic radii, do these trends work together or against each other? Which effect is larger?

SAMPLE EXERCISE 7.2 | Atomic Radii

Referring to a periodic table, arrange (as much as possible) the following atoms in order of increasing size: ^{15}P , ^{16}S , ^{33}As , ^{34}Se . (Atomic numbers are given for the elements to help you locate them quickly in the periodic table.)

SOLUTION

Analyze and Plan: We are given the chemical symbols for four elements. We can use their relative positions in the periodic table and the two periodic trends just described to predict the relative order of their atomic radii.

Solve: Notice that P and S are in the same row of the periodic table, with S to the right of P. Therefore, we expect the radius of S to be smaller than that of P. (Radii decrease as we move from left to right.) Likewise, the radius of Se is expected to be smaller than that of As. We also notice that As is directly below P and that Se is directly below S. We expect, therefore, that the radius of As is greater than that of P and the radius of Se is greater than that of S. From these observations, we predict $\text{S} < \text{P}$, $\text{P} < \text{As}$, $\text{S} < \text{Se}$, and $\text{Se} < \text{As}$. We can therefore conclude that S has the smallest radius of the four elements and that As has the largest radius.

Using just the two trends described above, we cannot determine whether P or Se has the larger radius. To go from P to Se in the periodic table, we must move down (radius tends to increase) and to the right (radius tends to decrease). In Figure 7.7 we see that the radius of Se (1.16 Å) is greater than that of P (1.06 Å). If you examine the figure carefully, you will discover that for the *s*- and *p*-block elements the increase in radius moving down a column tends to be the greater effect. There are exceptions, however.

Check: From Figure 7.7, we have $\text{S} (1.02 \text{ \AA}) < \text{P} (1.06 \text{ \AA}) < \text{Se} (1.16 \text{ \AA}) < \text{As} (1.19 \text{ \AA})$.

Comment: Note that the trends we have just discussed are for the *s*- and *p*-block elements. You will see in Figure 7.7 that the transition elements do not show a regular decrease upon moving from left to right across a row.

PRACTICE EXERCISE

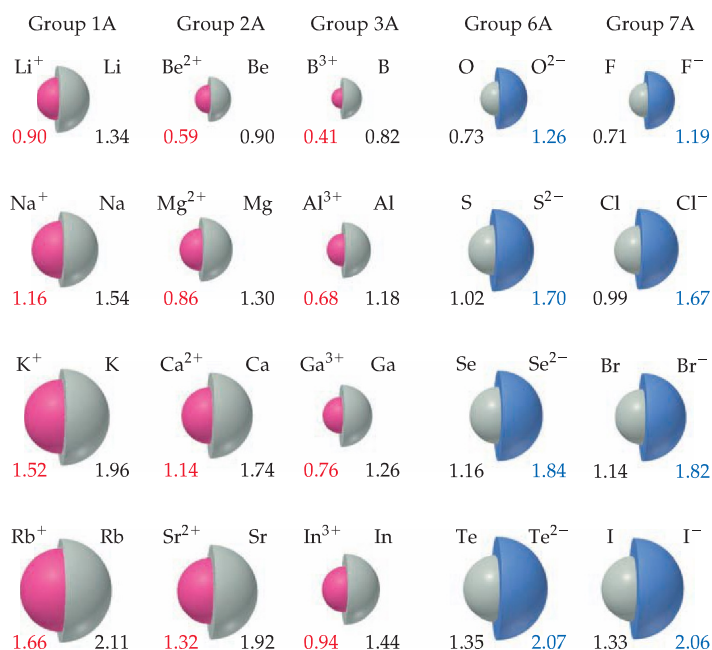
Arrange the following atoms in order of increasing atomic radius: ^{11}Na , ^4Be , ^{12}Mg .

Answer: $\text{Be} < \text{Mg} < \text{Na}$

Periodic Trends in Ionic Radii

Just as bonding atomic radii can be determined from interatomic distances in elements, 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. The formation of a cation vacates the most spatially extended occupied orbitals in an atom and decreases the number of electron–electron repulsions. Therefore, *cations are smaller than their parent atoms*, as illustrated in Figure 7.8. The opposite is true of anions. When electrons are added

► **Figure 7.8 Cation and anion size.** Comparisons of the radii, in Å, of neutral atoms and ions for several of the groups of representative elements. Neutral atoms are shown in gray, cations in red, and anions in blue.



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, size increases as we move down a column in the periodic table. This trend is also seen in Figure 7.8. As the principal quantum number of the outermost occupied orbital of an ion increases, the radius of the ion increases.

SAMPLE EXERCISE 7.3 | Atomic and Ionic Radii

Arrange these atoms and ions in order of decreasing size: Mg^{2+} , Ca^{2+} , and Ca.

SOLUTION

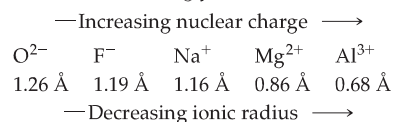
Cations are smaller than their parent atoms, and so the Ca^{2+} ion is smaller than the Ca atom. Because Ca is below Mg in group 2A of the periodic table, Ca^{2+} is larger than Mg^{2+} . Consequently, $\text{Ca} > \text{Ca}^{2+} > \text{Mg}^{2+}$.

PRACTICE EXERCISE

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

Answer: S^{2-}

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+} , Al^{3+} has 10 electrons. In any isoelectronic series we can list the members in order of increasing atomic number; therefore, nuclear charge increases as we move through the series. (Recall that the charge on the nucleus of an atom or monatomic ion is given by the atomic number of the element.) Because the number of electrons remains constant, the radius of the ion decreases with increasing nuclear charge, as the electrons are more strongly attracted to the nucleus:



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

SAMPLE EXERCISE 7.4 | Ionic Radii in an Isoelectronic Series

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

SOLUTION

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

PRACTICE EXERCISE

Which of the following ions is largest, Rb^+ , Sr^{2+} , or Y^{3+} ?

Answer: Rb^+

7.4 IONIZATION ENERGY

The ease with which electrons can be removed from an atom or ion has a major impact on chemical behavior. The **ionization energy** of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion. The *first ionization energy*, I_1 , is the energy

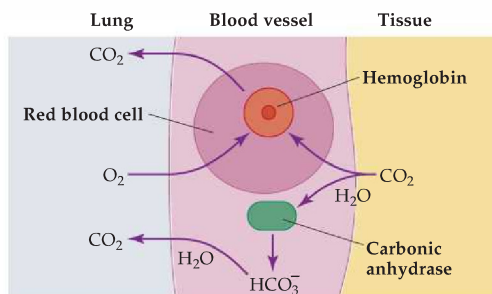
Ionic size plays a major role in determining the properties of ions in solution. For example, a small difference in ionic size is often sufficient for one metal ion to be biologically important and another not to be. To illustrate, let's examine some of the biological chemistry of the zinc ion (Zn^{2+}) and compare it with the cadmium ion (Cd^{2+}).

Recall from the "Chemistry and Life" box in Section 2.7 that zinc is needed in our diets in trace amounts. Zinc is an essential part of several enzymes—the proteins that facilitate or regulate the speeds of key biological reactions. For example, one of the most important zinc-containing enzymes is *carbonic anhydrase*. This enzyme is found in red blood cells. Its job is to facilitate the reaction of carbon dioxide (CO_2) with water to form the bicarbonate ion (HCO_3^-):



You might be surprised to know that our bodies need an enzyme for such a simple reaction. In the absence of carbonic anhydrase, however, the CO_2 produced in cells when they are oxidizing glucose or other fuels in vigorous exercise would be cleared out much too slowly. About 20% of the CO_2 produced by cell metabolism binds to hemoglobin and is carried to the lungs, where it is expelled. About 70% of the CO_2 produced is converted to bicarbonate ion through the action of carbonic anhydrase. When the CO_2 has been converted into bicarbonate ion, it diffuses into the blood plasma and eventually is passed into the lungs in the reverse of Equation 7.2. These processes are illustrated in Figure 7.9. In the absence of zinc, the carbonic anhydrase would be inactive, and serious imbalances would result in the amount of CO_2 present in blood.

Zinc is also found in several other enzymes, including some found in the liver and kidneys. It is obviously essential to life. By contrast, cadmium, zinc's neighbor in group 2B, is extremely toxic to humans. But why are two elements so dif-

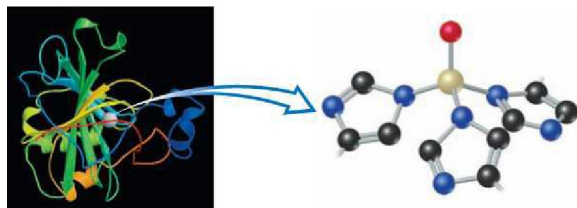


▲ **Figure 7.9 Ridding the body of carbon dioxide.**

Illustration of the flow of CO_2 from tissues into blood vessels and eventually into the lungs. About 20% of the CO_2 binds to hemoglobin and is released in the lungs. About 70% is converted by carbonic anhydrase into HCO_3^- ion, which remains in the blood plasma until the reverse reaction releases CO_2 into the lungs. Small amounts of CO_2 simply dissolve in the blood plasma and are released in the lungs.

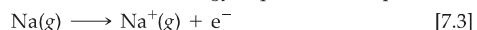
ferent? Both occur as $2+$ ions, but Zn^{2+} is smaller than Cd^{2+} . The radius of Zn^{2+} is 0.88 \AA ; that of Cd^{2+} is 1.09 \AA . Can this difference be the cause of such a dramatic reversal of biological properties? The answer is that while size is not the only factor, it is very important. In the carbonic anhydrase enzyme the Zn^{2+} ion is found electrostatically bonded to atoms on the protein, as shown in Figure 7.10. It turns out that Cd^{2+} binds in this same place preferentially over Zn^{2+} , thus displacing it. When Cd^{2+} is present instead of Zn^{2+} , however, the reaction of CO_2 with water is not facilitated. More seriously, Cd^{2+} inhibits reactions that are essential to the kidneys' functioning.

Related Exercises: 7.30, 7.91, and 7.92

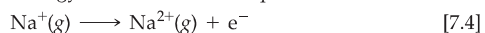


◀ **Figure 7.10 A zinc-containing enzyme.** The enzyme called carbonic anhydrase (left) catalyzes the reaction between CO_2 and water to form HCO_3^- . The ribbon represents the folding of the protein chain. The "active site" of the enzyme (represented by the ball-and-stick model) is where the reaction occurs. (H atoms have been excluded from this model for clarity.) The red sphere represents the oxygen of a water molecule that is bound to the zinc ion (gold sphere) at the center of the active site. The water molecule is replaced by CO_2 in the reaction. The bonds coming off the five-member rings attach the active site to the protein (nitrogen and carbon atoms are represented by blue and black spheres, respectively).

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



The greater the ionization energy, the more difficult it is to remove an electron.

GIVE IT SOME THOUGHT

Light can be used to ionize atoms and ions, as in Equations 7.3 and 7.4. Which of the two processes, [7.3] or [7.4], would require shorter wavelength radiation?

Variations in Successive Ionization Energies

Ionization energies for the elements sodium through argon are listed in Table 7.2. Notice that the values for a given element increase as successive electrons are removed: $I_1 < I_2 < I_3$, and so forth. This trend exists because with each successive removal, an electron is being pulled away from an increasingly more positive ion, requiring increasingly more energy.

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

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4562	(inner-shell electrons)				
Mg	738	1451	7733				
Al	578	1817	2745	11,577			
Si	786	1577	3232	4356	16,091		
P	1012	1907	2914	4964	6274	21,267	
S	1000	2252	3357	4556	7004	8496	27,107
Cl	1251	2298	3822	5159	6542	9362	11,018
Ar	1521	2666	3931	5771	7238	8781	11,995

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, whose electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^2$ or $[\text{Ne}]3s^2 3p^2$. The ionization energies increase steadily from 786 kJ/mol to 4356 kJ/mol for the loss of the four electrons in the outer 3s and 3p subshells. Removal of the fifth electron, which comes from the 2p subshell, requires a great deal more energy: 16,091 kJ/mol. The large increase occurs because the 2p electron is much more likely to be found close to the nucleus than are the four $n = 3$ electrons, and therefore the 2p electron experiences a much greater effective nuclear charge than do the 3s and 3p electrons.

GIVE IT SOME THOUGHT

Which would you expect to be greater, I_1 for a boron atom or I_2 for a carbon atom?

Every element exhibits a large increase in ionization energy when electrons are removed from its noble-gas core. This observation supports the idea that only the outermost electrons, those beyond the noble-gas core, are involved in the sharing and transfer of electrons that give rise to chemical bonding and reactions. The inner electrons are too tightly bound to the nucleus to be lost from the atom or even shared with another atom.

SAMPLE EXERCISE 7.5 | Trends in Ionization Energy

Three elements are indicated in the periodic table in the margin. Based on their locations, predict the one with 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 element in group 1A (Na), indicated by the red box, has only 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 box) and Ca (blue box), have two or more valence electrons. Thus, Na should have the largest second ionization energy.

Check: If we consult a chemistry handbook, we find the following values for the second ionization energies (I_2) of the respective elements: Ca (1,145 kJ/mol) < S (2,252 kJ/mol) < Na (4,562 kJ/mol).

PRACTICE EXERCISE

Which will have the greater third ionization energy, Ca or S?

Answer: Ca

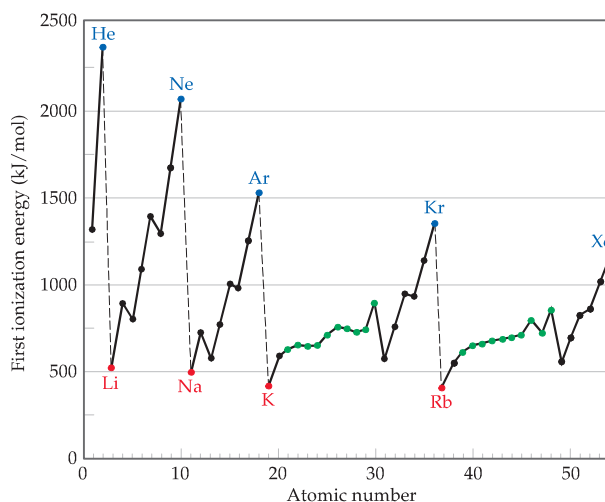
Periodic Trends in First Ionization Energies

We have seen that the ionization energy for a given element increases as we remove successive electrons. What trends do we observe in ionization energy as we move from one element to another in the periodic table? Figure 7.11 shows a graph of I_1 versus atomic number for the first 54 elements. The important trends are as follows:

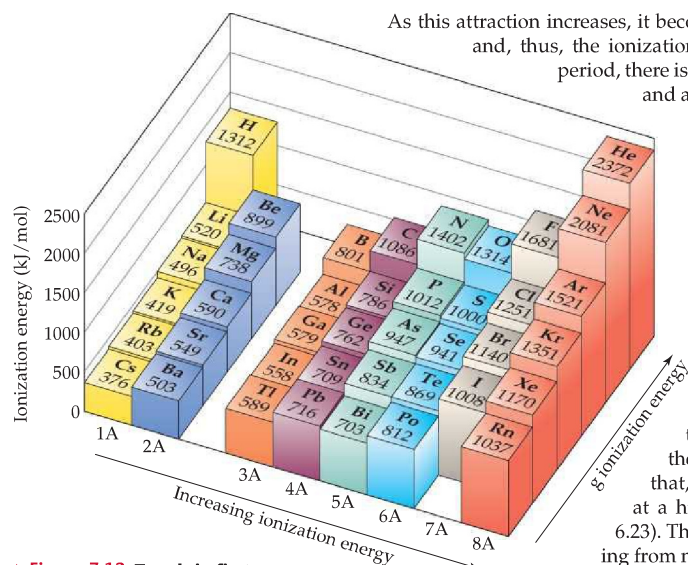
1. Within each row (period) of the table, I_1 generally increases with increasing atomic number. The alkali metals show the lowest ionization energy in each row, and the noble gases show the highest. There are slight irregularities in this trend that we will discuss shortly.
2. Within each column (group) of the table, the ionization energy generally decreases with increasing atomic number. For example, the ionization energies of the noble gases follow the order He > Ne > Ar > Kr > Xe.
3. The *s*- and *p*-block elements show a larger range of values of I_1 than do the transition-metal elements. Generally, the ionization energies of the transition metals increase slowly as we proceed from left to right in a period. The *f*-block metals, which are not shown in Figure 7.11, also show only a small variation in the values of I_1 .

The periodic trends in the first ionization energies of the *s*- and *p*-block elements are further illustrated in Figure 7.12.

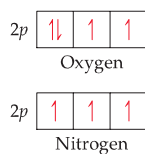
In general, smaller atoms have higher ionization energies. The same factors that influence atomic size also influence ionization energies. The energy needed to remove an electron from the outermost occupied shell depends on both the effective nuclear charge and the average distance of the electron from the nucleus. Either increasing the effective nuclear charge or decreasing the distance from the nucleus increases the attraction between the electron and the nucleus.



▲ **Figure 7.11 First ionization energy versus atomic number.** The red dots mark the beginning of a period (alkali metals), the blue dots mark the end of a period (noble gases), and the black dots indicate *s*- and *p*-block elements, while green dots are used to represent the transition metals.



▲ **Figure 7.12 Trends in first ionization energy.** First ionization energies for the s - and p -block elements in the first six periods. The ionization energy generally increases from left to right and decreases from top to bottom. The ionization energy of astatine has not been determined.



▲ **Figure 7.13 2p orbital filling in nitrogen and oxygen.** The presence of a fourth electron in the $2p$ orbitals of oxygen leads to an extra repulsion associated with putting two electrons in a single orbital. This repulsion is responsible for the lower first ionization energy of oxygen.

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, however, the atomic radius increases, while the effective nuclear charge increases rather gradually. Thus, the attraction between the nucleus and the electron decreases, causing the ionization energy to decrease.

The irregularities within a given row are somewhat subtler 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 Figures 7.11 and 7.12, occurs because the third valence electron of B must occupy the $2p$ subshell, which is empty for Be. Recall that, as we discussed earlier, the $2p$ subshell is at a higher energy than the $2s$ subshell (Figure 6.23). The decrease in ionization energy when moving from nitrogen ($[\text{He}]2s^22p^3$) to oxygen ($[\text{He}]2s^22p^4$) is because of the repulsion of paired electrons in the p^4 configuration, as shown in Figure 7.13. 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. ∞∞ (Section 6.8)

■ SAMPLE EXERCISE 7.6 | Periodic Trends in Ionization Energy

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

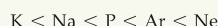
■ SOLUTION

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 row. It decreases as we move from the top of a group to the bottom. Because Na, P, and Ar are in the same row of the periodic table, we expect I_1 to vary in the order $\text{Na} < \text{P} < \text{Ar}$.

Because Ne is above Ar in group 8A, we expect Ne to have the greater first ionization energy: $\text{Ar} < \text{Ne}$. Similarly, K is the alkali metal directly below Na in group 1A, and so we expect I_1 for K to be less than that of Na: $\text{K} < \text{Na}$.

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



Check: The values shown in Figure 7.12 confirm this prediction.

■ PRACTICE EXERCISE

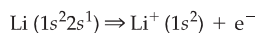
Which has the lowest first ionization energy, B, Al, C, or Si? Which has the highest first ionization energy?

Answer: Al lowest, C highest

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 ($1s^2 2s^1$), it is the $2s^1$ electron that is removed:



Likewise, when two electrons are removed from Fe ($[\text{Ar}]3d^6 4s^2$), the $4s^2$ electrons are the ones removed:

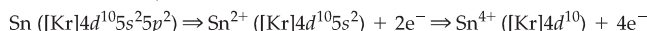


If an additional electron is removed, forming Fe^{3+} , it now comes from a $3d$ orbital because all the orbitals with $n = 4$ are empty:

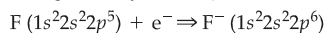


It may seem odd that the $4s$ electrons are removed before the $3d$ electrons in forming transition-metal cations. After all, in writing electron configurations, we added the $4s$ electrons before the $3d$ ones. In writing electron configurations for atoms, however, we are going through an imaginary 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.

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:



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



GIVE IT SOME THOUGHT

Would Cr^{3+} and V^{2+} have the same or different electron configurations?

SAMPLE EXERCISE 7.7 | Electron Configurations of Ions

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

SOLUTION

Analyze and Plan: We are asked to write electron configurations for three ions. To do so, we first write the electron configuration of the parent atom. We then remove electrons to form cations or add electrons to form anions. 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



To form a $2+$ ion, the two outer electrons must be removed, giving an ion that is isoelectronic with Ar:



(b) Cobalt (atomic number 27) has the electron configuration



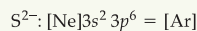
To form a $3+$ ion, three electrons must be removed. As discussed in the text preceding this Sample Exercise, the $4s$ electrons are removed before the $3d$ electrons. Consequently, the electron configuration for Co^{3+} is



(c) Sulfur (atomic number 16) has the electron configuration



To form a $2-$ ion, two electrons must be added. There is room for two additional electrons in the $3p$ orbitals. Thus, the S^{2-} electron configuration is



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

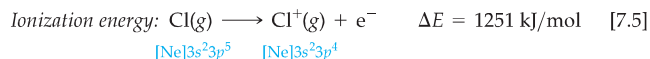
■ PRACTICE EXERCISE

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

Answers: (a) $[\text{Ar}]3d^{10}$, (b) $[\text{Ar}]3d^3$, (c) $[\text{Ar}]3d^{10}4s^24p^6 = [\text{Kr}]$

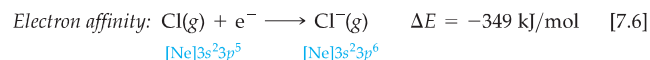
7.5 ELECTRON AFFINITIES

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 positively charged ion. For example, the first ionization energy of $\text{Cl}(\text{g})$, 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.

In addition, most atoms can gain electrons to form negatively charged ions. 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.*



It is important to understand the difference between ionization energy and electron affinity: Ionization energy measures the ease with which an atom *loses* an electron, whereas electron affinity measures the ease with which an atom *gains* an electron.

The greater the attraction between a given atom and an added electron, the more negative the atom's electron affinity will be. 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 a positive number means that an electron will not attach itself to an Ar atom; the Ar^- ion is unstable and does not form.

*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 the addition of an electron is an exothermic process, as in the electron affinity given 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 $\text{Cl}(\text{g})$, the electron affinity by this convention would be $+349$ kJ/mol.

Figure 7.14► shows the electron affinities for the *s*- and *p*-block elements in the first five rows of the periodic table. Notice that the trends in electron affinity as we proceed through the periodic table are not as evident as they were 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 negative ion that has a noble-gas configuration (Equation 7.6). 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 neutral atom (Equation 7.7). Because occupying a higher-energy subshell is energetically very 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 5A elements (N, P, As, Sb) 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 their neighbors to the left (P, As, Sb). Recall that we saw a discontinuity in the regular periodic trends for first ionization energy in Section 7.4 for the same reason.

Electron affinities do not change greatly as we move down a group. For example, consider the electron affinities of the halogens (Figure 7.14). For F, 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.

H –73						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 –47	Sr –5	In –30	Sn –107	Sb –103	Te –190	I –295	Xe > 0
1A	2A	3A	4A	5A	6A	7A	8A

▲ Figure 7.14 Electron affinity.

Electron affinities in kJ/mol for the *s*- and *p*-block elements in the first five rows of the periodic table. The more negative the electron affinity, the greater the attraction of the atom for an electron. An electron affinity > 0 indicates that the negative ion is higher in energy than the separated atom and electron.

GIVE IT SOME THOUGHT

Suppose you were asked for a value for the first ionization energy of a $\text{Cl}^-(g)$ ion. What is the relationship between this quantity and the electron affinity of $\text{Cl}(g)$?

7.6 METALS, NONMETALS, AND METALLOIDS

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

The elements can be broadly grouped into the categories of metals, nonmetals, and metalloids. ∞ (Section 2.5) This classification is shown in Figure 7.15►. Roughly three-quarters of the elements are metals, situated in the left and middle portions of the table. The nonmetals are located

▼ Figure 7.15 Metals, metalloids, and nonmetals.

The majority of elements are metals. Metallic character increases from right to left across a period and also increases from top to bottom in a group.

← Increasing metallic character →

1A 1 H	2A 2 He																			8A 18	
3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne			
11 Na	12 Mg	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8 9 10					1B 11	2B 12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr				
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe				
55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn				
87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	113	114	115	116						
			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb					
			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No					
			Metals																		
			Metalloids																		
			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, 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



▲ **Figure 7.16 The luster of metals.** Metallic objects are readily recognized by their characteristic shiny luster.

at the top right corner, and the metalloids lie between the metals and nonmetals. Hydrogen, which is located at the top left corner, is a nonmetal. This is why we set off hydrogen from the remaining group 1A elements in Figure 7.15 by inserting a space between the H box and the Li box. Some of the distinguishing properties of metals and nonmetals are summarized in Table 7.3▲.

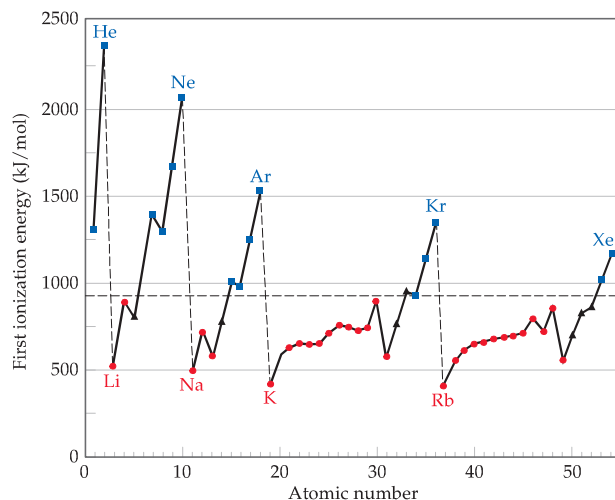
The more an element exhibits the physical and chemical properties of metals, the greater its **metallic character**. As indicated in Figure 7.15, metallic character generally increases as we proceed down a column of the periodic table and increases as we proceed from right to left in a row. Let's now examine the close relationships that exist between electron configurations and the properties of metals, nonmetals, and metalloids.

Metals

Most metallic elements exhibit the shiny luster that we associate with metals (Figure 7.16◀). Metals conduct heat and electricity. In general they are malleable (can be pounded into thin sheets) and ductile (can be drawn into wires). All are solids at room temperature except mercury (melting point = $-39\text{ }^{\circ}\text{C}$), which is a liquid. Two metals melt at slightly above room temperature, cesium at $28.4\text{ }^{\circ}\text{C}$ and gallium at $29.8\text{ }^{\circ}\text{C}$. At the other extreme, many metals melt at very high temperatures. For example, chromium melts at $1900\text{ }^{\circ}\text{C}$.

Metals tend to have low ionization energies and therefore tend to form positive ions relatively easily. As a result, metals are oxidized (lose electrons) when they undergo chemical reactions. This fact is illustrated in Figure 7.17▼, where the first ionization energies of the metals, nonmetals, and metalloids are compared.

Among the fundamental atomic properties (radius, electron configuration, electron affinity, and so forth), the first ionization energy is the best indicator of whether an element will behave as a metal or a nonmetal. The relative ease of oxidation of common metals was discussed earlier, in Section 4.4. As we noted there, many metals are oxidized by a variety of common substances, including O_2 and acids.



◀ **Figure 7.17 A comparison of the first ionization energies of metals vs. nonmetals.** Values of first ionization energy for metals are markedly lower than those of nonmetals. The red circles correspond to metallic elements, the blue squares to nonmetals, and the black triangles to metalloids. The dashed line at 925 kJ/mol separates the metals from the nonmetals.

1A												7A				8A	
H ⁺															H ⁻	N O B L E G A S E S	
Li ⁺														N ³⁻	O ²⁻		F ⁻
Na ⁺	Mg ²⁺	Transition metals										Al ³⁺		P ³⁻	S ²⁻		Cl ⁻
K ⁺	Ca ²⁺	Sc ³⁺	Ti ⁴⁺	V ⁵⁺ V ⁴⁺	Cr ³⁺	Mn ²⁺ Mn ⁴⁺	Fe ²⁺ Fe ³⁺	Co ²⁺ Co ³⁺	Ni ²⁺	Cu ⁺ Cu ²⁺	Zn ²⁺			Se ²⁻	Br ⁻		
Rb ⁺	Sr ²⁺								Pd ²⁺	Ag ⁺	Cd ²⁺		Sn ²⁺ Sn ⁴⁺	Sb ³⁺ Sb ⁵⁺	Te ²⁻		I ⁻
Cs ⁺	Ba ²⁺								Pt ²⁺	Au ⁺ Au ³⁺	Hg ²⁺ Hg ²⁺		Pb ²⁺ Pb ⁴⁺	Bi ³⁺ Bi ⁵⁺			

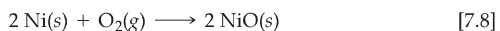
▲ **Figure 7.18 Representative oxidation states.** Oxidation states found in ionic compounds, including some examples of higher oxidation states adopted by *p*-block metals. Notice that the steplike line that divides metals from nonmetals also separates cations from anions.

Figure 7.18 ▲ shows the oxidation states of some representative ions of both metals and nonmetals. As we noted in Section 2.7, the charge on any alkali metal ion is always 1+, and that on any alkaline earth metal is always 2+ in their compounds. 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 3A–7A), the observed cations are formed either by losing only the outer *p* electrons (such as Sn²⁺) or the outer *s* and *p* electrons (such as Sn⁴⁺). The charge on transition-metal ions does not follow an obvious pattern. One of the characteristic features of the transition metals is their ability to form more than one positive ion. For example, iron may be 2+ in some compounds and 3+ in others.

GIVE IT SOME THOUGHT

Based on periodic trends discussed in this chapter, can you see a general relationship between the trends in metallic character and those for ionization energy?

Compounds of metals with nonmetals 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 Ni²⁺ and O²⁻ 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:

Metal oxide + water \longrightarrow metal hydroxide



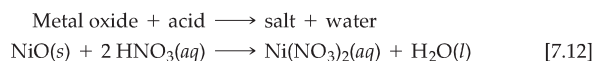
The basicity of metal oxides is due to the oxide ion, which reacts with water according to the net ionic equation



► **Figure 7.19 Metal oxides react with acids.** (a) Nickel oxide (NiO), nitric acid (HNO₃), and water. (b) NiO is insoluble in water, but reacts with HNO₃ to give a green solution of the salt Ni(NO₃)₂.



Metal oxides also demonstrate their basicity by reacting with acids to form a salt plus water, as illustrated in Figure 7.19▲:



In contrast, we will soon see that nonmetal oxides are acidic, dissolving in water to form acidic solutions and reacting with bases to form salts.

■ SAMPLE EXERCISE 7.8 | 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.

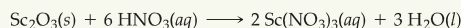
■ SOLUTION

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 would expect it to be an ionic solid. Indeed it is, with the very high melting point of 2485 °C.

(b) In its compounds, scandium has a 3+ charge, Sc³⁺; the oxide ion is O²⁻. Consequently, the formula of scandium oxide is Sc₂O₃. Metal oxides tend to be basic and therefore to react with acids to form a salt plus water. In this case the salt is scandium nitrate, Sc(NO₃)₃. The balanced chemical equation is



■ PRACTICE EXERCISE

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

Answer: $\text{CuO}(s) + \text{H}_2\text{SO}_4(aq) \longrightarrow \text{CuSO}_4(aq) + \text{H}_2\text{O}(l)$

▼ **Figure 7.20 The diversity of nonmetals.** Nonmetallic elements are diverse in their appearances. Shown here are (clockwise from top left) sulfur, bromine, phosphorus, iodine, and carbon.



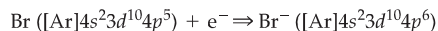
Nonmetals

Nonmetals vary greatly in appearance (Figure 7.20 ◀). 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, melts at 3570 °C). Under ordinary conditions, seven nonmetals exist as diatomic molecules. Five of these are gases (H₂, N₂, O₂, F₂, and Cl₂), one is a liquid (Br₂), and one is a volatile solid (I₂). Excluding the noble gases, the remaining nonmetals are solids that can be either hard, such as diamond, or soft, such as sulfur.

Because of their electron affinities, nonmetals tend to gain electrons when they react with metals. For example, the reaction of aluminum with bromine produces aluminum bromide, an ionic compound containing the aluminum ion, Al^{3+} , and the bromide ion, Br^- :

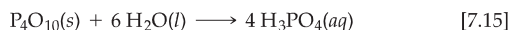
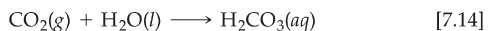
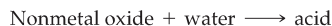


A nonmetal typically will gain enough electrons to fill its outermost occupied p subshell, giving a noble-gas electron configuration. For example, the bromine atom gains one electron to fill its $4p$ subshell:

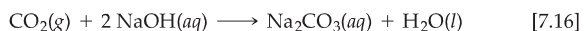


Compounds composed entirely of nonmetals are typically molecular substances. For example, the oxides, halides, and hydrides of the nonmetals are molecular substances that tend to be gases, liquids, or low-melting solids at room temperature.

Most nonmetal oxides are acidic; those that dissolve in water react to form acids, as in the following examples:

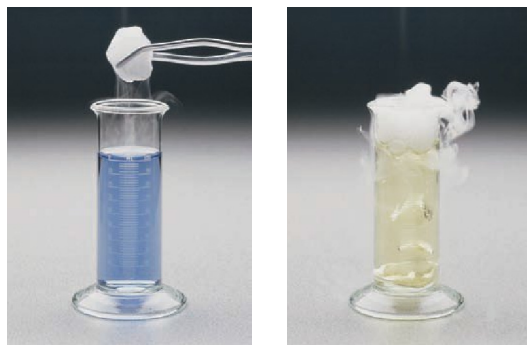


The reaction of carbon dioxide with water (Figure 7.21 ▼) accounts for the acidity of carbonated water and, to some extent, rainwater. Because sulfur is present in oil and coal, combustion of these common fuels produces sulfur dioxide and sulfur trioxide. These substances dissolve in water to produce *acid rain*, a major pollution problem in many parts of the world. Like acids, most nonmetal oxides dissolve in basic solutions to form a salt plus water:



GIVE IT SOME THOUGHT

A compound ACl_3 (A is an element) has a melting point of -112°C . Would you expect the compound to be a molecular or ionic substance? If you were told that element A was either scandium (Sc) or phosphorus (P), which do you think would be a more likely choice?



(a)

(b)

◀ **Figure 7.21 The reaction of CO_2 with water.** (a) The water has been made slightly basic and contains a few drops of bromthymol blue, an acid–base indicator that is blue in basic solution. (b) Upon the addition of a piece of solid carbon dioxide, $\text{CO}_2(s)$, the color changes to yellow, indicating an acidic solution. The mist is due to water droplets condensed from the air by the cold CO_2 gas.

SAMPLE EXERCISE 7.9 | Nonmetal Oxides

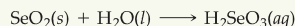
Write the balanced chemical equations for the reactions of solid selenium dioxide with (a) water, (b) aqueous sodium hydroxide.

SOLUTION

Analyze and Plan: We first note that selenium (Se) is a nonmetal. We therefore need to write chemical equations for the reaction of a nonmetal oxide, first with water and then 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) Selenium dioxide is SeO_2 . Its reaction with water is like that of carbon dioxide (Equation 7.14):



(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.)

(b) The reaction with sodium hydroxide is like the reaction summarized by Equation 7.16:

**PRACTICE EXERCISE**

Write the balanced chemical equation for the reaction of solid tetraphosphorus hexoxide with water.

Answer: $\text{P}_4\text{O}_6(\text{s}) + 6 \text{H}_2\text{O}(\text{l}) \longrightarrow 4 \text{H}_3\text{PO}_3(\text{aq})$



▲ **Figure 7.22 Elemental silicon.** Silicon is an example of a metalloid. Although it looks metallic, silicon is brittle and is a poor thermal and electrical conductor as compared to metals. Large crystals of silicon are sliced into thin wafers for use in integrated circuits.

▼ **Figure 7.23 Alkali metals.** Sodium and the other alkali metals are soft enough to be cut with a knife. The shiny metallic surface quickly tarnishes as the metal reacts with oxygen in the air.

**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, silicon *looks* like a metal (Figure 7.22 ◀), but it is brittle rather than malleable and is a much poorer conductor of heat and electricity than are metals. Compounds of metalloids can have characteristics of the compounds of metals or nonmetals, depending on the specific compound.

Several of the metalloids, most notably silicon, are electrical semiconductors and are the principal elements used in the manufacture of integrated circuits and computer chips. One of the reasons metalloids such as silicon can be used for integrated circuits is the fact that their electrical conductivity is intermediate between that of metals and nonmetals. Very pure silicon is an electrical insulator, but its conductivity can be dramatically increased with the addition of specific impurities (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.

7.7 GROUP TRENDS FOR THE ACTIVE METALS

Our discussion of atomic radius, ionization energy, electron affinity, and metallic character gives some idea of the way the periodic table can be used to organize and remember facts. As we have seen, elements in a group possess general similarities. However, trends also exist as we move through a group. In this section we will use the periodic table and our knowledge of electron configurations to examine the chemistry of the **alkali metals** (group 1A) and the **alkaline earth metals** (group 2A).

Group 1A: The Alkali Metals

The alkali metals are soft metallic solids (Figure 7.23 ◀). All have characteristic metallic properties such as a silvery, metallic luster and high thermal and electrical conductivities. 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.

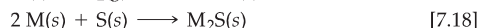
TABLE 7.4 ■ Some Properties of the Alkali Metals

Element	Electron Configuration	Melting Point (°C)	Density (g/cm ³)	Atomic Radius (Å)	I ₁ (kJ/mol)
Lithium	[He]2s ¹	181	0.53	1.34	520
Sodium	[Ne]3s ¹	98	0.97	1.54	496
Potassium	[Ar]4s ¹	63	0.86	1.96	419
Rubidium	[Kr]5s ¹	39	1.53	2.11	403
Cesium	[Xe]6s ¹	28	1.88	2.25	376

Sodium and potassium are relatively abundant in Earth's crust, in seawater, and in biological systems. We all have sodium ions in our bodies. However, ingesting too much sodium can raise our blood pressure. Potassium is also prevalent in our bodies; a 140-pound person contains about 130 g of potassium, as K⁺ ions in intracellular fluids. Plants require potassium for growth and development (Figure 7.24 ▶).

Some of the physical and chemical properties of the alkali metals are given in Table 7.4 ▲. The elements have low densities and melting points, and these properties vary in a fairly regular way with increasing atomic number. We can also see some of the usual trends as we move down the group, such as increasing atomic radius and decreasing first ionization energy. For each row of the periodic table, the alkali metal has the lowest I₁ value (Figure 7.11), which reflects the relative ease with which its outer s electron can be removed. As a result, the alkali metals are all very reactive, readily losing one electron to form ions carrying a 1+ charge. ∞ (Section 4.4)

The alkali metals exist in nature only as compounds. The metals combine directly with most nonmetals. For example, they react with hydrogen to form hydrides and with sulfur to form sulfides:



(The symbol M in Equations 7.17 and 7.18 represents any one of the alkali metals.) In hydrides of the alkali metals (LiH, NaH, and so forth), hydrogen is present as H⁻, called the **hydride ion**. The hydride ion, which is a hydrogen atom that has *gained* an electron, is distinct from the hydrogen ion, H⁺, formed when a hydrogen atom *loses* its electron.

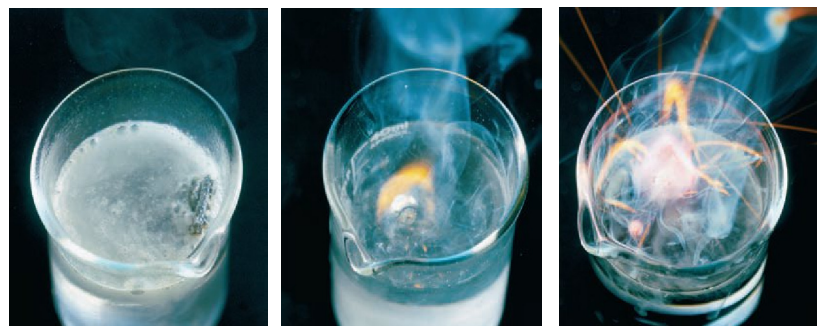
The alkali metals react vigorously with water, producing hydrogen gas and a solution of an alkali metal hydroxide:



These reactions are very exothermic. In many cases enough heat is generated to ignite the H₂, producing a fire or sometimes even an explosion (Figure 7.25 ▼).



▲ Figure 7.24 Elements in fertilizers. Fertilizers contain large quantities of potassium, phosphorus, and nitrogen to meet the needs of growing plants.



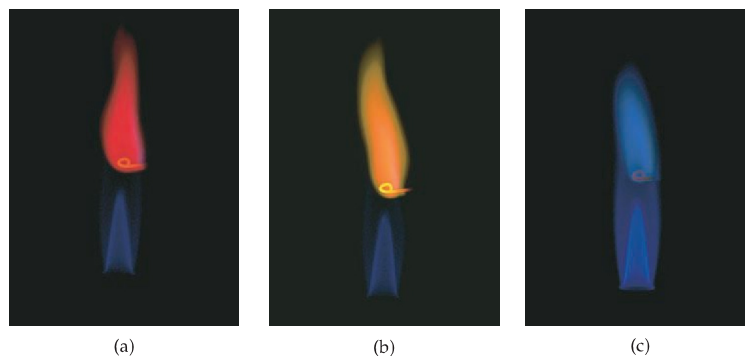
(a)

(b)

(c)

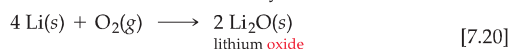
▼ Figure 7.25 The alkali metals react vigorously with water. (a) The reaction of lithium is evidenced by the bubbling of escaping hydrogen gas. (b) The reaction of sodium is more rapid and is so exothermic that the hydrogen gas produced burns in air. (c) Potassium reacts almost explosively.

► **Figure 7.26** Flame tests. (a) Li (crimson red), (b) Na (yellow), and (c) K (lilac).



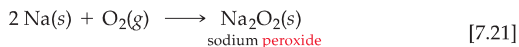
This reaction is most violent for the heavier members of the group, in keeping with their weaker hold on the single valence electron.

The reactions between the alkali metals and oxygen are more complex. When oxygen reacts with metals, metal oxides, which contain the O^{2-} ion, are usually formed. Indeed, lithium shows this reactivity:

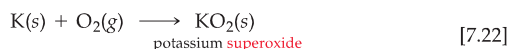


When dissolved in water, Li_2O and other soluble metal oxides react with water to form hydroxide ions from the reaction of O^{2-} ions with H_2O (Equation 7.11).

In contrast, the other alkali metals all react with oxygen to form metal *peroxides*, which contain the O_2^{2-} ion. For example, sodium forms sodium peroxide, Na_2O_2 .



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



You should be aware that the reactions shown in Equations 7.21 and 7.22 are somewhat surprising; in most cases, the reaction of oxygen with a metal forms the metal oxide.

As is evident from Equations 7.19 through 7.22, the alkali metals are extremely reactive toward water and oxygen. Because of this, 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 7.26 ▲). The ions are reduced to gaseous metal atoms in the central region of the flame. The high temperature of the flame then excites the valence electron 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. Sodium, for instance, gives a yellow flame because of emission at 589 nm. This wavelength is produced when the excited valence electron drops from the $3p$ subshell to the lower-energy $3s$ subshell. The characteristic yellow emission of sodium is the basis for sodium vapor lamps (Figure 7.27 ◀).



▲ **Figure 7.27** Light from sodium. Sodium vapor lamps, which are used for commercial and highway lighting, have a yellow glow because of the emission from excited sodium atoms.

GIVE IT SOME THOUGHT

Cesium metal tends to be the most reactive of the stable alkali metals (francium, element number 87, is radioactive and has not been extensively studied). What *atomic* property of Cs is most responsible for its high reactivity?

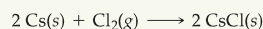
SAMPLE EXERCISE 7.10 | Reactions of an Alkali Metal

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

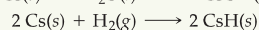
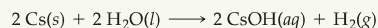
SOLUTION

Analyze and Plan: Cesium is an alkali metal (atomic number 55). We therefore expect that its chemistry will be dominated by oxidation of the metal to Cs^+ ions. Further, we recognize that Cs is far down the periodic table, which means it will be among the most active of all metals and will probably react with all three of the substances listed.

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



By analogy to Equations 7.19 and 7.17, respectively, we predict the reactions of cesium with water and hydrogen to proceed as follows:



All three of these reactions are redox reactions where cesium forms a Cs^+ ion in the product. The chloride (Cl^-), hydroxide (OH^-), and hydride (H^-) ions are all $1-$ ions, which means the final products have 1:1 stoichiometry with Cs^+ .

PRACTICE EXERCISE

Write a balanced equation for the reaction between potassium metal and elemental sulfur.

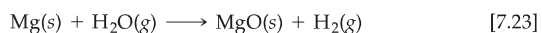
Answer: $2 \text{K}(\text{s}) + \text{S}(\text{s}) \longrightarrow \text{K}_2\text{S}(\text{s})$

Group 2A: The Alkaline Earth Metals

Like the alkali metals, the group 2A elements are all solids at room temperature and have typical metallic properties, some of which are listed in Table 7.5. Compared with the alkali metals, the alkaline earth metals are harder and more dense, and they melt at higher temperatures.

The first ionization energies of the alkaline earth elements are low, but they are not as low as those of the alkali metals. Consequently, the alkaline earth metals are less reactive than their alkali metal neighbors. As we noted in Section 7.4, the ease with which the elements lose electrons decreases as we move across the periodic table from left to right and increases as we move down a group. Thus, beryllium and magnesium, the lightest members of the 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 water or steam, even when heated red-hot. Magnesium reacts slowly with liquid water and more readily with steam to form magnesium oxide and hydrogen:



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

TABLE 7.5 ■ Some Properties of the Alkaline Earth Metals

Element	Electron Configuration	Melting Point ($^{\circ}\text{C}$)	Density (g/cm^3)	Atomic Radius (\AA)	I_1 (kJ/mol)
Beryllium	$[\text{He}]2s^2$	1287	1.85	0.90	899
Magnesium	$[\text{Ne}]3s^2$	650	1.74	1.30	738
Calcium	$[\text{Ar}]4s^2$	842	1.55	1.74	590
Strontium	$[\text{Kr}]5s^2$	777	2.63	1.92	549
Barium	$[\text{Xe}]6s^2$	727	3.51	1.98	503

The alkali metal ions tend to play a rather unexciting role in most chemical reactions in general chemistry. As noted in Section 4.2, all salts of the alkali metal ions are soluble, and the ions are spectators in most aqueous reactions (except for those involving the alkali metals in their elemental form, such as in Equations 7.17 through 7.22). However, the alkali metal 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. We will see in Chapter 20 that these ions are also two of the principal ions involved in regulation of the heart.

In contrast, the lithium ion (Li^+) has no known function in normal human physiology. Since the discovery of lithium in 1817, however, people thought 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, Mr. 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 Seven Up[®] (Figure 7.28 ▶).

Because of concerns of the Food and Drug Administration, lithium was removed from Seven Up[®] during the early 1950s. At nearly the same time, psychiatrists discovered that the lithium ion has a remarkable therapeutic effect on the mental disorder called *bipolar affective disorder*, or *manic-depressive illness*. Over 1 million Americans suffer from this psychosis, undergoing severe mood swings from deep depression to a manic euphoria. The lithium ion smooths these mood swings, allowing the bipolar patient to function more effectively in daily life.

The antipsychotic action of Li^+ was discovered by accident during the late 1940s by Australian psychiatrist John Cade 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 seemingly innocuous 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 the bipolar patients who take it.



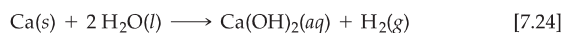
In this age of sophisticated drug design and biotechnology, the simple lithium ion is still the most effective treatment of this destructive psychological disorder. Remarkably, in spite of intensive research, scientists still do not fully understand the biochemical action of lithium that leads to its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

▲ **Figure 7.28 Lithium no more.** The soft drink Seven Up[®] originally contained lithium citrate, the lithium salt of citric acid. The lithium 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 same time that the antipsychotic action of Li^+ was discovered.

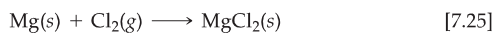


▲ **Figure 7.29 Elemental calcium solution.** Calcium metal reacts with water to form hydrogen gas and aqueous calcium hydroxide, $\text{Ca}(\text{OH})_2(\text{aq})$.

periodic table), as shown in Figure 7.29 ◀. The reaction between calcium and water, for example, is



The reactions represented in Equations 7.23 and 7.24 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 (Figure 3.5):



In the presence of O_2 , magnesium metal is protected from many chemicals by a thin surface coating of water-insoluble MgO . Thus, even though Mg is high in the activity series \rightleftharpoons (Section 4.4), 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 strongly heated in a flame. The colored flame produced by calcium is brick red, that of strontium is crimson red, and that of barium is green. Strontium salts produce the brilliant red color in fireworks, and barium salts produce the green color (Figure 7.30 ▶).

Both magnesium and calcium are essential for living organisms (Figure 2.24). Calcium is particularly important for growth and maintenance of bones and teeth (Figure 7.31 ▶). In humans 99% of the calcium is found in the skeletal system.



◀ **Figure 7.30 Fireworks display.** The colors in a fireworks display originate from the characteristic emissions of elements, including the alkaline earths. In this display the crimson color comes from strontium, while the green color comes from barium.



▲ **Figure 7.31 Calcium in the body.** This X-ray photograph shows the bone structure of the human hand. The primary mineral in bone and teeth is hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, in which calcium is present as Ca^{2+} .

GIVE IT SOME THOUGHT

Calcium carbonate, CaCO_3 , is often used as a dietary calcium supplement for bone health. Although $\text{CaCO}_3(s)$ is insoluble in water (Table 4.1), it can be taken orally to allow for the delivery of $\text{Ca}^{2+}(aq)$ ions to the musculoskeletal system. Why is this the case? [Hint: Recall the reactions of metal carbonates that were discussed in Section 4.3.]

7.8 GROUP TRENDS FOR SELECTED NONMETALS

Hydrogen

Hydrogen, the first element in the periodic table, has a $1s^1$ electron configuration, and for this reason its usual position in the table is above the alkali metals. However, hydrogen does not truly belong to any particular group. Unlike the alkali metals, hydrogen is a nonmetal that occurs as a colorless diatomic gas, $\text{H}_2(g)$, under most conditions. Nevertheless, hydrogen can be metallic under tremendous pressures. The interiors of the planets Jupiter and Saturn, for example, are believed to consist of a dense core of rock and ice surrounded by a thick shell of metallic hydrogen. The metallic hydrogen is in turn surrounded by a layer of liquid molecular hydrogen that gradually transforms to a mixture of gaseous hydrogen and helium upon moving closer to the surface. The Cassini–Huygens satellite mission, launched in 1997, has provided a wealth of new information regarding Saturn and its largest moon, Titan, including their chemical compositions. The spacecraft successfully entered orbit around Saturn in June 2004, and in January 2005 the Huygens probe descended through Titan’s atmosphere (Figure 7.32 ▶).

Owing to the complete absence of nuclear shielding of its sole electron, the ionization energy of hydrogen, 1312 kJ/mol, is more than double that of any of the alkali metals (Figure 7.11). In fact, hydrogen’s ionization energy is comparable to the I_1 values of other nonmetals, such as oxygen and chlorine. As a result, hydrogen does not lose its valence electron as easily as do the alkali metals. Whereas the alkali metals readily lose their valence electron to nonmetals to form ionic compounds, hydrogen shares its electron with nonmetals and thereby forms molecular compounds. The reactions between hydrogen and nonmetals can be quite exothermic, as evidenced by the combustion reaction between hydrogen and oxygen to form water (Figure 5.13):



▲ **Figure 7.32 Exploring Saturn.** This panoramic view of Saturn was taken from the Cassini spacecraft. From this perspective Saturn shelters the spacecraft from the Sun’s blinding glare.

We have also seen (Equation 7.17) 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 is not truly a member of the alkali metal family. In fact, in terms of chemical reactivity, hydrogen has more in common with the halogens (Group 7A) than with the alkali metals.

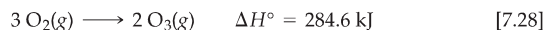
In addition to its ability to form covalent bonds and metal hydrides, probably the most important characteristic of hydrogen is its ability to lose its electron to form a cation. Indeed, the aqueous chemistry of hydrogen is dominated by the H^+ (*aq*) ion, which we first encountered in Chapter 4. ∞ (Section 4.1) We will study this important ion in greater detail in Chapter 16.

Group 6A: The Oxygen Group

As we proceed down group 6A, there is a change from nonmetallic to metallic character (Figure 7.15). Oxygen, sulfur, and selenium are typical nonmetals. Tellurium has some metallic properties and is classified as a metalloid. 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 6A are solids. Some of the physical properties of the group 6A elements are given in Table 7.6 \blacktriangledown .

As we saw in Section 2.6, oxygen is encountered in two molecular forms, O_2 and O_3 . The O_2 form is the more common one. People generally mean O_2 when they say “oxygen,” although the name *dioxygen* is more descriptive. The O_3 form is called **ozone**. The two forms of oxygen are examples of *allotropes*. Allotropes are different forms of the same element in the same state. (In this case both forms are gases.) About 21% of dry air consists of O_2 molecules. Ozone is present in very small amounts in the upper atmosphere and in polluted air. It is also formed from O_2 in electrical discharges, such as in lightning storms:



This reaction is strongly endothermic, telling us that O_3 is less stable than O_2 .

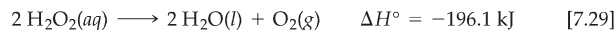
It is interesting to consider the differences in physical and chemical properties of the allotropes of oxygen. Although both O_2 and O_3 are colorless and therefore do not absorb visible light, O_3 absorbs certain wavelengths of ultraviolet light that O_2 does not. Because of this difference, the presence of ozone in the upper atmosphere is beneficial, filtering out harmful UV light ∞ (Section 18.3). Ozone and dioxygen 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, O^{2-} . This ion has a noble-gas configuration and is particularly stable. As shown in Equation 7.27, the formation of nonmetal oxides is also often very exothermic and thus energetically favorable.

TABLE 7.6 ■ Some Properties of the Group 6A Elements

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (Å)	I_1 (kJ/mol)
Oxygen	$[\text{He}]2s^2 2p^4$	-218	1.43 g/L	0.73	1314
Sulfur	$[\text{Ne}]3s^2 3p^4$	115	1.96 g/cm ³	1.02	1000
Selenium	$[\text{Ar}]3d^{10} 4s^2 4p^4$	221	4.82 g/cm ³	1.16	941
Tellurium	$[\text{Kr}]4d^{10} 5s^2 5p^4$	450	6.24 g/cm ³	1.35	869
Polonium	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^4$	254	9.20 g/cm ³	—	812

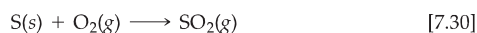
In our discussion of the alkali metals, we noted two less common oxygen anions—the peroxide (O_2^{2-}) ion and the superoxide (O_2^-) ion. Compounds of these ions often react with themselves to produce an oxide and O_2 . For example, aqueous hydrogen peroxide, H_2O_2 , slowly decomposes into water and O_2 at room temperature:



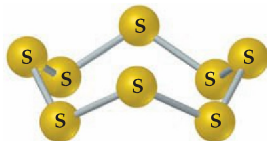
For this reason, bottles of aqueous hydrogen peroxide are topped with caps that are able to release the $\text{O}_2(g)$ produced before the pressure inside becomes too great (Figure 7.33 ▶).

After oxygen, the most important member of group 6A is sulfur. This element also exists in several allotropic forms, the most common and stable of which is the yellow solid having the molecular formula S_8 . This molecule consists of an eight-membered ring of sulfur atoms, as shown in Figure 7.34 ▼. Even though solid sulfur consists of S_8 rings, we usually write it simply as $\text{S}(s)$ in chemical equations to simplify the stoichiometric coefficients.

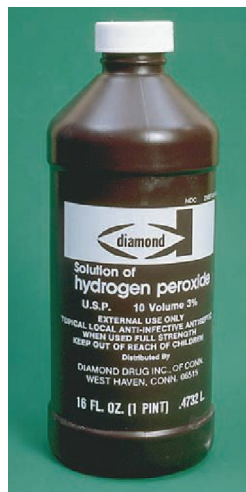
Like oxygen, sulfur has a tendency to gain electrons from other elements to form sulfides, which contain the S^{2-} ion. In fact, most sulfur in nature is present as metal sulfides. Sulfur is below oxygen in the periodic table, and the tendency of sulfur to form sulfide anions is not as great as that 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 pollutant:



We will discuss the environmental aspects of sulfur oxide chemistry in greater depth in Chapter 18.



◀ **Figure 7.34 Elemental sulfur.** At room temperature, the most common allotropic form of sulfur is an eight-member ring, S_8 .



▲ **Figure 7.33 Hydrogen peroxide solution.** Bottles of this common antiseptic are topped with a cap that allows any excess pressure created by $\text{O}_2(g)$ to be released from the bottle. Hydrogen peroxide is often stored in dark-colored or opaque bottles to minimize exposure to light, which accelerates its decomposition.

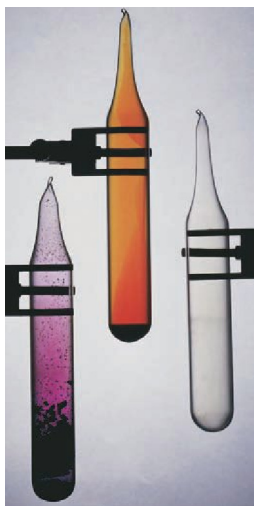
Group 7A: The Halogens

The group 7A elements are known as the **halogens**, after the Greek words *halos* and *gennao*, meaning “salt formers.” Some of the properties of these elements 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.

Unlike the group 6A elements, all the halogens are typical 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: F_2 , Cl_2 , Br_2 , and I_2 . Fluorine gas is pale yellow; chlorine gas is yellow-green; bromine liquid is reddish

TABLE 7.7 ■ Some Properties of the Halogens

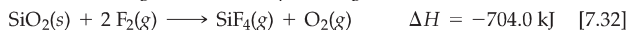
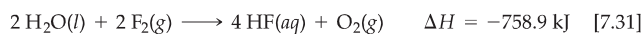
Element	Electron Configuration	Melting Point ($^\circ\text{C}$)	Density	Atomic Radius (\AA)	I_1 (kJ/mol)
Fluorine	$[\text{He}]2s^22p^5$	-220	1.69 g/L	0.71	1681
Chlorine	$[\text{Ne}]3s^23p^5$	-102	3.12 g/L	0.99	1251
Bromine	$[\text{Ar}]3d^{10}4s^24p^5$	-7.3	3.12 g/cm ³	1.14	1140
Iodine	$[\text{Kr}]4d^{10}5s^25p^5$	114	4.94 g/cm ³	1.33	1008



▲ **Figure 7.35 Elemental halogens.** All three of these elements—from left to right, iodine (I_2), bromine (Br_2), and chlorine (Cl_2)—exist as diatomic molecules.

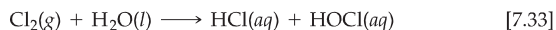
brown and readily forms a reddish brown vapor; and solid iodine is grayish black and readily forms a violet vapor (Figure 7.35 ◀).

The halogens have highly negative electron affinities (Figure 7.14). 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:



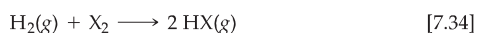
As a result, fluorine gas is difficult and dangerous to use in the laboratory, requiring specialized equipment.

Chlorine is the most industrially useful of the halogens. In 2005, total production was 22 billion pounds, making it the eighth most produced chemical in the United States. 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, where 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.

GIVE IT SOME THOUGHT

Can you use data in Table 7.7 to provide estimates for the atomic radius and first ionization energy of an astatine atom?

Group 8A: The Noble Gases

The group 8A 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 8A 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

TABLE 7.8 ■ Some Properties of the Noble Gases

Element	Electron Configuration	Boiling Point (K)	Density (g/L)	Atomic Radius* (Å)	I_1 (kJ/mol)
Helium	$1s^2$	4.2	0.18	0.32	2372
Neon	$[He]2s^22p^6$	27.1	0.90	0.69	2081
Argon	$[Ne]3s^23p^6$	87.3	1.78	0.97	1521
Krypton	$[Ar]3d^{10}4s^24p^6$	120	3.75	1.10	1351
Xenon	$[Kr]4d^{10}5s^25p^6$	165	5.90	1.30	1170
Radon	$[Xe]4f^{14}5d^{10}6s^26p^6$	211	9.73	1.45	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.

1960s the elements were called the *inert gases* because they were thought to be incapable of forming chemical compounds. In 1962, Neil Bartlett at the University of British Columbia reasoned that the ionization energy of Xe might be low enough to allow it to form compounds. In order 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 PtF_6 . Xenon also reacts directly with $\text{F}_2(\text{g})$ to form the molecular compounds XeF_2 , XeF_4 , and XeF_6 (Figure 7.36▶). 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, KrF_2 . In 2000, Finnish scientists reported the first neutral molecule that contains argon, the HArF molecule, which is stable only at low temperatures.



▲ **Figure 7.36 A compound of xenon.** Crystals of XeF_4 , which is one of the very few compounds that contain a group 8A element.

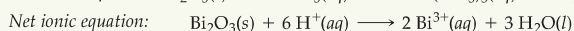
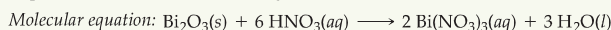
SAMPLE INTEGRATIVE EXERCISE | Putting Concepts Together

The element bismuth (Bi, atomic number 83) is the heaviest member of group 5A. A salt of the element, bismuth subsalicylate, is the active ingredient in Pepto-Bismol[®], an over-the-counter medication for gastric distress.

- The covalent atomic radii of thallium (Tl) and lead (Pb) are 1.48 Å and 1.47 Å, respectively. Using these values and those in Figure 7.7, predict the covalent atomic radius of the element bismuth (Bi). Explain your answer.
- What accounts for the general increase in atomic radius going down the group 5A elements?
- 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?
- 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?
- ^{209}Bi is the heaviest stable isotope of any element. How many protons and neutrons are present in this nucleus?
- 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

- Note that there is a gradual decrease in radius of the elements in Groups 3A–5A as we proceed across the fifth period, that is, in the series In–Sn–Sb. Therefore, it is reasonable to expect a decrease of about 0.02 Å as we move from Pb to Bi, leading to an estimate of 1.45 Å. The tabulated value is 1.46 Å.
- The general increase in radius with increasing atomic number in the group 5A elements occurs because additional shells of electrons are being added, with corresponding increases in nuclear charge. The core electrons in each case largely shield 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.
- 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.
- Following the procedures described in Section 4.2 for writing molecular and net ionic equations, we have the following:



In the net ionic equation, nitric acid is a strong acid and $\text{Bi}(\text{NO}_3)_3$ is a soluble salt, so we need show only the reaction of the solid with the hydrogen ion forming the $\text{Bi}^{3+}(\text{aq})$ ion and water.

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

$$\frac{6.77 \text{ g Bi}_2\text{O}_3}{0.500 \text{ L soln}} \times \frac{1 \text{ mol Bi}_2\text{O}_3}{466.0 \text{ g Bi}_2\text{O}_3} \times \frac{2 \text{ mol Bi}^{3+}}{1 \text{ mol Bi}_2\text{O}_3} = \frac{0.0581 \text{ mol Bi}^{3+}}{\text{L soln}} = 0.0581 \text{ M}$$

(e) We can proceed as in Section 2.3. 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 proceed as in Sections 1.4 and 3.4: the volume of the cube is $(5.00)^3 \text{ cm}^3 = 125 \text{ cm}^3$. Then we have

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

$$5.87 \text{ mol Bi} \times \frac{6.022 \times 10^{23} \text{ atom Bi}}{1 \text{ mol Bi}} = 3.54 \times 10^{24} \text{ atoms Bi}$$

CHAPTER REVIEW

SUMMARY AND KEY TERMS

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 recognize 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. The differences among elements in the same group arise because their valence orbitals are in different shells.

Section 7.2 Many properties of atoms are due to the average distance of the outer electrons from the nucleus and to the **effective nuclear charge** experienced by these electrons. 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 effectively. As a result, the effective nuclear charge experienced by valence electrons increases as we move left to right across a period.

Section 7.3 The size of an atom can be gauged by its **bonding atomic radius**, based on measurements of the distances separating atoms in their chemical compounds. In general, atomic radii increase as we go down a column in the periodic table and decrease as we proceed 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 nuclear charge as the electrons are attracted more strongly to the nucleus.

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. Electrons are removed first from the orbitals 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, $4p$). Electrons are added to orbitals in the reverse order.

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 the anion is stable; a positive electron affinity means that the anion is not stable relative to the separated atom and electron, in which case its exact value cannot be measured. 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.

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.

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 1A) 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 2A) are harder and more dense 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^- .

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 6A. 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 7A) are nonmetals that 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 8A) are nonmetals that 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.

KEY SKILLS

- Understand the meaning of effective nuclear charge, Z_{eff} , and how Z_{eff} depends upon nuclear charge and electron configuration.
- Use the periodic table to predict the trends in atomic radii, ionic radii, ionization energy, and electron affinity.
- Understand how the radius of an atom changes upon losing electrons to form a cation or gaining electrons to form an anion.
- Understand how the ionization energy changes as we remove successive electrons. Recognize the jump in ionization energy that occurs when the ionization corresponds to removing a core electron.
- Be able to write the electron configurations of ions.
- Understand how irregularities in the periodic trends for electron affinity can be related to electron configuration.
- Recognize the differences in chemical and physical properties of metals and nonmetals, including the basicity of metal oxides and the acidity of nonmetal oxides.
- Understand how the atomic properties, such as ionization energy and electron configuration, are related to the chemical reactivity and physical properties of the alkali and alkaline earth metals (groups 1A and 2A).
- Be able to write balanced equations for the reactions of the group 1A and 2A metals with water, oxygen, hydrogen, and the halogens.
- Understand and recognize the unique characteristics of hydrogen.
- Understand how the atomic properties (such as ionization energy, electron configuration, and electron affinity) of group 6A, 7A, and 8A elements are related to their chemical reactivity and physical properties.

KEY EQUATIONS

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

VISUALIZING CONCEPTS

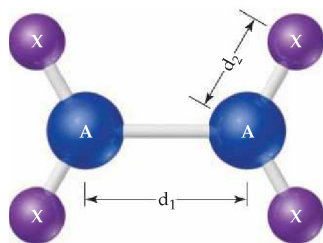
- 7.1 We can draw an analogy between the attraction of an electron to a nucleus and seeing a lightbulb—in essence, the more nuclear charge the electron “sees,” the greater the attraction. (a) Within this analogy, discuss how the shielding by core electrons is analogous to putting a frosted-glass lampshade between the lightbulb and your eyes, as shown in the illustration. (b) Explain how we could mimic moving to the right in a row of the periodic table by changing the wattage of the lightbulb. (c) How would you change the wattage of the bulb and/or the frosted glass to mimic the effect of moving down a column of the periodic table? [Section 7.2]



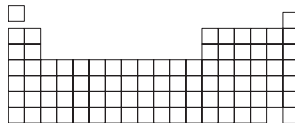
- 7.2 Fluorine has atomic number 9. If we represent the radius of a fluorine atom with the billiard ball illustrated here, would the analogy be more appropriate for the bonding or nonbonding atomic radius? If we used the same billiard ball to illustrate the concept of fluorine's bonding atomic radius, would we overestimate or underestimate the bonding atomic radius? Explain. [Section 7.3]



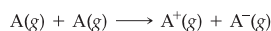
- 7.3 Consider the A_2X_4 molecule depicted below, where A and X are elements. The A—A bond length in this molecule is d_1 , and the four A—X bond lengths are each d_2 . (a) In terms of d_1 and d_2 , how could you define the bonding atomic radii of atoms A and X? (b) In terms of d_1 and d_2 , what would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



- 7.4 Make a simple sketch of the shape of the main part of the periodic table, as shown. (a) Ignoring H and He, write a single straight arrow from the element with the smallest bonding atomic radius to the element with the largest. (b) Ignoring H and He, write a single straight arrow from the element with the smallest first ionization energy to the element with the largest. (c) What significant observation can you make from the arrows you drew in parts (a) and (b)? [Sections 7.3 and 7.4]

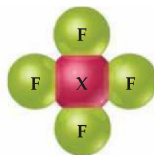


- 7.5 In the chemical process called *electron transfer*, an electron is transferred from one atom or molecule to another (We will talk about electron transfer extensively in Chapter 20.) A simple electron transfer reaction is



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? [Sections 7.4 and 7.5]

- 7.6 An element X reacts with $F_2(g)$ to form the molecular product shown below. (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? Explain. [Section 7.6]



EXERCISES

Periodic Table; Effective Nuclear Charge

- 7.7 Why did Mendeleev leave blanks in his early version of the periodic table? How did he predict the properties of the elements that belonged in those blanks?
- 7.8 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 7.2, what do we now call the element Mendeleev called *eka-manganese*?
- 7.9 In Chapter 1 we learned that silicon is the second most abundant element in Earth's crust, accounting for more than one-fourth of the mass of the crust (Figure 1.6). Yet we see that silicon is not among the elements that have been known since ancient times (Figure 7.2), whereas iron, which accounts for less than 5% of Earth's crust, has been known since prehistoric times. Given silicon's abundance how do you account for its relatively late discovery?
- 7.10 (a) During the period from about 1800 to about 1865, the atomic weights of many elements were accurately measured. Why was this important to Mendeleev's formulation of the periodic table? (b) What property of the atom did Moseley associate with the wavelength of X-rays emitted from an element in his experiments? (c) Why are chemical and physical properties of the elements more closely related to atomic number than they are to atomic weight?
- 7.11 (a) What is meant by the term *effective nuclear charge*? (b) How does the effective nuclear charge experienced by the valence electrons of an atom vary going from left to right across a period of the periodic table?
- 7.12 (a) How is the concept of effective nuclear charge used to simplify the numerous electron-electron repulsions in a many-electron atom? (b) Which experiences a greater effective nuclear charge in a Be atom, the 1s electrons or the 2s electrons? Explain.
- 7.13 Detailed calculations show that the value of Z_{eff} for 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?
- 7.14 Detailed calculations show that the value of Z_{eff} for 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?
- 7.15 Which will experience the greater effective nuclear charge, the electrons in the $n = 3$ shell in Ar or the $n = 3$ shell in Kr? Which will be closer to the nucleus? Explain.
- 7.16 Arrange the following atoms in order of increasing effective nuclear charge experienced by the electrons in the $n = 3$ electron shell: K, Mg, P, Rh, and Ti. Explain the basis for your order.

Atomic and Ionic Radii

- 7.17 (a) Because an exact outer boundary cannot be measured or even calculated for an atom, how are atomic radii determined? (b) What is the difference between a bonding radius and a nonbonding radius? (c) For a given element, which one is larger?
- 7.18 (a) Why does the quantum mechanical description of many-electron atoms make it difficult to define a precise atomic radius? (b) When nonbonded atoms come up against one another, what determines how closely the nuclear centers can approach?
- 7.19 The distance between W atoms in tungsten metal is 2.74 Å. What is the atomic radius of a tungsten atom in this environment? (This radius is called the *metallic radius*.)
- 7.20 Based on the radii presented in Figure 7.7, predict the distance between Si atoms in solid silicon.
- 7.21 Estimate the As—I bond length from the data in Figure 7.7, and compare your value to the experimental As—I bond length in arsenic triiodide, AsI_3 , 2.55 Å.
- 7.22 The experimental Bi—I bond length in bismuth triiodide, BiI_3 , is 2.81 Å. Based on this value and data in Figure 7.7, predict the atomic radius of Bi.
- 7.23 How do the sizes of atoms change as we move (a) from left to right across a row in the periodic table, (b) from top to bottom in a group in the periodic table? (c) Arrange the following atoms in order of increasing atomic radius: F, P, S, As.

7.24 (a) Among the nonmetallic elements, the change in atomic radius in moving one place left or right in a row is smaller than the change in moving one row up or down. Explain these observations. (b) Arrange the following atoms in order of increasing atomic radius: Si, Al, Ge, Ga.

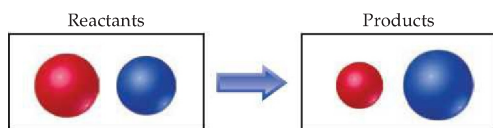
7.25 Using only the periodic table, arrange each set of atoms in order of increasing radius: (a) Ca, Mg, Be; (b) Ga, Br, Ge; (c) Al, Tl, Si.

7.26 Using only the periodic table, arrange each set of atoms in order of increasing radius: (a) Ba, Ca, Na; (b) Sn, Sb, As; (c) Al, Be, Si.

7.27 (a) Why are monatomic cations smaller than their corresponding neutral atoms? (b) Why are monatomic anions larger than their corresponding neutral atoms? (c) Why does the size of ions increase as one proceeds down a column in the periodic table?

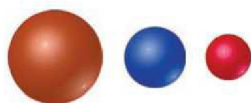
7.28 Explain the following variations in atomic or ionic radii: (a) $I^- > I > I^+$, (b) $Ca^{2+} > Mg^{2+} > Be^{2+}$, (c) $Fe > Fe^{2+} > Fe^{3+}$.

7.29 Consider a reaction represented by the following spheres:



Which sphere represents a metal and which a nonmetal? Explain.

7.30 Consider the following spheres:



Which one represents Ca, which Ca^{2+} , and which Mg^{2+} ?

7.31 (a) What is an isoelectronic series? (b) Which neutral atom is isoelectronic with each of the following ions: Al^{3+} , Ti^{4+} , Br^- , Sn^{2+} .

7.32 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. If such an atom does not exist explain why: (a) Cl^- , (b) Sc^{3+} , (c) Fe^{2+} , (d) Zn^{2+} , (e) Sn^{4+} .

7.33 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?

7.34 Consider the isoelectronic ions Cl^- and K^+ . (a) Which ion is smaller? (b) Use 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?

7.35 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.

7.36 For each of the following sets of atoms and ions, arrange the members in order of increasing size: (a) Se^{2-} , Te^{2-} , Se; (b) Co^{3+} , Fe^{2+} , Fe^{3+} ; (c) Ca, Ti^{4+} , Sc^{3+} ; (d) Be^{2+} , Na^+ , Ne.

7.37 For each of the following statements, provide an explanation: (a) O^{2-} is larger than O; (b) S^{2-} is larger than O^{2-} ; (c) S^{2-} is larger than K^+ ; (d) K^+ is larger than Ca^{2+} .

7.38 In the ionic compounds LiF, NaCl, KBr, and RbI, the measured cation–anion distances are 2.01 Å (Li–F), 2.82 Å (Na–Cl), 3.30 Å (K–Br), and 3.67 Å (Rb–I), respectively. (a) Predict the cation–anion distance using the values of ionic radii given in Figure 7.8. (b) Is the agreement between the prediction and the experiment perfect? If not, why not? (c) What estimates of the cation–anion distance would you obtain for these four compounds using *bonding atomic radii*? Are these estimates as accurate as the estimates using ionic radii?

Ionization Energies; Electron Affinities

7.39 Write equations that show the processes that describe the first, second, and third ionization energies of a boron atom.

7.40 Write equations that show the process for (a) the first two ionization energies of tin and (b) the fourth ionization energy of titanium.

7.41 (a) Why are ionization energies always positive quantities? (b) Why does F have a larger first ionization energy than O? (c) Why is the second ionization energy of an atom always greater than its first ionization energy?

7.42 (a) Why does Li have a larger first ionization energy than Na? (b) The difference between the third and fourth ionization energies of scandium is much larger than the difference between the third and fourth ionization energies of titanium. Why? (c) Why does Li have a much larger second ionization energy than Be?

7.43 (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?

7.44 (a) What is the trend in first ionization energies as one proceeds down the group 7A 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?

7.45 Based on their positions in the periodic table, predict which atom of the following pairs will have the larger first ionization energy: (a) Cl, Ar; (b) Be, Ca; (c) K, Co; (d) S, Ge; (e) Sn, Te.

- 7.46 For each of the following pairs, indicate which element has the larger first ionization energy: (a) Ti, Ba; (b) Ag, Cu; (c) Ge, Cl; (d) Pb, Sb. (In each case use electron configuration and effective nuclear charge to explain your answer.)
- 7.47 Write the electron configurations for the following ions: (a) In^{3+} , (b) Sb^{3+} , (c) Te^{2-} , (d) Te^{6+} , (e) Hg^{2+} , (f) Rh^{3+} .
- 7.48 Write electron configurations for the following ions, and determine which have noble-gas configurations: (a) Cr^{3+} , (b) N^{3-} , (c) Sc^{3+} , (d) Cu^{2+} , (e) Tl^{+} , (f) Au^{+} .
- 7.49 Write the electron configuration for (a) the Ni^{2+} ion and (b) the Sn^{2+} ion. How many unpaired electrons does each contain?
- 7.50 Identify the element whose ions have the following electron configurations: (a) a $2+$ ion with $[\text{Ar}]3d^9$, (b) a $1+$ ion with $[\text{Xe}]4f^{14}5d^{10}6s^2$. How many unpaired electrons does each ion contain?
- 7.51 The first ionization energy of Ar and the electron affinity of Ar are both positive values. What is the significance of the positive value in each case?
- 7.52 The electron affinity of lithium is a negative value, whereas the electron affinity of beryllium is a positive value. Use electron configurations to account for this observation.
- 7.53 While the electron affinity of bromine is a negative quantity, it is positive for Kr. Use the electron configurations of the two elements to explain the difference.
- 7.54 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?
- 7.55 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 will 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? Explain your answer.
- 7.56 Write an equation for the process that corresponds to the electron affinity of the Mg^+ ion. Also write the electron configurations of the species involved. What is the magnitude of the energy change in the process? [Hint: The answer is in Table 7.2.]

Properties of Metals and Nonmetals

- 7.57 How are metallic character and first ionization energy related?
- 7.58 Arrange the following pure solid elements in order of increasing electrical conductivity: Ge, Ca, S, and Si. Explain the reasoning you used.
- 7.59 If we look at groups 3A through 5A, we see two metalloids for groups 4A (Si, Ge) and 5A (As, Sb), but only one metalloid in group 3A (B). To maintain a regular geometric pattern one might expect that aluminum would also be a metalloid, giving group 3A two metalloids. What can you say about the metallic character of aluminum with respect to its neighbors based on its first ionization energy?
- 7.60 For each of the following pairs, which element will have the greater metallic character: (a) Li or Be, (b) Li or Na, (c) Sn or P, (d) Al or B?
- 7.61 Predict whether each of the following oxides is ionic or molecular: SO_2 , MgO , Li_2O , P_2O_5 , Y_2O_3 , N_2O , and XeO_3 . Explain the reasons for your choices.
- 7.62 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.
- 7.63 (a) What is meant by the terms acidic oxide and basic oxide? (b) How can we predict whether an oxide will be acidic or basic, based on its composition?
- 7.64 Arrange the following oxides in order of increasing acidity: CO_2 , CaO , Al_2O_3 , SO_3 , SiO_2 , and P_2O_5 .
- 7.65 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) Under usual conditions, Cl_2O_7 is a colorless liquid with a boiling point of 81°C . Is this boiling point expected or surprising? (d) Would you expect Cl_2O_7 to be more reactive toward $\text{H}^+(aq)$ or $\text{OH}^-(aq)$? Explain.
- [7.66] 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? Explain. (c) By using a sourcebook such as the *CRC Handbook of Chemistry and Physics*, try to determine the identity of element X.
- 7.67 Write balanced equations for the following reactions: (a) barium oxide with water, (b) iron(II) oxide with perchloric acid, (c) sulfur trioxide with water, (d) carbon dioxide with aqueous sodium hydroxide.
- 7.68 Write balanced equations for the following reactions: (a) potassium oxide with water, (b) diphosphorus trioxide with water, (c) chromium(III) oxide with dilute hydrochloric acid, (d) selenium dioxide with aqueous potassium hydroxide.

Group Trends in Metals and Nonmetals

- 7.69** Compare the elements sodium and magnesium with respect to the following properties: (a) electron configuration, (b) most common ionic charge, (c) first ionization energy, (d) reactivity toward water, (e) atomic radius. Account for the differences between the two elements.
- 7.70** (a) Compare the electron configurations and atomic radii (see Figure 7.7) of rubidium and silver. In what respects are their electronic configurations similar? Account for the difference in radii of the two elements. (b) As with rubidium, silver is most commonly found as the $1+$ ion, Ag^+ . However, silver is far less reactive. Explain these observations.
- 7.71** (a) Why is calcium generally more reactive than magnesium? (b) Why is calcium generally less reactive than potassium?
- 7.72** (a) Why is cesium more reactive toward water than is lithium? (b) 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? (c) Write a balanced chemical equation for reaction of the white substance with water.
- 7.73** Write a balanced equation for the reaction that occurs in each of the following cases: (a) Potassium metal burns in 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 is reacted with molten sulfur.
- 7.74** Write a balanced equation for the reaction that occurs in each of the following cases: (a) Cesium is added to water. (b) Strontium is added to water. (c) Sodium reacts with oxygen. (d) Calcium reacts with iodine.
- 7.75** (a) If we arrange the elements of the second period (Li–Ne) in order of increasing first ionization energy, where would hydrogen fit into this series? (b) If we now arrange the elements of the third period (Na–Ar) in order of increasing first ionization energy, where would lithium fit into this series? (c) Are these series consistent with the assignment of hydrogen as a nonmetal and lithium as a metal?
- 7.76** (a) As described in Section 7.7, the alkali metals react with hydrogen to form hydrides and react with halogens—for example, fluorine—to form halides. Compare the roles of hydrogen and the halogen in these reactions. In what sense are the forms of hydrogen and halogen in the products alike? (b) Write balanced equations for the reaction of fluorine with calcium and for the reaction of hydrogen with calcium. What are the similarities among the products of these reactions?
- 7.77** Compare the elements fluorine 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.
- 7.78** 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) What is the chemical formula of the compound it forms with Na?
- 7.79** Until the early 1960s the group 8A elements were called the inert gases; before that they were called the rare gases. The term rare gases was dropped after it was discovered that argon accounts for roughly 1% of Earth's atmosphere. (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?
- 7.80** Why does xenon react with fluorine, whereas neon does not?
- 7.81** Write a balanced equation for the reaction that occurs in each of the following cases: (a) Ozone decomposes to dioxygen. (b) Xenon reacts with fluorine. (Write three different equations.) (c) Sulfur reacts with hydrogen gas. (d) Fluorine reacts with water.
- 7.82** Write a balanced equation for the reaction that occurs in each of the following cases: (a) Chlorine reacts with water. (b) Barium metal is heated in an atmosphere of hydrogen gas. (c) Lithium reacts with sulfur. (d) Fluorine reacts with magnesium metal.

ADDITIONAL EXERCISES

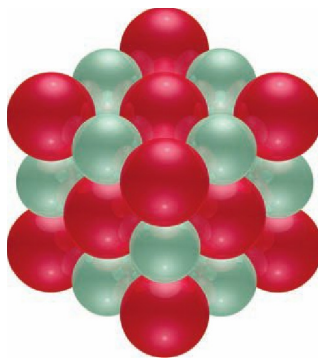
- 7.83** Consider the stable elements through lead ($Z = 82$). In how many instances are the atomic weights of the elements in the reverse order relative to the atomic numbers of the elements? What is the explanation for these cases?
- 7.84** (a) Which will have the lower energy, a $4s$ or a $4p$ electron in an As atom? (b) How can we use the concept of effective nuclear charge to explain your answer to part (a)?
- 7.85** (a) If the core electrons were totally effective at shielding the valence electrons and the valence electrons provided no shielding 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? Explain.

- 7.86 Nearly all the mass of an atom is in the nucleus, which has a very small radius. When atoms bond together (for example, two fluorine atoms in F_2), why is the distance separating the nuclei so much larger than the radii of the nuclei?
- [7.87] Consider the change in effective nuclear charge experienced by a $2p$ electron as we proceed from C to N. (a) Based on a simple model in which core electrons screen the valence electrons completely and valence electrons do not screen other valence electrons, what do you predict for the change in Z_{eff} from C to N? (b) What change do you predict using Slater's rules? (c) The actual change in Z_{eff} from C to N is $0.70+$. Which approach to estimating Z_{eff} is more accurate? (d) The change in Z_{eff} from N to O is smaller than that from C to N. Can you provide an explanation for this observation?
- 7.88 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?
- 7.89 In the series of group 5A hydrides, of general formula MH_3 , the measured bond distances are P—H, 1.419 Å; As—H, 1.519 Å; Sb—H, 1.707 Å. (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 electronic configurations of the M atoms.
- 7.90 It is possible to produce compounds of the form $GeClH_3$, $GeCl_2H_2$, and $GeCl_3H$. What values do you predict for the Ge—H and Ge—Cl bond lengths in these compounds?
- 7.91 Note from the following table that the increase in atomic radius in moving from Zr to Hf is smaller than in moving from Y to La. Suggest an explanation for this effect.

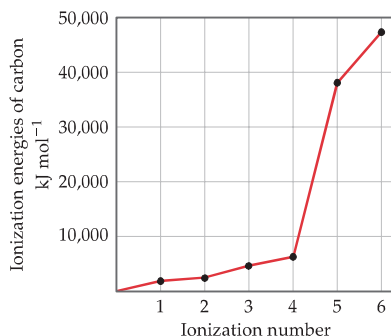
Atomic Radii (Å)			
Sc	1.44	Ti	1.36
Y	1.62	Zr	1.48
La	1.69	Hf	1.50

- 7.92 The "Chemistry and Life" box on ionic size in Section 7.3 compares the ionic radii of Zn^{2+} and Cd^{2+} . (a) The $2+$ ion of which other element seems the most obvious one to compare to Zn^{2+} and Cd^{2+} ? (b) With reference to Figure 2.24, is the element in part (a) essential for life? (c) Estimate the ionic radius of the $2+$ ion of the element in part (a). Explain any assumptions you have made. (d) Would you expect the $2+$ ion of the element in part (a) to be physiologically more similar to Zn^{2+} or to Cd^{2+} ? (e) Use a sourcebook or a Web search to determine whether the element in part (a) is toxic to humans.
- [7.93] The ionic substance strontium oxide, SrO, forms from the direct reaction of strontium metal with molecular oxygen. The arrangement of the ions in solid SrO is analogous to that in solid NaCl (see Figure 2.23) and is shown here. (a) Write a balanced equation for the formation of SrO(s) from the 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 experimental density of SrO is 5.10 g/cm^3 . Given your answer to part (b), what is the number of formula units of SrO that are contained in the cube in the figure? (We will examine structures like those in the figure more closely in Chapter 11.)



- 7.94 Explain the variation in ionization energies of carbon, as displayed in the following graph:

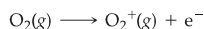


- 7.95 Do you agree with the following statement? "A negative value for the electron affinity of an atom occurs when the outermost electrons incompletely shield one another from the nucleus." If not, change it to make it more nearly correct in your view. Apply either the statement as given or your revised statement to explain why the electron affinity of bromine is -325 kJ/mol and that for its neighbor Kr is > 0 .
- 7.96 Use orbital diagrams to illustrate what happens when an oxygen atom gains two electrons. Why is it extremely difficult to add a third electron to the atom?
- [7.97] 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.

- 7.98** The following table gives the electron affinities, in kJ/mol, for the group 1B and group 2B metals: (a) Why are the electron affinities of the group 2B elements greater than zero? (b) Why do the electron affinities of the group 1B elements become more negative as we move down the group? [Hint: Examine the trends in the electron affinity of other groups as we proceed down the periodic table.]

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

- 7.99** Hydrogen is an unusual element because it behaves in some ways like the alkali metal elements and in other ways like a nonmetal. 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.
- [7.100]** 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.

- 7.101** Based on your reading of this chapter, arrange the following in order of increasing melting point: K, Br_2 , Mg, and O_2 . Explain the factors that determine the order.
- 7.102** The element strontium is used in a variety of industrial processes. It is not an extremely hazardous substance, but low levels of strontium ingestion could affect the health of children. Radioactive strontium is very hazardous; it was a by-product of nuclear weapons testing and was found widely distributed following nuclear tests. Calcium is quite common in the environment, including food products, and is frequently present in drinking water. Discuss the similarities and differences between calcium and strontium, and indicate how and why strontium might be expected to accompany calcium in water supplies, uptake by plants, and so on.
- [7.103]** There are certain similarities in properties that exist between the first member of any periodic family and the element located below it and to the right in the periodic table. For example, in some ways Li resembles Mg, Be resembles Al, and so forth. This observation is called the diagonal relationship. Using what we have learned in this chapter, offer a possible explanation for this relationship.
- [7.104]** A historian discovers a nineteenth-century notebook in which some observations, dated 1822, on a substance thought to be a new element, were recorded. 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/cm^3 . 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 a handbook of chemistry, 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 7.2, might this nineteenth-century investigator have been the first to discover a new element?

INTEGRATIVE EXERCISES

- [7.105]** 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 (\AA)
Ne	14.610
Ca	3.358
Zn	1.435
Zr	0.786
Sn	0.491

(a) Calculate the frequency, ν , of the X-rays emitted by each of the elements, in Hz. (b) Using graph paper (or

suitable computer software), plot the square root of ν 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 0.980 \AA . What element do you think it is?

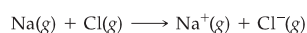
- [7.106]** (a) Write the electron configuration for Li, and estimate the effective nuclear charge experienced by the valence electron. (b) The energy of an electron in a one-electron atom or ion equals $(-2.18 \times 10^{-18}\text{ J})\left(\frac{Z^2}{n^2}\right)$ where Z is the nuclear charge and n 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 (c)?

- [7.107] One way to measure ionization energies is photoelectron spectroscopy (PES), a technique based on the photoelectric effect. ∞ (Section 6.2) 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 eV? (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 10.75 eV. What is the first ionization energy of Hg, in kJ/mol? (d) With reference to Figure 7.11, determine which of the halogen elements has a first ionization energy closest to that of mercury.

- 7.108 Consider the gas-phase transfer of an electron from a sodium atom to a chlorine atom:



(a) Write this reaction as the sum of two reactions, one that relates to an ionization energy and one that relates to an electron affinity. (b) Use the result from part (a), data in this chapter, and Hess's law to calculate the enthalpy of the above reaction. Is the reaction exothermic or endothermic? (c) The reaction between sodium metal and chlorine gas is highly exothermic and produces NaCl(s), whose structure was discussed in Section 2.7. Comment on this observation relative to the calculated enthalpy for the aforementioned gas-phase reaction.

- [7.109] 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 NH₃(g) and the reaction goes to completion, which component is the limiting reactant? What mass of H₂(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.

- 7.110 (a) The experimental Bi—Br bond length in bismuth tribromide, BiBr₃, is 2.63 Å. Based on this value and the data in Figure 7.7, 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 NaOH(aq). Based on these properties, is bismuth characterized as a metallic, metalloid, or non-metallic element? (d) Treating bismuth with fluorine gas forms BiF₅. Use the electron configuration of Bi to explain the formation of a compound with this formulation. (e) While it is possible to form BiF₅ 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?
- 7.111 Potassium superoxide, KO₂, is often used in oxygen masks (such as those used by firefighters) because KO₂ reacts with CO₂ to release molecular oxygen. Experiments indicate that 2 mol of KO₂(s) react with each mole of CO₂(g). (a) The products of the reaction are K₂CO₃(s) and O₂(g). Write a balanced equation for the reaction between KO₂(s) and CO₂(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 KO₂(s) is needed to consume 18.0 g CO₂(g)? What mass of O₂(g) is produced during this reaction?