

Chemical properties depend on valence shell electron configurations

For the representative elements (those in the longer columns), the only electrons that are normally important in controlling chemical properties are the ones in the outer shell. This outer shell is known as the **valence shell**, and it is always the occupied shell with the largest value of n . The electrons in the valence shell are called **valence electrons**. (The term *valence* comes from the study of chemical bonding and relates to the combining capacity of an element, but that's not important here.)

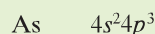
For the representative elements it is very easy to determine the electron configuration of the valence shell by using the periodic table. *The valence shell always consists of just the s and p subshells that we encounter crossing the period that contains the element in question.* Thus, to determine the valence shell configuration of sulfur, a Period 3 element, we note that to reach sulfur in Period 3 we place two electrons into the $3s$ and four electrons into the $3p$. The valence shell configuration of sulfur is therefore



Predict the electron configuration of the valence shell of arsenic ($Z = 33$).

ANALYSIS: For the valence shell configuration, we are only interested in s and p subshell electrons. The principal quantum number for them is the same as the period number.

SOLUTION: To reach arsenic in Period 4, we add electrons to the $4s$, $3d$, and $4p$ subshells. But the $3d$ is not part of the fourth shell and therefore not part of the valence shell, so all we need be concerned with are the electrons in the $4s$ and $4p$ subshells. This gives us the valence shell configuration of arsenic,



Is the Answer Reasonable?

The total number of valence electrons (i.e., those in valence shell orbitals) equals the group number. Arsenic is in Group V, and that's how many electrons we have shown in the answer, so it is correct.

PRACTICE EXERCISE 9: What is the valence shell electron configuration of (a) Se, (b) Sn, and (c) I?

EXAMPLE 8.6

Writing Valence Shell Configurations

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Configurations for transition and rare earth elements are sometimes unexpected

The rules you've learned for predicting electron configurations work most of the time, but not always. Appendix A gives the electron configurations of all of the elements as determined experimentally. Close examination reveals that there are quite a few exceptions to the rules. Some of these exceptions are important to us because they occur with common elements.

Two important exceptions are for chromium and copper. Following the rules, we would expect the configurations to be



However, the actual electron configurations, determined experimentally, are



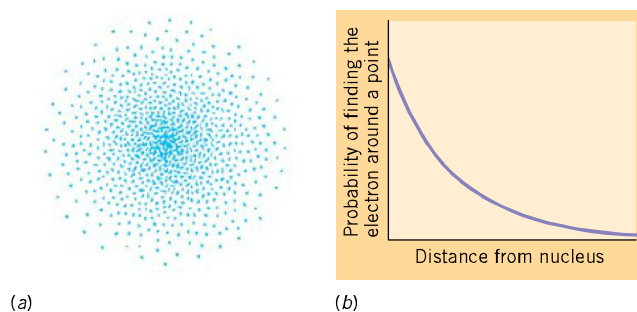


FIGURE 8.23 *Electron distribution in a 1s orbital.* (a) A dot-density diagram that illustrates the electron probability distribution for a 1s electron. (b) A graph that shows how the probability of finding the electron around a given point, ψ^2 , decreases as the distance from the nucleus increases.

In those places where the dot density is large (i.e., where there are large numbers of dots per unit volume), the amplitude of the wave is large and the probability of finding the electron is also large. Figure 8.23b shows how the electron probability for a 1s orbital varies as we move away from the nucleus. As you might expect, the probability of finding the electron close to the nucleus is large and decreases with increasing distance from the nucleus.

The other important concept that stems from the notion that the electron probability varies from place to place is **electron density**, which relates to how much of the electron's charge is packed into a given volume. In regions of high probability there is a high concentration of electrical charge (and mass) and the electron density is large; in regions of low probability, the electron density is small.

Remember that an electron confined to a tiny space no longer behaves much like a particle. It's more like a cloud of negative charge. Like clouds made of water vapor, the density of the cloud varies from place to place. In some places the cloud is dense; in others the cloud is thinner and may be entirely absent. This is a useful picture to keep in mind as you try to visualize the shapes of atomic orbitals.

Shapes and sizes of s and p orbitals

In looking at the way the electron density distributes itself in atomic orbitals, we are interested in three things—the *shape* of the orbital, its *size*, and its *orientation* in space relative to other orbitals.

The electron density in an orbital doesn't end abruptly at some particular distance from the nucleus. It gradually fades away. Therefore, to define the size and shape of an orbital, it is useful to picture some imaginary surface enclosing, say, 90% of the electron density of the orbital and on which the probability of finding the electron is everywhere the same. For the 1s orbital in Figure 8.23, we find that if we go out a given distance from the nucleus in *any* direction, the probability of finding the electron is the same. This means that all the points of equal probability lie on the surface of a sphere, so we can say that the shape of the orbital is spherical. In fact, all s orbitals are spherical. As suggested earlier, their sizes increase with increasing n . This is illustrated in Figure 8.24. Notice that beginning with the 2s

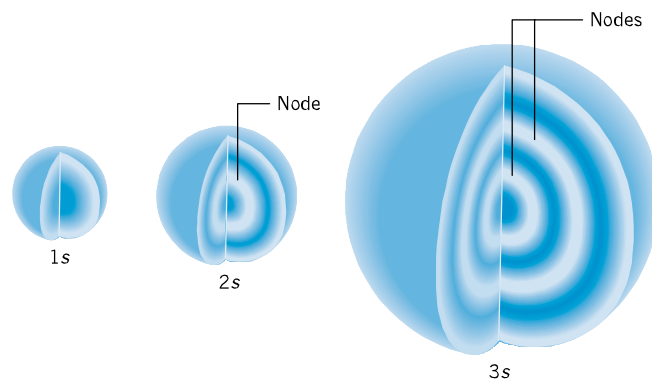


FIGURE 8.24 *Size variations among s orbitals.* The orbitals become larger as the principal quantum number, n , becomes larger.

FIGURE 8.25 *Distribution of electron density in p orbitals.* (a) Dot-density diagram that represents a cross section of the probability distribution in a $2p$ orbital. There is a nodal plane between the two lobes of the orbital. (b) Cross section of a $3p$ orbital. Note the nodes in the electron density that are in addition to the nodal plane passing through the nucleus.

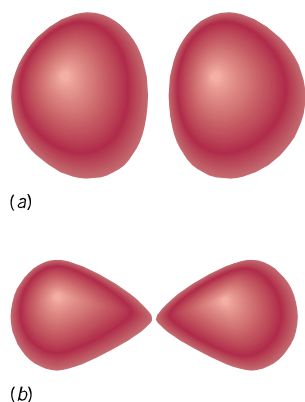
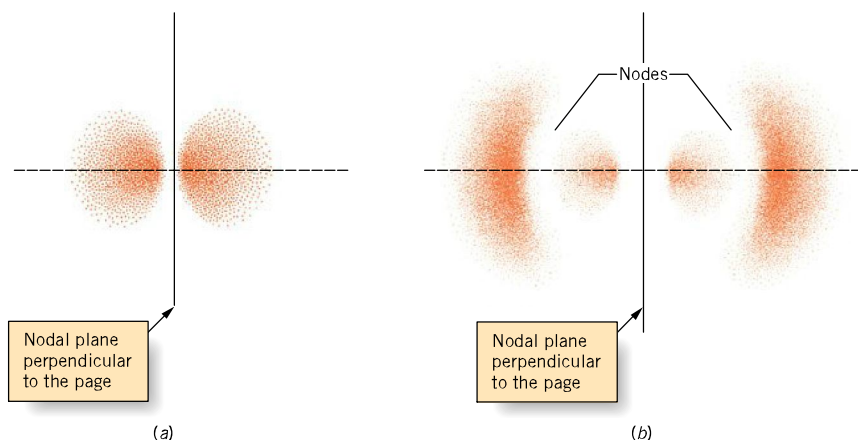


FIGURE 8.26 *Representations of the shapes of p orbitals.* (a) Shape of a surface of constant probability for a $2p$ orbital. (b) A simplified representation of a p orbital that emphasizes the directional nature of the orbital.

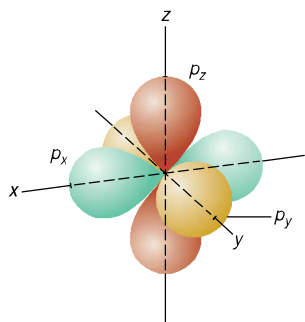


FIGURE 8.27 *The orientations of the three p orbitals in a p subshell.* Because the directions of maximum electron density lie along lines that are mutually perpendicular, like the axes of an xyz coordinate system, it is convenient to label the orbitals p_x , p_y , and p_z .

orbital, there are certain places where the electron density drops to zero. These are the nodes of the electron wave. It is interesting that electron waves have nodes just like the waves on a guitar string. For electron waves, however, the nodes consist of imaginary *surfaces* on which the electron density is zero.

The p orbitals are quite different from s orbitals, as shown in Figure 8.25. Notice that the electron density is equally distributed in two regions on opposite sides of the nucleus. Figure 8.25a illustrates the two “lobes” of *one* $2p$ orbital. Between the lobes is a *nodal plane*—an imaginary flat surface on which every point has an electron density of zero. Because of this nodal plane, electrons in p orbitals cannot reach or “penetrate” to the nucleus as well as electrons in s orbitals can. This is why p orbitals have slightly higher energies than s orbitals in the same shell, for all atoms but hydrogen.

The size of the p orbitals also increases with increasing n as illustrated by the cross section of a $3p$ orbital in Figure 8.25b. The $3p$ and higher p orbitals have additional nodes besides the nodal plane that passes through the nucleus.

Figure 8.26a illustrates the shape of a surface of constant probability for a $2p$ orbital. Often chemists will simplify this shape by drawing two “balloons” connected at the nucleus and pointing in opposite directions, as shown in Figure 8.26b. Both representations emphasize the point that a p orbital has two equal-sized lobes that extend in opposite directions along a line that passes through the nucleus.

Orientations of orbitals in a p subshell

As you’ve learned, a p subshell consists of three orbitals of equal energy. Wave mechanics tells us that the lines along which the orbitals have their maximum electron densities are oriented at 90° angles to each other, corresponding to the axes of an imaginary xyz coordinate system (Figure 8.27). For convenience in referring to the individual p orbitals they are often labeled according to the axis along which they lie. The p orbital concentrated along the x axis is labeled p_x , and so forth.

Shapes and orientations of d orbitals in a d subshell

The shapes of the d orbitals, illustrated in Figure 8.28, are a bit more complex than are those of the p orbitals. Because of this, and because there are five orbitals in a d subshell, we haven’t attempted to draw all of them at the same time on the same set of coordinate axes. Notice that four of the five d orbitals have the same shape and consist of four lobes of electron density. These orbitals differ only in their orientations around the nucleus (their labels come from the mathematics of wave

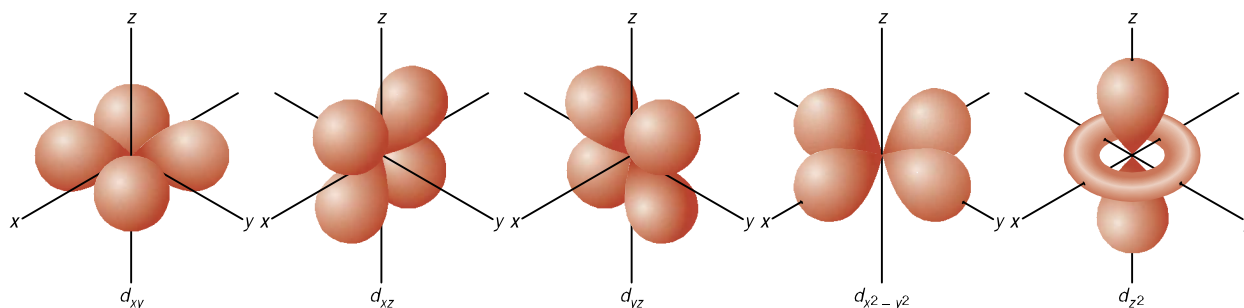


FIGURE 8.28 The shapes and directional properties of the five d orbitals of a d subshell.

mechanics). The fifth d orbital, labeled d_z^2 , has two lobes that point in opposite directions along the z axis plus a doughnut-shaped ring of electron density around the center that lies in the x - y plane. We will see that the d orbitals are important in the formation of chemical bonds in certain molecules and that their shapes and orientations are important in understanding the properties of the transition metals, which will be discussed in Chapter 23.

The f orbitals are even more complex than the d orbitals, but we will have no need to discuss their shapes.

8.8 Atomic properties correlate with an atom's electron configuration

There are many chemical and physical properties that vary in a more or less systematic way according to an element's position in the periodic table. For example, in Chapter 1 we noted that the metallic character of the elements increases from top to bottom in a group and decreases from left to right across a period. In this section we discuss several physical properties of the elements that have an important influence on chemical properties. We will see how these properties correlate with an atom's electron configuration, and because electron configuration is also related to the location of an element in the periodic table, we will study their periodic variations as well.

Effective nuclear charge is the positive charge "felt" by outer electrons

Many of an atom's properties are determined by the amount of positive charge felt by the atom's outer electrons. Except for hydrogen, this positive charge is always *less* than the full nuclear charge, because the negative charge of the electrons in inner shells partially offsets, or "neutralizes," the positive charge of the nucleus.

To gain a better understanding of this, consider the element lithium, which has the electron configuration $1s^2 2s^1$. The core electrons ($1s^2$), which lie beneath the valence shell ($2s^1$), are tightly packed around the nucleus and for the most part lie between the nucleus and the electron in the outer shell. This core has a charge of $2-$ and it surrounds a nucleus that has a charge of $3+$. When the outer $2s$ electron "looks toward" the center of the atom, it "sees" the $3+$ charge of the nucleus reduced to only about $1+$ because of the intervening $2-$ charge of the core. In other words, the $2-$ charge of the core effectively neutralizes two of the positive charges of the nucleus, so the net charge that the outer electron feels, which we call the **effective nuclear charge**, is only about $1+$. This is illustrated in an overly simplified way in Figure 8.29.

Although electrons in inner shells shield the electrons in outer shells quite effectively from the nuclear charge, electrons in the *same* shell are much less effective at shielding each other. For example, in the element beryllium ($1s^2 2s^2$)

The inner electrons partially shield the outer electrons from the nucleus, so the outer electrons "feel" only a fraction of the full nuclear charge.

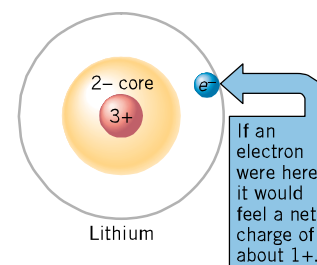


FIGURE 8.29 **Effective nuclear charge.** If the $2-$ charge of the $1s^2$ core of lithium were 100% effective at shielding the $2s$ electron from the nucleus, the valence electron would feel an effective nuclear charge of only about $1+$.

An electron spends very little time between the nucleus and another electron in the same shell, so it shields that other electron poorly.

The C—H distance in most hydrocarbons is about 110 pm (110×10^{-12} m).

The angstrom is named after Anders Jonas Ångström (1814–1874), a Swedish physicist who was the first to measure the wavelengths of the four most prominent lines of the hydrogen spectrum.

each of the electrons in the outer $2s$ orbital is shielded quite well from the nuclear charge by the inner $1s^2$ core, but one $2s$ electron doesn't shield the other $2s$ electron very well at all. This is because electrons in the same shell are at about the same average distance from the nucleus, and in attempting to stay away from each other they only spend a very small amount of time one below the other, which is what's needed to provide shielding. Since electrons in the same shell hardly shield each other at all from the nuclear charge, *the effective nuclear charge felt by the outer electrons is determined primarily by the difference between the charge on the nucleus and the charge on the core*. With this as background, let's examine some properties controlled by the effective nuclear charge.

Atomic and ionic sizes increase with increasing n and decreasing effective nuclear charge

The wave nature of the electron makes it difficult to define exactly what we mean by the "size" of an atom or ion. As we've seen, the electron cloud doesn't simply stop at some particular distance from the nucleus; instead it gradually fades away. Nevertheless, atoms and ions do behave in many ways as though they have characteristic sizes. For example, in a whole host of hydrocarbons, ranging from methane (CH_4 , natural gas) to octane (C_8H_{18} , in gasoline) to many others, the distance between the nuclei of carbon and hydrogen atoms is virtually the same. This would suggest that carbon and hydrogen have the same relative sizes in each of these compounds.

Experimental measurements reveal that the diameters of atoms range from about 1.4×10^{-10} to 5.7×10^{-10} m. Their radii, which is the usual way that size is specified, range from about 7.0×10^{-11} to 2.9×10^{-10} m. Such small numbers are difficult to comprehend. A million carbon atoms placed side by side in a line would extend a little less than 0.2 mm, or about the diameter of the period at the end of this sentence.

The sizes of atoms and ions are rarely expressed in meters because the numbers are so cumbersome. Instead, a unit is chosen that makes the values easier to comprehend. A unit that scientists have traditionally used is called the **angstrom** (symbolized \AA), which is defined as

$$1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$$

However, the angstrom is not an SI unit, and in many current scientific journals, atomic dimensions are given in picometers, or sometimes in nanometers ($1 \text{ pm} = 10^{-12} \text{ m}$ and $1 \text{ nm} = 10^{-9} \text{ m}$). In this book, we will normally express atomic dimensions in picometers, but because much of the scientific literature has these quantities in angstroms, you may someday find it useful to remember the conversions:

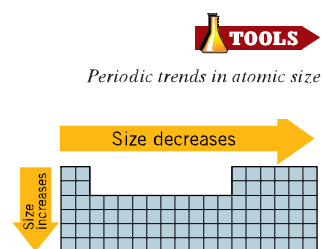
$$1 \text{ \AA} = 100 \text{ pm}$$

$$1 \text{ \AA} = 0.1 \text{ nm}$$

Atomic size varies periodically

The variations in atomic radii within the periodic table are illustrated in Figure 8.30. Here we see that atoms generally become larger going from top to bottom in a group, and they become smaller going from left to right across a period. To understand these variations we must consider two factors. One is the value of the principal quantum number of the valence electrons, and the other is the effective nuclear charge felt by the valence electrons.

Going from top to bottom within a group, the effective nuclear charge felt by the outer electrons remains nearly constant, while the principal quantum number of the valence shell increases. For example, consider the elements of Group IA. For



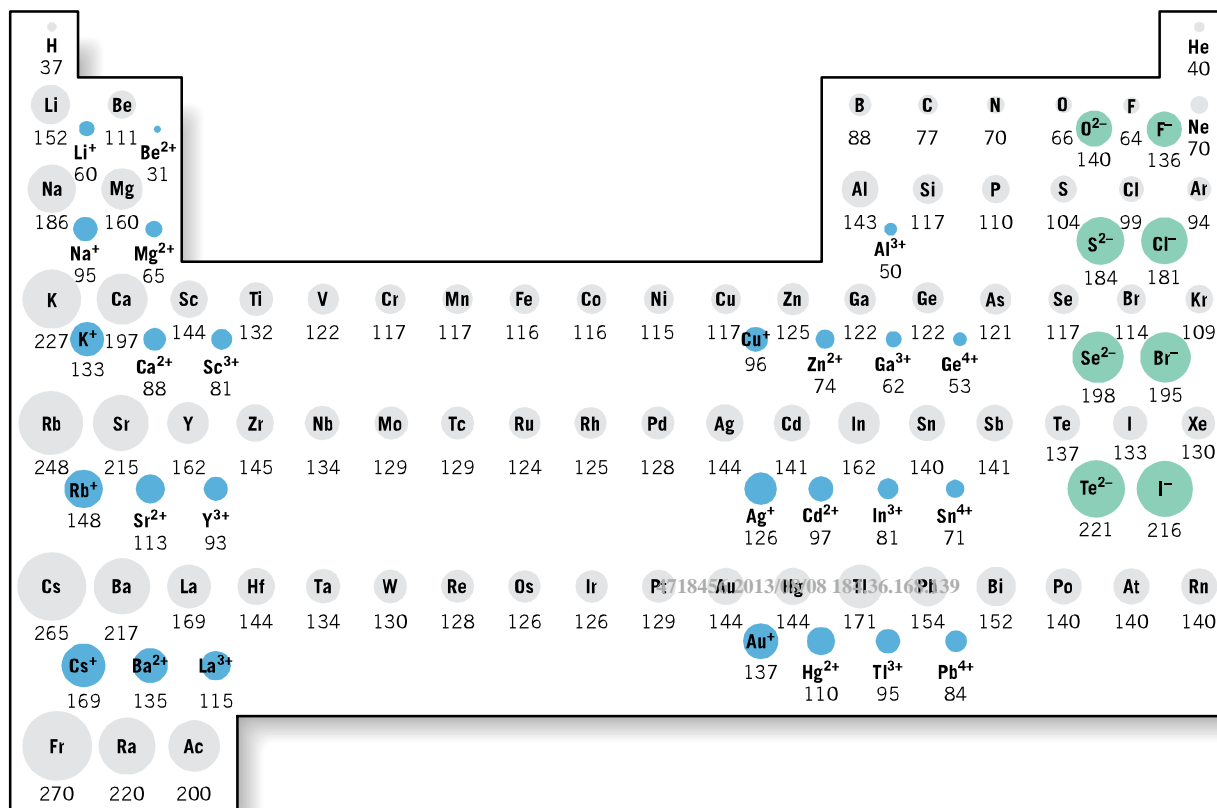


FIGURE 8.30 Variation in atomic and ionic radii in the periodic table. Values are in picometers.

lithium, the valence shell configuration is $2s^1$; for sodium, it is $3s^1$; for potassium, it is $4s^1$; and so forth. For each of these elements, the core has a negative charge that is 1 less than the nuclear charge, so the valence electron of each experiences a nearly constant effective nuclear charge of about $1+$. However, as we descend the group, the value of n for the valence shell increases, and as you learned earlier, the larger the value of n , the larger is the orbital. Therefore, the atoms become larger as we go down a group simply because the orbitals containing the valence electrons become larger. This same argument applies whether the valence shell orbitals are s or p .

Moving from left to right across a period, electrons are added to the same shell. The orbitals holding the valence electrons all have the *same* value of n . In this case we have to examine the variation in the effective nuclear charge felt by the valence electrons.

As we move from left to right across a period, the nuclear charge increases, the outer shells of the atoms become more populated, but the inner core remains the same. For example, from lithium to fluorine the nuclear charge increases from $3+$ to $9+$. The core ($1s^2$) stays the same, however. As a result, the outer electrons feel an increase in positive charge (i.e., effective nuclear charge) that causes them to be drawn inward, and thereby causes the sizes of the atoms to decrease.

Across a row of transition elements or inner transition elements, the size variations are less pronounced than among the representative elements. This is because the outer shell configuration remains essentially the same while an inner shell is filled. From atomic numbers 21 to 30, for example, the outer electrons occupy the $4s$ subshell while the underlying $3d$ subshell is gradually completed. The amount of shielding provided by the addition of electrons to this inner $3d$ level is greater than the amount of shielding that would occur if the electrons were added to the outer shell, so the

effective nuclear charge felt by the outer electrons increases more gradually. As a result, the decrease in size with increasing atomic number is also more gradual.



Trends in ionic size

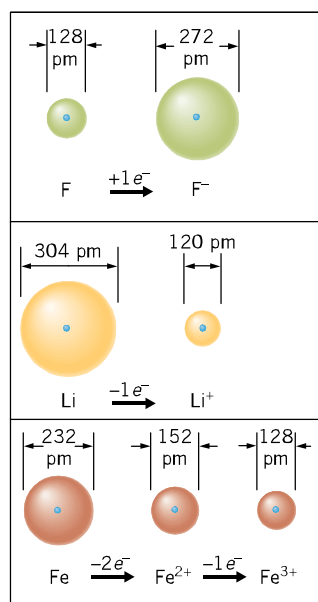


FIGURE 8.31 Changes in size when atoms gain or lose electrons to form ions. Adding electrons leads to an increase in the size of the particle, as illustrated for fluorine. Removing electrons leads to a decrease in the size of the particle, as shown for lithium and iron.

Ion sizes parallel atom sizes, but anions are bigger and cations are smaller

Figure 8.30 also illustrates how sizes of the ions compare with those of the neutral atoms. As you can see, when atoms gain or lose electrons to form ions, rather significant size changes take place. The reasons are easy to understand and remember.

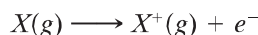
When electrons are added to an atom, the mutual repulsions between them increase. This causes the electrons to push apart and occupy a larger volume. Therefore, *negative ions are always larger than the atoms from which they are formed* (Figure 8.31).

When electrons are removed from an atom, the electron–electron repulsions decrease, which allows the remaining electrons to be pulled closer together around the nucleus. Therefore, *positive ions are always smaller than the atoms from which they are formed*. This is also illustrated in Figure 8.31 for the elements lithium and iron. For lithium, removal of the outer 2s electron completely empties the valence shell and exposes the smaller 1s² core. When a metal is able to form more than one positive ion, the sizes of the ions decrease as the amount of positive charge on the ion increases. To form the Fe²⁺ ion, an iron atom loses its outer 4s electrons. To form the Fe³⁺ ion, an additional electron is lost from the 3d subshell that lies beneath the 4s. Comparing sizes, we see that the radius of an iron atom is 116 pm, whereas the radius of the Fe²⁺ ion is 76 pm. Removing yet another electron to give Fe³⁺ decreases electron–electron repulsions in the d subshell and gives the Fe³⁺ ion a radius of 64 pm.

PRACTICE EXERCISE 10: Use the periodic table to choose the largest atom or ion in each set: (a) Ge, Te, Se, Sn; (b) C, F, Br, Ga; (c) Cr, Cr²⁺, Cr³⁺; (d) O, O²⁻, S, S²⁻.

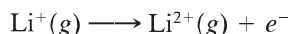
Ionization Energy

The **ionization energy** (abbreviated **IE**) is the energy required to remove an electron from an isolated, gaseous atom or ion in its ground state. For an atom of an element X, it is the increase in potential energy associated with the change



In effect, the ionization energy is a measure of how much work is required to pull an electron from an atom, so it reflects how tightly the electron is held by the atom. Usually, the ionization energy is expressed in units of kilojoules per mole (kJ/mol), so we can also view it as the energy needed to remove 1 mol of electrons from 1 mol of gaseous atoms.

Table 8.2 gives the ionization energies of the first 12 elements. As you can see, atoms with more than one electron have more than one ionization energy. These correspond to the stepwise removal of electrons, one after the other. Lithium, for example, has three ionization energies because it has three electrons. Removing the outer 2s electrons from 1 mol of isolated lithium atoms to give 1 mol of gaseous lithium ions, Li⁺, requires 520 kJ; so the *first ionization energy* of lithium is 520 kJ/mol. The second IE of lithium is 7297 kJ/mol and corresponds to the process



This involves the removal of an electron from the now-exposed 1s core of lithium. Removal of the third (and last) electron requires the third IE, which is 11,810 kJ/mol. In general, successive ionization energies always increase because each subsequent electron is being pulled away from an increasingly more positive ion, and that requires more work.

Ionization energies are additive. For example,

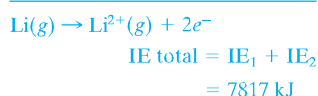
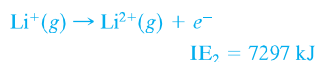
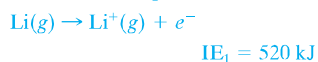


TABLE 8.2 SUCCESSIVE IONIZATION ENERGIES IN kJ/mol FOR HYDROGEN THROUGH MAGNESIUM

Note the sharp increase in ionization energy when crossing the “staircase,” indicating that the last of the valence electrons has been removed.

	1st	2nd	3rd	4th	5th	6th	7th	8th
H	1312							
He	2372	5250						
Li	520	7297	11,810					
Be	899	1757	14,845	21,000				
B	800	2426	3659	25,020	32,820			
C	1086	2352	4619	6221	37,820	47,260		
N	1402	2855	4576	7473	9442	53,250	64,340	
O	1314	3388	5296	7467	10,987	13,320	71,320	84,070
F	1680	3375	6045	8408	11,020	15,160	17,860	92,010
Ne	2080	3963	6130	9361	12,180	15,240	—	—
Na	496	4563	6913	9541	13,350	16,600	20,113	25,666
Mg	737	1450	7731	10,545	13,627	17,995	21,700	25,662

Larger atoms have lower ionization energies

Within the periodic table there are trends in the way IE varies that are useful to know and to which we will refer in later discussions. We can see these by examining a graph that shows how the first ionization energy varies with an element's position in the table, which is shown in Figure 8.32. Notice that the elements with the largest ionization energies are the nonmetals in the upper right of the periodic table and that those with the smallest ionization energies are the metals in the lower left of the table. In general, then, the following trends are observed:

Ionization energy generally increases from bottom to top within a group and increases from left to right within a period.



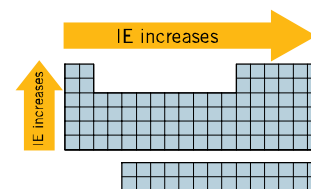
Periodic trends in ionization energy

The same factors that affect atomic size also affect ionization energy. As the value of n increases going down a group, the orbitals become larger and the outer electrons are farther from the nucleus. Electrons farther from the nucleus are bound less tightly, so IE decreases from top to bottom. Of course, this is just the same as saying that it increases from bottom to top.

As you can see, there is a gradual overall increase in IE as we move from left to right across a period, although the horizontal variation of IE is somewhat irregular (see Facets of Chemistry 8.2). The reason for the overall trend is the increase in effective nuclear charge felt by the valence electrons as we move across a period. As we've seen, this draws the valence electrons closer to the nucleus and leads to a decrease in atomic size as we move from left to right. But the increasing effective nuclear charge also causes the valence electrons to be held more tightly, which makes it more difficult to remove them.

The results of these trends place elements with the largest IE in the upper right-hand corner of the periodic table. It is very difficult to cause these atoms to lose electrons. In the lower left-hand corner of the table are elements that have loosely held valence electrons. These elements form positive ions relatively easily, as you learned in Chapter 2.

It is often helpful to remember that the trends in IE are just the opposite of the trends in atomic size within the periodic table: when size increases, IE decreases.



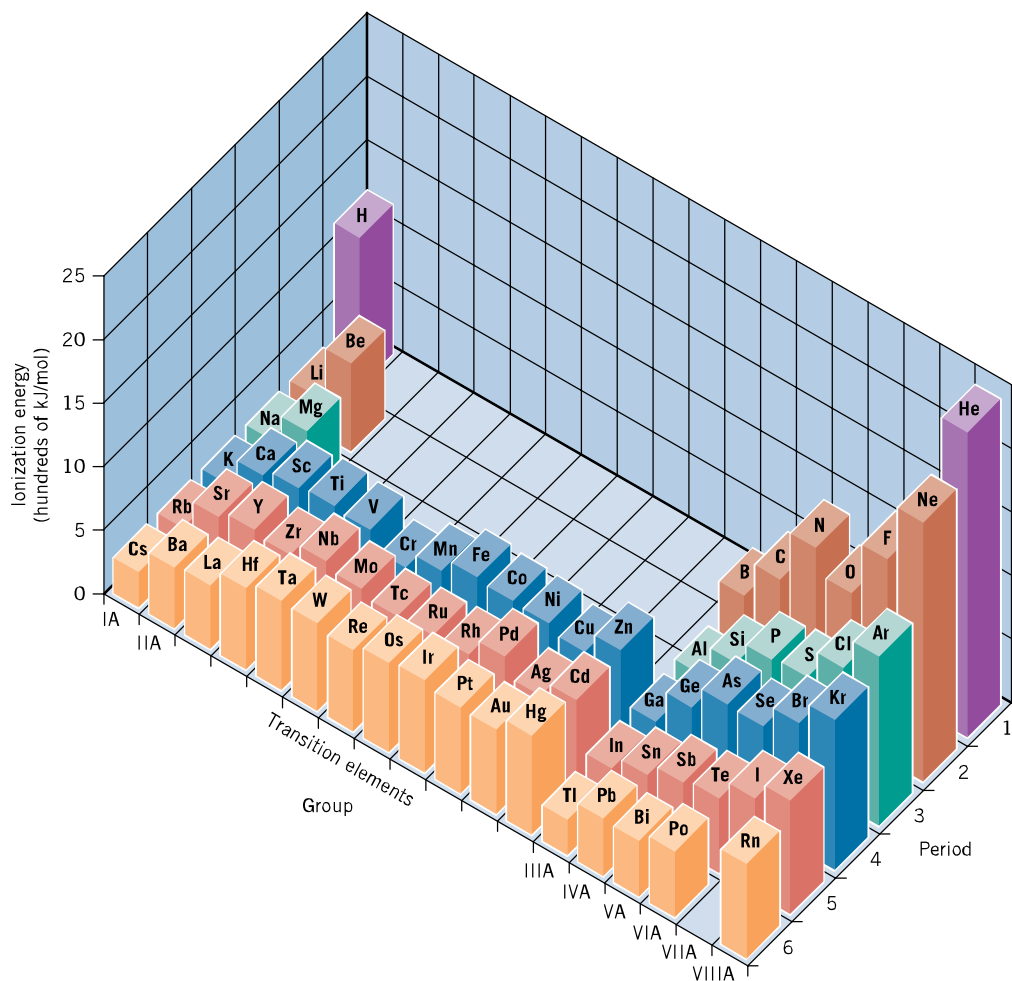


FIGURE 8.32 Variation in first ionization energy with location in the periodic table. Elements with the largest ionization energies are in the upper right of the periodic table. Those with the smallest ionization energies are at the lower left.

Noble gas configurations are extremely stable

Table 8.2 shows that, for a given element, successive ionization energies increase gradually until the valence shell is emptied. Then a very much larger increase in IE occurs as the core is broken into. This is illustrated graphically in Figure 8.33 for the Period 2 elements lithium through fluorine. For lithium, we see that the first electron (the $2s$ electron) is removed rather easily, but the second and third electrons, which come from the $1s$ core, are much more difficult to dislodge. For beryllium, the large jump in IE occurs after two electrons (the two $2s$ electrons) are removed. In fact, for all of these elements, the big jump in IE happens when the core is broken into.

The data displayed in Figure 8.33 suggest that although it may be moderately difficult to empty the valence shell of an atom, it is *extremely* difficult to break into the noble gas configuration of the core electrons. As you will learn, this is one of the factors that influences the number of positive charges on ions formed by the representative metals.

PRACTICE EXERCISE 11: Use the periodic table to select the atom with the largest IE: (a) Na, Sr, Be, Rb; (b) B, Al, C, Si.