

**Beginning students of chemistry often think of the science as a mere collection of disconnected data to be memorized by brute force.**

**Not at all! Just look at it properly and everything hangs together and makes sense.**

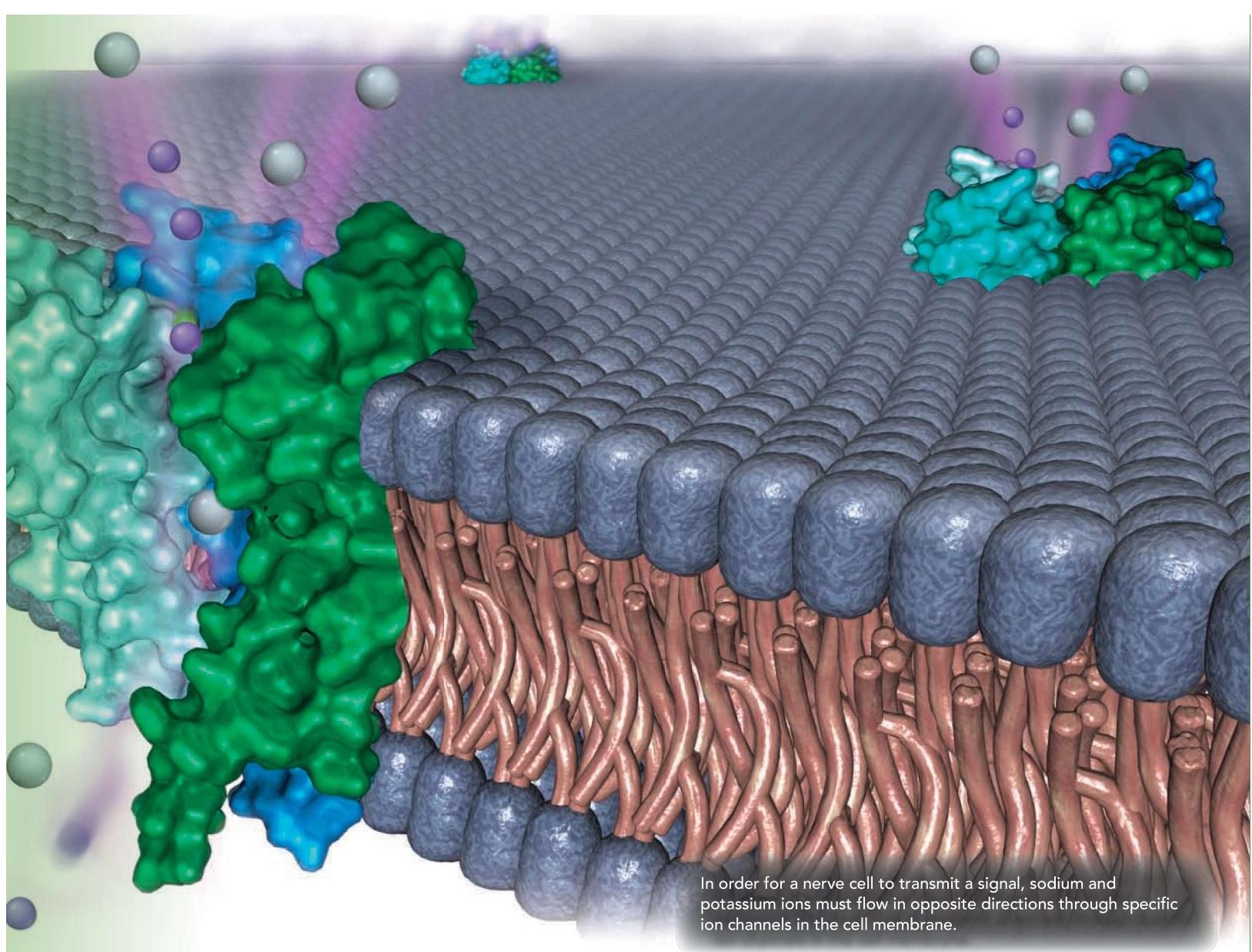
—ISAAC ASIMOV (1920–1992)

CHAPTER

# 9

## Periodic Properties of the Elements

**G**reat advances in science occur not only when a scientist sees something new, but also when a scientist sees what everyone else has seen in a new way. In other words, great scientists often see patterns where others have seen only disjointed facts. Such was the case in 1869 when Dmitri Mendeleev (1834–1907), a Russian chemist, saw a pattern in the properties of elements. Mendeleev's insight led to the periodic table, arguably the single most important tool for chemists. Recall that scientists devise theories that explain the underlying reasons for observations. Mendeleev's periodic table is a compact way to summarize a large number of observations; quantum mechanics (covered in Chapter 8) is the theory that explains the underlying reasons for the periodic table. Quantum mechanics explains how electrons are arranged in atoms, which in turn determines the element's properties. Since the periodic table is organized according to those properties, quantum mechanics beautifully accounts for Mendeleev's periodic table. In this chapter, we see a continuation of the theme we have been developing since page one of this book—the properties of macroscopic substances (in this case, the elements in the periodic table) are explained by the properties of the particles that compose them (in this case, atoms and their electrons).



In order for a nerve cell to transmit a signal, sodium and potassium ions must flow in opposite directions through specific ion channels in the cell membrane.

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#### LEARNING OUTCOMES 385

## 9.1 Nerve Signal Transmission

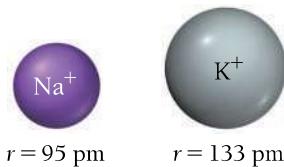
As you sit reading this book, tiny pumps in the membranes of your cells are working hard to transport ions—especially sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ )—through those membranes. Amazingly, the ions are pumped in opposite directions. Sodium ions are pumped *out of cells*, while potassium ions are pumped *into cells*. The result is a *chemical gradient* for each ion: the concentration of sodium is higher outside the cell than within,

whereas just the opposite is true for potassium. These ion pumps are analogous to the water pumps in a high-rise building that pump water against the force of gravity to a tank on the roof. Other structures within the membrane, called ion channels, are like the building's faucets. When these open, sodium and potassium ions flow back down their gradients—sodium flowing in and potassium flowing out. This movement of ions is the basis for the transmission of nerve signals in the brain and throughout the body. Every move you make, every thought you have, and every sensation you experience is mediated by these ion movements.

How do the pumps and channels differentiate between sodium and potassium ions to selectively move one out of the cell and the other into the cell? To answer this question, we must examine the ions more closely. Both ions are cations of group 1A metals. All group 1A metals tend to lose one electron to form cations with a  $1+$  charge, so that cannot be the decisive factor. Potassium (atomic number 19) lies directly below sodium in the periodic table (atomic number 11), indicating that it has more protons, neutrons, and electrons than sodium. How do these additional subatomic particles affect the properties of potassium? As we will see in this chapter, although a higher atomic number does not always result in a larger ion (or atom), it does in the case of potassium (relative to sodium). The potassium ion has a radius of 133 pm, whereas the sodium ion has a radius of 95 pm. (Recall that  $1\text{pm} = 10^{-12}\text{ m}$ .) The pumps and channels within cell membranes are so sensitive that they distinguish between the sizes of these two ions and selectively allow only one or the other to pass.

3 Li 6.94
11 Na 22.99
19 K 39.10
37 Rb 85.47
55 Cs 132.91
87 Fr (223.02)

▲ The group 1A metals. Potassium is directly beneath sodium in the periodic table.



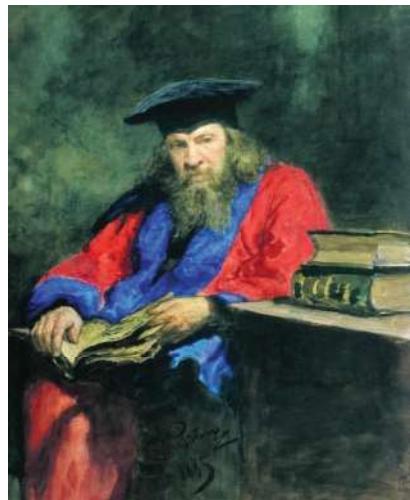
The relative size of sodium and potassium ions is an example of a **periodic property**: one that is predictable based on an element's position within the periodic table. In this chapter, we examine several periodic properties of elements, including atomic radius, ionization energy, and electron affinity. We will see that these properties, as well as the overall arrangement of the periodic table, are explained by quantum-mechanical theory, which we examined in Chapter 8. The arrangement of elements in the periodic table—originally based on similarities in the properties of the elements—reflects how electrons fill quantum-mechanical orbitals.

## 9.2

## The Development of the Periodic Table

Prior to the 1700s, the number of known elements was relatively small, consisting mostly of the metals that had long been used for coinage, jewelry, and weapons. From the early 1700s to the mid-1800s, however, chemists discovered over 50 new elements. The first attempt to organize these elements according to similarities in their properties was made by the German chemist Johann Döbereiner (1780–1849), who grouped elements into *triads*: three elements with similar properties. For example, Döbereiner formed a triad out of barium, calcium, and strontium, three fairly reactive metals. About 50 years later, English chemist John Newlands (1837–1898) organized elements into *octaves*, in analogy to musical notes. When arranged this way, the properties of every eighth element were similar, much as every eighth note in the musical scale is similar. Newlands endured some ridicule for drawing an analogy between chemistry and music, including the derisive comments of one colleague who asked Newlands if he had ever tried ordering the elements according to the first letters of their names.

The modern periodic table is credited primarily to the Russian chemist Dmitri Mendeleev, even though a similar organization had been suggested by the German chemist Julius Lothar Meyer (1830–1895). Recall from Chapter 2 that Mendeleev's table is based on the periodic law, which states that when elements are arranged in order of increasing mass, certain properties recur periodically. Mendeleev arranged the elements in a table in which mass increases from left to right and elements with similar properties fall in the same columns.



▲ Dmitri Mendeleev is credited with the arrangement of the periodic table.

**Gallium (eka-aluminum)**

	Mendeleev's predicted properties	Actual properties
Atomic mass	About 68 amu	69.72 amu
Melting point	Low	29.8 °C
Density	5.9 g/cm³	5.90 g/cm³
Formula of oxide	X₂O₃	Ga₂O₃
Formula of chloride	XCl₃	GaCl₃

**Germanium (eka-silicon)**

	Mendeleev's predicted properties	Actual properties
Atomic mass	About 72 amu	72.64 amu
Density	5.5 g/cm³	5.35 g/cm³
Formula of oxide	XO₂	GeO₂
Formula of chloride	XCl₄	GeCl₄

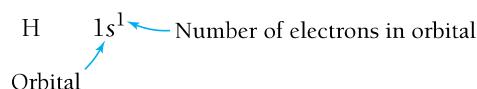
Mendeleev's arrangement was a huge success, allowing him to predict the existence and properties of yet undiscovered elements such as eka-aluminum (later discovered and named gallium) and eka-silicon (later discovered and named germanium). The properties of these two elements are summarized in Figure 9.1▲. (As noted in Chapter 2, *eka* means “the one beyond” or “the next one” in a family of elements.) However, Mendeleev did encounter some difficulties. For example, according to accepted values of atomic masses, tellurium (with higher mass) should come *after* iodine. But based on their properties, Mendeleev placed tellurium *before* iodine and suggested that the mass of tellurium was erroneous. The mass was correct; later work by the English physicist Henry Moseley (1887–1915) showed that listing elements according to *atomic number*, rather than atomic mass, resolves this problem and results in even better correlation with elemental properties.

Notice the scientific approach in practice in the history of the periodic table. A number of related observations led to a scientific law—the periodic law. Mendeleev's table, an expression of the periodic law, had predictive power as laws usually do. However, it did not explain *why* the properties of elements recurred or *why* certain elements had similar properties. Recall from Chapter 1 that laws *summarize* behavior while theories *explain* behavior. The theory that explains the reasons behind the periodic law is quantum-mechanical theory. In this chapter, we explore the connection between the periodic table and quantum-mechanical theory.

▲ **FIGURE 9.1 Eka-aluminum and Eka-silicon** Mendeleev's arrangement of elements in the periodic table allowed him to predict the existence of these elements, now known as gallium and germanium, and anticipate their properties.

**9.3****Electron Configurations: How Electrons Occupy Orbitals**

Quantum-mechanical theory describes the behavior of electrons in atoms. Since chemical bonding involves the transfer or sharing of electrons, quantum-mechanical theory helps us understand and describe chemical behavior. As we saw in Chapter 8, electrons in atoms exist within orbitals. An **electron configuration** for an atom shows the particular orbitals that electrons occupy for that atom. For example, consider the **ground state**—or lowest energy state—electron configuration for a hydrogen atom:



The electron configuration indicates that hydrogen's one electron is in the 1s orbital. Electrons generally occupy the lowest energy orbitals available. Since the 1s orbital is the lowest energy orbital in hydrogen (see Section 8.5), hydrogen's electron occupies that orbital. If we could write electron configurations for all the elements, we could see how the arrangements of the electrons within their atoms correlate with the element's chemical properties. However, the Schrödinger equation solutions (the atomic orbitals and their energies) that we described in Chapter 8 are for the hydrogen atom. What do the atomic orbitals of *other atoms* look like? What are their relative energies?

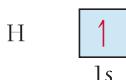
**WATCH NOW!**

**KEY CONCEPT VIDEO 9.3**  
*Electron Configurations*

The Schrödinger equation for multielectron atoms has terms to account for the interactions of the electrons with one another that make it too complicated to solve exactly. However, approximate solutions indicate that the orbitals in multielectron atoms are hydrogen-like—they are similar to the  $s$ ,  $p$ ,  $d$ , and  $f$  orbitals that we examined in Chapter 8. In order to see how the electrons in multielectron atoms occupy these hydrogen-like orbitals, we must examine two additional concepts: *the effects of electron spin*, a fundamental property of all electrons that affects the number of electrons allowed in any one orbital; and *sublevel energy splitting*, which determines the order of orbital filling within a level.

## Electron Spin and the Pauli Exclusion Principle

We can represent the electron configuration of hydrogen ( $1s^1$ ) in a slightly different way with an **orbital diagram**, which gives similar information but symbolizes the electron as an arrow and the orbital as a box. The orbital diagram for a hydrogen atom is:



In an orbital diagram, the direction of the arrow (pointing up or pointing down) represents the orientation of the *electron's spin*. Recall from Section 8.5 that the orientation of the electron's spin is quantized, with only two possibilities—spin up ( $m_s = +\frac{1}{2}$ ) and spin down ( $m_s = -\frac{1}{2}$ ). In an orbital diagram,  $m_s = +\frac{1}{2}$  is represented with a half-arrow pointing up ( $\uparrow$ ) and  $m_s = -\frac{1}{2}$  is represented with a half-arrow pointing down ( $\downarrow$ ). In a collection of hydrogen atoms, the electrons in about half of the atoms are spin up and the electrons in the other half are spin down. Since no additional electrons are present within the hydrogen atom, we conventionally represent the hydrogen atom electron configuration with its one electron as spin up.

Helium is the first element on the periodic table that contains two electrons. Its two electrons occupy the 1s orbital:

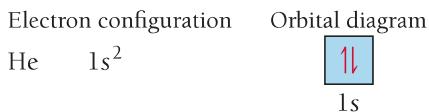


How do the spins of the two electrons in helium align relative to each other? The answer to this question is addressed by the **Pauli exclusion principle**, formulated by Wolfgang Pauli (1900–1958) in 1925:

**Pauli exclusion principle: no two electrons in an atom can have the same four quantum numbers.**

Since two electrons occupying the same orbital have three identical quantum numbers ( $n$ ,  $l$ , and  $m_l$ ), they must have different spin quantum numbers. Because there are only two possible spin quantum numbers ( $+\frac{1}{2}$  and  $-\frac{1}{2}$ ), the Pauli exclusion principle implies that *each orbital can have a maximum of only two electrons, with opposing spins*.

By applying the exclusion principle, we write an electron configuration and orbital diagram for helium as follows:



The following table shows the four quantum numbers for each of the two electrons in helium:

The two electrons have three quantum numbers in common (because they are in the same orbital) but have different spin quantum numbers (as indicated by the opposing half-arrows in the orbital diagram).

## Sublevel Energy Splitting in Multielectron Atoms

Understanding the underlying reasons for sublevel energy splitting routinely causes my students confusion. This section of text, beginning here and extending to p. 367, is generally well-written and clear, but I have a few suggestions for improvement.

1. a key aspect that is somewhat glossed over is that electrons are particles and waves. And in looking at the three factors that influence sublevel energy splitting, two reflect the particle nature (Coulomb's Law and shielding, which is somewhat of an

$n$	$l$	$m_l$	$m_s$
1	0	0	$+\frac{1}{2}$
1	0	0	$-\frac{1}{2}$

extension of Coulomb's Law), and one reflects the wave nature of electrons (penetration). I would suggest making this more explicit.

2. The penetration concept is particularly difficult for students to grasp. And I think that this is partly due to the fact that when shielding is described, the text uses a fictitious scenario: that of an electron (particle) being physically moved closer to the nucleus. That to me seems an overly hypothetical scenario – I'm not aware that this is even experimentally feasible, but I could be ignorant of such things – and then students are presented with graphs that portray radial distribution functions without being reminded that these reflect/depict the wave nature of electrons. (I realize that this is a nuanced point that I am trying to make, and if necessary, I am happy to clarify further by phone.)
3. I suggest making the x-axis labels of Figures 9.3 and 9.4 more consistent with each other, for improved clarity, e.g., “r (pm), distance from nucleus” I have often found that students don't necessarily look at Fig. 9.3 and understand that “r” means distance from the nucleus.

A major difference in the (approximate) solutions to the Schrödinger equation for multi-electron atoms compared to the solutions for the hydrogen atom is the energy ordering of the orbitals. In the hydrogen atom, the energy of an orbital depends only on  $n$ , the principal quantum number. For example, the  $3s$ ,  $3p$ , and  $3d$  orbitals (which are empty for hydrogen in its lowest energy state) all have the same energy—they are **degenerate**. The orbitals within a principal level of a *multielectron atom*, in contrast, are not degenerate—their energy depends on the value of  $l$ . We say that the energies of the sublevels are *split*. In general, the lower the value of  $l$  *within a principal level*, the lower the energy ( $E$ ) of the corresponding orbital. Thus, for a given value of  $n$ :

$$E(s \text{ orbital}) < E(p \text{ orbital}) < E(d \text{ orbital}) < E(f \text{ orbital})$$

In order to understand why the sublevels split in this way, we must examine three key concepts associated with the energy of an electron in the vicinity of a nucleus: (1) Coulomb's law, which describes the interactions between charged particles; (2) shielding, which describes how one electron can shield another electron from the full charge of the nucleus; and (3) penetration, which describes how one atomic orbital can overlap spatially with another, thus penetrating into a region that is close to the nucleus (and therefore less shielded from nuclear charge). We then discuss how these concepts, together with the spatial distributions of electron probability for each orbital, result in the energy ordering that we just saw.

## Coulomb's Law

The attractions and repulsions between charged particles, first introduced in Section 2.4, are described by **Coulomb's law**, which states that the potential energy ( $E$ ) of two charged particles depends on their charges ( $q_1$  and  $q_2$ ) and on their separation ( $r$ ):

$$E = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r} \quad [9.1]$$

In this equation,  $\epsilon_0$  is a constant ( $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{J} \cdot \text{m}$ ). The potential energy is positive for charges of the same sign (plus  $\times$  plus, or minus  $\times$  minus) and negative for charges of opposite sign (plus  $\times$  minus, or minus  $\times$  plus). The *magnitude* of the potential energy depends inversely on the separation between the charged particles. We can draw three important conclusions from Coulomb's law:

- For like charges, the potential energy ( $E$ ) is positive and decreases as the particles get *farther apart* (as  $r$  increases). Since systems tend toward lower potential energy, like charges repel each other (in much the same way that like poles of two magnets repel each other).
- For opposite charges, the potential energy is negative and becomes more negative as the particles get *closer together* (as  $r$  decreases). Therefore, opposite charges (like opposite poles on a magnet) *attract each other*.
- The *magnitude* of the interaction between charged particles increases as the charges of the particles increase. Consequently, an electron with a charge of 1– is more strongly attracted to a nucleus with a charge of 2+ than it is to a nucleus with a charge of 1+.

ANSWER NOW!



## 9.1 Cc

Conceptual Connection

**COULOMB'S LAW** According to Coulomb's law, what happens to the potential energy of two oppositely charged particles as they get closer together?

- (a) Their potential energy decreases.
- (b) Their potential energy increases.
- (c) Their potential energy does not change.

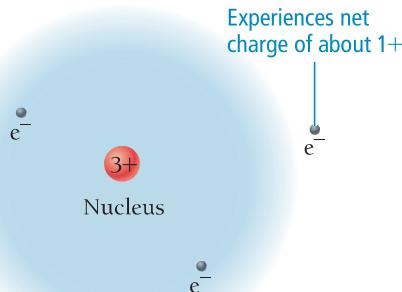
## Shielding

In multielectron atoms, any one electron experiences both the positive charge of the nucleus (which is attractive) and the negative charges of the other electrons (which are repulsive). We can think of the repulsion of one electron by other electrons as *screening* or **shielding** that electron from the full effects of the nuclear charge. For example, consider a lithium ion ( $\text{Li}^+$ ). The lithium ion contains two electrons, so its electron configuration is identical to that of helium:



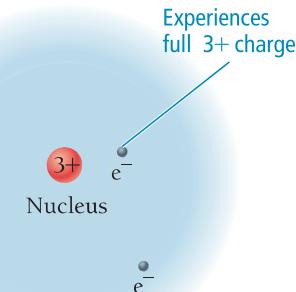
Imagine bringing a third electron toward the lithium ion. When the third electron is far from the nucleus, it experiences the  $3+$  charge of the nucleus through the *screen* or *shield* of the  $2-$  charge of the two  $1s$  electrons, as shown in Figure 9.2(a)▼. We can think of the third electron as experiencing an **effective nuclear charge ( $Z_{\text{eff}}$ )** of approximately  $1+$  ( $3+$  from the nucleus and  $2-$  from the electrons, for a net charge of  $1+$ ). The inner electrons in effect *shield* the outer electron from the full nuclear charge.

### Shielding



(a)

### Penetration



(b)

▲ **FIGURE 9.2 Shielding and Penetration** (a) An electron far from the nucleus is partly shielded by the electrons in the  $1s$  orbital, reducing the effective net nuclear charge that it experiences. (b) An electron that penetrates the electron cloud of the  $1s$  orbital experiences more of the nuclear charge.

## Penetration

The probability of an electron penetrating into the region occupied by inner electrons is described by its radial distribution function (which reflects the wave nature of the electron).

Now imagine allowing this third electron to come closer to the nucleus. As the third electron *penetrates* the electron cloud of the  $1s$  electrons, it begins to experience the  $3+$  charge of the nucleus more fully because it is less shielded by the intervening electrons. If the electron could somehow get closer to the nucleus than the  $1s$  electrons, it would experience the full  $3+$  charge, as shown in Figure 9.2(b)▲. In other words, as the outer electron undergoes **penetration** into the region occupied by the inner electrons, it experiences a greater nuclear charge and therefore (according to Coulomb's law) a lower energy.

## Electron Spatial Distributions and Sublevel Splitting

We now have examined the concepts we need to understand the energy splitting of the sublevels within a principal level. The splitting is a result of the spatial distributions of electrons within a sublevel. Recall from Section 8.6 that the radial distribution function

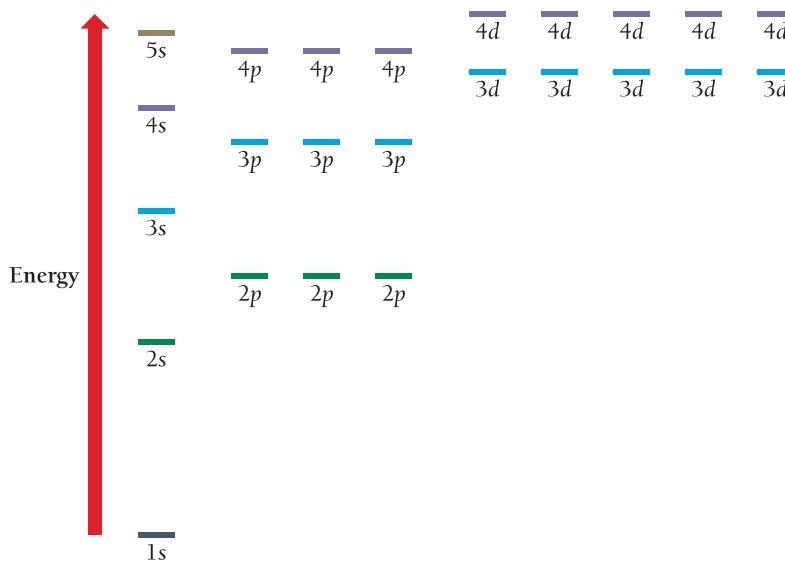
for an atomic orbital shows the total probability of finding the electron within a thin spherical shell at a distance  $r$  from the nucleus.

Figure 9.3► shows the radial distribution functions of the 2s and 2p orbitals superimposed on one another (the radial distribution function of the 1s orbital is also shown). Notice that, in general, an electron in a 2p orbital has a greater probability of being found closer to the nucleus than an electron in a 2s orbital. We might initially expect, therefore, that the 2p orbital would be lower in energy. However, exactly the opposite is true—the 2s orbital is actually lower in energy, *but only when the 1s orbital is occupied*. (When the 1s orbital is empty, the 2s and 2p orbitals are degenerate.) Why? The reason is the bump near  $r = 0$  (near the nucleus) for the 2s orbital. This bump represents a significant probability of the electron being found very close to the nucleus. Even more importantly, this area of the probability penetrates into the 1s orbital—it gets into the region where shielding by the 1s electrons is less effective. In contrast, most of the probability in the radial distribution function of the 2p orbital lies *outside* the radial distribution function of the 1s orbital. Consequently, almost all of the 2p orbital is shielded from nuclear charge by the 1s orbital. The end result is that the 2s orbital—since it experiences more of the nuclear charge due to its greater *penetration*—is lower in energy than the 2p orbital. The results are similar when we compare the 3s, 3p, and 3d orbitals. The s orbitals penetrate more fully than the p orbitals, which in turn penetrate more fully than the d orbitals, as shown in Figure 9.4►.

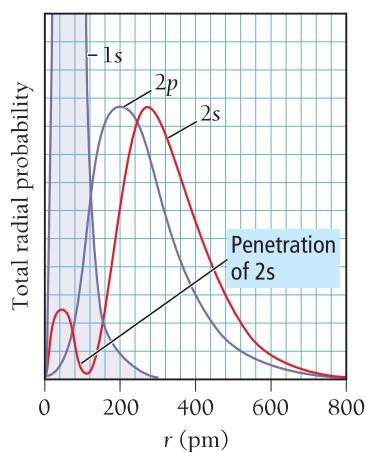
Figure 9.5▼ shows the energy ordering of a number of orbitals in multielectron atoms. Notice these features of Figure 9.5:

- Because of penetration, the sublevels of each principal level are *not* degenerate for multielectron atoms.
- In the fourth and fifth principal levels, the effects of penetration become so important that the 4s orbital lies lower in energy than the 3d orbitals and the 5s orbital lies lower in energy than the 4d orbitals.
- The energy separations between one set of orbitals and the next become smaller for 4s orbitals and beyond, and the relative energy ordering of these orbitals can actually vary among elements. These variations result in irregularities in the electron configurations of the transition metals and their ions (as we shall see later).

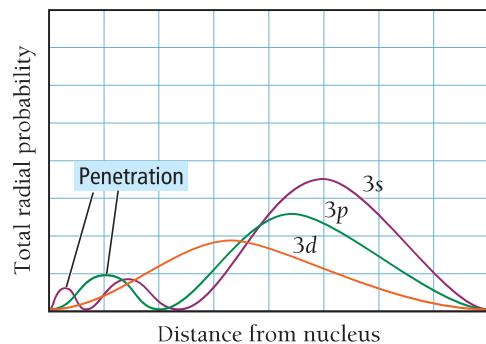
### General Energy Ordering of Orbitals for Multielectron Atoms



▲ FIGURE 9.5 General Energy Ordering of Orbitals for Multielectron Atoms



▲ FIGURE 9.3 Radial Distribution Functions for the 1s, 2s, and 2p Orbitals



▲ FIGURE 9.4 Radial Distribution Functions for the 3s, 3p, 3d Orbitals The 3s electrons penetrate most deeply into the inner orbitals, are least shielded, and experience the "greatest" effective nuclear charge. The 3d electrons penetrate least. This accounts for the energy ordering of the sublevels:  $s < p < d$ .

ANSWER NOW!



## 9.2 Cc

Conceptual Connection

### PENETRATION AND SHIELDING

Which statement is true?

- (a) An orbital that penetrates into the region occupied by core electrons is more shielded from nuclear charge than an orbital that does not penetrate and therefore has a higher energy.
- (b) An orbital that penetrates into the region occupied by core electrons is less shielded from nuclear charge than an orbital that does not penetrate and therefore has a higher energy.
- (c) An orbital that penetrates into the region occupied by core electrons is less shielded from nuclear charge than an orbital that does not penetrate and therefore has a lower energy.
- (d) An orbital that penetrates into the region occupied by core electrons is more shielded from nuclear charge than an orbital that does not penetrate and therefore has a lower energy.

### Electron Configurations for Multielectron Atoms

Unless otherwise specified, we use the term *electron configuration* to mean the ground state (or lowest energy) configuration.

Remember that the number of electrons in a neutral atom is equal to its atomic number.

Electrons with parallel spins have correlated motion that minimizes their mutual repulsion.

Now that we know the energy ordering of orbitals in multielectron atoms, we can determine ground state electron configurations for the rest of the elements. Since we know that electrons occupy the lowest energy orbitals available when the atom is in its ground state and that only two electrons (with opposing spins) are allowed in each orbital, we can systematically build up the electron configurations for the elements. This pattern of orbital filling is known as the **aufbau principle** (the German word *aufbau* means “build up”). For lithium, with three electrons, the electron configuration and orbital diagram are:

Electron configuration	Orbital diagram
Li $1s^2 2s^1$	

For carbon, which has six electrons, the electron configuration and orbital diagram are:

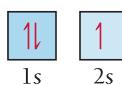
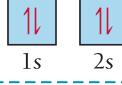
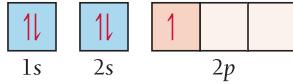
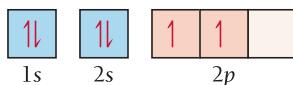
Electron configuration	Orbital diagram
C $1s^2 2s^2 2p^2$	

Notice that the  $2p$  electrons occupy the  $p$  orbitals (of equal energy) singly, rather than pairing in one orbital. This way of filling orbitals is known as **Hund's rule**, which states that *when filling degenerate orbitals, electrons fill them singly first, with parallel spins*. Hund's rule is a result of an atom's tendency to find the lowest energy state possible. When two electrons occupy separate orbitals of equal energy, the repulsive interaction between them is lower than when they occupy the same orbital because the electrons are spread out over different regions of space. By convention, we denote these parallel spins with half-arrows pointing up.

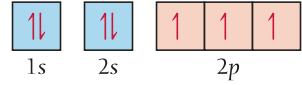
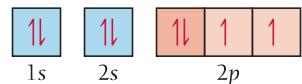
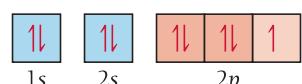
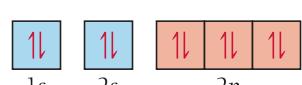
#### Summarizing Orbital Filling

- Electrons occupy orbitals so as to minimize the energy of the atom; therefore, lower energy orbitals fill before higher energy orbitals. Orbitals fill in the following order:  $1s\ 2s\ 2p\ 3s\ 3p\ 4s\ 3d\ 4p\ 5s\ 4d\ 5p\ 6s$ .
- Orbitals can hold no more than two electrons each. When two electrons occupy the same orbital, their spins are opposite. This is another way of expressing the Pauli exclusion principle (no two electrons in one atom can have the same four quantum numbers).
- When orbitals of identical energy are available, electrons first occupy these orbitals singly with parallel spins rather than in pairs. Once the orbitals of equal energy are half full, the electrons start to pair (Hund's rule).

Consider the electron configurations and orbital diagrams for elements with atomic numbers 3–10:

Symbol	Number of electrons	Electron configuration	Orbital diagram
Li	3	$1s^2 2s^1$	
Be	4	$1s^2 2s^2$	
B	5	$1s^2 2s^2 2p^1$	
C	6	$1s^2 2s^2 2p^2$	

Notice that, as a result of Hund's rule, the  $p$  orbitals fill with single electrons before the electrons pair:

N	7	$1s^2 2s^2 2p^3$	
O	8	$1s^2 2s^2 2p^4$	
F	9	$1s^2 2s^2 2p^5$	
Ne	10	$1s^2 2s^2 2p^6$	

The electron configuration of neon represents the complete filling of the  $n = 2$  principal level. When writing electron configurations for elements beyond neon, or beyond any other noble gas, we can abbreviate the electron configuration of the previous noble gas—sometimes called the *inner electron configuration*—by the symbol for the noble gas in square brackets. For example, the electron configuration of sodium is:



We can write this configuration more compactly by using [Ne] to represent the inner electrons:



[Ne] represents  $1s^2 2s^2 2p^6$ , the electron configuration for neon.

## How to Write an Electron Configuration for an Element

- Locate the element on the periodic table and determine its atomic number (this number equals the number of electrons).
- Use the order of filling (Figure 9.5) to distribute the electrons in the appropriate orbitals. Remember that each orbital can hold a maximum of two electrons. Consequently,
  - the  $s$  sublevel has only one orbital and can therefore hold only 2 electrons.
  - the  $p$  sublevel has three orbitals and can hold 6 electrons.
  - the  $d$  sublevel has five orbitals and can hold 10 electrons.
  - the  $f$  sublevel has seven orbitals and can hold 14 electrons.

**EXAMPLE 9.1** Electron Configurations

Write electron configurations for each element.

- (a) Mg      (b) P      (c) Br      (d) Al

**SOLUTION**

- (a) Mg

Magnesium has 12 electrons. Distribute 2 of these into the 1s orbital, 2 into the 2s orbital, 6 into the 2p orbitals, and 2 into the 3s orbital.

$$\text{Mg} \quad 1s^2 2s^2 2p^6 3s^2 \text{ or } [\text{Ne}] 3s^2$$

- (b) P

Phosphorus has 15 electrons. Distribute 2 of these into the 1s orbital, 2 into the 2s orbital, 6 into the 2p orbitals, 2 into the 3s orbital, and 3 into the 3p orbitals.

$$\text{P} \quad 1s^2 2s^2 2p^6 3s^2 3p^3 \text{ or } [\text{Ne}] 3s^2 3p^3$$

- (c) Br

Bromine has 35 electrons. Distribute 2 of these into the 1s orbital, 2 into the 2s orbital, 6 into the 2p orbitals, 2 into the 3s orbital, 6 into the 3p orbitals, 2 into the 4s orbital, 10 into the 3d orbitals, and 5 into the 4p orbitals.

$$\text{Br} \quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5 \text{ or } [\text{Ar}] 4s^2 3d^{10} 4p^5$$

- (d) Al

Aluminum has 13 electrons. Distribute 2 of these into the 1s orbital, 2 into the 2s orbital, 6 into the 2p orbitals, 2 into the 3s orbital, and 1 into the 3p orbital.

$$\text{Al} \quad 1s^2 2s^2 2p^6 3s^2 3p^1 \text{ or } [\text{Ne}] 3s^2 3p^1$$

**FOR PRACTICE 9.1** Write electron configurations for each element.

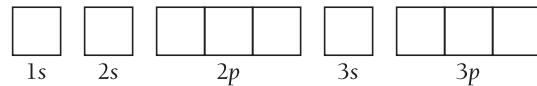
- (a) Cl      (b) Si      (c) Sr      (d) O

**WATCH NOW!****INTERACTIVE WORKED EXAMPLE 9.2****EXAMPLE 9.2** Writing Orbital Diagrams

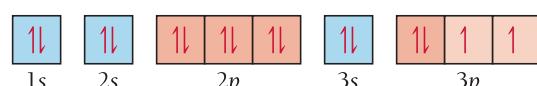
Write the orbital diagram for sulfur and determine the number of unpaired electrons.

**SOLUTION**

Sulfur's atomic number is 16; it therefore has 16 electrons, and the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^4$ . Draw a box for each orbital, putting the lowest energy orbital (1s) on the far left and proceeding to orbitals of higher energy to the right.



Distribute the 16 electrons into the boxes representing the orbitals, allowing a maximum of two electrons per orbital and remembering Hund's rule. You can see from the diagram that sulfur has two unpaired electrons.



Two unpaired electrons

**FOR PRACTICE 9.2** Write the orbital diagram for Ar and determine the number of unpaired electrons.

**ANSWER NOW!****ELECTRON CONFIGURATIONS AND QUANTUM NUMBERS**

What are the four quantum numbers for each of the two electrons in a 4s orbital?

- |   |   |
|---|---|
| <p>(a) <math>n = 4, l = 0, m_l = 0, m_s = +\frac{1}{2}</math></p> <p>(b) <math>n = 4, l = 0, m_l = 0, m_s = -\frac{1}{2}</math></p> <p>(c) <math>n = 3, l = 0, m_l = 0, m_s = +\frac{1}{2}</math></p> <p>(d) <math>n = 4, l = 1, m_l = 0, m_s = +\frac{1}{2}</math></p> | <p><math>n = 4, l = 0, m_l = 0, m_s = +\frac{1}{2}</math></p> <p><math>n = 4, l = 0, m_l = 0, m_s = -\frac{1}{2}</math></p> <p><math>n = 3, l = 0, m_l = 0, m_s = -\frac{1}{2}</math></p> <p><math>n = 4, l = 1, m_l = 0, m_s = -\frac{1}{2}</math></p> |
|---|---|

## 9.4

## Electron Configurations, Valence Electrons, and the Periodic Table

Recall that Mendeleev arranged the periodic table so that elements with similar chemical properties lie in the same column. We can begin to make the connection between an element's properties and its electron configuration by superimposing the electron configurations of the first 18 elements onto a partial periodic table, as shown in Figure 9.6►. As we move to the right across a row, the orbitals fill in the correct order. With each subsequent row, the highest principal quantum number increases by one. Notice that as we move down a column, *the number of electrons in the outermost principal energy level (highest n value) remains the same*. The key connection between the macroscopic world (an element's chemical properties) and the atomic world (an atom's electronic structure) lies in these outermost electrons.

An atom's **valence electrons** are those that are important in chemical bonding. *For main-group elements, the valence electrons are those in the outermost principal energy level.* For transition elements, we also count the outermost *d* electrons among the valence electrons (even though they are not in an outermost principal energy level). The chemical properties of an element depend on its valence electrons, which are instrumental in bonding because they are held most loosely (and are therefore the easiest to lose or share). We can now see why the elements in a column of the periodic table have similar chemical properties: *they have the same number of valence electrons.*

We distinguish between valence electrons and all the other electrons in an atom, which are called **core electrons**. For example, silicon, with the electron configuration  $1s^22s^22p^63s^23p^2$ , has four valence electrons (those in the  $n = 3$  principal level) and ten core electrons as shown in the margin.

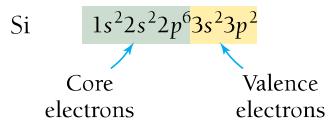
### WATCH NOW!

**KEY CONCEPT VIDEO 9.4**  
Writing an Electron Configuration based on an Element's Position on the Periodic Table

### Outer Electron Configurations of Elements 1–18

1A								8A
1 H $1s^1$	2A	3A	4A	5A	6A	7A		2 He $1s^2$
3 Li $2s^1$	4 Be $2s^2$	5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$		10 Ne $2s^22p^6$
11 Na $3s^1$	12 Mg $3s^2$	13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$		18 Ar $3s^23p^6$

▲FIGURE 9.6 Outer Electron Configurations of the First 18 Elements in the Periodic Table



### EXAMPLE 9.3 Valence Electrons and Core Electrons

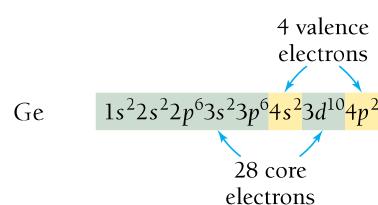
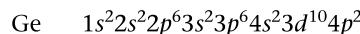
Write the electron configuration for Ge. Identify the valence electrons and the core electrons.

#### SOLUTION

Determine the total number of electrons from germanium's atomic number (32). Distribute the electrons into the appropriate orbitals according to the information in *Summarizing Orbital Filling* on p. 358.

Since germanium is a main-group element, its valence electrons are those in the outermost principal energy level. For germanium the  $n = 4$  principal level is outermost. Consequently, the  $n = 4$  electrons are valence electrons and the rest are core electrons.

*Note:* In this book, we write electron configurations with the orbitals in the order of filling. However, electron configurations are sometimes written in order of increasing principal quantum number. The electron configuration of germanium written in order of increasing principal quantum number is Ge  $1s^22s^22p^63s^23p^63d^{10}4s^24p^2$ .



**FOR PRACTICE 9.3** Write the electron configuration for phosphorus. Identify the valence electrons and core electrons.

## Orbital Blocks in the Periodic Table

A pattern similar to what we just saw for the first 18 elements exists for the entire periodic table, as shown in Figure 9.7▼. Note that because of the filling order of orbitals, we can divide the periodic table into blocks representing the filling of particular sublevels.

- s block** The first two columns on the left side of the periodic table comprise the *s* block, with outer electron configurations of  $ns^1$  (the alkali metals) and  $ns^2$  (the alkaline earth metals).
- p block** The six columns on the right side of the periodic table comprise the *p* block, with outer electron configurations of  $ns^2np^1$ ,  $ns^2np^2$ ,  $ns^2np^3$ ,  $ns^2np^4$ ,  $ns^2np^5$  (halogens), and  $ns^2np^6$  (noble gases).
- d block** The transition elements comprise the *d* block.
- f block** The lanthanides and actinides (also called the inner transition elements) comprise the *f* block. (For compactness, the *f* block is normally printed below the *d* block instead of being embedded within it.)

You can see that *the number of columns in a block corresponds to the maximum number of electrons that can occupy the particular sublevel of that block*. The *s* block has two columns (corresponding to one *s* orbital holding a maximum of two electrons); the *p* block has six columns (corresponding to three *p* orbitals with two electrons each); the *d* block has 10 columns (corresponding to five *d* orbitals with two electrons each); and the *f* block has 14 columns (corresponding to seven *f* orbitals with two electrons each).

Notice also that, except for helium, *the number of valence electrons in any main-group element is equal to its lettered group number*. For example, we know that chlorine has seven valence electrons because it is in group 7A.

Lastly, note that, for main-group elements, *the row number in the periodic table is equal to the number (or n value) of the highest occupied principal level*. For example, because chlorine is in row 3, its highest principal level is the  $n = 3$  level.

Helium is an exception. Even though it lies in the column with an outer electron configuration of  $ns^2np^6$ , its electron configuration is simply  $1s^2$ .

▼ FIGURE 9.7 The *s*, *p*, *d*, and *f* Blocks of the Periodic Table

### Orbital Blocks of the Periodic Table

The following table illustrates the orbital blocks of the periodic table, showing the arrangement of elements based on their electron configurations and the filling of atomic orbitals.

Groups		Periods																																			
1	1A																																				
1	H $1s^1$	2	2A																																		
2	Li $2s^1$	4	Be $2s^2$																																		
3	Na $3s^1$	12	Mg $3s^2$	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	He $1s^2$																		
4	K $4s^1$	20	Ca $4s^2$	21	Sc $4s^23d^1$	22	Ti $4s^23d^2$	23	V $4s^23d^3$	24	Cr $4s^23d^5$	25	Mn $4s^23d^6$	26	Fe $4s^23d^7$	27	Co $4s^23d^8$	28	Ni $4s^23d^10$	29	Cu $4s^23d^{10}$	30	Zn $4s^24p^1$	31	Ga $4s^24p^2$	32	Ge $4s^24p^3$	33	As $4s^24p^4$	34	Se $4s^24p^5$	35	Br $4s^24p^6$				
5	Rb $5s^1$	38	Sr $5s^2$	39	Y $5s^24d^1$	40	Zr $5s^24d^2$	41	Nb $5s^14d^4$	42	Mo $5s^14d^5$	43	Tc $5s^24d^5$	44	Ru $5s^14d^7$	45	Rh $5s^14d^8$	46	Pd $4d^{10}$	47	Ag $5s^14d^{10}$	48	Cd $5s^25p^1$	49	In $5s^25p^2$	50	Sn $5s^25p^3$	51	Sb $5s^25p^4$	52	Te $5s^25p^5$	53	I $5s^25p^6$	54	Xe		
6	Cs $6s^1$	55	Cs $6s^2$	56	Ba $6s^25d^1$	57	La $6s^25d^2$	72	Hf $6s^25d^3$	73	Ta $6s^25d^4$	74	W $6s^25d^5$	75	Re $6s^25d^6$	76	Os $6s^25d^7$	77	Ir $6s^25d^8$	78	Pt $6s^25d^9$	79	Au $6s^25d^{10}$	80	Hg $6s^26p^1$	81	Tl $6s^26p^2$	82	Pb $6s^26p^3$	83	Bi $6s^26p^4$	84	Po $6s^26p^5$	85	At $6s^26p^6$	86	Rn
7	Fr $7s^1$	87	Ra $7s^2$	88	Ac $7s^26d^1$	89	Rf $7s^26d^2$	104	Db $7s^26d^3$	105	Sg $7s^26d^4$	106	Bh $7s^26d^5$	107	Hs $7s^26d^6$	108	Mt $7s^26d^7$	109	Ds $7s^26d^8$	110	Rg $7s^26d^9$	111	Cn $7s^26d^{10}$	112	Nh $7s^25f^1$	113	Fl $7s^25f^2$	114	Mc $7s^25f^3$	115	Lv $7s^25f^4$	116	Ts $7s^25f^5$	117	Og $7s^25f^6$	118	Og

Lanthanides	Ce $6s^24f^15d^1$	Pr $6s^24f^3$	Nd $6s^24f^4$	Pm $6s^24f^5$	Sm $6s^24f^6$	Eu $6s^24f^7$	Gd $6s^24f^75d^1$	Tb $6s^24f^9$	Dy $6s^24f^{10}$	Ho $6s^24f^{11}$	Er $6s^24f^{12}$	Tm $6s^24f^{13}$	Yb $6s^24f^{14}$	Lu $6s^24f^{14}5d^1$
Actinides	Th $7s^26d^2$	Pa $7s^25f^26d^1$	U $7s^25f^16d^1$	Np $7s^25f^46d^1$	Pu $7s^25f^6$	Am $7s^25f^7$	Cm $7s^25f^76d^1$	Bk $7s^25f^9$	Cf $7s^25f^{10}$	Es $7s^25f^{11}$	Fm $7s^25f^{12}$	Md $7s^25f^{13}$	No $7s^25f^{14}$	Lr $7s^25f^{14}6d^1$

Recall from Chapter 2 that main-group elements are those in the two far left columns (groups 1A, 2A) and the six far right columns (groups 3A–8A) of the periodic table.

### Summarizing Periodic Table Organization

- The periodic table is divisible into four blocks corresponding to the filling of the four quantum sublevels (*s*, *p*, *d*, and *f*).
- The lettered group number of a main-group element is equal to the number of valence electrons in that element.
- The row number of a main-group element is equal to the highest principal quantum number of that element.

**VALENCE ELECTRONS AND GROUP NUMBER** Without writing an electron configuration, determine the number of valence electrons in nitrogen.

- (a) 3      (b) 4      (c) 5      (d) 6



ANSWER NOW!



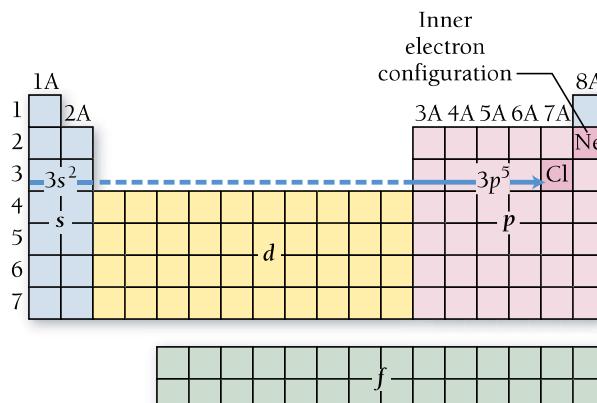
## Writing an Electron Configuration for an Element from Its Position in the Periodic Table

The organization of the periodic table allows us to write the electron configuration for an element based on its position in the periodic table.

### How to Write an Electron Configuration for an Element from Its Position in the Periodic Table

1. Locate the element on the periodic table.
2. Locate the noble gas that precedes the element.
3. Represent the inner electron configuration by writing the symbol of the noble gas in brackets.
4. Determine the outer electron configuration by tracing the elements between the noble gas and the element of interest; assign electrons to the appropriate orbitals as you trace across the blocks on the periodic table.

For example, suppose we want to write an electron configuration for Cl. The *inner electron configuration* of Cl is that of the noble gas that precedes it in the periodic table, Ne. So we can represent the inner electron configuration with [Ne]. We can determine the *outer electron configuration*—the configuration of the electrons beyond the previous noble gas—by tracing the elements between Ne and Cl and assigning electrons to the appropriate orbitals, as shown here. Remember that the highest *n* value is indicated by the row number (in this case, 3 for chlorine).



We begin with [Ne], then add in the two 3s electrons as we trace across the *s* block, followed by five 3*p* electrons as we trace across the *p* block to Cl, which is in the fifth column of the *p* block. The electron configuration is:



Notice that Cl is in column 7A and therefore has seven valence electrons and an outer electron configuration of  $ns^2np^5$ .

### WATCH NOW!

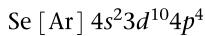
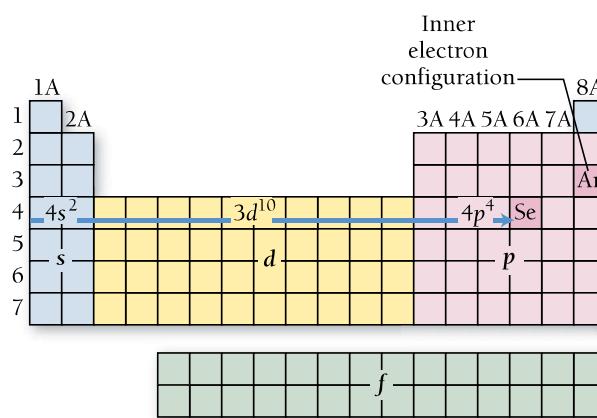
### INTERACTIVE WORKED EXAMPLE 9.4

## EXAMPLE 9.4 Writing Electron Configurations from the Periodic Table

Refer to the periodic table to write the electron configuration for selenium (Se).

### SOLUTION

The atomic number of Se is 34. The noble gas that precedes Se in the periodic table is argon, so the inner electron configuration is [Ar]. Obtain the outer electron configuration by tracing the elements between Ar and Se and assigning electrons to the appropriate orbitals. Begin with [Ar]. Because Se is in row 4, add two 4s electrons as you trace across the *s* block ( $n = \text{row number}$ ). Next, add ten 3*d* electrons as you trace across the *d* block ( $n = \text{row number} - 1$ ). Lastly, add four 4*p* electrons as you trace across the *p* block to Se, which is in the fourth column of the *p* block ( $n = \text{row number}$ ).



**FOR PRACTICE 9.4** Refer to the periodic table to write the electron configuration of bismuth (Bi).

**FOR MORE PRACTICE 9.4** Refer to the periodic table to write the electron configuration for iodine (I).

## The Transition and Inner Transition Elements

The electron configurations of the transition elements (*d* block) and inner transition elements (*f* block) exhibit trends that differ somewhat from those of the main-group elements. As we move to the right across a row in the *d* block, the *d* orbitals fill as shown here:

21 Sc $4s^23d^1$	22 Ti $4s^23d^2$	23 V $4s^23d^3$	24 Cr $4s^13d^5$	25 Mn $4s^23d^5$	26 Fe $4s^23d^6$	27 Co $4s^23d^7$	28 Ni $4s^23d^8$	29 Cu $4s^13d^{10}$	30 Zn $4s^23d^{10}$
39 Y $5s^24d^1$	40 Zr $5s^24d^2$	41 Nb $5s^14d^4$	42 Mo $5s^14d^5$	43 Tc $5s^24d^5$	44 Ru $5s^14d^7$	45 Rh $5s^14d^8$	46 Pd $4d^{10}$	47 Ag $5s^14d^{10}$	48 Cd $5s^24d^{10}$

Notice that *the principal quantum number of the *d* orbitals that fill across each row in the transition series is equal to the row number minus one*. In the fourth row, the 3*d* orbitals fill; in the fifth row, the 4*d* orbitals fill; and so on. This happens because, as we discussed in Section 9.3, the 4s orbital is generally lower in energy than the 3*d* orbital (because it more efficiently penetrates into the region occupied by the core electrons). The result is that the 4s orbital fills before the 3*d* orbital, even though the 4s orbital's principal quantum number ( $n = 4$ ) is higher.

Keep in mind, however, that the 4s and the 3*d* orbitals are extremely close to each other in energy, so their relative energy ordering depends on the exact species

under consideration; this causes some irregular behavior in the transition metals. For example, in the first transition series of the *d* block, the outer configuration is  $4s^23d^x$  with two exceptions: Cr is  $4s^13d^5$  and Cu is  $4s^13d^{10}$ . This behavior is related to the closely spaced  $3d$  and  $4s$  energy levels and the stability associated with a half-filled (as in Cr) or completely filled (as in Cu) sublevel. Actual electron configurations are definitively determined experimentally (through spectroscopy) and do not always conform to the general pattern. Nonetheless, the patterns described here allow us to accurately predict electron configurations for most of the elements in the periodic table.

As we move across the *f* block (the inner transition series), the *f* orbitals fill. For these elements, the principal quantum number of the *f* orbitals that fill across each row is the row number *minus two*. (In the sixth row, the  $4f$  orbitals fill, and in the seventh row, the  $5f$  orbitals fill.) In addition, within the inner transition series, the close energy spacing of the  $5d$  and  $4f$  orbitals sometimes causes an electron to enter a  $5d$  orbital instead of the expected  $4f$  orbital. For example, the electron configuration of gadolinium is  $[Xe]6s^24f^75d^1$  (instead of the expected  $[Xe]6s^24f^8$ ).

## 9.5

### The Explanatory Power of the Quantum-Mechanical Model

We can now see how the quantum-mechanical model accounts for the chemical properties of the elements, such as the inertness of helium or the reactivity of hydrogen, and (more generally) how it accounts for the periodic law. *The chemical properties of elements are largely determined by the number of valence electrons they contain.* Their properties are periodic because the number of valence electrons is periodic.

Because elements within a column in the periodic table have the same number of valence electrons, they have similar chemical properties. The noble gases, for example, all have eight valence electrons, except for helium, which has two. Although we do not cover the quantitative (or numerical) aspects of the quantum-mechanical model in this book, calculations of the overall energy of the electrons within atoms with eight valence electrons (or two, in the case of helium) show that they are particularly stable. In other words, when *s* and *p* quantum sublevels are completely full, the overall energy of the electrons that occupy that level is particularly low. Therefore, those electrons *cannot* lower their energy by reacting with other atoms or molecules, so the corresponding atom is relatively unreactive or inert. The noble gases are the most chemically stable and relatively unreactive family in the periodic table.

Elements with electron configurations *close* to those of the noble gases are the most reactive because they can attain noble gas electron configurations by losing or gaining a small number of electrons. For example, alkali metals (group 1A) are among the most reactive metals because their outer electron configuration ( $ns^1$ ) is one electron beyond a noble gas configuration. They readily react to lose the  $ns^1$  electron, obtaining a noble gas configuration. This explains why—as we saw in Chapter 2—the group 1A metals tend to form  $1+$  cations. Similarly, alkaline earth metals, with an outer electron configuration of  $ns^2$ , also tend to be reactive metals, losing their  $ns^2$  electrons to form  $2+$  cations. This does not mean that forming an ion with a noble gas configuration is in itself energetically favorable. In fact, forming cations always *requires energy*. But when the cation formed has a noble gas configuration, the energy cost of forming the cation is often less than the energy payback that occurs when that cation forms ionic bonds with anions, as we shall see in Chapter 10.

On the right side of the periodic table, halogens are among the most reactive non-metals because of their  $ns^2np^5$  electron configurations. They are only one electron short of a noble gas configuration and tend to react to gain that one electron, forming  $1-$  ions. Figure 9.8►, which is similar to Figure 2.13 in Chapter 2, shows the elements that form predictable ions. The charges of these ions reflect their electron configurations—in their reactions, these elements form ions with noble gas electron configurations.

8A	1A
2 He $1s^2$	3 Li $2s^1$
10 Ne $2s^22p^6$	11 Na $3s^1$
18 Ar $3s^23p^6$	19 K $4s^1$
36 Kr $4s^24p^6$	37 Rb $5s^1$
54 Xe $5s^25p^6$	55 Cs $6s^1$
86 Rn $6s^26p^6$	87 Fr $7s^1$

Noble gases

Alkali metals

2A	7A
4 Be $2s^2$	9 F $2s^22p^5$
12 Mg $3s^2$	17 Cl $3s^23p^5$
20 Ca $4s^2$	35 Br $4s^24p^5$
38 Sr $5s^2$	53 I $5s^25p^5$
56 Ba $6s^2$	85 At $6s^26p^5$
88 Ra $7s^2$	

Halogens

Alkaline earth metals

### Elements That Form Ions with Predictable Charges

	1A	2A											3A	4A	5A	6A	7A	8A
1	Li <sup>+</sup>														N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>	
2	Na <sup>+</sup>	Mg <sup>2+</sup>	3B	4B	5B	6B	7B	8B		1B		2B	Al <sup>3+</sup>	P <sup>3-</sup>	S <sup>2-</sup>	Cl <sup>-</sup>		
3	K <sup>+</sup>	Ca <sup>2+</sup>													Se <sup>2-</sup>	Br <sup>-</sup>		
4	Rb <sup>+</sup>	Sr <sup>2+</sup>													Te <sup>2-</sup>	I <sup>-</sup>		
5	Cs <sup>+</sup>	Ba <sup>2+</sup>																

▲ FIGURE 9.8 Elements That Form Ions with Predictable Charges Notice that each ion has a noble gas electron configuration.

ANSWER NOW!



9.5

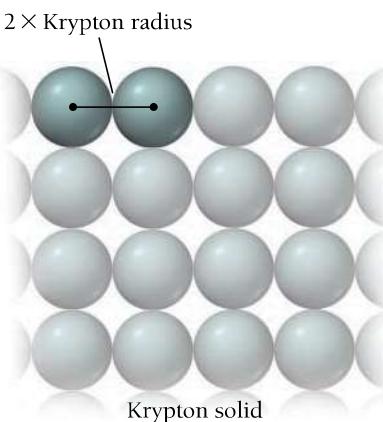
**Cc**  
Conceptual Connection

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**KEY CONCEPT VIDEO 9.6**  
Periodic Trends in the Size of Atoms and Effective Nuclear Charge

### van der Waals Radius for Krypton

The van der Waals radius of an atom is one-half the distance between adjacent nuclei in the atomic solid.



The bonding radii of some elements, such as helium and neon, must be approximated because they do not form chemical bonds or metallic crystals.

### ELECTRON CONFIGURATIONS AND ION CHARGE

A main-group element has an outer electron configuration of  $ns^2np^4$ . What charge is likely for an ion of this element?

- (a) 1-      (b) 2-      (c) 1+      (d) 2+

### 9.6 Periodic Trends in the Size of Atoms and Effective Nuclear Charge

In previous chapters, we saw that the volume of an atom is taken up primarily by its electrons (Chapter 2) occupying quantum-mechanical orbitals (Chapter 8). We also discussed how these orbitals do not have a definite boundary but represent only a statistical probability distribution for where the electron is found. So how do we define the size of an atom? One way to define atomic radii is to consider the distance between *nond bonding* atoms that are in direct contact. For example, krypton can be frozen into a solid in which the krypton atoms are touching each other but are not bonded together. The distance between the centers of adjacent krypton atoms—which we can determine from the solid’s density—is then twice the radius of a krypton atom. An atomic radius determined in this way is called the **nonbonding atomic radius** or the **van der Waals radius**. The van der Waals radius represents the radius of an atom when it is not bonded to another atom.

Another way to define the size of an atom—the **bonding atomic radius** or **covalent radius**—differs for nonmetals and metals, as follows:

Nonmetals: one-half the distance between two of the atoms bonded together

Metals: one-half the distance between two of the atoms next to each other in a crystal of the metal

For example, the distance between Br atoms in Br<sub>2</sub> is 228 pm; therefore, the Br covalent radius is one-half of 228 pm or 114 pm.

Using this method, we can assign radii to all elements in the periodic table that form chemical bonds or metallic crystals. A more general term, the **atomic radius**, refers to a set of average bonding radii determined from measurements on a large number of elements and compounds. The atomic radius represents the radius of an atom when it is bonded to another atom and is always smaller than the van der Waals radius. The approximate bond length of any two covalently bonded atoms is the sum of their atomic radii. For example, the approximate bond length for ICl is iodine’s atomic radius (133 pm) plus chlorine’s atomic radius (99 pm), a bond length of 232 pm. (The actual experimentally measured bond length in ICl is 232.07 pm.)

Figure 9.9▶ plots atomic radius as a function of atomic number for the first 57 elements in the periodic table. Notice the periodic trend in the radii. Atomic radii peak with each alkali metal. Figure 9.10▶ is a relief map of atomic radii for most of the

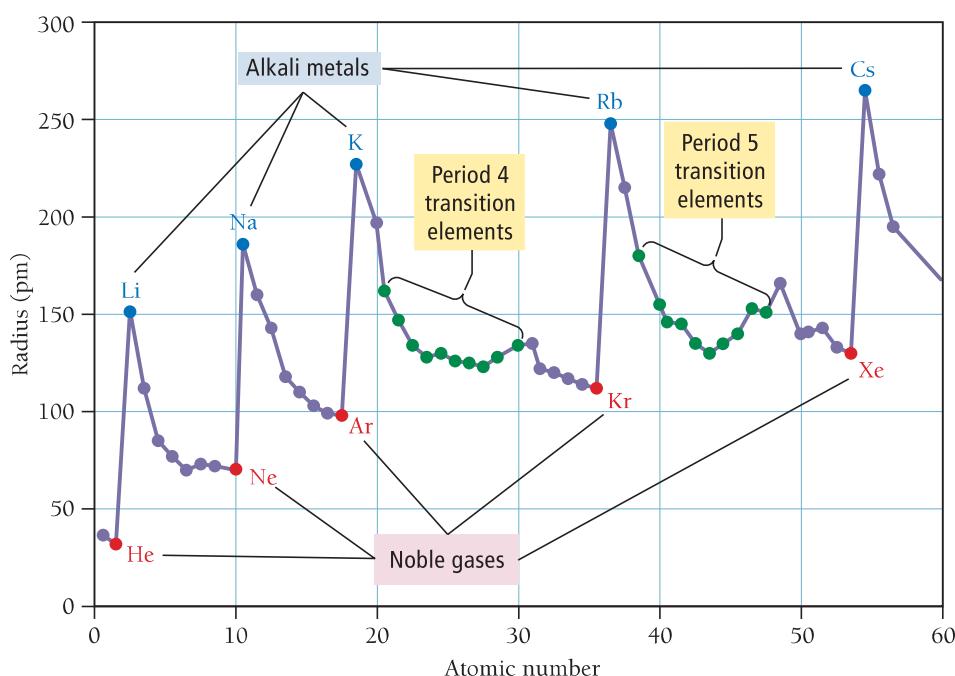
elements in the periodic table. The general trends in the atomic radii of main-group elements, which are the same as trends observed in van der Waals radii, are:

- As we move down a column (or family) in the periodic table, atomic radius increases.
- As we move to the right across a period (or row) in the periodic table, atomic radius decreases.

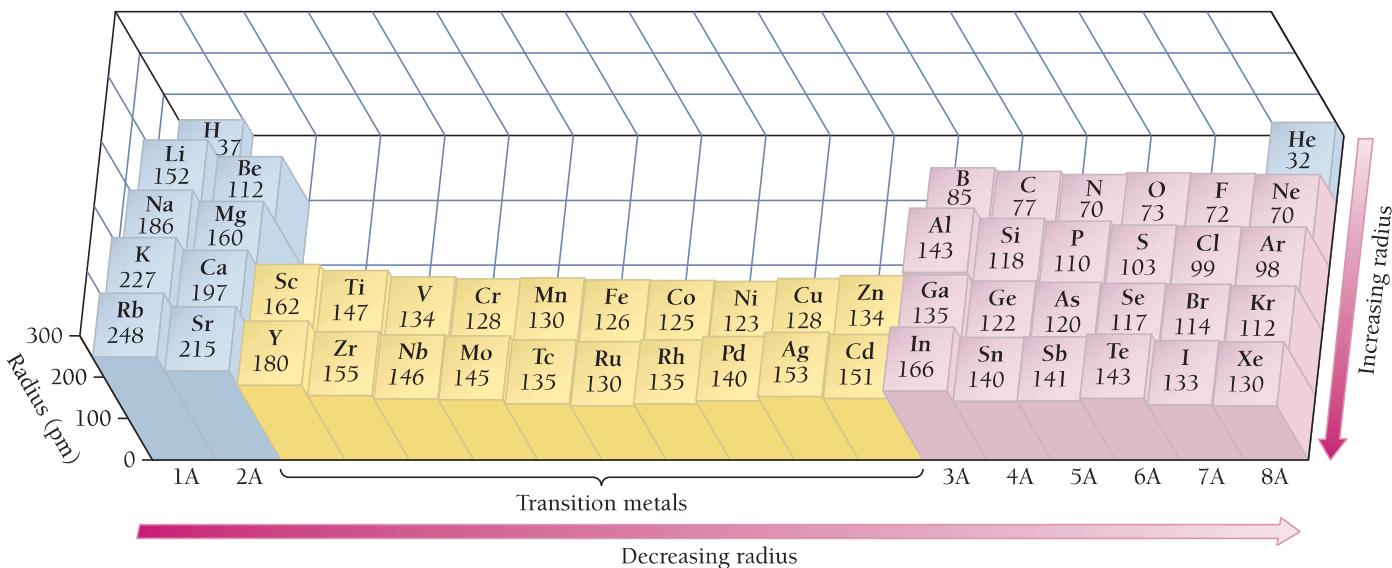
We can understand the observed trend in radii as we move down a column based on the trends in the sizes of atomic orbitals. Atomic radius is largely determined by the valence electrons, the electrons farthest from the nucleus. As we move down a column in the periodic table, the highest principal quantum number ( $n$ ) of the valence electrons increases. Consequently, the valence electrons occupy larger orbitals, resulting in larger atoms.

The observed trend in atomic radii as we move to the right across a row, however, is a bit more complex. To understand this trend, we must revisit some concepts from Section 9.3, including effective nuclear charge and shielding.

### Atomic Radii

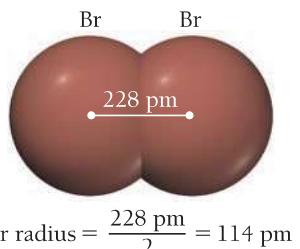


### Trends in Atomic Radius



### Covalent Radius for Bromine

The covalent radius is one-half the distance between two bonded atoms.



◀ FIGURE 9.9 Atomic Radius versus Atomic Number Notice the periodic trend in atomic radius, starting at a peak with each alkali metal and falling to a minimum with each noble gas.

▼ FIGURE 9.10 Trends in Atomic Radius In general, atomic radii increase as we move down a column and decrease as we move to the right across a period in the periodic table.

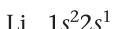
## Effective Nuclear Charge

The trend in atomic radius as we move to the right across a row in the periodic table is determined by the inward pull of the nucleus on the electrons in the outermost principal energy level (highest  $n$  value). According to Coulomb's law, the attraction between a nucleus and an electron increases with increasing magnitude of nuclear charge. For example, compare the H atom to the  $\text{He}^+$  ion:



It takes 1312 kJ/mol of energy to remove the  $1s$  electron from hydrogen but 5251 kJ/mol of energy to remove it from  $\text{He}^+$ . Why? Although each electron is in a  $1s$  orbital, the electron in the helium ion is attracted to the nucleus by a  $2+$  charge, while the electron in the hydrogen atom is attracted to the nucleus by only a  $1+$  charge. Therefore, the electron in the helium ion is held more tightly (it has lower potential energy according to Coulomb's law), making it more difficult to remove and making the helium ion smaller than the hydrogen atom.

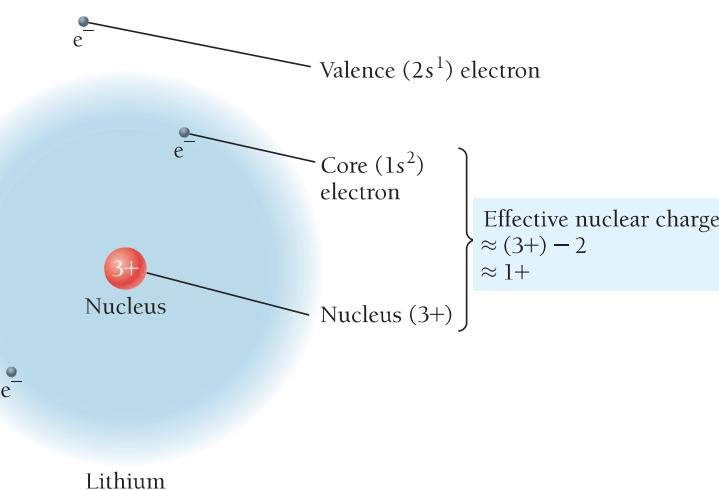
As we saw in Section 9.3, any one electron in a multielectron atom experiences both the positive charge of the nucleus (which is attractive) and the negative charges of the other electrons (which are repulsive). Consider again the outermost electron in the lithium atom:



Even though the  $2s$  orbital penetrates into the  $1s$  orbital to some degree, the majority of the  $2s$  orbital is outside of the  $1s$  orbital. Therefore, the electron in the  $2s$  orbital is partially *screened* or *shielded* from the  $3+$  charge of the nucleus by the  $2-$  charge of the  $1s$  (core) electrons. This reduces the net charge experienced by the  $2s$  electron, as shown in Figure 9.11▼.

**► FIGURE 9.11** Shielding and Effective Nuclear Charge The valence electron in lithium experiences the  $3+$  charge of the nucleus through the screen of the  $2-$  charge of the core electrons. The effective nuclear charge acting on the valence electron is approximately  $1+$ .

### Shielding and Effective Nuclear Charge



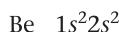
As we have seen, we can define the average or net charge experienced by an electron as the *effective nuclear charge*. The effective nuclear charge experienced by a particular electron in an atom is the *actual nuclear charge* ( $Z$ ) minus the *charge shielded by other electrons* ( $S$ ):

$$Z_{\text{eff}} = Z - S$$

Effective nuclear charge      Actual nuclear charge      Charge screened by other electrons

For lithium, we estimate that the two core electrons shield the valence electron from the nuclear charge with high efficiency ( $s$  is nearly 2). The effective nuclear charge experienced by lithium's valence electron is therefore slightly greater than  $1+$ .

Now consider the valence electrons in beryllium (Be), with atomic number 4. Its electron configuration is:



To estimate the effective nuclear charge experienced by the  $2s$  electrons in beryllium, we must distinguish between two different types of shielding: (1) the shielding of the outermost electrons by the core electrons and (2) the shielding of the outermost electrons by *each other*. The key to understanding the trend in atomic radius is the difference between these two types of shielding:

**Core electrons efficiently shield electrons in the outermost principal energy level from nuclear charge, but outermost electrons do not efficiently shield one another from nuclear charge.**

For example, the two outermost electrons in beryllium experience the  $4+$  charge of the nucleus through the shield of the two  $1s$  core electrons without shielding each other from that charge very much. We estimate that the shielding ( $S$ ) experienced by any one of the outermost electrons due to the core electrons is nearly 2, but that the shielding due to the other outermost electron is nearly 0. The effective nuclear charge experienced by beryllium's outermost electrons is therefore slightly greater than  $2+$ .

The effective nuclear charge experienced by *beryllium*'s outermost electrons is greater than that experienced by *lithium*'s outermost electron. Consequently, beryllium's outermost electrons are held more tightly than lithium's, resulting in a smaller atomic radius for beryllium. The effective nuclear charge experienced by an atom's outermost electrons continues to become more positive as we move to the right across the rest of the second row in the periodic table, resulting in successively smaller atomic radii. The same trend is generally observed in all main-group elements.

#### Summarizing Atomic Radii for Main-Group Elements

- As we move down a column in the periodic table, the principal quantum number ( $n$ ) of the electrons in the outermost principal energy level increases, resulting in larger orbitals and therefore larger atomic radii.
- As we move to the right across a row in the periodic table, the effective nuclear charge ( $Z_{\text{eff}}$ ) experienced by the electrons in the outermost principal energy level increases, resulting in a stronger attraction between the outermost electrons and the nucleus, and smaller atomic radii.

**EFFECTIVE NUCLEAR CHARGE** Which electrons experience the greatest effective nuclear charge?

- the valence electrons in Mg
- the valence electrons in Al
- the valence electrons in S



ANSWER NOW!



## Atomic Radii and the Transition Elements

In Figure 9.10, we can see that as we move down the first two rows of a column within the transition metals, the elements follow the same general trend in atomic radii as the main-group elements (the radii get larger). However, with the exception of the first couple of elements in each transition series, the atomic radii of the transition elements *do not* follow the same trend as the main-group elements as we move to the right across a row. Instead of decreasing in size, *the radii of transition elements stay roughly constant across each row*. Why? The difference is that, across a row of transition elements, the number of electrons in the outermost principal energy level (highest  $n$  value) is nearly constant (recall from Section 9.3, for example, that the  $4s$  orbital fills before the  $3d$ ). As another

proton is added to the nucleus of each successive element, another electron is added as well, but the electron goes into an  $n_{\text{highest}} - 1$  orbital. The number of outermost electrons stays constant, and they experience a roughly constant effective nuclear charge, keeping the radius approximately constant.

## WATCH NOW!

## INTERACTIVE WORKED EXAMPLE 9.5

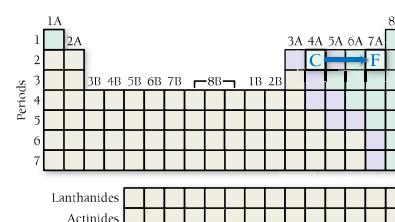
**EXAMPLE 9.5** Atomic Size

On the basis of periodic trends, choose the larger atom in each pair (if possible). Explain your choices.

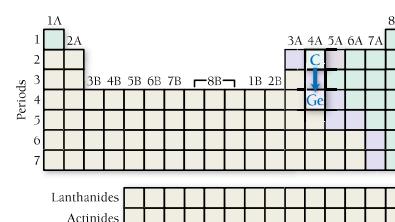
- (a) C or F
- (b) C or Ge
- (c) N or Al
- (d) Al or Ge

**SOLUTION**

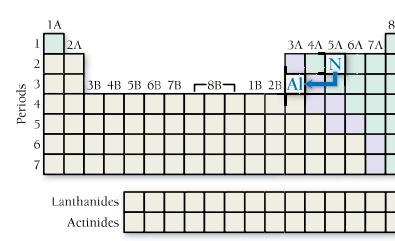
- (a) C atoms are larger than F atoms because as you trace the path between C and F on the periodic table, you move to the right within the same period. As you move to the right across a period, the effective nuclear charge experienced by the outermost electrons increases, resulting in a smaller radius.



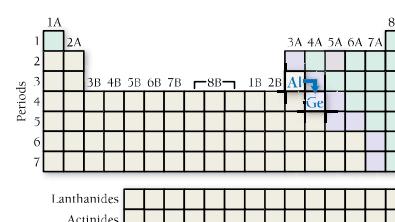
- (b) Ge atoms are larger than C atoms because as you trace the path between C and Ge on the periodic table, you move down a column. Atomic size increases as you move down a column because the outermost electrons occupy orbitals with a higher principal quantum number that are therefore larger, resulting in a larger atom.



- (c) Al atoms are larger than N atoms because as you trace the path between N and Al on the periodic table, you move down a column (atomic size increases) and then to the left across a period (atomic size increases). These effects add together for an overall increase.



- (d) Based on periodic trends alone, you cannot tell which atom is larger because as you trace the path between Al and Ge you move to the right across a period (atomic size decreases) and then down a column (atomic size increases). These effects tend to counter each other, and it is not easy to tell which will predominate.



**FOR PRACTICE 9.5** On the basis of periodic trends, choose the larger atom in each pair (if possible):

- (a) Sn or I
- (b) Ge or Po
- (c) Cr or W
- (d) F or Se

**FOR MORE PRACTICE 9.5** Arrange the elements in order of decreasing radius: S, Ca, F, Rb, Si.

## 9.7

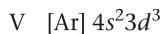
## Ions: Electron Configurations, Magnetic Properties, Ionic Radii, and Ionization Energy

Recall that ions are atoms (or groups of atoms) that have lost or gained electrons. In this section, we examine periodic trends in ionic electron configurations, magnetic properties, ionic radii, and ionization energies.

### Electron Configurations and Magnetic Properties of Ions

We can deduce the electron configuration of a main-group monoatomic ion from the electron configuration of the neutral atom and the charge of the ion. For anions, we *add* the number of electrons indicated by the magnitude of the charge of the anion. For example, the electron configuration of fluorine (F) is  $1s^22s^22p^5$  and that of the fluoride ion ( $F^-$ ) is  $1s^22s^22p^6$ .

We determine the electron configuration of cations by *subtracting* the number of electrons indicated by the magnitude of the charge. For example, the electron configuration of lithium (Li) is  $1s^22s^1$  and that of the lithium ion ( $Li^+$ ) is  $1s^22s^0$  (or simply  $1s^2$ ). For main-group cations, we remove the required number of electrons in the reverse order of filling. However, for transition metal cations, the trend is different. When writing the electron configuration of a transition metal cation, we *remove the electrons in the highest  $n$ -value orbitals first, even if this does not correspond to the reverse order of filling*. For example, the electron configuration of vanadium is:



The  $V^{2+}$  ion, however, has the following electron configuration:

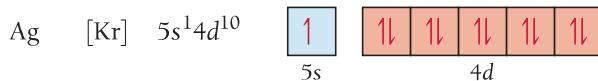


In other words, for transition metal cations, the order in which electrons are removed upon ionization is *not* the reverse of the filling order. During filling, the  $4s$  orbital normally fills before the  $3d$  orbital. When a fourth-period transition metal ionizes, however, it loses its  $4s$  electrons before its  $3d$  electrons. Why this unexpected behavior? The full answer to this question is beyond our scope, but the following two factors contribute to this phenomenon:

- As discussed previously, the  $ns$  and  $(n - 1)d$  orbitals are extremely close in energy and, depending on the exact configuration, can vary in relative energy ordering.
- As the  $(n - 1)d$  orbitals begin to fill in the first transition series, the increasing nuclear charge stabilizes the  $(n - 1)d$  orbitals relative to the  $ns$  orbitals. This happens because the  $(n - 1)d$  orbitals are not the outermost (or highest  $n$ ) orbitals and are therefore not effectively shielded from the increasing nuclear charge by the  $ns$  orbitals.

The bottom-line experimental observation is that an  $ns^0(n - 1)d^x$  configuration is lower in energy than an  $ns^2(n - 1)d^{x-2}$  configuration for transition metal ions. Therefore, we remove the  $ns$  electrons before the  $(n - 1)d$  electrons when we write electron configurations for transition metal ions.

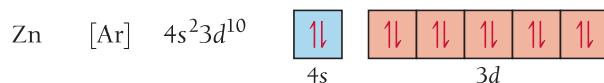
The magnetic properties of transition metal ions support these assignments. An unpaired electron generates a magnetic field due to its spin. Consequently, an atom or ion that contains unpaired electrons is attracted to an external magnetic field, and we say that the atom or ion is **paramagnetic**. For example, consider the electron configuration of silver:



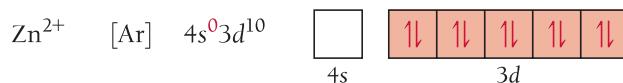
Silver's unpaired  $5s$  electron causes silver to be paramagnetic. In fact, an early demonstration of electron spin—called the Stern–Gerlach experiment—involved the interaction of a beam of silver atoms with a magnetic field.

The order of removing electrons is not the reverse of the filling order because the energy levels in a cation shift relative to the neutral atom.

An atom or ion in which all electrons are paired is not attracted to an external magnetic field—it is instead slightly repelled—and we say that the atom or ion is **diamagnetic**. The zinc atom is diamagnetic:



The magnetic properties of the zinc ion provide confirmation that the 4s electrons are indeed lost before 3d electrons in the ionization of zinc. If zinc lost two 3d electrons upon ionization, then the  $Zn^{2+}$  would be paramagnetic (because the two electrons would come out of two different filled d orbitals, leaving each of them with one unpaired electron). That does not happen and the zinc ion, like the zinc atom, is diamagnetic because the 4s electrons are lost instead:



Observations in other transition metals confirm that the  $ns$  electrons are lost before the  $(n - 1)d$  electrons upon ionization.

**EXAMPLE 9.6** Electron Configurations and Magnetic Properties for Ions



## WATCH NOW!

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### INTERACTIVE WORKED EXAMPLE 9.6

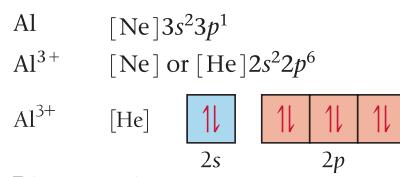
Write the electron configuration and orbital diagram for each ion and determine whether each is diamagnetic or paramagnetic.

- (a)**  $\text{Al}^{3+}$       **(b)**  $\text{S}^{2-}$       **(c)**  $\text{Fe}^{3+}$

## SOLUTION

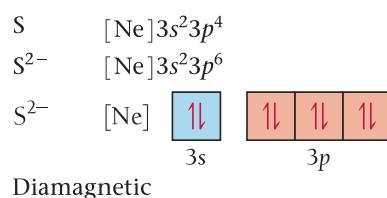
- (a)  $\text{Al}^{3+}$

Begin by writing the electron configuration of the neutral atom. This ion has a  $3+$  charge, so you remove three electrons to write the electron configuration of the ion. Write the orbital diagram by drawing half-arrows to represent each electron in boxes representing the orbitals. Because there are no unpaired electrons,  $\text{Al}^{3+}$  is diamagnetic.



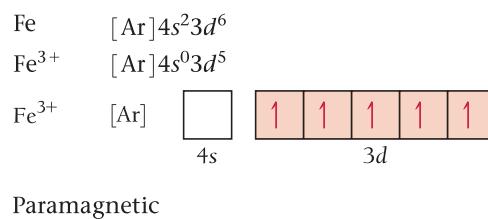
- (b)  $S^{2-}$

Begin by writing the electron configuration of the neutral atom. Because this ion has a -2 charge, add two electrons to write the electron configuration of the ion. Write the orbital diagram by drawing half-arrows to represent each electron in boxes representing the orbitals. Because there are no unpaired electrons,  $S^{2-}$  is diamagnetic.



- (c)  $\text{Fe}^{3+}$

Begin by writing the electron configuration of the neutral atom. Since this ion has a  $3+$  charge, remove three electrons to write the electron configuration of the ion. Because it is a transition metal, remove the electrons from the  $4s$  orbital before removing electrons from the  $3d$  orbitals. Write the orbital diagram by drawing half-arrows to represent each electron in boxes representing the orbitals. There are unpaired electrons, so  $\text{Fe}^{3+}$  is paramagnetic.



**FOR PRACTICE 9.6** Write the electron configuration and orbital diagram for each ion and predict whether each is paramagnetic or diamagnetic.

- (a)** Co<sup>2+</sup>      **(b)** N<sup>3-</sup>      **(c)** Ca<sup>2+</sup>

## Ionic Radii

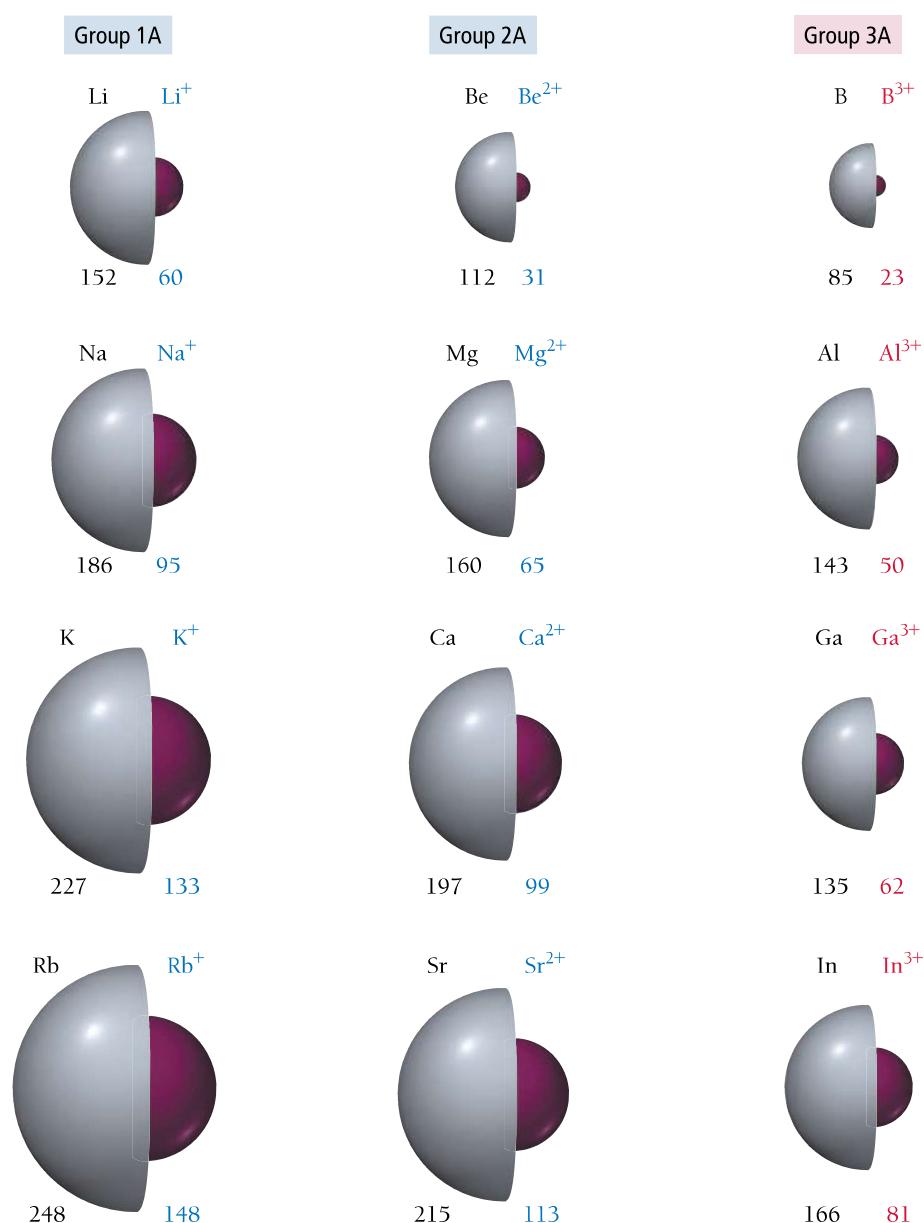
What happens to the radius of an atom when it becomes a cation? An anion? Consider, for example, the difference between the Na atom and the  $\text{Na}^+$  ion. Their electron configurations are:



The sodium atom has an outer  $3s$  electron and a neon core. Because the  $3s$  electron is the outermost electron and it is shielded from the nuclear charge by the core electrons, it contributes greatly to the size of the sodium atom. The sodium cation, having lost the outermost  $3s$  electron, has only the neon core and carries a charge of  $1+$ . Without the  $3s$  electron, the sodium cation (ionic radius = 95 pm) is much smaller than the sodium atom (covalent radius = 186 pm). The trend is the same with all cations and their atoms, as shown in Figure 9.12▼:

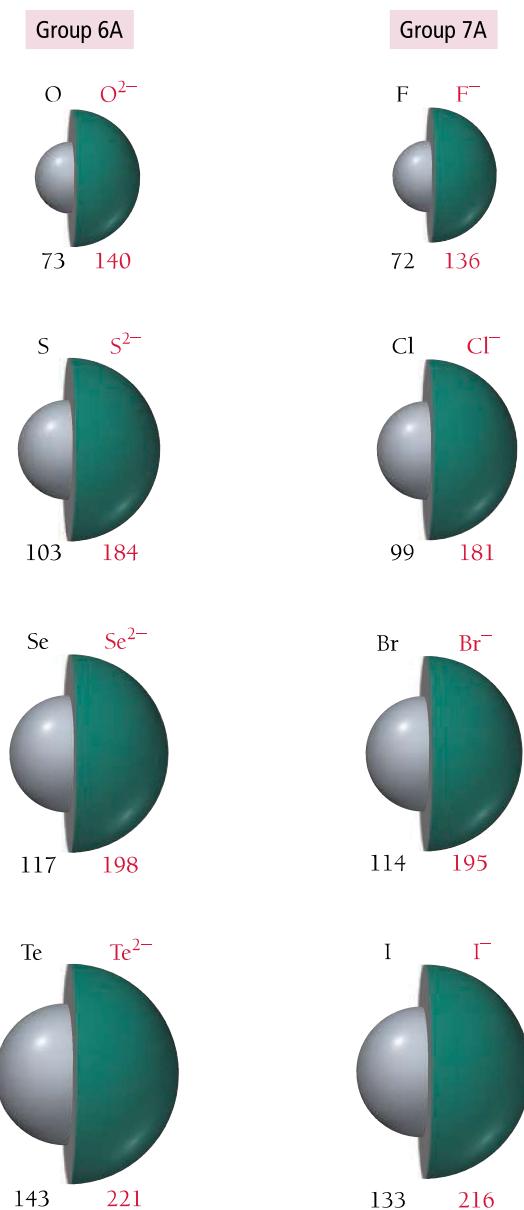
**Cations are much smaller than their corresponding atoms.**

### Radii of Atoms and Their Cations (pm)



◀ FIGURE 9.12 Sizes of Atoms and Their Cations Atomic and ionic radii (pm) for the first three columns of main-group elements.

## Radii of Atoms and Their Anions (pm)



What about anions? Consider the difference between Cl and  $Cl^{-}$ . Their electron configurations are:



The chloride anion has one additional outermost electron but no additional proton to increase the nuclear charge. The extra electron increases the repulsions among the outermost electrons, resulting in a chloride anion that is larger than the chlorine atom. The trend is the same with all anions and their atoms, as shown in Figure 9.13.

### Anions are much larger than their corresponding atoms.

We can observe an interesting trend in ionic size when we examine the radii of an *isoelectronic* series of ions—ions with the same number of electrons. Consider the following ions and their radii:

$S^{2-}$ (184 pm)	$Cl^{-}$ (181 pm)	$K^{+}$ (133 pm)	$Ca^{2+}$ (99 pm)
18 electrons	18 electrons	18 electrons	18 electrons
16 protons	17 protons	19 protons	20 protons

All of these ions have 18 electrons in exactly the same orbitals, but the radius of each ion gets successively smaller. Why? The reason is the progressively greater number of protons. The  $S^{2-}$  ion has 16 protons and therefore a charge of 16+ pulling on 18 electrons. The  $Ca^{2+}$  ion, in contrast, has 20 protons, and therefore a charge of 20+ pulling on the same 18 electrons. The result is a much smaller radius for the calcium ion. For a given number of electrons, a greater nuclear charge results in a smaller atom or ion.

◀ FIGURE 9.13 Sizes of Atoms and Their Anions Atomic and ionic radii for groups 6A and 7A in the periodic table.

## EXAMPLE 9.7 Ion Size

Choose the larger atom or ion from each pair.

- (a) S or  $S^{2-}$       (b) Ca or  $Ca^{2+}$       (c)  $Br^{-}$  or Kr

### SOLUTION

- (a) The  $S^{2-}$  ion is larger than an S atom because anions are larger than the atoms from which they are formed.  
 (b) A Ca atom is larger than  $Ca^{2+}$  because cations are smaller than the atoms from which they are formed.  
 (c) A  $Br^{-}$  ion is larger than a Kr atom because, although they are isoelectronic,  $Br^{-}$  has one fewer proton than Kr, resulting in less pull on the electrons and therefore a larger radius.

FOR PRACTICE 9.7 Choose the larger atom or ion from each pair.

- (a) K or  $K^{+}$       (b) F or  $F^{-}$       (c)  $Ca^{2+}$  or  $Cl^{-}$

**IONS, ISOTOPES, AND ATOMIC SIZE** In the previous sections, we have seen how the number of electrons and the number of protons affect the size of an atom or ion. However, we have not considered how the number of neutrons affects the size of an atom. Would you expect isotopes—for example, C-12 and C-13—to have different atomic radii?

- (a) C-12 is larger than C-13.
- (b) C-12 and C-13 are the same size.
- (c) C-13 is larger than C-12.

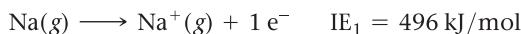


ANSWER NOW!



## Ionization Energy

The **ionization energy (IE)** of an atom or ion is the energy required to remove an electron from the atom or ion in the gaseous state. Ionization energy is always positive because removing an electron always takes energy. (The process is similar to an endothermic reaction, which absorbs heat and therefore has a positive  $\Delta H$ .) The energy required to remove the first electron is the *first ionization energy (IE<sub>1</sub>)*. For example, we represent the first ionization of sodium with the equation:



The energy required to remove the second electron is the *second ionization energy (IE<sub>2</sub>)*, the energy required to remove the third electron is the *third ionization energy (IE<sub>3</sub>)*, and so on. We represent the second ionization energy of sodium as:

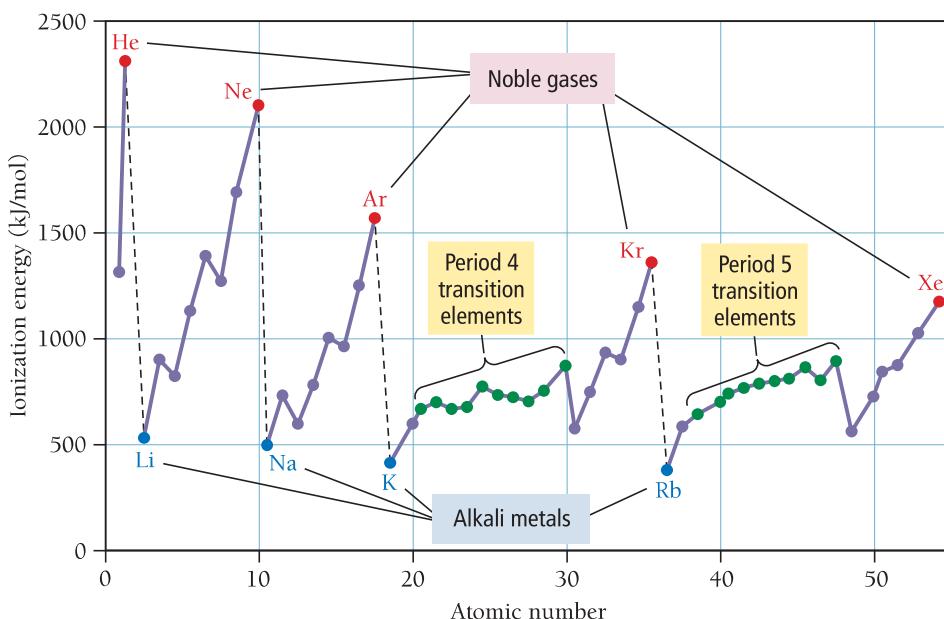


Notice that the second ionization energy is not the energy required to remove *two* electrons from sodium (that quantity is the sum of IE<sub>1</sub> and IE<sub>2</sub>), but rather the energy required to remove one electron from Na<sup>+</sup>. We look at trends in IE<sub>1</sub> and IE<sub>2</sub> separately.

## Trends in First Ionization Energy

The first ionization energies of the elements through Xe are shown in Figure 9.14▼. Notice the periodic trend in ionization energy, peaking at each noble gas and bottoming at each alkali metal. Based on what we have learned about electron configurations and effective nuclear charge, how can we account for the observed trend? As we have seen,

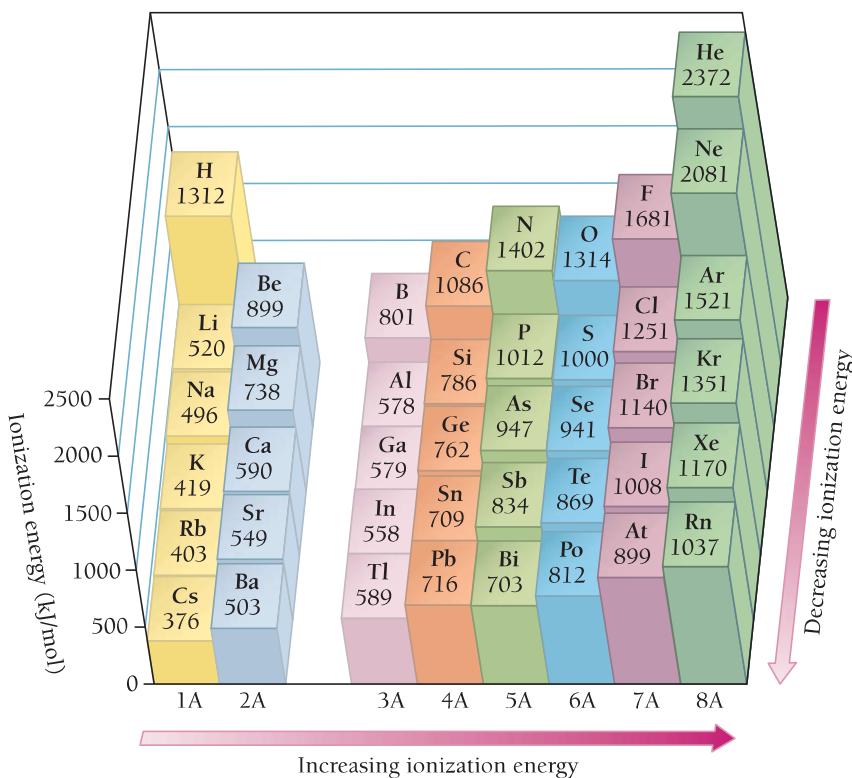
### First Ionization Energies



◀ FIGURE 9.14 First Ionization Energy versus Atomic Number for the Elements through Xenon First ionization energy starts at a minimum with each alkali metal and rises to a peak with each noble gas.

the principal quantum number,  $n$ , increases as we move down a column. Within a given sublevel, orbitals with higher principal quantum numbers are larger than orbitals with smaller principal quantum numbers. Consequently, electrons in the outermost principal level are farther away from the positively charged nucleus—and are therefore held less tightly—as we move down a column. This results in a lower ionization energy as we move down a column, as shown in Figure 9.15▼.

### Trends in First Ionization Energy



▲ **FIGURE 9.15 Trends in Ionization Energy** First ionization energy increases as we move to the right across a period and decreases as we move down a column in the periodic table.

What about the trend as we move to the right across a row? For example, would it take more energy to remove an electron from Na or from Cl, two elements on either end of the third row in the periodic table? We know that Na has an outer electron configuration of  $3s^1$  and Cl has an outer electron configuration of  $3s^23p^5$ . As discussed previously, the outermost electrons in chlorine experience a higher effective nuclear charge than the outermost electrons in sodium (which is why chlorine has a smaller atomic radius than sodium). Consequently, we would expect chlorine to have a higher ionization energy than sodium, which is indeed the case. We can make a similar argument for the other main-group elements: first ionization energy generally increases as we move to the right across a row in the periodic table, as shown in Figure 9.15.

#### Summarizing First Ionization Energy for Main-Group Elements

- First ionization energy generally *decreases* as we move down a column (or family) in the periodic table because electrons in the outermost principal level are increasingly farther away from the positively charged nucleus and are therefore held less tightly.
- First ionization energy generally *increases* as we move to the right across a row (or period) in the periodic table because electrons in the outermost principal energy level generally experience a greater effective nuclear charge ( $Z_{\text{eff}}$ ) and are therefore held more tightly.

WATCH NOW!

## INTERACTIVE WORKED EXAMPLE 9.8

**EXAMPLE 9.8 First Ionization Energy**

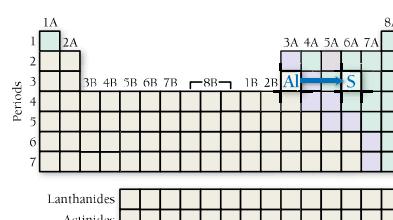
On the basis of periodic trends, determine which element in each pair has the higher first ionization energy (if possible).

- (a) Al or S      (b) As or Sb      (c) N or Si      (d) O or Cl

**SOLUTION**

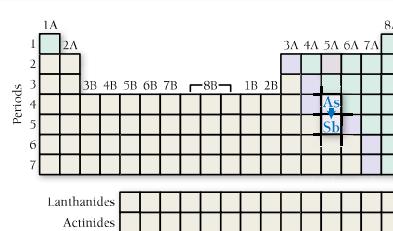
- (a) Al or S**

S has a higher ionization energy than Al because as you trace the path between Al and S on the periodic table, you move to the right within the same row. Ionization energy increases as you go to the right due to increasing effective nuclear charge.



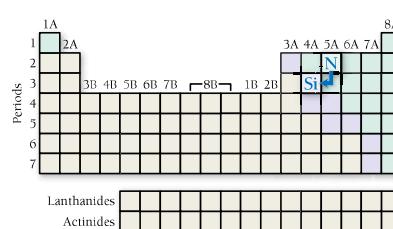
- (b) As or Sb**

As has a higher ionization energy than Sb because as you trace the path between As and Sb on the periodic table, you move down a column. Ionization energy decreases as you go down a column as a result of the increasing size of orbitals with increasing  $n$ .



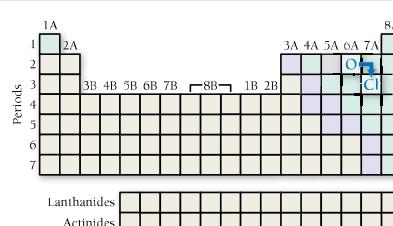
- (c) N or Si**

N has a higher ionization energy than Si because as you trace the path between N and Si on the periodic table, you move down a column (ionization energy decreases) and then to the left across a row (ionization energy decreases). These effects sum together for an overall decrease.



- (d) O or Cl**

Based on periodic trends alone, it is impossible to tell which has a higher ionization energy because, as you trace the path between O and Cl, you go to the right across a row (ionization energy increases) and then down a column (ionization energy decreases). These effects tend to counter each other, and it is not obvious which will dominate.



**FOR PRACTICE 9.8** On the basis of periodic trends, determine the element in each pair with the higher first ionization energy (if possible).

- (a) Sn or I      (b) Ca or Sr      (c) C or P      (d) F or S

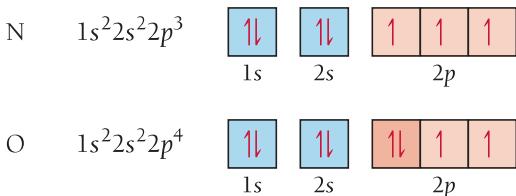
**FOR MORE PRACTICE 9.8** Arrange the following elements in order of decreasing first ionization energy: S, Ca, F, Rb, Si.

**Exceptions to Trends in First Ionization Energy**

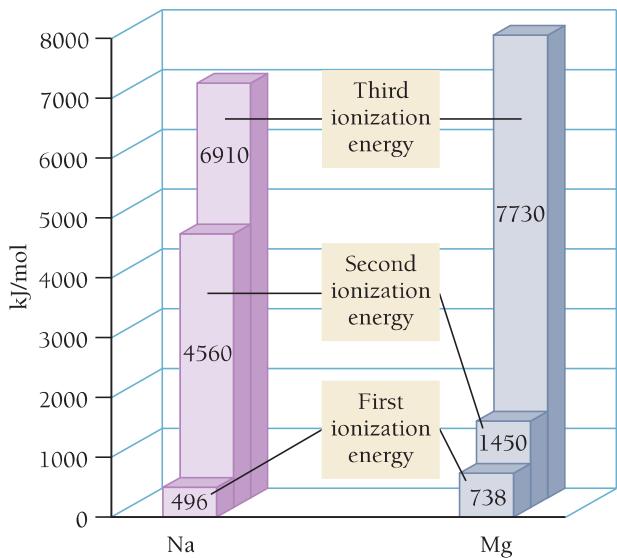
If we carefully examine Figure 9.15, we can see some exceptions to the trends in first ionization energies. For example, boron has a smaller ionization energy than beryllium, even though it lies to the right of beryllium in the same row. This exception is caused by the difference between the *s* block and the *p* block. Recall from Section 9.3 that the  $2p$  orbital penetrates into the nuclear region *less than* the  $2s$  orbital. Consequently, the  $1s$  electrons shield the electron in the  $2p$  orbital from nuclear charge more than they shield the electrons in the  $2s$  orbital. The result, as we saw in Section 9.3, is that the

$2p$  orbitals are higher in energy, and therefore the electron is easier to remove (it has a lower first ionization energy). Similar exceptions occur for aluminum and gallium, both directly below boron in group 3A.

Another exception occurs between nitrogen and oxygen. Although oxygen is to the right of nitrogen in the same row, it has a lower first ionization energy. This exception is caused by the repulsion between electrons when they occupy the same orbital. Examine the electron configurations and orbital diagrams of nitrogen and oxygen shown here:



Nitrogen has three electrons in three  $p$  orbitals, whereas oxygen has four. In nitrogen, the  $2p$  orbitals are half-filled (which makes the configuration particularly stable). One of oxygen's four  $2p$  electrons must pair with another electron, making it easier to remove (and less stable). Exceptions for similar reasons occur for S and Se, directly below oxygen in group 6A.



## Trends in Second and Successive Ionization Energies

Notice the trends in the first, second, and third ionization energies of sodium (group 1A) and magnesium (group 2A), as shown at left.

For sodium, there is a huge jump between the first and second ionization energies. For magnesium, the ionization energy roughly doubles from the first to the second, but then a huge jump occurs between the second and third ionization energies. What is the reason for these jumps?

We can understand these trends by examining the electron configurations of sodium and magnesium:



The first ionization of sodium involves removing the valence electron in the  $3s$  orbital. Recall that these valence electrons are held more loosely than the core electrons and that the resulting ion has a noble gas configuration, which is particularly stable. Consequently, the first ionization energy is fairly low. The second ionization of sodium, however, involves removing a core electron from an ion with a noble gas configuration. This requires a tremendous amount of energy, making the value of  $\text{IE}_2$  very high.

As with sodium, the first ionization of magnesium involves removing a valence electron in the  $3s$  orbital. This requires a bit more energy than the corresponding ionization of sodium because of the trends in  $Z_{\text{eff}}$  that we discussed earlier ( $Z_{\text{eff}}$  increases as we move to the right across a row). The second ionization of magnesium also involves removing an outer electron in the  $3s$  orbital, but this time from an ion with a  $1+$  charge (instead of from a neutral atom). This requires roughly twice the energy as removing the electron from the neutral atom. The third ionization of magnesium is analogous to the second ionization of sodium—it requires removing a core electron from an ion with a noble gas configuration. This requires a tremendous amount of energy, making the value of  $\text{IE}_3$  very high.

As shown in Table 9.1, similar trends exist for the successive ionization energies of many elements. The ionization energy increases fairly uniformly with each successive removal of an outermost electron, but then takes a large jump with the removal of the first core electron.

**TABLE 9.1** ■ Successive Ionization Energies for the Elements Sodium through Argon (kJ/mol)

Element	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>	IE <sub>6</sub>	IE <sub>7</sub>
Na	496	4560					
Mg	738	1450	7730				
Al	578	1820	2750	11,600			
Si	786	1580	3230	4360	16,100		
P	1012	1900	2910	4960	6270	22,200	
S	1000	2250	3360	4560	7010	8500	27,100
Cl	1251	2300	3820	5160	6540	9460	11,000
Ar	1521	2670	3930	5770	7240	8780	12,000

**SUCCESSIVE IONIZATION ENERGIES** A second row element has a large jump between its third and fourth ionization energies. What is the element?

- (a) Li      (b) Be      (c) B      (d) C



ANSWER NOW!



**IONIZATION ENERGIES AND CHEMICAL BONDING** Based on what you just learned about ionization energies, explain why valence electrons are more important than core electrons in determining the reactivity and bonding in atoms.

- (a) Since bonding involves the transfer or sharing of electrons, valence electrons are most important because they are held most tightly.  
 (b) Since bonding involves the transfer or sharing of electrons, valence electrons are most important because they are held most loosely.



ANSWER NOW!



## 9.8

## Electron Affinities and Metallic Character

Electron affinity and metallic character also exhibit periodic trends. Electron affinity is a measure of how easily an atom will accept an additional electron; it is crucial to chemical bonding because bonding involves the transfer or sharing of electrons. Metallic character is important because of the high proportion of metals in the periodic table and the large role they play in our lives. Of the 118 elements, 92 are metals. We examine each of these periodic properties individually in this section.

### Electron Affinity

The **electron affinity (EA)** of an atom (or ion) is the energy change associated with the gaining of an electron by the atom in the gaseous state. Electron affinity is usually—though not always—negative because an atom or ion usually releases energy when it gains an electron. (The process is analogous to an exothermic reaction, which releases heat and therefore has a negative  $\Delta H$ .) In other words, the coulombic attraction between the nucleus of an atom and the incoming electron usually results in the release of energy as the electron is gained. For example, we represent the electron affinity of chlorine with the equation:

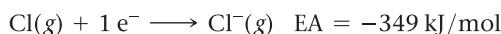


Figure 9.16▶ displays the electron affinities for a number of main-group elements. As you can see from this figure, the trends in electron affinity are not as regular as trends in other properties we examined in Sections 9.6 and 9.7. For instance, we might expect

### Electron Affinities (kJ/mol)

1A		8A						
H -73	2A	3A	4A	5A	6A	7A	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	

▲ FIGURE 9.16 Electron Affinities of Selected Main-Group Elements

electron affinities to become relatively more positive (so that the addition of an electron is less exothermic) as we move down a column because the electron is located in orbitals with successively higher principal quantum numbers and therefore is farther from the nucleus. This trend applies to the group 1A metals but does not hold for the other columns in the periodic table.

A more regular trend in electron affinity occurs across rows, however. For main-group elements, electron affinity generally becomes more negative (more exothermic) as we move to the right across a row in the periodic table. We can understand this trend by considering Na and Cl. Based on other periodic trends, would you expect Na or Cl to have the more negative (more exothermic) electron affinity? We know that Na has an outer electron configuration of  $3s^1$  and Cl has an outer electron configuration of  $3s^23p^5$ . Since adding an electron to chlorine gives it a noble gas configuration and adding an electron to sodium does not, and since the outermost electrons in chlorine experience a higher  $Z_{eff}$

experience a higher  $Z_{eff}$  than the outermost electrons in sodium, we would expect chlorine to have a more negative electron affinity—the process should be more exothermic for chlorine. This is in fact the case. The halogens (group 7A) have the most negative electron affinities. But exceptions do occur. For example, notice that nitrogen and the other group 5A elements do not follow the general trend. These elements have  $ns^2np^3$  outer electron configurations. When an electron is added to this configuration, it must pair with another electron in an already occupied  $p$  orbital. The repulsion between two electrons occupying the same orbital causes the electron affinity to be more positive than for elements in the previous column.

#### Summarizing Electron Affinity for Main-Group Elements

- Most groups (columns) of the periodic table do not exhibit any definite trend in electron affinity. Among the group 1A metals, however, electron affinity becomes more positive as we move down a column (adding an electron becomes less exothermic).
- Electron affinity generally becomes more negative (adding an electron becomes more exothermic) as we move to the right across a period (row) in the periodic table.

### Metallic Character

As we discussed in Chapter 2, metals are good conductors of heat and electricity: they can be pounded into flat sheets (malleability), they can be drawn into wires (ductility), they are often shiny, and they tend to lose electrons in chemical reactions. Nonmetals, in contrast, have more varied physical properties; some are solids at room temperature, others are gases. However, in general, nonmetals are typically poor conductors of heat and electricity, and they all tend to gain electrons in chemical reactions.

As we move to the right across a row in the periodic table, ionization energy increases and electron affinity becomes more negative; therefore, elements on the left side of the periodic table are more likely to lose electrons than elements on the right side (which are more likely to gain them). The other properties associated with metals follow the same general trend (even though we do not quantify them here). Consequently, as shown in Figure 9.17▶:

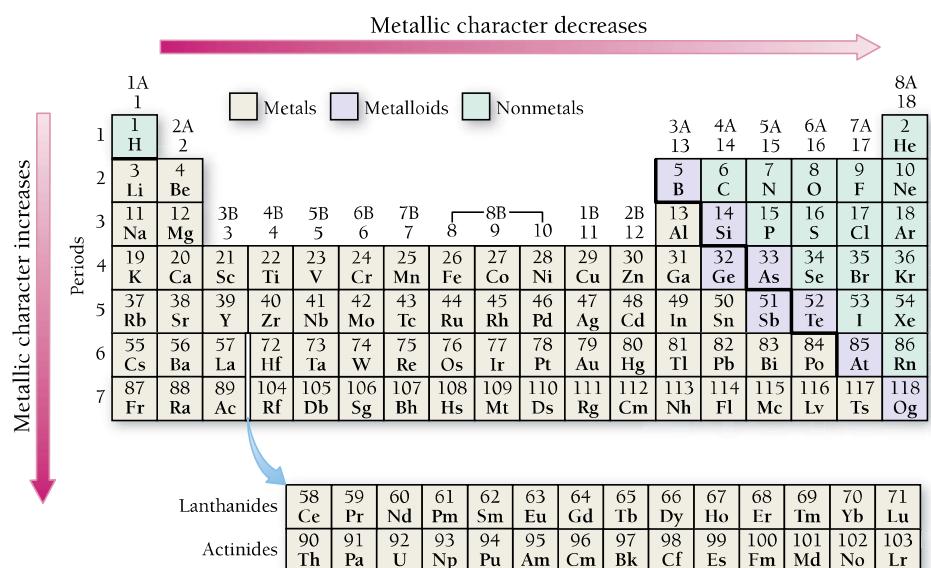
#### As we move to the right across a row (or period) in the periodic table, metallic character decreases.

As we move down a column in the periodic table, ionization energy decreases, making electrons more likely to be lost in chemical reactions. Therefore,

#### As we move down a column (or family) in the periodic table, metallic character increases.

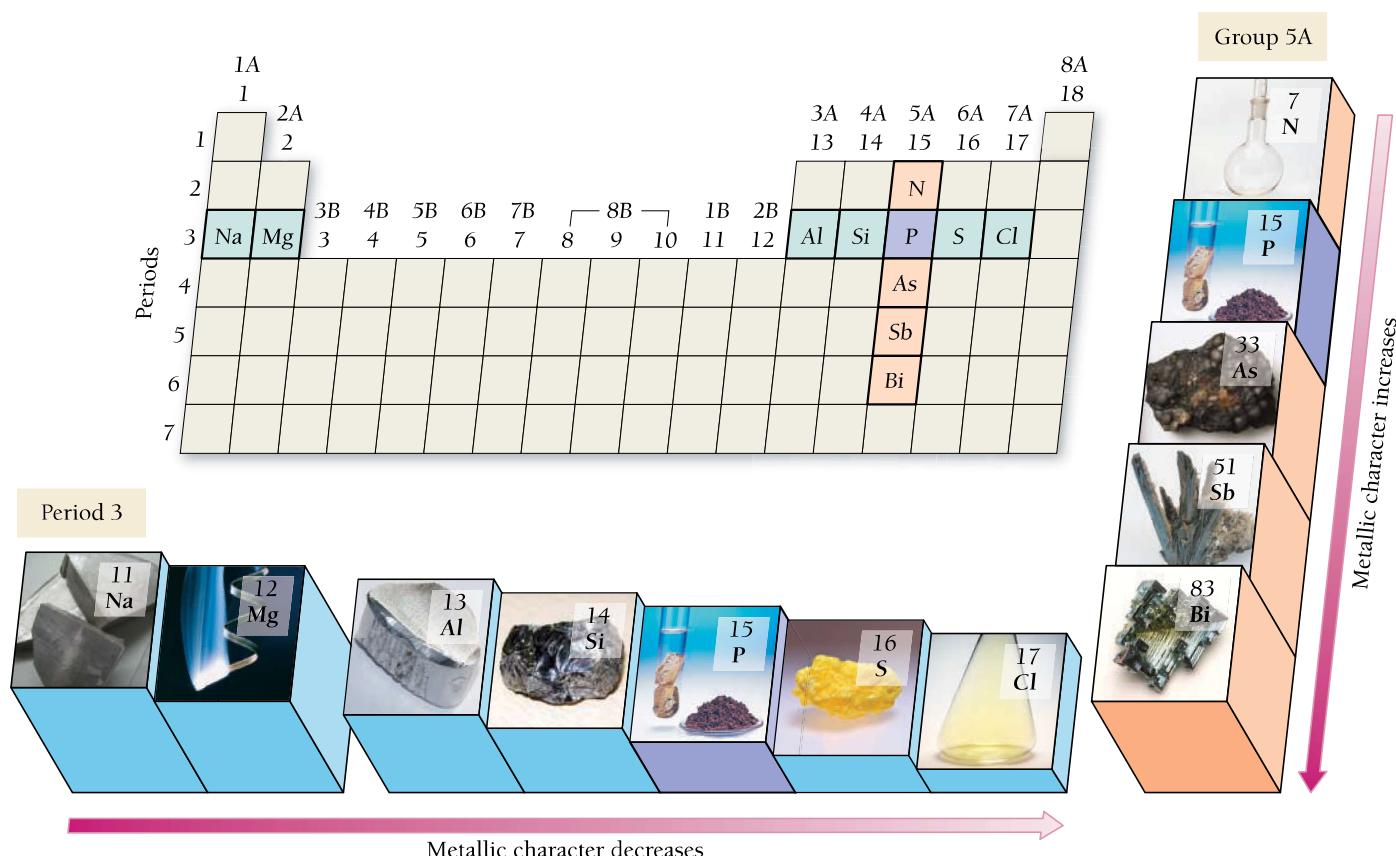
These trends, based on the quantum-mechanical model, explain the distribution of metals and nonmetals in the periodic table discussed in Chapter 2. Metals are found on the left side and toward the center and nonmetals on the upper right side. The change in chemical behavior from metallic to nonmetallic can be seen most clearly as we proceed to the right across period 3, or down along group 5A as we can see in Figure 9.18▶.

## Trends in Metallic Character



▲ FIGURE 9.17 Trends in Metallic Character I Metallic character decreases as we move to the right across a period and increases as we move down a column in the periodic table.

## Trends in Metallic Character



▲ FIGURE 9.18 Trends in Metallic Character II As we move down group 5A in the periodic table, metallic character increases. As we move across period 3, metallic character decreases.

**EXAMPLE 9.9** Metallic Character

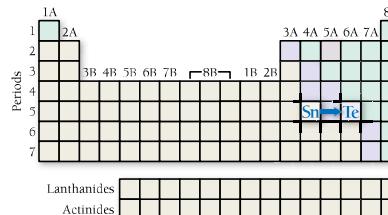
On the basis of periodic trends, choose the more metallic element from each pair (if possible).

- (a) Sn or Te      (b) P or Sb      (c) Ge or In      (d) S or Br

**SOLUTION**

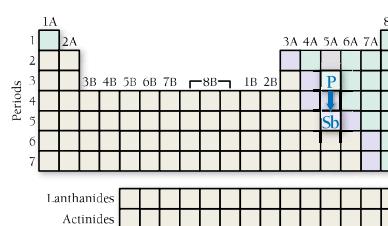
- (a) Sn or Te

Sn is more metallic than Te because as you trace the path between Sn and Te on the periodic table, you move to the right within the same period. Metallic character decreases as we move to the right.



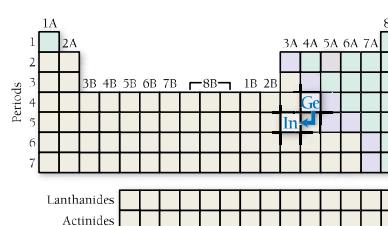
- (b) P or Sb

Sb is more metallic than P because as you trace the path between P and Sb on the periodic table, you move down a column. Metallic character increases as we move down a column.



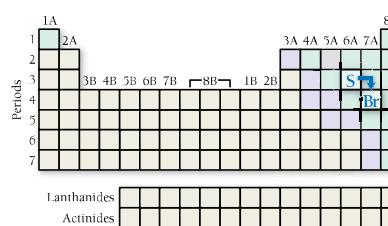
- (c) Ge or In

In is more metallic than Ge because as you trace the path between Ge and In on the periodic table, you move down a column (metallic character increases) and then to the left across a period (metallic character increases). These effects add together for an overall increase.



- (d) S or Br

Based on periodic trends alone, we cannot tell which is more metallic because as you trace the path between S and Br, you move to the right across a period (metallic character decreases) and then down a column (metallic character increases). These effects tend to counter each other, and it is not easy to tell which will predominate.



**FOR PRACTICE 9.9** On the basis of periodic trends, choose the more metallic element from each pair (if possible).

- (a) Ge or Sn      (b) Ga or Sn      (c) P or Bi      (d) B or N

**FOR MORE PRACTICE 9.9** Arrange the following elements in order of increasing metallic character: Si, Cl, Na, Rb.

**ANSWER NOW!**



## 9.10 Cc

Conceptual Connection

**PERIODIC TRENDS** Which statement best explains why sodium commonly forms a 1+ ion and not a 2+ ion?

- (a) Sodium only has one electron, so it has only one to lose.
- (b) All metals form 1+ ions, and sodium is a metal.
- (c) Sodium has only one valence electron that is easily removed; removing a second electron would be more difficult because it would be a core electron.

**9.9****Periodic Trends Summary**

In this chapter, we have examined various trends in properties that we can understand in terms of electron configurations. We have seen how electronic structure determines the size, ionization energy, electron affinity, and metallic character of atoms. We summarize these four important properties and their periodic trends in Table 9.2.

**TABLE 9.2 ■ Summary of Periodic Properties**

Property	Trend Moving Down a Column	Reason for Trend Moving Down	Trend Moving Across a Row	Reason for Trend Moving Across
<b>Atomic Radii</b>	Increasing ↑	Size of outermost occupied orbital increases	Decreasing ↓	Effective nuclear charge increases
<b>First Ionization Energy</b>	Decreasing ↓	Outermost electrons further away from nucleus (and therefore easier to remove)	Increasing ↑	Effective nuclear charge increases
<b>Electron Affinity</b>	No definite trend		Decreasing (more negative) ↓	Effective nuclear charge increases
<b>Metallic Character</b>	Increasing ↑	Ionization energy decreases	Decreasing ↓	Ionization energy increases

**QUIZ YOURSELF NOW!**

## Self-Assessment Quiz



- Q1.** According to Coulomb's law, if the separation between two particles of the same charge is doubled, what happens to the potential energy of the two particles?

**MISSED THIS? Read Section 9.3**

- a) It is twice as high as it was before the distance separation.
- b) It is one-half as high as it was before the separation.
- c) It does not change.
- d) It is one-fourth as high as it was before the separation.

- Q2.** Which electron in sulfur is most shielded from nuclear charge?

**MISSED THIS? Read Section 9.3**

- a) an electron in the 1s orbital
- b) an electron in a 2p orbital
- c) an electron in a 3p orbital
- d) none of the above (All of these electrons are equally shielded from nuclear charge.)

- Q3.** Choose the correct electron configuration for Se.

**MISSED THIS? Read Section 9.3; Watch KCV 9.3**

- a)  $1s^2 2s^2 2p^6 3s^2 3p^4$
- b)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
- c)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^4$
- d)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

- Q4.** Choose the correct orbital diagram for vanadium.

**MISSED THIS? Read Section 9.3; Watch KCV 9.3, IWE 9.3**

- a) [Ar]   
4s                    3d
- b) [Ar]   
4s                    3d
- c) [Ar]   
4s                    3d
- d) [Ar]   
4s                    3d

- Q5.** Which set of four quantum numbers corresponds to an electron in a 4p orbital?

**MISSED THIS? Read Section 9.3**

- a)  $n = 4, l = 1, m_l = 0, m_s = \frac{1}{2}$
- b)  $n = 4, l = 3, m_l = 3, m_s = -\frac{1}{2}$
- c)  $n = 4, l = 2, m_l = 0, m_s = \frac{1}{2}$
- d)  $n = 4, l = 4, m_l = 3, m_s = -\frac{1}{2}$

- Q6.** Which element has the smallest atomic radius?

**MISSED THIS? Read Section 9.6; Watch KCV 9.6, IWE 9.5**

- a) C                    b) Si                    c) Be                    d) F

- Q7.** Which statement is true about electron shielding of nuclear charge? **MISSED THIS? Read Section 9.6; Watch KCV 9.6**

- a) Outermost electrons efficiently shield one another from nuclear charge.
- b) Core electrons efficiently shield one another from nuclear charge.
- c) Outermost electrons efficiently shield core electrons from nuclear charge.
- d) Core electrons efficiently shield outermost electrons from nuclear charge.

- Q8.** Which statement is true about effective nuclear charge?

**MISSED THIS? Read Section 9.6; Watch KCV 9.6**

- a) Effective nuclear charge *decreases* as you move to the right across a row in the periodic table.
- b) Effective nuclear charge *increases* as you move to the right across a row in the periodic table.
- c) Effective nuclear charge *remains constant* as you move to the right across a row in the periodic table.
- d) Effective nuclear charge *increases and decreases* at regular intervals as you move to the right across a row in the periodic table.

—Continued on the next page

**Q9.** Which is the correct electron configuration for  $\text{Fe}^{2+}$ ?

- MISSED THIS? Read Section 9.7; Watch IWE 9.6**
- [Ar]4s<sup>2</sup>3d<sup>6</sup>
  - [Ar]4s<sup>2</sup>3d<sup>4</sup>
  - [Ar]4s<sup>0</sup>3d<sup>6</sup>
  - [Ar]4s<sup>2</sup>3d<sup>8</sup>

**Q10.** Which species is diamagnetic?

- MISSED THIS? Read Section 9.7; Watch IWE 9.6**
- $\text{Cr}^{2+}$
  - Zn
  - Mn
  - C

**Q11.** Arrange these atoms and ions in order of increasing radius:

- $\text{Cs}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{I}^-$ . **MISSED THIS? Read Section 9.7**
- $\text{I}^- < \text{Ba}^{2+} < \text{Cs}^+$
  - $\text{Cs}^+ < \text{Ba}^{2+} < \text{I}^-$
  - $\text{Ba}^{2+} < \text{Cs}^+ < \text{I}^-$
  - $\text{I}^- < \text{Cs}^+ < \text{Ba}^{2+}$

**Q12.** Arrange these elements in order of increasing first ionization energy: Cl, Sn, Si.

- MISSED THIS? Read Section 9.7; Watch IWE 9.8**
- $\text{Cl} < \text{Si} < \text{Sn}$
  - $\text{Sn} < \text{Si} < \text{Cl}$
  - $\text{Si} < \text{Cl} < \text{Sn}$
  - $\text{Sn} < \text{Cl} < \text{Si}$

**Q13.** The ionization energies of an unknown third-period element are listed here. Identify the element.  $\text{IE}_1 = 786 \text{ kJ/mol}$ ;

$\text{IE}_2 = 1580 \text{ kJ/mol}$ ;  $\text{IE}_3 = 3230 \text{ kJ/mol}$ ;

$\text{IE}_4 = 4360 \text{ kJ/mol}$ ;  $\text{IE}_5 = 16,100 \text{ kJ/mol}$

- MISSED THIS? Read Section 9.7**

- Mg
- Al
- Si
- P

**Q14.** Which statement is true about trends in metallic character?

- MISSED THIS? Read Section 9.8**

- Metallic character *increases* as you move to the right across a row in the periodic table and *increases* as you move down a column.
- Metallic character *decreases* as you move to the right across a row in the periodic table and *increases* as you move down a column.
- Metallic character *decreases* as you move to the right across a row in the periodic table and *decreases* as you move down a column.
- Metallic character *increases* as you move to the right across a row in the periodic table and *decreases* as you move down a column.

**Q15.** For which element is the gaining of an electron most exothermic? **MISSED THIS? Read Section 9.8**

- Li
- N
- F
- B

**Answers:** 1. (b) 2. (c) 3. (b) 4. (d) 5. (a) 6. (d) 7. (d)

## CHAPTER 9 IN REVIEW

### TERMS

#### Section 9.1

periodic property (352)

#### Section 9.3

electron configuration (353)  
ground state (353)  
orbital diagram (354)  
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Coulomb's law (355)

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effective nuclear charge ( $Z_{\text{eff}}$ ) (356)  
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#### Section 9.6

van der Waals radius (nonbonding atomic radius) (366)  
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atomic radius (366)

#### Section 9.7

paramagnetic (371)  
diamagnetic (372)  
ionization energy (IE) (375)

#### Section 9.8

electron affinity (EA) (379)

### CONCEPTS

#### Periodic Properties and the Development of the Periodic Table (9.1, 9.2)

- In the nineteenth century, Dmitri Mendeleev arranged the elements in an early version of the periodic table so that atomic mass increased from left to right in a row and elements with similar properties fell in the same columns.
- Periodic properties are predictable based on an element's position within the periodic table. Periodic properties include atomic radius, ionization energy, electron affinity, density, and metallic character.
- Quantum mechanics explains the periodic table by describing how electrons fill the quantum-mechanical orbitals within the atoms that compose the elements.

#### Electron Configurations (9.3)

- An electron configuration for an atom shows which quantum-mechanical orbitals the atom's electrons occupy. For example, the electron configuration of helium ( $1s^2$ ) indicates that helium's two electrons occupy the  $1s$  orbital.
- The order of filling quantum-mechanical orbitals in multielectron atoms is  $1s$   $2s$   $2p$   $3s$   $3p$   $4s$   $3d$   $4p$   $5s$   $4d$   $5p$   $6s$ .
- According to the Pauli exclusion principle, each orbital can hold a maximum of two electrons and those electrons have opposing spins.
- According to Hund's rule, orbitals of the same energy first fill singly with electrons having parallel spins before pairing.

## Electron Configurations and the Periodic Table (9.4, 9.5)

- Because quantum-mechanical orbitals fill sequentially with increasing atomic number, we can infer the electron configuration of an element from its position in the periodic table.
- The most stable electron configurations are those with completely full *s* and *p* sublevels. Therefore, the most stable and unreactive elements—those with the lowest energy electron configurations—are the noble gases.
- Elements with one or two valence electrons are among the most active metals, readily losing their valence electrons to attain noble gas configurations.
- Elements with six or seven valence electrons are among the most active nonmetals, readily gaining enough electrons to attain a noble gas configuration.

## Effective Nuclear Charge and Periodic Trends in Atomic Size (9.6)

- The size of an atom is largely determined by its outermost electrons. As we move down a column in the periodic table, the principal quantum number (*n*) of the outermost electrons increases, resulting in successively larger orbitals and therefore larger atomic radii.
- As we move across a row in the periodic table, atomic radii decrease because the effective nuclear charge—the net or average charge experienced by the atom's outermost electrons—increases.
- The atomic radii of the transition elements stay roughly constant as we move across each row because electrons are added to the  $n_{\text{highest}} - 1$  orbitals, while the number of highest *n* electrons stays roughly constant.

## EQUATIONS AND RELATIONSHIPS

### Order of Filling Quantum-Mechanical Orbitals (9.3)

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s

## LEARNING OUTCOMES

Chapter Objectives	Assessment
Write electron configurations for elements (9.3)	Example 9.1 For Practice 9.1 Exercises 39–40
Draw orbital diagrams for elements (9.3)	Example 9.2 For Practice 9.2 Exercises 41–42
Write electron configurations based on periodic table location (9.4)	Examples 9.3, 9.4 For Practice 9.3, 9.4 For More Practice 9.4 Exercises 43–52
Predict relative atomic sizes of elements (9.6)	Example 9.5 For Practice 9.5 For More Practice 9.5 Exercises 53–62
Analyze ions in terms of magnetic properties (9.7)	Example 9.6 For Practice 9.6 Exercises 63–66
Predict the relative size of ions from periodic trends (9.7)	Example 9.7 For Practice 9.7 Exercises 67–70
Predict relative ionization energies for atoms and ions based on periodic trends (9.7)	Example 9.8 For Practice 9.8 For More Practice 9.8 Exercises 71–76
Predict the metallic character of atoms based on periodic trends (9.8)	Example 9.9 For Practice 9.9 For More Practice 9.9 Exercises 77–82

# EXERCISES

## REVIEW QUESTIONS

- Mastering Chemistry** provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.
- What are periodic properties?
  - Which periodic property is particularly important to nerve signal transmission? Why?
  - Explain the contributions of Johann Döbereiner and John Newlands to the organization of elements according to their properties.
  - Who is credited with arranging the periodic table? How are the elements arranged in the modern periodic table?
  - Explain the contributions of Meyer and Moseley to the periodic table.
  - The periodic table is a result of the periodic law. What observations led to the periodic law? What theory explains the underlying reasons for the periodic law?
  - What is an electron configuration? Give an example.
  - What is Coulomb's law? Explain how the potential energy of two charged particles depends on the distance between the charged particles and on the magnitude and sign of their charges.
  - What is shielding? In an atom, which electrons tend to do the most shielding (core electrons or valence electrons)?
  - What is penetration? How does the penetration of an orbital into the region occupied by core electrons affect the energy of an electron in that orbital?
  - Why are the sublevels within a principal level split into different energies for multielectron atoms but not for the hydrogen atom?
  - What is an orbital diagram? Provide an example.
  - Why is electron spin important when writing electron configurations? Explain in terms of the Pauli exclusion principle.
  - What are degenerate orbitals? According to Hund's rule, how are degenerate orbitals occupied?
  - List all orbitals from 1s through 5s according to increasing energy for multielectron atoms.
  - What are valence electrons? Why are they important?
  - Copy this blank periodic table onto a sheet of paper and label each of the blocks within the table: s block, p block, d block, and f block.

	1A															8A		
1	2															18		
2		3B	4B	5B	6B	7B		8B		1B	2B							
3		3	4	5	6	7		8		9	10	11	12					
4																		
5																		
6																		
7																		
Periods																		
	Lanthanides																	
	Actinides																	

  - Explain why the s block in the periodic table has only two columns while the p block has six.
  - Why do the rows in the periodic table get progressively longer as you move down the table? For example, the first row contains 2 elements, the second and third rows each contain 8 elements, and the fourth and fifth rows each contain 18 elements. Explain.
  - Describe the relationship between a main-group element's lettered group number (the number of the element's column) and its valence electrons.
  - Describe the relationship between an element's row number in the periodic table and the highest principal quantum number in the element's electron configuration. How does this relationship differ for main-group elements, transition elements, and inner transition elements?
  - Which of the transition elements in the first transition series have anomalous electron configurations?
  - Describe how to write the electron configuration for an element based on its position in the periodic table.
  - Describe the relationship between the properties of an element and the number of valence electrons that it contains.
  - List the number of valence electrons for each family, and explain the relationship between the number of valence electrons and the resulting chemistry of the elements in the family.
    - a. alkali metals
    - b. alkaline earth metals
    - c. halogens
    - d. oxygen family
  - Define atomic radius. For main-group elements, describe the observed trends in atomic radius as you move:
    - a. across a period in the periodic table
    - b. down a column in the periodic table
  - What is effective nuclear charge? What is shielding?
  - Use the concepts of effective nuclear charge, shielding, and  $n$  value of the valence orbital to explain the trend in atomic radius as you move across a period in the periodic table.
  - For transition elements, describe and explain the observed trends in atomic radius as you move:
    - a. across a period in the periodic table
    - b. down a column in the periodic table
  - How is the electron configuration of an anion different from that of the corresponding neutral atom? How is the electron configuration of a cation different?
  - Describe how to write an electron configuration for a transition metal cation. Is the order of electron removal upon ionization simply the reverse of electron addition upon filling? Why or why not?
  - Describe the relationship between
    - a. the radius of a cation and that of the atom from which forms
    - b. the radius of an anion and that of the atom from which it forms
  - What is ionization energy? What is the difference between first ionization energy and second ionization energy?
  - What is the general trend in first ionization energy as you move down a column in the periodic table? As you move across a row?
  - What are the exceptions to the periodic trends in first ionization energy? Why do they occur?
  - Examination of the first few successive ionization energies for a given element usually reveals a large jump between two ionization energies. For example, the successive ionization energies of magnesium show a large jump between  $IE_2$  and  $IE_3$ . The successive ionization energies of aluminum show a large jump between  $IE_3$  and  $IE_4$ . Explain why these jumps occur and how you might predict them.
  - What is electron affinity? What are the observed periodic trends in electron affinity?
  - What is metallic character? What are the observed periodic trends in metallic character?

## PROBLEMS BY TOPIC

### Electron Configurations

**39.** Write the full electron configuration for each element.

**MISSED THIS?** Read Section 9.3; Watch KCV 9.3

- a. Si      b. O      c. K      d. Ne

**40.** Write the full electron configuration for each element.

- a. C      b. P      c. Ar      d. Na

**41.** Write the full orbital diagram for each element.

**MISSED THIS?** Read Section 9.3; Watch KCV 9.3, IWE 9.2

- a. N      b. F      c. Mg      d. Al

**42.** Write the full orbital diagram for each element.

- a. S      b. Ca      c. Ne      d. He

**43.** Use the periodic table to write an electron configuration for each element. Represent core electrons with the symbol of the previous noble gas in brackets.

**MISSED THIS?** Read Section 9.4; Watch KCV 9.4, IWE 9.4

- a. P      b. Ge      c. Zr      d. I

**44.** Use the periodic table to determine the element corresponding to each electron configuration.

- a.  $[\text{Ar}] 4s^2 3d^{10} 4p^6$       b.  $[\text{Ar}] 4s^2 3d^2$   
c.  $[\text{Kr}] 5s^2 4d^{10} 5p^2$       d.  $[\text{Kr}] 5s^2$

**45.** Use the periodic table to determine each quantity.

**MISSED THIS?** Read Section 9.4; Watch KCV 9.4, IWE 9.4

- a. the number of  $2s$  electrons in Li  
b. the number of  $3d$  electrons in Cu  
c. the number of  $4p$  electrons in Br  
d. the number of  $4d$  electrons in Zr

**46.** Use the periodic table to determine each quantity.

- a. the number of  $3s$  electrons in Mg  
b. the number of  $3d$  electrons in Cr  
c. the number of  $4d$  electrons in Y  
d. the number of  $6p$  electrons in Pb

**47.** Name an element in the fourth period (row) of the periodic table with the following:

**MISSED THIS?** Read Section 9.4; Watch KCV 9.4, IWE 9.4

- a. five valence electrons  
b. four  $4p$  electrons  
c. three  $3d$  electrons  
d. full  $s$  and  $p$  sublevels

**48.** Name an element in the third period (row) of the periodic table with the following:

- a. three valence electrons  
b. four  $3p$  electrons  
c. six  $3p$  electrons  
d. two  $3s$  electrons and no  $3p$  electrons

### Valence Electrons and Simple Chemical Behavior from the Periodic Table

**49.** Determine the number of valence electrons in an atom of each element. **MISSED THIS?** Read Section 9.4; Watch KCV 9.4

- a. Ba      b. Cs      c. Ni      d. S

**50.** Determine the number of valence electrons in an atom of each element. Which elements do you expect to lose electrons in their chemical reactions? Which do you expect to gain electrons?

- a. Al      b. Sn      c. Br      d. Se

**51.** Which outer electron configuration would you expect to belong to a reactive metal? To a reactive nonmetal?

**MISSED THIS?** Read Section 9.5

- a.  $ns^2$       b.  $ns^2 np^6$       c.  $ns^2 np^5$       d.  $ns^2 np^2$

**52.** Which outer electron configurations would you expect to belong to a noble gas? To a metalloid?

- a.  $ns^2$       b.  $ns^2 np^6$       c.  $ns^2 np^5$       d.  $ns^2 np^2$

### Coulomb's Law and Effective Nuclear Charge

**53.** According to Coulomb's law, which pair of charged particles has the lowest potential energy? **MISSED THIS?** Read Section 9.3

- a. a particle with a  $1-$  charge separated by 150 pm from a particle with a  $2+$  charge  
b. a particle with a  $1+$  charge separated by 150 pm from a particle with a  $1+$  charge  
c. a particle with a  $1-$  charge separated by 100 pm from a particle with a  $3+$  charge

**54.** According to Coulomb's law, rank the interactions between charged particles from lowest potential energy to highest potential energy.

- a. a  $1+$  charge and a  $1-$  charge separated by 100 pm  
b. a  $2+$  charge and a  $1-$  charge separated by 100 pm  
c. a  $1+$  charge and a  $1+$  charge separated by 100 pm  
d. a  $1+$  charge and a  $1-$  charge separated by 200 pm

**55.** Which experience a greater effective nuclear charge: the valence electrons in beryllium or the valence electrons in nitrogen? Why? **MISSED THIS?** Read Section 9.6; Watch KCV 9.6

**56.** Arrange the atoms according to decreasing effective nuclear charge experienced by their valence electrons: S, Mg, Al, Si.

**57.** If core electrons completely shielded valence electrons from nuclear charge (i.e., if each core electron reduced nuclear charge by 1 unit) and if valence electrons did not shield one another from nuclear charge at all, what would be the effective nuclear charge experienced by the valence electrons of each atom?

**MISSED THIS?** Read Section 9.6; Watch KCV 9.6

- a. K      b. Ca      c. O      d. C

**58.** In Section 9.6, we estimated the effective nuclear charge on beryllium's valence electrons to be slightly greater than  $2+$ . What would a similar process predict for the effective nuclear charge on boron's valence electrons? Would you expect the effective nuclear charge to be different for boron's  $2s$  electrons compared to its  $2p$  electron? In what way? (Hint: Consider the shape of the  $2p$  orbital compared to that of the  $2s$  orbital.)

### Atomic Radius

**59.** Choose the larger atom from each pair.

**MISSED THIS?** Read Section 9.6; Watch KCV 9.6, IWE 9.5

- a. Al or In      b. Si or N  
c. P or Pb      d. C or F

**60.** Choose the larger atom from each pair, if possible.

- a. Sn or Si      b. Br or Ga  
c. Sn or Bi      d. Se or Sn

**61.** Arrange these elements in order of increasing atomic radius: Ca, Rb, S, Si, Ge, F.

**MISSED THIS?** Read Section 9.6; Watch KCV 9.6, IWE 9.5

**62.** Arrange these elements in order of decreasing atomic radius: Cs, Sb, S, Pb, Se.

### Ionic Electron Configurations, Ionic Radii, Magnetic Properties, and Ionization Energy

**63.** Write the electron configuration for each ion.

**MISSED THIS?** Read Section 9.7; Watch IWE 9.6

- a.  $\text{O}^{2-}$       b.  $\text{Br}^-$       c.  $\text{Sr}^{2+}$       d.  $\text{Co}^{3+}$       e.  $\text{Cu}^{2+}$

- 64.** Write the electron configuration for each ion.  
 a.  $\text{Cl}^-$    b.  $\text{P}^{3-}$    c.  $\text{K}^+$    d.  $\text{Mo}^{3+}$    e.  $\text{V}^{3+}$
- 65.** Write orbital diagrams for each ion and indicate whether the ion is diamagnetic or paramagnetic.  
**MISSED THIS? Read Section 9.7; Watch IWE 9.6**  
 a.  $\text{V}^{5+}$    b.  $\text{Cr}^{3+}$    c.  $\text{Ni}^{2+}$    d.  $\text{Fe}^{3+}$
- 66.** Write orbital diagrams for each ion and indicate whether the ion is diamagnetic or paramagnetic.  
 a.  $\text{Cd}^{2+}$    b.  $\text{Au}^+$    c.  $\text{Mo}^{3+}$    d.  $\text{Zr}^{2+}$
- 67.** Which is the larger species in each pair?  
**MISSED THIS? Read Section 9.7**  
 a.  $\text{Li}$  or  $\text{Li}^+$    b.  $\text{I}^-$  or  $\text{Cs}^+$   
 c.  $\text{Cr}$  or  $\text{Cr}^{3+}$    d.  $\text{O}$  or  $\text{O}^{2-}$
- 68.** Which is the larger species in each pair?  
 a.  $\text{Sr}$  or  $\text{Sr}^{2+}$    b.  $\text{N}$  or  $\text{N}^{3-}$   
 c.  $\text{Ni}$  or  $\text{Ni}^{2+}$    d.  $\text{S}^{2-}$  or  $\text{Ca}^{2+}$
- 69.** Arrange this isoelectronic series in order of decreasing radius:  
 $\text{F}^-$ ,  $\text{O}^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ . **MISSED THIS? Read Section 9.7**
- 70.** Arrange this isoelectronic series in order of increasing atomic radius:  $\text{Se}^{2-}$ ,  $\text{Sr}^{2+}$ ,  $\text{Rb}^+$ ,  $\text{Br}^-$ .
- 71.** Choose the element with the higher first ionization energy from each pair. **MISSED THIS? Read Section 9.7; Watch IWE 9.8**  
 a.  $\text{Br}$  or  $\text{Bi}$    b.  $\text{Na}$  or  $\text{Rb}$   
 c.  $\text{As}$  or  $\text{At}$    d.  $\text{P}$  or  $\text{Sn}$
- 72.** Choose the element with the higher first ionization energy from each pair.  
 a.  $\text{P}$  or  $\text{I}$    b.  $\text{Si}$  or  $\text{Cl}$   
 c.  $\text{P}$  or  $\text{Sb}$    d.  $\text{Ga}$  or  $\text{Ge}$
- 73.** Arrange these elements in order of increasing first ionization energy:  $\text{Si}$ ,  $\text{F}$ ,  $\text{In}$ ,  $\text{N}$ . **MISSED THIS? Read Section 9.7; Watch IWE 9.8**
- 74.** Arrange these elements in order of decreasing first ionization energy:  $\text{Cl}$ ,  $\text{S}$ ,  $\text{Sn}$ ,  $\text{Pb}$ .

- 75.** For each element, predict where the “jump” occurs for successive ionization energies. (For example, does the jump occur between the first and second ionization energies, the second and third, or the third and fourth?) **MISSED THIS? Read Section 9.7**

a.  $\text{Be}$    b.  $\text{N}$    c.  $\text{O}$    d.  $\text{Li}$

- 76.** Consider this set of ionization energies.

$$\text{IE}_1 = 578 \text{ kJ/mol}$$

$$\text{IE}_2 = 1820 \text{ kJ/mol}$$

$$\text{IE}_3 = 2750 \text{ kJ/mol}$$

$$\text{IE}_4 = 11,600 \text{ kJ/mol}$$

To which third-period element do these ionization values belong?

### Electron Affinities and Metallic Character

- 77.** Choose the element with the more negative (more exothermic) electron affinity from each pair. **MISSED THIS? Read Section 9.8**  
 a.  $\text{Na}$  or  $\text{Rb}$    b.  $\text{B}$  or  $\text{S}$   
 c.  $\text{C}$  or  $\text{N}$    d.  $\text{Li}$  or  $\text{F}$
- 78.** Choose the element with the more negative (more exothermic) electron affinity from each pair.  
 a.  $\text{Mg}$  or  $\text{S}$    b.  $\text{K}$  or  $\text{Cs}$   
 c.  $\text{Si}$  or  $\text{P}$    d.  $\text{Ga}$  or  $\text{Br}$
- 79.** Choose the more metallic element from each pair.  
**MISSED THIS? Read Section 9.8**  
 a.  $\text{Sr}$  or  $\text{Sb}$    b.  $\text{As}$  or  $\text{Bi}$    c.  $\text{Cl}$  or  $\text{O}$    d.  $\text{S}$  or  $\text{As}$
- 80.** Choose the more metallic element from each pair.  
 a.  $\text{Sb}$  or  $\text{Pb}$    b.  $\text{K}$  or  $\text{Ge}$    c.  $\text{Ge}$  or  $\text{Sb}$    d.  $\text{As}$  or  $\text{Sn}$
- 81.** Arrange these elements in order of increasing metallic character:  $\text{Fr}$ ,  $\text{Sb}$ ,  $\text{In}$ ,  $\text{S}$ ,  $\text{Ba}$ ,  $\text{Se}$ . **MISSED THIS? Read Section 9.8**
- 82.** Arrange these elements in order of decreasing metallic character:  $\text{Sr}$ ,  $\text{N}$ ,  $\text{Si}$ ,  $\text{P}$ ,  $\text{Ga}$ ,  $\text{Al}$ .

## CUMULATIVE PROBLEMS

- 83.** Bromine is a highly reactive liquid while krypton is an inert gas. Explain this difference based on their electron configurations.
- 84.** Potassium is a highly reactive metal while argon is an inert gas. Explain this difference based on their electron configurations.
- 85.** Both vanadium and its  $3+$  ion are paramagnetic. Refer to their electron configurations to explain this statement.
- 86.** Refer to their electron configurations to explain why copper is paramagnetic while its  $1+$  ion is not.
- 87.** Suppose you were trying to find a substitute for  $\text{K}^+$  in nerve signal transmission. Where would you begin your search? What ions would be most like  $\text{K}^+$ ? For each ion you propose, explain the ways in which it would be similar to  $\text{K}^+$  and the ways it would be different. Refer to periodic trends in your discussion.
- 88.** Suppose you were trying to find a substitute for  $\text{Na}^+$  in nerve signal transmission. Where would you begin your search? What ions would be most like  $\text{Na}^+$ ? For each ion you propose, explain the ways in which it would be similar to  $\text{Na}^+$  and the ways it would be different. Use periodic trends in your discussion.
- 89.** Life on Earth evolved based on the element carbon. Based on periodic properties, what two or three elements would you expect to be most like carbon?
- 90.** Which pair of elements would you expect to have the most similar atomic radii, and why?  
 a.  $\text{Si}$  and  $\text{Ga}$   
 b.  $\text{Si}$  and  $\text{Ge}$   
 c.  $\text{Si}$  and  $\text{As}$

- 91.** Consider these elements:  $\text{N}$ ,  $\text{Mg}$ ,  $\text{O}$ ,  $\text{F}$ ,  $\text{Al}$ .  
 a. Write the electron configuration for each element.  
 b. Arrange the elements in order of decreasing atomic radius.  
 c. Arrange the elements in order of increasing ionization energy.  
 d. Use the electron configurations in part a to explain the differences between your answers to parts b and c.
- 92.** Consider these elements:  $\text{P}$ ,  $\text{Ca}$ ,  $\text{Si}$ ,  $\text{S}$ ,  $\text{Ga}$ .  
 a. Write the electron configuration for each element.  
 b. Arrange the elements in order of decreasing atomic radius.  
 c. Arrange the elements in order of increasing ionization energy.  
 d. Use the electron configurations in part a to explain the differences between your answers to parts b and c.
- 93.** Explain why atomic radius decreases as you move to the right across a period for main-group elements but not for transition elements.
- 94.** Explain why vanadium (radius = 134 pm) and copper (radius = 128 pm) have nearly identical atomic radii, even though the atomic number of copper is about 25% higher than that of vanadium. What would you predict about the relative densities of these two metals? Look up the densities in a reference book, periodic table, or on the Internet. Are your predictions correct?
- 95.** The lightest noble gases, such as helium and neon, are completely inert—they do not form any chemical compounds whatsoever. The heavier noble gases, in contrast, do form a limited number of compounds. Explain this difference in terms of trends in fundamental periodic properties.

- 96.** The lightest halogen is also the most chemically reactive, and reactivity generally decreases as you move down the column of halogens in the periodic table. Explain this trend in terms of periodic properties.
- 97.** Write general outer electron configurations ( $ns^x np^y$ ) for groups 6A and 7A in the periodic table. The electron affinity of each group 7A element is more negative than that of each corresponding group 6A element. Use the electron configurations to explain why this is so.
- 98.** The electron affinity of each group 5A element is more positive than that of each corresponding group 4A element. Use the outer electron configurations for these columns to suggest a reason for this observation.
- 99.** The elements with atomic numbers 35 and 53 have similar chemical properties. Based on their electronic configurations, predict the atomic number of a heavier element that also should share these chemical properties.
- 100.** Write the electron configurations of the six cations that form from sulfur by the loss of one to six electrons. For those cations that have unpaired electrons, write orbital diagrams.
- 101.** You have cracked a secret code that uses elemental symbols to spell words. The code uses numbers to designate the elemental symbols. Each number is the sum of the atomic number and the highest principal quantum number of the highest occupied orbital of the element whose symbol is to be used. The message

may be written forward or backward. Decode the following messages:

- 10, 12, 58, 11, 7, 44, 63, 66
  - 9, 99, 30, 95, 19, 47, 79
- 102.** The electron affinity of sodium is lower than that of lithium, while the electron affinity of chlorine is higher than that of fluorine. Suggest an explanation for this observation.
- 103.** Use Coulomb's law to calculate the ionization energy in kJ/mol of an atom composed of a proton and an electron separated by 100.00 pm. What wavelength of light has sufficient energy to ionize the atom?
- 104.** The first ionization energy of sodium is 496 kJ/mol. Use Coulomb's law to estimate the average distance between the sodium nucleus and the 3s electron. How does this distance compare to the atomic radius of sodium? Explain the difference.
- 105.** Consider the elements: B, C, N, O, F.
- Which element has the highest first ionization energy?
  - Which element has the largest atomic radius?
  - Which element is most metallic?
  - Which element has three unpaired electrons?
- 106.** Consider the elements: Na, Mg, Al, Si, P.
- Which element has the highest second ionization energy?
  - Which element has the smallest atomic radius?
  - Which element is least metallic?
  - Which element is diamagnetic?

## CHALLENGE PROBLEMS

- 107.** Consider the densities and atomic radii of the noble gases at 25 °C:

Element	Atomic Radius (pm)	Density (g/L)
He	32	0.18
Ne	70	0.90
Ar	98	-
Kr	112	3.75
Xe	130	-
Rn	-	9.73

- Estimate the densities of argon and xenon by interpolation from the data.
- Estimate the density of the element with atomic number 118 by extrapolation from the data.
- Use the molar mass of neon to estimate the mass of a neon atom. Then use the atomic radius of neon to calculate the average density of a neon atom. How does this density compare to the density of neon gas? What does this comparison suggest about the nature of neon gas?
- Use the densities and molar masses of krypton and neon to calculate the number of atoms of each element found in a volume of 1.0 L. Use these values to estimate the number of atoms present in 1.0 L of Ar. Now use the molar mass of argon to estimate the density of Ar. How does this estimate compare to that in part a?

- 108.** As you have seen, the periodic table is a result of empirical observation (i.e., the periodic law), but quantum-mechanical theory explains *why* the table is so arranged. Suppose that, in another universe, quantum theory was such that there were one s orbital but only two p orbitals (instead of three) and only three d orbitals (instead of five). Draw out the first four periods of the periodic table in this alternative universe. Which elements would be the equivalent of the noble gases? Halogens? Alkali metals?

- 109.** Consider the metals in the first transition series. Use periodic trends to predict a trend in density as you move to the right across the series.

- 110.** Imagine a universe in which the value of  $m_s$  can be  $+\frac{1}{2}$ , 0, and  $-\frac{1}{2}$ . Assuming that all the other quantum numbers can take only the values possible in our world and that the Pauli exclusion principle applies, determine:

- the new electronic configuration of neon
- the atomic number of the element with a completed  $n = 2$  shell
- the number of unpaired electrons in fluorine

- 111.** A carbon atom can absorb radiation of various wavelengths with resulting changes in its electron configuration. Write orbital diagrams for the electron configuration of carbon that results from absorption of the three longest wavelengths of radiation it can absorb.

- 112.** Only trace amounts of the synthetic element darmstadtium, atomic number 110, have been obtained. The element is so highly unstable that no observations of its properties have been possible. Based on its position in the periodic table, propose three different reasonable valence electron configurations for this element.

- 113.** What is the atomic number of the as yet undiscovered element in which the  $8s$  and  $8p$  electron energy levels fill? Predict the chemical behavior of this element.
- 114.** The trend in second ionization energy for the elements from lithium to fluorine is not a regular one. Predict which of these elements has the highest second ionization energy and which has the lowest and explain. Of the elements N, O, and F, O has the highest and N the lowest second ionization energy. Explain.
- 115.** Unlike the elements in groups 1A and 2A, those in group 3A do not show a regular decrease in first ionization energy as you move down the column. Explain the irregularities.
- 116.** Using the data in Figures 9.15 and 9.16, calculate  $\Delta E$  for the reaction  $\text{Na}(g) + \text{Cl}(g) \longrightarrow \text{Na}^+(g) + \text{Cl}^-(g)$ .
- 117.** Even though adding two electrons to O or S forms an ion with a noble gas electron configuration, the second electron affinity of both of these elements is positive. Explain.
- 118.** In Section 2.7 we discussed the metalloids, which form a diagonal band separating the metals from the nonmetals. There are other instances in which elements such as lithium and magnesium that are diagonal to each other have comparable metallic character. Suggest an explanation for this observation.
- 119.** The heaviest known alkaline earth metal is radium, atomic number 88. Find the atomic numbers of the as yet undiscovered next two members of the series.
- 120.** Predict the electronic configurations of the first two excited states (next higher-energy states beyond the ground state) of Pd.
- 121.** Table 9.2 does not include francium because none of francium's isotopes are stable. Predict the values of the entries for Fr in Table 9.2. Predict the nature of the products of the reaction of Fr with: (a) water, (b) oxygen, and (c) chlorine.
- 122.** From its electronic configuration, predict which of the first 10 elements would be most similar in chemical behavior to the as yet undiscovered element 165.

## CONCEPTUAL PROBLEMS

- 123.** Imagine that in another universe atoms and elements are identical to ours, except that atoms with six valence electrons have particular stability (in contrast to our universe where atoms with eight valence electrons have particular stability). Give an example of an element in the alternative universe that corresponds to each of the following:
- a noble gas
  - a reactive nonmetal
  - a reactive metal
- 124.** The outermost valence electron in atom A experiences an effective nuclear charge of  $2+$  and is on average 225 pm from the nucleus. The outermost valence electron in atom B experiences an effective nuclear charge of  $1+$  and is on average 175 pm from the nucleus. Which atom (A or B) has the higher first ionization energy? Explain.
- 125.** Determine whether each statement regarding penetration and shielding is true or false. (Assume that all lower energy orbitals are fully occupied.)
- An electron in a  $3s$  orbital is more shielded than an electron in a  $2s$  orbital.
  - An electron in a  $3s$  orbital penetrates into the region occupied by core electrons more than electrons in a  $3p$  orbital penetrates into the region occupied by core electrons.
  - An electron in an orbital that penetrates closer to the nucleus always experiences more shielding than an electron in an orbital that does not penetrate as far.
  - An electron in an orbital that penetrates close to the nucleus tends to experience a higher effective nuclear charge than an electron in an orbital that does not penetrate close to the nucleus.
- 126.** Give a combination of four quantum numbers that could be assigned to an electron occupying a  $5p$  orbital. Do the same for an electron occupying a  $6d$  orbital.
- 127.** Use the trends in ionization energy and electron affinity to explain why calcium fluoride has the formula  $\text{CaF}_2$  and not  $\text{Ca}_2\text{F}$  or  $\text{CaF}$ .

## QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

- 128.** In a complete sentence describe the relationship between shielding and penetration.
- 129.** Play a game to memorize the order in which orbitals fill. Have each group member in turn state the name of the next orbital to fill and the maximum number of electrons it can hold (for example, "1s two," "2s two," "2p six"). If a member gets stuck, other group members can help, consulting Figure 9.5 and the accompanying text summary if necessary. However, when a member gets stuck, the next player starts back at "1s two." Keep going until each group member can list all the orbitals in order up to "6s two."

### Active Classroom Learning

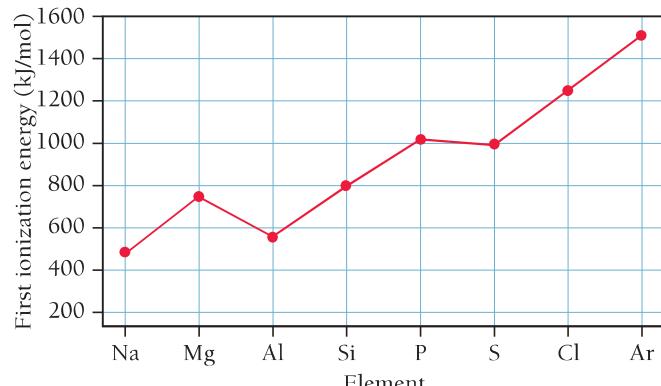
- 130.** Sketch a periodic table (without element symbols). Include the correct number of rows and columns in the  $s$ ,  $p$ ,  $d$ , and  $f$  blocks. Shade in the squares for elements that have irregular electron configurations.
- 131.** In complete sentences, explain: (a) why  $\text{Se}^{2-}$  and  $\text{Br}^-$  are about the same size; (b) why  $\text{Br}^-$  is slightly smaller than  $\text{Se}^{2-}$ ; and (c) which singly charged cation you would expect to be approximately the same size as  $\text{Se}^{2-}$  and  $\text{Br}^-$  and why.
- 132.** Have each member of your group sketch a periodic table indicating a periodic trend (atomic size, first ionization energy, metallic character, etc.). Have each member present his or her table to the rest of the group and explain the trend based on concepts such as orbital size or effective nuclear charge.



## DATA INTERPRETATION AND ANALYSIS

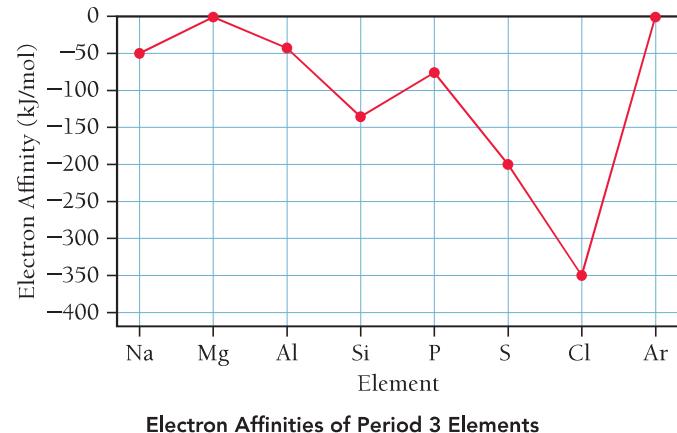
### Periodic Properties of Period 3 Elements

- 133.** The accompanying graphs show the first ionization energies and electron affinities of the period 3 elements. Refer to the graphs to answer the questions that follow.



First Ionization Energies of Period 3 Elements

- Describe the general trend in period 3 first ionization energies as you move from left to right across the periodic table. Explain why this trend occurs.
- The trend in first ionization energy has two exceptions: one at Al and another at S. Explain why the first ionization energy of Al is lower than that of Mg and why the first ionization of S is less than that of P.



Electron Affinities of Period 3 Elements

- Describe the general trend in period 3 electron affinities as you move from left to right across the periodic table. Explain why this trend occurs.
- The trend in electron affinities has exceptions at Mg and P. Explain why the electron affinity of Mg is more positive (less exothermic) than that of Na and why the electron affinity of P is more positive (less exothermic) than that of Si.
- Determine the overall energy change for removing one electron from Na and adding that electron to Cl. Is the exchange of the electron exothermic or endothermic?



## ANSWERS TO CONCEPTUAL CONNECTIONS

### Coulomb's Law

- 9.1 (a)** Since the charges are opposite, the potential energy of the interaction is negative. As the charges get closer together,  $r$  becomes smaller and the potential energy decreases (becomes more negative).

### Penetration and Shielding

- 9.2 (c)** Penetration results in less shielding from nuclear charge and therefore lower energy.

### Electron Configurations and Quantum Numbers

- 9.3 (b)**  $n = 4$ ,  $l = 0$ ,  $m_l = 0$ ,  $m_s = +\frac{1}{2}$ ;  $n = 4$ ,  $l = 0$ ,  $m_l = 0$ ,  $m_s = -\frac{1}{2}$

### Valence Electrons and Group Number

- 9.4 (c)** Nitrogen has five valence electrons. Since nitrogen is a main-group element, it has the same number of valence electrons as its lettered group number in the periodic table.

### Electron Configuration and Ion Charge

- 9.5 (b)** Elements with electron configurations close to those of the noble gases gain or lose electrons to attain a noble gas configuration. The 2-charge implies that the element gained two electrons, which results in the configuration  $ns^2np^6$ , which is a noble gas configuration.

### Effective Nuclear Charge

- 9.6 (c)** Since  $Z_{\text{eff}}$  increases from left to right across a row in the periodic table, the valence electrons in S experience a greater effective nuclear charge than the valence electrons in Al or in Mg.

### Ions, Isotopes, and Atomic Size

- 9.7 (b)** The isotopes of an element all have the same radius for two reasons: (1) neutrons are negligibly small compared to the size of an atom and therefore extra neutrons do not increase atomic size, and (2) neutrons have no charge and therefore do not attract electrons in the way that protons do.

### Successive Ionization Energies

- 9.8 (c)** Since B has three valence electrons, it would have a huge jump between its third and fourth ionization energies. The third ionization energy corresponds to removing the third valence electron, while the fourth ionization energy corresponds to removing the first core electron.

### Ionization Energies and Chemical Bonding

- 9.9 (b)** As you can see from the successive ionization energies of any element, valence electrons are held most loosely and can therefore be transferred or shared most easily. Core electrons, however, are held tightly and are not easily transferred or shared. Consequently, valence electrons are most important to chemical bonding.

### Periodic Trends

- 9.10 (c)** The 3s electron in sodium has a relatively low ionization energy (496 kJ/mol) because it is a valence electron. The energetic cost for sodium to lose a second electron is extraordinarily high (4560 kJ/mol) because the next electron to be lost is a core electron ( $2p$ ).