The majority of the material that composes most aircraft is aluminum.

CHAPTER 3

Periodic Properties of the Elements

GREAT ADVANCES IN SCIENCE occur not only when a scientist sees something new, but also when a scientist sees something everyone else has seen in a new way. That is what happened in 1869 when Dmitri Mendeleev, a Russian chemistry professor, saw a pattern in the properties of elements. Mendeleev's insight led to the development of the periodic table. Recall from Chapter 1 that theories explain the underlying reasons for observations. If we think of Mendeleev's periodic table as a compact way to summarize a large number of observations, then quantum mechanics is the theory that explains the underlying reasons. Quantum mechanics explains how electrons are arranged in an element's atoms, which in turn determines the element's properties. Because the periodic table is organized according to those properties, quantum mechanics elegantly accounts for Mendeleev's periodic table. In this chapter, we see a continuation of this book's theme—the properties of matter (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).

> "It is the function of science to discover the existence of a general reign of order in nature and to find the causes governing this order."
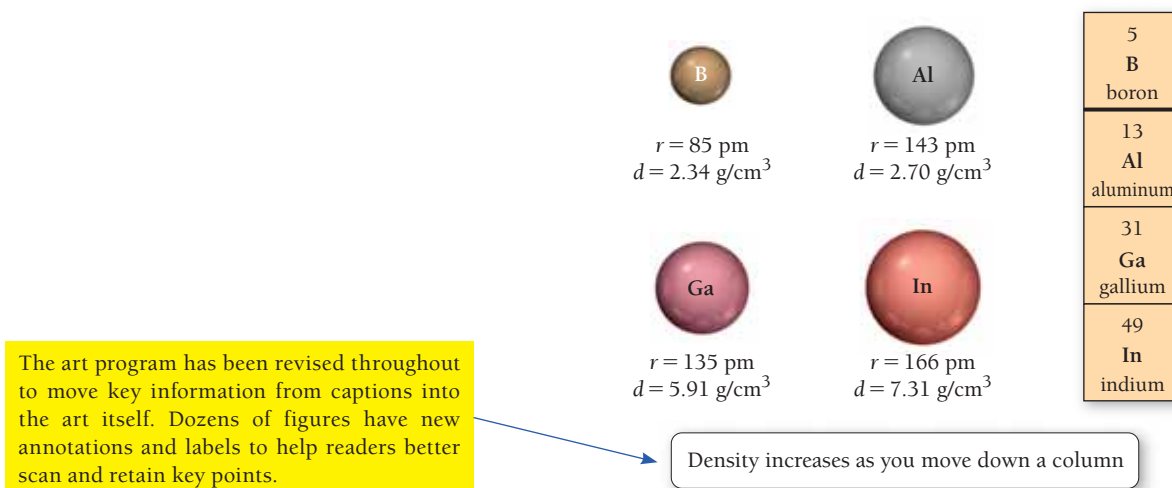>
> —Dmitri Mendeleev (1834–1907)

3.1 Aluminum: Low-Density Atoms Result in Low-Density Metal

Look out the window of almost any airplane and you will see the large sheets of aluminum that compose the aircraft's wing. In fact, the majority of the plane is most likely made out of aluminum. Aluminum has several properties that make it suitable for airplane construction, but among the most important is its low density. Aluminum has a density of only 2.70 g/cm^3. For comparison, iron's density is 7.86 g/cm^3, and platinum's density is 21.4 g/cm^3. Why is the density of aluminum metal so low?

The density of aluminum metal is low because the density of an aluminum atom is low. Few metal atoms have a lower mass-to-volume ratio than aluminum, and those that do can't be used in airplanes for other reasons (such as their high chemical reactivity). Although the *arrangements* of atoms in a solid must also be considered when evaluating the density of the solid, the mass-to-volume ratio of the composite atoms

Dynamic chapter-opening images introduce relevancy and grab students' attention.

113

is a very important factor. For this reason, the densities of the elements generally follow a fairly well-defined trend: *The density of elements tends to increase as we move down a column in the periodic table*. For example, consider the densities of several elements in the column that includes aluminum in the periodic table:

5
B
boron

13
Al
aluminum

31
Ga
gallium

49
In
indium

B $r = 85$ pm $d = 2.34$ g/cm^3

Al $r = 143$ pm $d = 2.70$ g/cm^3

Ga $r = 135$ pm $d = 5.91$ g/cm^3

In $r = 166$ pm $d = 7.31$ g/cm^3

Density increases as you move down a column

The art program has been revised throughout to move key information from captions into the art itself. Dozens of figures have new annotations and labels to help readers better scan and retain key points.

As we move down the column in the periodic table, the density of the elements increases even though the radius generally increases as well (with the exception of Ga whose radius decreases a bit). Why? *Because the mass of each successive atom increases even more than its volume does*. As we move down a column in the periodic table, the additional protons and neutrons add more mass to the atoms. This increase in mass is greater than the increase in volume, resulting in a higher denstity.

The densities of elements and the radii of their atoms are examples of *periodic properties*. A **periodic property** is one that is generally 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. As we do, we will see that these properties—as well as the overall arrangement of the periodic table—are explained by quantum-mechanical theory, which we first examined in Chapter 2. *Quantum-mechanical theory explains the electronic structure of atoms—this in turn determines the properties of those atoms*.

The theme of *structure determines properties* is emphasized throughout the text (in both first-semester content as well as second-semester topics).

Notice again that *structure determines properties*. 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. Understanding the structure of atoms as explained by quantum mechanics allows us to predict the properties of elements from their position on the periodic table. If we need a metal with a high density, for example, we look toward the bottom of the periodic table. Platinum (as we saw previously) has a density of 21.4 g/cm^3. It is among the densest metals and is found near the bottom of the periodic table. If we need a metal with a low density, we look toward the top of the periodic table. Aluminum is among the least dense metals and is found near the top of the periodic table.

3.2 The Periodic Law and the Periodic Table

Prior to the 1700s, the number of known elements was relatively small, consisting mostly of the metals 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*: A triad consisted of 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 Periodic Law

| 1 H | 2 He | 3 Li | 4 Be | 5 B | 6 C | 7 N | 8 O | 9 F | 10 Ne | 11 Na | 12 Mg | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar | 19 K | 20 Ca |

Elements with similar properties recur in a regular pattern.

▲ **FIGURE 3.1 Recurring Properties** These elements are listed in order of increasing atomic number. Elements with similar properties are represented with the same color. Notice that the colors form a repeating pattern, much like musical notes form a repeating pattern on a piano keyboard.

The modern periodic table is credited primarily to the Russian chemist Dmitri Mendeleev (1834–1907), even though a similar organization had been suggested by the German chemist Julius Lothar Meyer (1830–1895). In 1869, Mendeleev noticed that certain groups of elements had similar properties. He also found that when he listed elements in order of increasing mass, these similar properties recurred in a periodic pattern (**Figure 3.1 ▲**). Mendeleev summarized these observations in the **periodic law**:

> When the elements are arranged in order of increasing mass, certain sets of properties recur periodically.

Mendeleev organized the known elements in a table consisting of a series of rows in which mass increases from left to right. He arranged the rows so that elements with similar properties fall in the same vertical columns (**Figure 3.2 ▶**).

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. (*Eka* means the one beyond or the next one in a family of elements. So, eka-silicon means the element beyond silicon in the same family as silicon.) The properties of these two elements are summarized in **Figure 3.3 ▼**.

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, resolved this problem and resulted in even better correlation with elemental properties. Mendeleev's original listing evolved into the modern periodic

Photos throughout the book have been replaced to ensure clarity and relevance.

▲ Dmitri Mendeleev, a Russian chemistry professor who proposed the periodic law and arranged early versions of the periodic table, was honored on a Soviet postage stamp.

A Simple Periodic Table

1 H									2 He
3 Li	4 Be			5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg			13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca								

Elements with similar properties fall into columns.

▲ **FIGURE 3.2 Making a Periodic Table** We can arrange the elements from Figure 3.1 in a table where atomic number increases from left to right and elements with similar properties (as represented by the different colors) are aligned in columns.

The revised art program teaches and presents complex information clearly and concisely. These labels make the figures useful learning and study aides for students who focus on the art in a textbook.

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/cm^3	5.90 g/cm^3
Formula of oxide	X$_2$O$_3$	Ga$_2$O$_3$
Formula of chloride	XCl$_3$	GaCl$_3$

Germanium (eka-silicon)

	Mendeleev's predicted properties	Actual properties
Atomic mass	About 72 amu	72.64 amu
Density	5.5 g/cm^3	5.35 g/cm^3
Formula of oxide	XO$_2$	GeO$_2$
Formula of chloride	XCl$_4$	GeCl$_4$

▲ **FIGURE 3.3 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 to anticipate their properties.

| Main-group elements | | | Transition elements | | | | | | | | | | | | | Main-group elements | | | | | |

Periods

	1A 1	Group number																			8A 18
1	1 H	2A 2											3A 13	4A 14	5A 15	6A 16	7A 17	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg	3B 3	4B 4	5B 5	6B 6	7B 7	8	8B 9	10	1B 11	2B 12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

58 Ce cerium	59 Pr praseodymium	60 Nd neodymium	61 Pm promethium	62 Sm samarium	63 Eu europium	64 Gd gadolinium	65 Tb terbium	66 Dy dysprosium	67 Ho holmium	68 Er erbium	69 Tm thulium	70 Yb ytterbium	71 Lu lutetium
90 Th thorium	91 Pa protactinium	92 U uranium	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

Inner transition elements

▲ **FIGURE 3.4 The Modern Periodic Table**   The elements in the periodic table fall into columns. The two columns at the left and the six columns at the right constitute the main-group elements. The elements that constitute any one column are a *group* or *family*. The properties of main-group elements can generally be predicted from their position in the periodic table. The properties of the elements in the middle of the table, known as transition elements, and those at the bottom of the table, known as the inner transition elements, are less predictable based on their position within the table.

table shown in **Figure 3.4** ▲. In the modern table, elements are listed in order of increasing atomic number rather than increasing relative mass. The modern periodic table also contains more elements than Mendeleev's original table because more have been discovered since then. The discovery of new elements continues to this day. In 2015, four new elements—113, 115, 117, and 118—were discovered and added to the periodic table. One of those elements (element 113) was the first to be attributed to researchers in Asia.

We divide the periodic table, as shown in Figure 3.4, into **main-group elements**, whose properties tend to be largely predictable based on their position in the periodic table, and **transition elements** (or **transition metals**) and inner transition elements, whose properties tend to be less predictable based simply on their position in the periodic table. Main-group elements are in columns labeled with a number and the letter A. Transition elements are in columns labeled with a number and the letter B. An alternative numbering system does not use letters, but only the numbers 1–18. Both numbering systems are shown in most of the periodic tables in this book. Each column within the main-group regions of the periodic table is a **family** or **group** of elements. A family of elements has similar properties as observed by Mendeleev.

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, has predictive power, as laws usually do. However, it does not explain *why* the properties of elements recur or *why* certain elements have similar properties. Quantum-mechanical theory explains the electronic structure of atoms, which in turn determines their properties. Since a family of elements has similar properties, we expect the electronic structure of their atoms to have similarities as well. We now turn to examining those similarities.

3.1

The Periodic Table

**Cc**

Conceptual Connection

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Which element is a transition metal?

(a) Ca   (b) Pb   (c) Xe   (d) Cr

Conceptual Connections throughout each chapter ask students to think about key concepts in context and solve problems without doing any complex calculations.

The eText 2.0 icon indicates that this Conceptual Connection is embedded and interactive in the eText.

3.3 Electron Configurations: How Electrons Occupy Orbitals

KEY CONCEPT VIDEO
Electron Configurations

PEARSON
eText 2.0

As we saw in Chapter 2, 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:

H $1s^1$ — Number of electrons in orbital

Orbital

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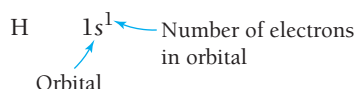
The electron configuration indicates that hydrogen's one electron is in the $1s$ orbital. Electrons generally occupy the lowest energy orbitals available. Since the $1s$ orbital is the lowest energy orbital in hydrogen (see Section 2.5), hydrogen's electron occupies that orbital. If we could write electron 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) described in Chapter 2 are for the hydrogen atom only. What do the atomic orbitals of *other atoms* look like? What are their relative energies?

The Schrödinger equation for multi-electron atoms includes 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 multi-electron atoms are hydrogen-like—they are similar to the *s*, *p*, *d*, and *f* orbitals we examined in Chapter 2. In order to see how the electrons in multi-electron 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 is similar to an electron configuration but symbolizes the electron as an arrow and the orbital as a box. The orbital diagram for a hydrogen atom is:

H   ⬆
      $1s$
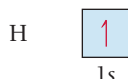
In an orbital diagram, the direction of the arrow (pointing up or pointing down) represents the orientation of the *electron's spin*. Recall from Section 2.5 that the orientation of the electron's spin is quantized, with only two possibilities: spin up ($m_s = +\frac{1}{2}$) and spin down ($m_s = -\frac{1}{2}$). In an orbital diagram, we represent $m_s = +\frac{1}{2}$ with a half-arrow pointing up (↑) and $m_s = -\frac{1}{2}$ with a half-arrow pointing down (↓). 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.

He $1s^2$

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.

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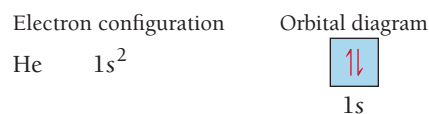
quantum numbers ($+\frac{1}{2}$ and $-\frac{1}{2}$), the Pauli exclusion principle implies that *each orbital can have a maximum of only two electrons, with opposing spins.* By applying the exclusion principle, we can write an electron configuration and orbital diagram for helium:

Electron configuration	Orbital diagram
He $1s^2$	⇅
	$1s$

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

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

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

Sublevel Energy Splitting in Multi-electron Atoms

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—we say they are **degenerate**. The orbitals within a principal level of a *multi-electron 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:

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

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 is less shielded from nuclear charge). We then examine how these concepts, together with the spatial distributions of electron probability for each orbital, result in the energy ordering presented above.

Coulomb's Law   The attractions and repulsions between charged particles, first introduced in Section 1.6, 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):

$$E = \frac{1}{4\pi\varepsilon_0} \frac{q_1 \, q_2}{r} \qquad [3.1]$$

In this equation, ε_0 is a constant ($\varepsilon_0 = 8.85 \times 10^{-12}\ \text{C}^2/\text{J} \cdot \text{m}$). The potential energy is positive for the interaction of charges with the same sign (plus × plus, or minus × minus) and negative for charges of the opposite sign (plus × minus, or minus × 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:

- The potential energy (E) associated with the interaction of like charges is positive but decreases as the particles get *farther apart* (as r increases). Since systems tend toward lower potential energy (see Section I.6), like charges that are close together have high potential energy and tend to move away from each other (toward lower potential energy). Like charges therefore repel one another (in much the same way that like poles of two magnets repel each other).

Tro's writing style is concise and friendly, breaking down difficult concepts into clear discussions that promote comprehension.

- The potential energy (E) associated with the interaction of unlike charges is negative and becomes more negative as the particles get closer together. Since systems tend toward lower potential energy, the interaction of unlike charges draws them closer together (toward lower potential energy). Unlike charges therefore attract one another (like the opposite poles of a magnet).

- 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 $1+$.

Coulomb's Law

3.2

Cc

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Conceptual Connection

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.

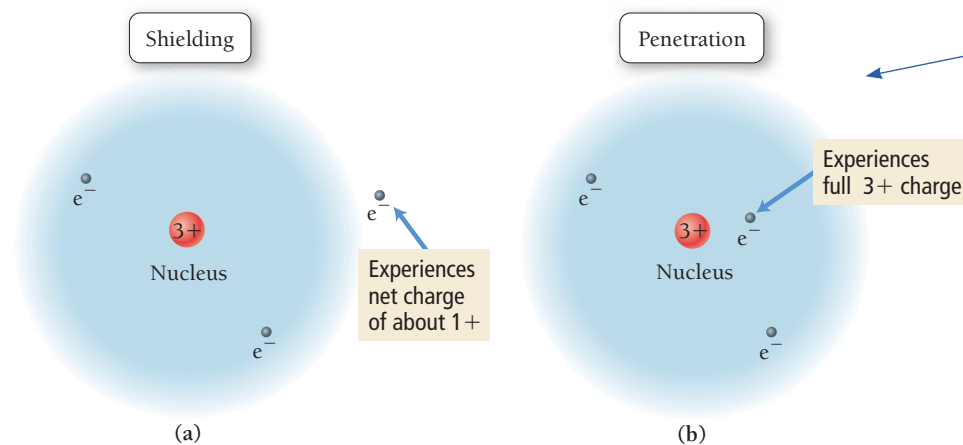(c) Their potential energy does not change.

Shielding For multi-electron atoms, any single 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 (Li^+). Because the lithium ion contains two electrons, its electron configuration is identical to that of helium:

$$Li^+ \quad 1s^2$$

Now 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 3.5a** ▼. We can think of the third electron as experiencing an **effective nuclear charge** (Z_{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.

Penetration Now imagine that this third electron comes closer to the nucleus. As the electron *penetrates* the electron cloud of the 1s electrons, it begins to experience the $3+$ charge of the nucleus more fully because the third electron 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 3.5b** ▼. 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.

Shielding

Penetration

Experiences full $3+$ charge

e^-

$3+$

Nucleus

e^-

Experiences net charge of about $1+$

e^-

e^-

$3+$

Nucleus

e^-

e^-

(a)

(b)

◀ **FIGURE 3.5 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.
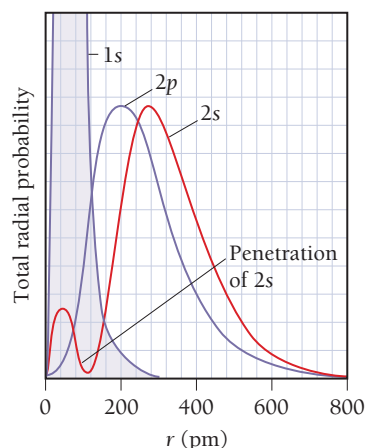
▲ FIGURE 3.6 Radial Distribution Functions for the 1s, 2s, and 2p Orbitals
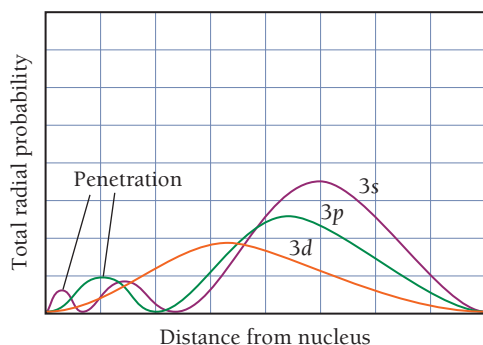
Electron Spatial Distributions and Sublevel Splitting We have now examined all of the concepts we need to understand the energy splitting of the sublevels within a principal level. The splitting is a result of the spatial distributions of electrons within a sublevel. Recall from Section 2.6 that the 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 3.6 ◄** 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?
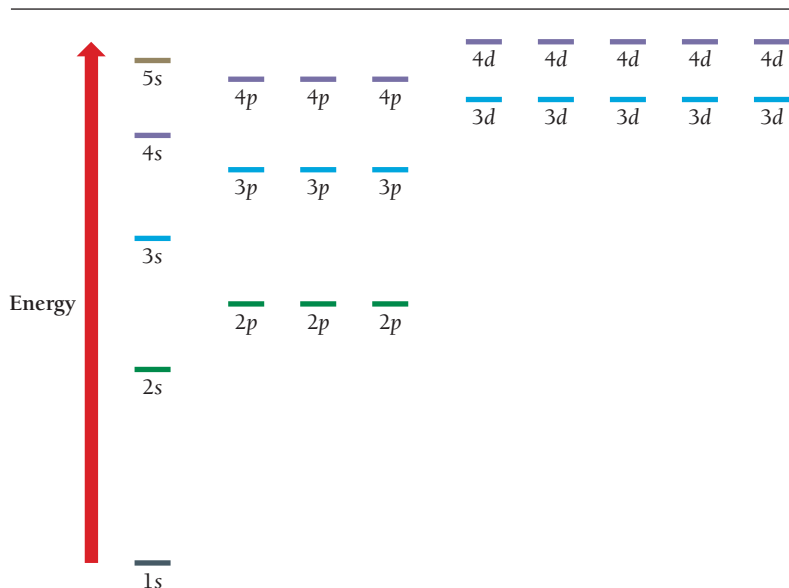
The reason is the bump near $r = 0$, the nucleus for the 2s orbital. This bump represents a significant probability of the electron being found very close to the nucleus. Even more importantly, this area of the probability penetrates into the 1s orbital—it gets into the region where shielding by the 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 2s orbital—because it experiences more of the nuclear charge due to its greater *penetration*—is lower in energy than the 2p orbital.

The situation is 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 3.7 ◄**.

Figure 3.8 ▼ shows the energy ordering of a number of orbitals in multi-electron atoms. Notice these features of Figure 3.8:

- Because of penetration, the sublevels of each principal level are *not* degenerate for multi-electron atoms.

- In the fourth and fifth principal levels, the effects of penetration become so important that the 4s orbital is lower in energy than the 3d orbitals and the 5s orbital is 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 in Section 3.4).

▲ FIGURE 3.7 Radial Distribution Functions for the 3s, 3p, and 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: $s < p < d$.

General Energy Ordering of Orbitals for Multi-electron Atoms

▶ FIGURE 3.8 General Energy Ordering of Orbitals for Multi-electron Atoms

3.3

Cc

Conceptual
Connection

PEARSON
eText
2.0

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 Multi-electron Atoms

Now that we know the energy ordering of orbitals in multi-electron atoms, we can determine ground state electron configurations for the rest of the elements. Because electrons occupy the lowest energy orbitals available when the atom is in its ground state, and 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 $1s^2 2s^1$

1s   2s
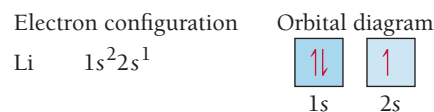
For carbon, which has six electrons, the electron configuration and orbital diagram are:

Electron configuration   Orbital diagram

C $1s^2 2s^2 2p^2$

1s   2s   2p
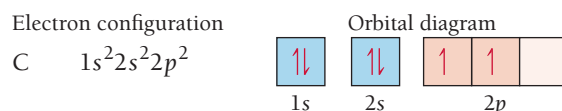
Notice that the 2p electrons occupy the *p* orbitals (of equal energy) singly, rather than pairing in one orbital. This way of filling orbitals follows **Hund's rule**, which states that *when filling degenerate orbitals, electrons fill them singly first, with parallel spins*. Hund's rule is a result 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 a larger region of space. By convention, we denote these parallel spins with half arrows pointing up.

Summarizing Orbital Filling
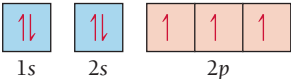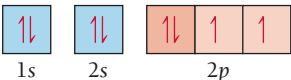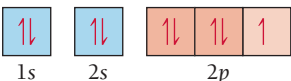
- Electrons occupy orbitals so as to minimize the energy of the atom; therefore, lower-energy orbitals fill before higher-energy orbitals. Orbitals fill in the following order: $1s\,2s\,2p\,3s\,3p\,4s\,3d\,4p\,5s\,4d\,5p\,6s$.

- 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 (Hund's rule). Once the orbitals of equal energy are half-full, the electrons start to pair.

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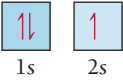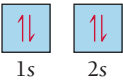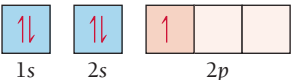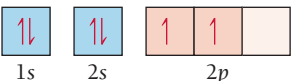
Electrons with parallel spins have correlated motion that minimizes their mutual repulsion.

Consider the electron configurations and orbital diagrams for the elements with atomic numbers 3–10:
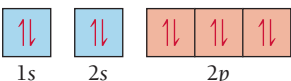
Symbol	Number of electrons	Electron configuration	Orbital diagram
Li	3	$1s^2 2s^1$	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow}$ — 1s 2s
Be	4	$1s^2 2s^2$	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ — 1s 2s
B	5	$1s^2 2s^2 2p^1$	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\ \ }$ — 1s 2s 2p
C	6	$1s^2 2s^2 2p^2$	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\ \uparrow\ }$ — 1s 2s 2p

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

N	7	$1s^2 2s^2 2p^3$	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\ \uparrow\ \uparrow}$ — 1s 2s 2p
O	8	$1s^2 2s^2 2p^4$	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow\ \uparrow\ \uparrow}$ — 1s 2s 2p
F	9	$1s^2 2s^2 2p^5$	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow}$ — 1s 2s 2p
Ne	10	$1s^2 2s^2 2p^6$	$\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow}$ $\boxed{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}$ — 1s 2s 2p

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 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:

$$\text{Na} \quad 1s^2 2s^2 2p^6 3s^1$$

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

$$\text{Na} \quad [\text{Ne}]\, 3s^1$$

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

To write an electron configuration for an element, we first find its atomic number from the periodic table—this number equals the number of electrons. Then we use the order of filling 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 two electrons.
- The *p* sublevel has three orbitals and can hold six electrons.
- The *d* sublevel has five orbitals and can hold ten electrons.
- The *f* sublevel has seven orbitals and can hold 14 electrons.

EXAMPLE 3.1

Worked Examples feature Tro's hallmark problem-solving approach. The left column echoes what a professor would say while teaching and the right column shows what a professor would write while teaching.

Electron Configurations

Write the electron configuration for each element.

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

SOLUTION

(a) Mg Magnesium has 12 electrons. Distribute two electrons into the 1s orbital, two into the 2s orbital, six into the 2p orbitals, and two into the 3s orbital.	Mg $1s^2 2s^2 2p^6 3s^2$ or [Ne] $3s^2$
(b) P Phosphorus has 15 electrons. Distribute two electrons into the 1s orbital, two into the 2s orbital, six into the 2p orbitals, two into the 3s orbital, and three into the 3p orbitals.	P $1s^2 2s^2 2p^6 3s^2 3p^3$ or [Ne] $3s^2 3p^3$
(c) Br Bromine has 35 electrons. Distribute two electrons into the 1s orbital, two into the 2s orbital, six into the 2p orbitals, two into the 3s orbital, six into the 3p orbitals, two into the 4s orbital, ten into the 3d orbitals, and five into the 4p orbitals.	Br $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$ or [Ar] $4s^2 3d^{10} 4p^5$
(d) Al Aluminum has 13 electrons. Distribute two electrons into the 1s orbital, two into the 2s orbital, six into the 2p orbitals, two into the 3s orbital, and one into the 3p orbital.	Al $1s^2 2s^2 2p^6 3s^2 3p^1$ or [Ne] $3s^2 3p^1$

FOR PRACTICE 3.1

Write the electron configuration for each element.

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

EXAMPLE 3.2

Writing Orbital Diagrams

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

SOLUTION

Sulfur's atomic number is 16, so it 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.	 1s 2s 2p 3s 3p
Distribute the 16 electrons into the boxes representing the orbitals, allowing a maximum of two electrons per orbital and obeying Hund's rule. You can see from the diagram that sulfur has two unpaired electrons.	 1s 2s 2p 3s 3p Two unpaired electrons
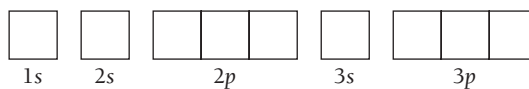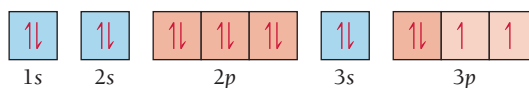
FOR PRACTICE 3.2

For Practice Problems follow every worked example and are assignable in MasteringChemistry™.
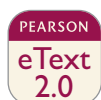
Write the orbital diagram for Ar and determine its number of unpaired electrons.

PEARSON
eText
2.0

3.4

Cc

Conceptual
Connection

Electron Configurations and Quantum Numbers

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

PEARSON
eText
2.0

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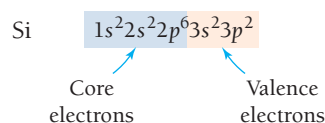on the Periodic Table**

eText 2.0 icons throughout the chapter indicate where students can view Key Concept Videos and Interactive Worked Example videos, embedded in eText 2.0. All videos and in-video assessment questions are assignable in MasteringChemistry™ and accessible on mobile devices.

3.4 **Electron Configurations, Valence Electrons, and the Periodic Table**

Recall from Section 3.2 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 3.9 ▼**. As we move to the right across a row (which is also called a period), 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 particulate world (an atom's electronic structure) lies in these outermost electrons.

An atom's **valence electrons** are the most 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 valence electrons from all the other electrons in an atom, which we call **core electrons**. The core electrons are those in *complete* principal energy levels and those in *complete d* and *f* sublevels. For example, silicon, with the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^2$ has four valence electrons (those in the $n = 3$ principal level) and ten core electrons:

Si $1s^2 2s^2 2p^6 3s^2 3p^2$

Core
electrons

Valence
electrons

NEW! Annotations added to art to direct student attention to key elements in the figure and promote understanding of the processes depicted. Numerous figures in the second edition have better, more helpful labels and annotations to focus readers on key concepts.

Outer Electron Configurations of Elements 1–18

Number of electrons
in outermost level
remains constant.

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** $2s^2 2p^1$	6 **C** $2s^2 2p^2$	7 **N** $2s^2 2p^3$	8 **O** $2s^2 2p^4$	9 **F** $2s^2 2p^5$	10 **Ne** $2s^2 2p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$	13 **Al** $3s^2 3p^1$	14 **Si** $3s^2 3p^2$	15 **P** $3s^2 3p^3$	16 **S** $3s^2 3p^4$	17 **Cl** $3s^2 3p^5$	18 **Ar** $3s^2 3p^6$

▲ **FIGURE 3.9 Outer Electron Configurations of the First 18 Elements in the Periodic Table**

EXAMPLE **3.3**

Valence Electrons and Core Electrons

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

SOLUTION

To write the electron configuration for Ge, determine the total number of electrons from germanium's atomic number (32) and distribute them into the appropriate orbitals.	Ge $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^2$

Because germanium is a main-group element, its valence electrons are those in the outermost principal energy level. For germanium, the $n = 1, 2,$ and 3 principal levels are complete (or full), and 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 always write electron configurations with the orbitals in the order of filling. However, it is also common to write electron configurations in the order of increasing principal quantum number. The electron configuration of germanium written in order of increasing principal quantum number is:

$$\text{Ge} \quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^2$$

4 valence electrons

Ge $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$
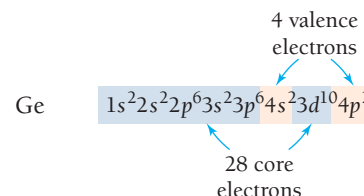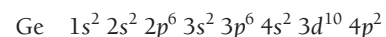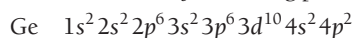
28 core electrons

FOR PRACTICE 3.3

Write the electron configuration for phosphorus. Identify its valence electrons and core electrons.

Orbital Blocks in the Periodic Table

A pattern similar to what we saw for the first 18 elements exists for the entire periodic table, as shown in **Figure 3.10** ▼. Note that, because of the filling order of orbitals, the periodic table can be divided

Orbital Blocks of the Periodic Table

▲ **FIGURE 3.10** The *s*, *p*, *d*, and *f* Blocks of the Periodic Table

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

Recall from Section 3.2 that main-group elements are those in the two far-left columns (groups 1A and 2A) and the six far-right columns (groups 3A–8A) of the periodic table.

into blocks representing the filling of particular sublevels. The first two columns on the left side of the periodic table constitute the s block, with outer electron configurations of ns^1 (group 1A) and ns^2 (group 2A). The six columns on the right side of the periodic table constitute the p block, with outer electron configurations of $ns^2 np^1$, $ns^2 np^2$, $ns^2 np^3$, $ns^2 np^4$, $ns^2 np^5$, and $ns^2 np^6$. Together, the s and p blocks constitute the *main-group* elements. The *transition* elements consitute the d block, and the lanthanides and actinides (also called the inner transition elements) constitute the f block. (For compactness, the f block is typically printed below the d block instead of being embedded within it.)

Note also 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 ten 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).

Except for helium, *the number of valence electrons for 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 number 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 principal level*. For example, because chlorine is in row 3, its highest principal level is the $n = 3$ level.

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 for that element.

- The row number of a main-group element is equal to the highest principal quantum number of that element.

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 any element based on its position in 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 represent the inner electron configuration with [Ne]. We obtain 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 (3 for chlorine).

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

$$\text{Cl} \quad [\text{Ne}]\, 3s^2 3p^5$$

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

EXAMPLE **3.4**

Writing Electron Configurations from the Periodic Table

Interactive
Worked Example
Video 3.4

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 ($n =$ row number). Next, add ten $3d$ electrons as you trace across the d block ($n =$ row number $-$ 1). (See explanation after example.) Lastly, add four $4p$ electrons as you trace across the p block to Se, which is in the fourth column of the p block ($n =$ row number).

Se $[Ar]\, 4s^2 3d^{10} 4p^4$
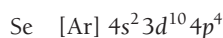
FOR PRACTICE 3.4

Refer to the periodic table to write the electron configuration of bismuth (Bi).

FOR MORE PRACTICE 3.4

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

Note 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 $3d$ orbitals fill; in the fifth row, the $4d$ orbitals fill; and so on. This happens because, as we discussed in Section 3.3, the $4s$ orbital is generally lower in energy than the $3d$ orbital (because the $4s$ orbital more efficiently penetrates into the region occupied by the core electrons). The result is that the $4s$ orbital fills before the $3d$ orbital, even though its principal quantum number ($n = 4$) is higher.

Keep in mind, however, that the $4s$ and the $3d$ orbitals are extremely close to each other in energy so that 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 $4s^2 3d^x$ with two exceptions: Cr is $4s^1 3d^5$ and Cu is $4s^1 3d^{10}$.

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 determined experimentally (through spectroscopy) and do not always conform to the general pattern. Nonetheless, the patterns we have described 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] $6s^2\,4f^7\,5d^1$ (instead of the expected [Xe] $6s^2 4f^8$).

3.5 Electron Configurations and Elemental Properties

As we discussed in Section 3.4, *the chemical properties of elements are largely determined by the number of valence electrons the elements contain.* The properties of elements are periodic because the number of valence electrons is periodic. Mendeleev grouped elements into families (or columns) based on observations about their properties. We now know that elements in a family have the same number of valence electrons. In other words, elements in a family have similar properties because they have the same number of valence electrons.

Perhaps the most striking family in the periodic table is the column labeled 8A, known as the **noble gases**. The noble gases are generally inert—they are the most unreactive elements in the entire periodic table. Why? Notice that each noble gas has eight valence electrons (or two in the case of helium), and they all have full outer quantum levels. We do not cover the quantitative (or numerical) aspects of the quantum-mechanical model in this book, but calculations of the overall energy of the electrons within atoms with eight valence electrons (or two for helium) show that these atoms are particularly stable. *In other words, when a quantum level is completely full, the overall potential energy of the electrons that occupy that level is particularly low.*

Recall from Section E.6 that, on the one hand, systems with high potential energy tend to change in ways that lower their potential energy. Systems with low potential energy, on the other hand, tend not to change—they are stable. Because atoms with eight electrons (or two for helium) have particularly low potential energy, the noble gases are stable—they *cannot* lower their energy by reacting with other atoms or molecules.

We can explain a great deal of chemical behavior with the simple idea that *elements without a noble gas electron configuration react to attain a noble gas configuration.* This idea applies particularly well to main-group elements. In this section, we first apply this idea to help differentiate between metals and nonmetals. We then apply the idea to understand the properties of several individual families of elements. Lastly, we apply the idea to the formation of ions.

Metals and Nonmetals

We can understand the broad chemical behavior of the elements by superimposing one of the most general properties of an element—whether it is a metal or nonmetal—with its outer electron configuration in the form of a periodic table (**Figure 3.11** ▶). **Metals** lie on the lower left side and middle of the periodic table and share some common properties: They 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 most importantly, *they tend to lose electrons when they undergo chemical changes.*

For example, sodium is among the most reactive metals. Its electron configuration is $1s^2\,2s^2\,2p^6\,3s^1$. Notice that its electron configuration is one electron beyond the configuration of neon, a noble gas. Sodium can attain a noble gas electron configuration by losing that one valence electron—and that is exactly what it does. When we find sodium in nature, we most often find it as Na$^+$, which has the electron configuration of neon ($1s^2\,2s^2\,2p^6$). The other main-group metals in the periodic table behave similarly: They tend to lose their valence electrons in chemical changes to attain noble gas electron configurations. The transition metals also tend to lose electrons in their chemical changes, but they do not generally attain noble gas electron configurations.

8A

2
He
$1s^2$

10
Ne
$2s^2 2p^6$

18
Ar
$3s^2 3p^6$

36
Kr
$4s^2 4p^6$

54
Xe
$5s^2 5p^6$

86
Rn
$6s^2 6p^6$

Noble gases

▲ The noble gases each have eight valence electrons except for helium, which has two. They have full outer quantum levels and are particularly stable and unreactive.

Major Divisions of the Periodic Table

Metals	Metalloids	Nonmetals

Silicon · Arsenic · Carbon · Sulfur · Strontium · Chromium · Gold · Copper · Lead · Bromine · Iodine

1A 1	2A 2	3B 3	4B 4	5B 5	6B 6	7B 7	8B 8	8B 9	8B 10	1B 11	2B 12	13	14	15	16	17	18
1 H $1s^1$																	2 He $1s^2$
3 Li $2s^1$	4 Be $2s^2$											5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^1 3d^5$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^1 3d^{10}$	30 Zn $4s^2 3d^{10}$	31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$
37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^2 4d^1$	40 Zr $5s^2 4d^2$	41 Nb $5s^1 4d^4$	42 Mo $5s^1 4d^5$	43 Tc $5s^2 4d^5$	44 Ru $5s^1 4d^7$	45 Rh $5s^1 4d^8$	46 Pd $4d^{10}$	47 Ag $5s^1 4d^{10}$	48 Cd $5s^2 4d^{10}$	49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$
55 Cs $6s^1$	56 Ba $6s^2$	57 La $6s^2 5d^1$	72 Hf $6s^2 5d^2$	73 Ta $6s^2 5d^3$	74 W $6s^2 5d^4$	75 Re $6s^2 5d^5$	76 Os $6s^2 5d^6$	77 Ir $6s^2 5d^7$	78 Pt $6s^1 5d^9$	79 Au $6s^1 5d^{10}$	80 Hg $6s^2 5d^{10}$	81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$
87 Fr $7s^1$	88 Ra $7s^2$	89 Ac $7s^2 6d^1$	104 Rf $7s^2 6d^2$	105 Db $7s^2 6d^3$	106 Sg $7s^2 6d^4$	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Lanthanides

58 Ce $6s^2 4f^1 5d^1$	59 Pr $6s^2 4f^3$	60 Nd $6s^2 4f^4$	61 Pm $6s^2 4f^5$	62 Sm $6s^2 4f^6$	63 Eu $6s^2 4f^7$	64 Gd $6s^2 4f^7 5d^1$	65 Tb $6s^2 4f^9$	66 Dy $6s^2 4f^{10}$	67 Ho $6s^2 4f^{11}$	68 Er $6s^2 4f^{12}$	69 Tm $6s^2 4f^{13}$	70 Yb $6s^2 4f^{14}$	71 Lu $6s^2 4f^{14} 5d^1$

Actinides

90 Th $7s^2 6d^2$	91 Pa $7s^2 5f^2 6d^1$	92 U $7s^2 5f^3 6d^1$	93 Np $7s^2 5f^4 6d^1$	94 Pu $7s^2 5f^6$	95 Am $7s^2 5f^7$	96 Cm $7s^2 5f^7 6d^1$	97 Bk $7s^2 5f^9$	98 Cf $7s^2 5f^{10}$	99 Es $7s^2 5f^{11}$	100 Fm $7s^2 5f^{12}$	101 Md $7s^2 5f^{13}$	102 No $7s^2 5f^{14}$	103 Lr $7s^2 5f^{14} 6d^1$

▲ **FIGURE 3.11 Metallic Behavior and Electron Configuration** The elements in the periodic table fall into three broad classes: metals, metalloids, and nonmetals. Notice the correlations between elemental properties and electron configurations.

Nonmetals lie on the upper right side of the periodic table. The division between metals and nonmetals is the zigzag diagonal line running from boron to astatine. Nonmetals have varied properties—some are solids at room temperature, others are liquids or gases—but as a whole they tend to be poor conductors of heat and electricity, and most importantly *they all tend to gain electrons when they undergo chemical changes.*

Chlorine is among the most reactive nonmetals. Its electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^5$. Notice that its electron configuration is one electron short of the configuration of argon, a noble gas. Chlorine can attain a noble gas electron configuration by gaining one electron—and that is exactly what it does. When we find chlorine in nature, we often find it as Cl^-, which has the electron configuration of argon ($1s^2 2s^2 2p^6 3s^2 3p^6$). The other nonmetals in the periodic table behave similarly: They tend to gain electrons in chemical changes to attain noble gas electron configurations.

Many of the elements that lie along the zigzag diagonal line that divides metals and nonmetals are **metalloids** and exhibit mixed properties. Several metalloids are classified as **semiconductors** because of their intermediate (and highly temperature-dependent) electrical conductivity. Our ability to change and control the conductivity of semiconductors makes them useful in the manufacture of the electronic chips and circuits central to computers, cellular telephones, and many other devices. Examples of metalloids include silicon, arsenic, and antimony.

> Multi-part images include symbolic, macroscopic, and molecular perspectives that are fundamental to visualizing and understanding chemistry. Tro's art program helps students see the relationship between the formulas they write down on paper (symbolic), the world they see around them (macroscopic), and the atoms and molecules that compose the world (molecular).

> Metalloids are sometimes called semimetals.

Families of Elements

We can also understand the properties of families of elements (those in the same column in the periodic table) based on their electron configurations. We have already seen that the group 8A elements, called the *noble gases*, have eight valence electrons and are mostly unreactive. The most familiar noble gas is

2A
4 **Be** $2s^2$
12 **Mg** $3s^2$
20 **Ca** $4s^2$
38 **Sr** $5s^2$
56 **Ba** $6s^2$
88 **Ra** $7s^2$

Alkaline earth
metals

7A
9 **F** $2s^2 2p^5$
17 **Cl** $3s^2 3p^5$
35 **Br** $4s^2 4p^5$
53 **I** $5s^2 5p^5$
85 **At** $6s^2 6p^5$

Halogens

probably helium, used to fill buoyant balloons. Helium is chemically stable—it does not combine with other elements to form compounds—and is therefore safe to put into balloons. Other noble gases are neon (often used in electronic signs), argon (a small component of our atmosphere), krypton, and xenon.

The group 1A elements, called the **alkali metals**, all have an outer electron configuration of ns^1. Like sodium, a member of this family, the alkali metals have electron configurations that are one electron beyond a noble gas electron configuration. In their reactions, alkali metals readily, and sometimes violently, lose the ns^1 electron to form ions with a 1+ charge. A marble-sized piece of sodium, for example, explodes violently when dropped into water. Lithium, potassium, and rubidium are also alkali metals.

The group 2A elements, called the **alkaline earth metals**, all have an outer electron configuration of ns^2. They have electron configurations that are two electrons beyond a noble gas configuration. In their reactions, they tend to lose the two ns^2 electrons—though not quite as violently as the alkali metals—to form ions with a 2+ charge. Calcium, for example, reacts fairly vigorously when dropped into water but does not explode as dramatically as sodium. Magnesium (a common low-density structural metal), strontium, and barium are other alkaline earth metals.

The group 7A elements, the **halogens**, all have an outer electron configuration of $ns^2 np^5$. Like chlorine, a member of this family, their electron configurations are one electron short of a noble gas configuration. Consequently, in their reactions with metals, halogens tend to gain one electron to form ions with a 1− charge. Chlorine, a greenish-yellow gas with a pungent odor, is one of the most familiar halogens. Because of its reactivity, chlorine is used as a sterilizing and disinfecting agent. Other halogens are bromine, a red-brown liquid that easily evaporates into a gas; iodine, a purple solid; and fluorine, a pale-yellow gas.

The Formation of Ions

In Section 1.8, we learned that atoms can lose or gain electrons to form ions. We have just seen that metals tend to form positively charged ions (cations) and nonmetals tend to form negatively charged ions (anions). A number of main-group elements in the periodic table always form ions with a noble gas electron configuration. Consequently, we can reliably predict their charges (**Figure 3.12 ▼**).

As we have already seen, the alkali metals tend to form cations with a 1+ charge, the alkaline earth metals tend to form ions with a 2+ charge, and the halogens tend to form ions with a 1− charge. In each of these cases, the ions have noble gas electron configurations. This is true of the rest of the ions in Figure 3.12. Nitrogen, for example, has an electron configuration of $1s^2 2s^2 2p^3$. The N^{3-} ion has three additional electrons and an electron configuration of $1s^2 2s^2 2p^6$, which is the same as the configuration of neon, the nearest noble gas.

Notice that, for the main-group elements that form cations with predictable charge, the charge is equal to the group number. For main-group elements that form anions with predictable charge, the charge is equal to the group number minus eight. Transition elements may form various ions with different charges.

The tendency for many main-group elements to form ions with noble gas electron configurations *does not* mean that the process is in itself energetically favorable. In fact, forming cations always requires energy, and forming anions sometimes requires energy as well. However, the energy cost of forming a cation or anion with *a noble gas configuration* is often less than the energy payback that occurs when that cation or anion forms chemical bonds, as we shall see in Chapter 4.

Elements That Form Ions with Predictable Charges

	1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
1	Li^+														N^{3-}	O^{2-}	F^-	
2	Na^+	Mg^{2+}											Al^{3+}			S^{2-}	Cl^-	
3	K^+	Ca^{2+}														Se^{2-}	Br^-	
4	Rb^+	Sr^{2+}														Te^{2-}	I^-	
5	Cs^+	Ba^{2+}																

▲ **FIGURE 3.12 Elements That Form Ions with Predictable Charges**

EXAMPLE **3.5**

Predicting the Charge of Ions

Predict the charges of the monoatomic (single atom) ions formed by each main-group element.

(a) Al

(b) S

SOLUTION

(a) Aluminum is a main-group metal and tends to lose electrons to form a cation with the same electron configuration as the nearest noble gas. The electron configuration of aluminum is $1s^2 2s^2 2p^6 3s^2 3p^1$. The nearest noble gas is neon, which has an electron configuration of $1s^2 2s^2 2p^6$. Therefore, aluminum loses three electrons to form the cation Al^{3+}.

(b) Sulfur is a nonmetal and tends to gain electrons to form an anion with the same electron configuration as the nearest noble gas. The electron configuration of sulfur is $1s^2 2s^2 2p^6 3s^2 3p^4$. The nearest noble gas is argon, which has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6$. Therefore, sulfur gains two electrons to form the anion S^{2-}.

FOR PRACTICE 3.5

Predict the charges of the monoatomic ions formed by each main-group element.

(a) N

(b) Rb

3.6 Periodic Trends in Atomic Size and Effective Nuclear Charge

In previous chapters, we saw that the volume of an atom is taken up primarily by its electrons (Chapter 1) occupying quantum-mechanical orbitals (Chapter 2). We also saw that 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 *nonbonding* 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 can be determined from the solid's density—is then twice the radius of a krypton atom. An atomic radius determined in this way is 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**, is defined differently 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_2 is 228 pm; therefore, the Br covalent radius is assigned to be 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 form 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), for a bond length of 232 pm. (The actual experimentally measured bond length in ICl is 232.07 pm.)

van der Waals radius

$2 \times$ Krypton radius

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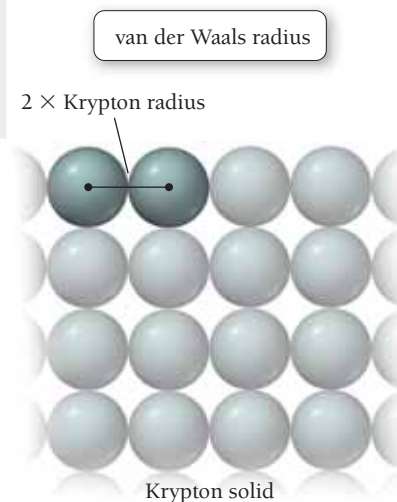
▲ The van der Waals radius of an atom is one-half the distance between adjacent nuclei in the atomic solid.

Covalent radius

Br   Br

228 pm

Br radius $= \dfrac{228 \text{ pm}}{2} = 114$ pm
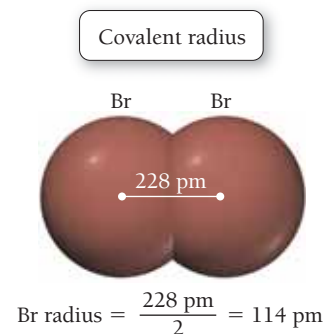
▲ The covalent radius of bromine is one-half the distance between two bonded bromine atoms.

▶ **FIGURE 3.13 Atomic Radius versus Atomic Number**   Notice the periodic trend in the atomic radius, starting at a peak with each alkali metal and falling to a minimum with each noble gas.

Annotated art features a hierarchy for learning:
• **White** boxes contain the most important information
• **Beige** boxes are of secondary importance.

Atomic Radii

Alkali metals

Period 4 transition elements

Period 5 transition elements

Noble gases
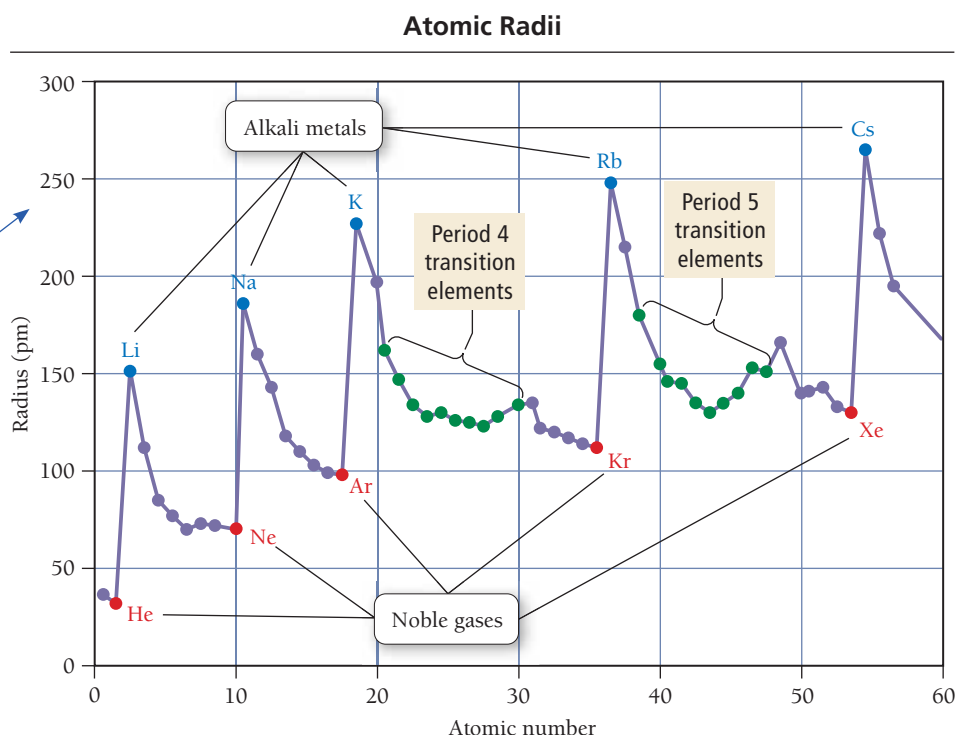
Figure 3.13 ▲ shows the atomic radius plotted as a function of atomic number for the first 57 elements in the periodic table. Notice the periodic trend in the radii. Atomic radii peak with each alkali metal. **Figure 3.14** ▼ is a relief map of atomic radii for most of the elements in the periodic table.

Trends in Atomic Radius
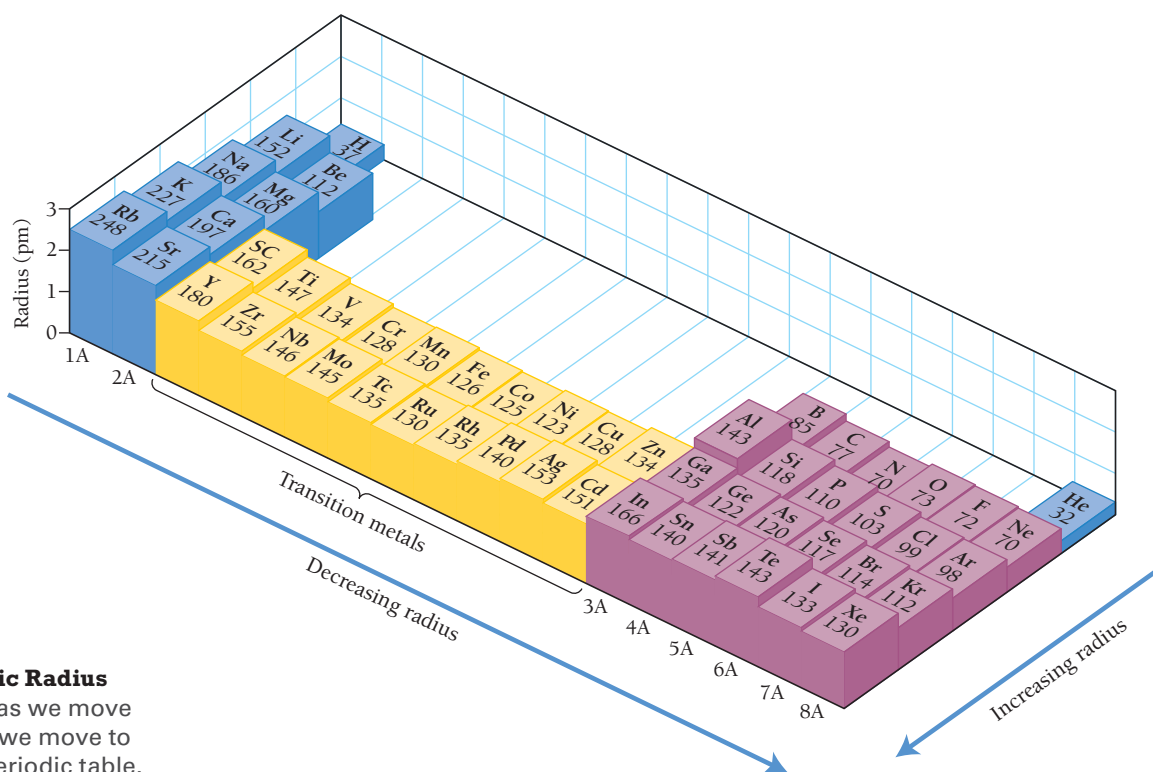
▶ **FIGURE 3.14 Trends in Atomic Radius**
In general, atomic radii increase as we move down a column and decrease as we move to the right across a period in the periodic table.

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 follows:

1. As we move down a column (or family) in the periodic table, the atomic radius increases.

2. As we move to the right across a period (or row) in the periodic table, the atomic radius decreases.

We can understand the observed trend in radius as we move down a column based on the trends in the sizes of atomic orbitals. The 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 radius as we move to the right across a row, however, is a bit more complex. To understand this trend, we now revisit some concepts from Section 3.3, including effective nuclear charge and shielding.

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 He^+ ion:

$$H \quad 1s^1$$
$$He^+ \quad 1s^1$$
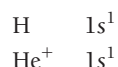
It takes 1312 kJ/mol of energy to remove the $1s$ electron from H, but 5251 kJ/mol of energy to remove it from He^+. Why? Although each electron is in a $1s$ orbital, the electron in the helium ion is attracted to the nucleus by a 2+ charge, while the electron in the hydrogen atom is attracted to the 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 3.3, any one electron in a multi-electron 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:

$$Li \quad 1s^2 2s^1$$

As shown in **Figure 3.15** ▶, 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 $1s$ (or core) electrons, reducing the net charge experienced by the $2s$ electron.

Recall from Section 3.3 that we 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):

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

Effective nuclear charge ↗ ↑ ↖ Charge shielded by other electrons

Actual nuclear charge

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+.

Shielding and Effective Nuclear Charge

Valence ($2s^1$) electron

Core ($1s^2$) electrons

Nucleus

Nucleus (3+)

Effective nuclear charge
$\approx (3+) - 2$
$\approx 1+$
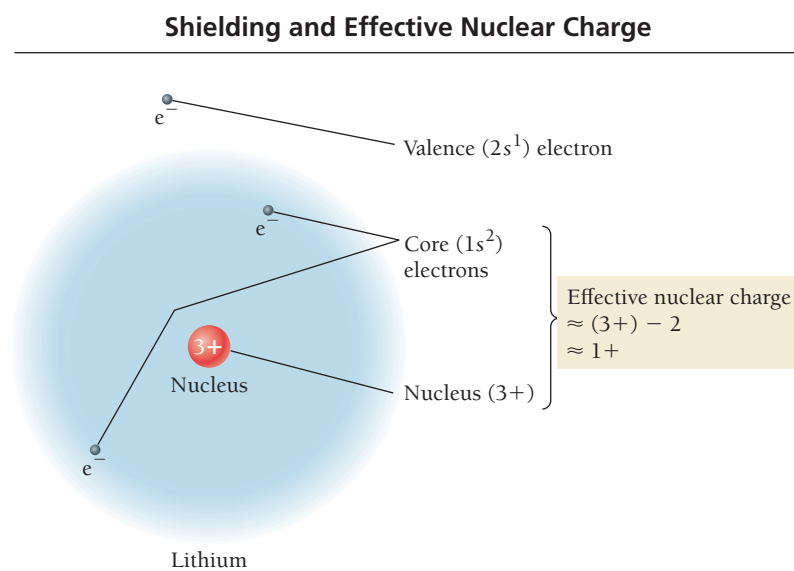
Lithium

▲ **FIGURE 3.15 Shielding and Effective Nuclear Charge** The valence electron in lithium experiences the 3+ charge of the nucleus through the shield of the 2− charge of the core electrons. The effective nuclear charge acting on the valence electron is approximately 1+.

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

$$Be \quad 1s^2 2s^2$$
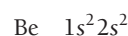
To estimate the effective nuclear charge experienced by the 2s electrons in beryllium, we must distinguish between two different types of shielding: (1) the shielding of the outermost electrons by the core electrons and (2) the shielding of the outermost electrons by *each other.* The key to understanding 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_{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.

PEARSON eText 2.0

3.5 Cc Conceptual Connection

Effective Nuclear Charge

Which atom's valence electrons experience the greatest effective nuclear charge?
(a) the valence electrons in Mg
(b) the valence electrons in Al
(c) the valence electrons in S

Atomic Radii and the Transition Elements

Notice in Figure 3.14 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). In contrast, 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 3.3, 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 $n_{highest} - 1$ orbital. The number of outermost electrons stays constant, and the electrons experience a roughly constant effective nuclear charge, keeping the radius approximately constant.

EXAMPLE 3.6

Atomic Size

Interactive
Worked Example
Video 3.6

PEARSON
eText
2.0

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

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

SOLUTION

(a) N atoms are larger than F atoms because, as you trace the path between N 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 go 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 3.6

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 3.6

Arrange the elements in order of decreasing radius: S, Ca, F, Rb, Si.

<div style="border:1px solid #000; padding:4px;">**3.7**</div> ## Ions: Electron Configurations, Magnetic Properties, 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, radii, and ionization energies.

Electron Configurations and Magnetic Properties of Ions

As we saw in Section 3.5, 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 $1s^2 2s^2 2p^5$, and that of the fluoride ion (F^-) is $1s^2 2s^2 2p^6$.

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 $1s^2 2s^1$, and that of the lithium ion (Li^+) is $1s^2 2s^0$ (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:

$$V \quad [Ar]\, 4s^2 3d^3$$

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

$$V^{2+} \quad [Ar]\, 4s^0 3d^3$$

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 normally 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 writing electron configurations for transition metal ions.

The magnetic properties of transition metal ions support these assignments. Recall from Section 3.3 that an unpaired electron has spin. This spin generates a tiny magnetic field. 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:

$$Ag \quad [Kr] \quad 5s^1 4d^{10}$$
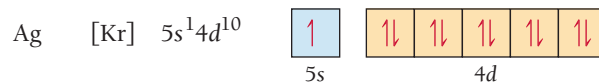
Silver's unpaired $5s$ electron causes silver to be paramagnetic. In fact, an early demonstration of electron spin—called the Stern–Gerlach experiment—involved the interaction of a beam of silver atoms with a magnetic field.

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.

$$Zn \quad [Ar] \quad 4s^2 3d^{10}$$
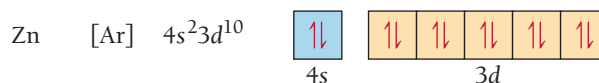
The magnetic properties of the zinc ion provide confirmation that the $4s$ electrons are indeed lost before $3d$ electrons in the ionization of zinc. If zinc lost two $3d$ electrons upon ionization, then the Zn^{2+} would become paramagnetic (because the two electrons would come out of two different filled d orbitals, leaving each of them with one unpaired electron). But the zinc ion, like the zinc atom, is diamagnetic because the $4s$ electrons are lost instead.

$$Zn^{2+} \quad [Ar] \quad 4s^0 3d^{10}$$

$4s \qquad 3d$

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

The consistent step-by-step framework within the In-Chapter Worked Examples encourages students to think logically through the problem-solving process and develop transferrable problem-solving skills.

EXAMPLE 3.7

Interactive
Worked Example
Video 3.7

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Electron Configurations and Magnetic Properties for Ions

Write the electron configuration and orbital diagram for each ion and determine whether each is diamagnetic or paramagnetic.
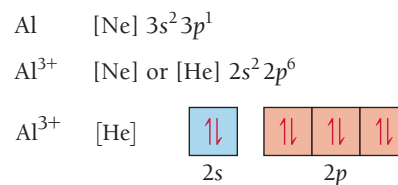
(a) Al^{3+} (b) S^{2-} (c) Fe^{3+}

SOLUTION

(a) Al^{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. Write the orbital diagram by drawing half-arrows to represent each electron in boxes representing the orbitals. Because there are no unpaired electrons, Al^{3+} is diamagnetic.

Al   [Ne] $3s^2 3p^1$

Al^{3+} [Ne] or [He] $2s^2 2p^6$

Al^{3+} [He]
$2s \qquad 2p$

Diamagnetic

(b) S^{2-}

Begin by writing the electron configuration of the neutral atom.

Since 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.

S   [Ne] $3s^2 3p^4$

S^{2-} [Ne] $3s^2 3p^6$

S^{2-} [Ne]
$3s \qquad 3p$
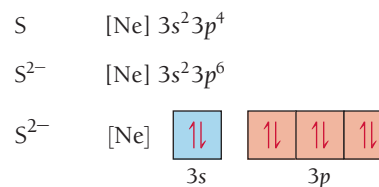
Diamagnetic

(c) 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. Since 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 Fe^{3+} is paramagnetic.

Fe   [Ar] $4s^2 3d^6$

Fe^{3+} [Ar] $4s^0 3d^5$

Fe^{3+} [Ar]
$4s \qquad 3d$
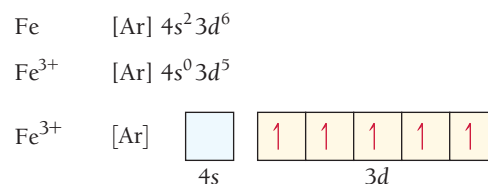
Paramagnetic

FOR PRACTICE 3.7

Write the electron configuration and orbital diagram for each ion and predict whether each will be paramagnetic or diamagnetic.

(a) Co^{2+} (b) N^{3-} (c) Ca^{2+}

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 Na^+ ion. Their electron configurations are:

$$Na \quad [Ne]\,3s^1$$
$$Na^+ \quad [Ne]\,3s^0$$
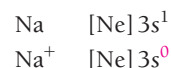
The sodium atom has an outer 3s electron and a neon core. Because the 3s electron is the outermost electron and that electron is shielded from the nuclear charge by the core electrons, it contributes greatly to the size of the sodium atom. The sodium cation, having lost the outermost 3s electron, has 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 illustrated in **Figure 3.16 ▼**.

Cations are much smaller than their corresponding neutral atoms.

Radii of Atoms and Their Cations (pm)

Group 1A		Group 2A		Group 3A	
Li	Li^+	Be	Be^{2+}	B	B^{3+}
152	60	112	31	85	23
Na	Na^+	Mg	Mg^{2+}	Al	Al^{3+}
186	95	160	65	143	50
K	K^+	Ca	Ca^{2+}	Ga	Ga^{3+}
227	133	197	99	135	62
Rb	Rb^+	Sr	Sr^{2+}	In	In^{3+}
248	148	215	113	166	81
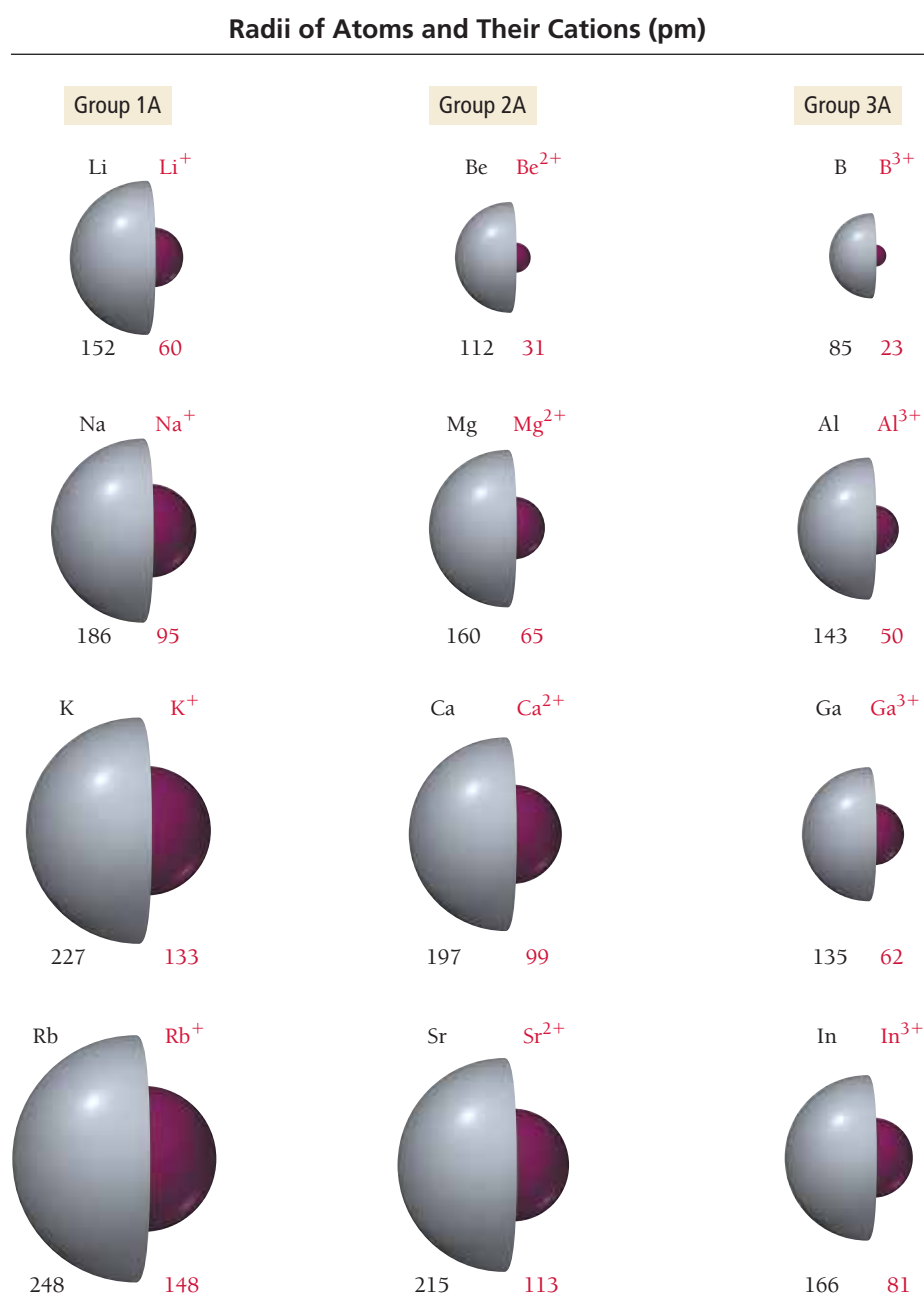
▶ **FIGURE 3.16 Sizes of Atoms and Their Cations** Atomic and ionic radii (pm) for the first three columns of main-group elements.

What about anions? Consider, for example, the difference between Cl and Cl⁻. Their electron configurations are:

$$\text{Cl} \quad [\text{Ne}]\, 3s^2 3p^5$$
$$\text{Cl}^- \quad [\text{Ne}]\, 3s^2 3p^6$$
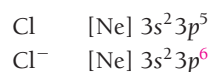
The chlorine anion has one additional outermost electron but no additional proton to increase the nuclear charge. The extra electron increases the repulsions among the outermost electrons, resulting in a chloride anion that is larger than the chlorine atom. The trend is the same with all anions and their atoms, as shown in **Figure 3.17** ▶.

Anions are much larger than their corresponding neutral atoms.

We can observe an interesting trend in ionic size by examining 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, however, has 20 protons, and therefore a charge of 20+ pulling on the same 18 electrons. The result is a much smaller radius. In general, the greater the nuclear charge in atoms or ions with the same number of electrons, the smaller the atom or ion.

Radii of Atoms and Their Anions (pm)

▶ **FIGURE 3.17 Sizes of Atoms and Their Anions** Atomic and ionic radii for groups 6A and 7A in the periodic table.

Group 6A		Group 7A	
O O²⁻		F F⁻	
73 140		72 136	
S S²⁻		Cl Cl⁻	
103 184		99 181	
Se Se²⁻		Br Br⁻	
117 198		114 195	
Te Te²⁻		I I⁻	
143 221		133 216	

EXAMPLE 3.8

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 the S^{2-} ion has the same number of protons as S but two more electrons. The additional electron–electron repulsions cause the anion to be larger than the neutral atom.

(b) A Ca atom is larger than a Ca^{2+} ion because the Ca atom has an argon core and two 4s electrons. Because the 4s electrons are the outermost electrons and they are shielded from the nuclear charge by the core electrons, they contribute greatly to the size of the Ca atom. The Ca^{2+} cation, having lost the outermost 4s electrons, has only the argon core and carries a charge of 2+, which makes it smaller than the Ca atom.

(c) A Br^- ion is larger than a Kr atom because, although they are isoelectronic, Br^- has one fewer proton than Kr, resulting in a smaller pull on the electrons and therefore a larger radius.

FOR PRACTICE 3.8

Choose the larger atom or ion from each pair.

(a) K or K^+

(b) F or F^-

(c) Ca^{2+} or Cl^-

3.6

Cc

Conceptual
Connection

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. Why not? Would you expect isotopes—for example, C-12 and C-13—to have different atomic radii?

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 endothermic, which, as we discussed in Chapter E, absorbs heat and therefore carries a positive sign.) The energy required to remove the first electron is the *first ionization energy* (IE_1). For example, we represent the first ionization of sodium with the equation:

$$Na(g) \longrightarrow Na^+(g) + 1\ e^- \quad IE_1 = 496\ kJ/mol$$
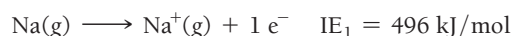
The energy required to remove the second electron is the *second ionization energy* (IE_2), the energy required to remove the third electron is the *third ionization energy* (IE_3), and so on. We represent the second ionization energy of sodium as:

$$Na^+(g) \longrightarrow Na^{2+}(g) + 1\ e^- \quad IE_2 = 4560\ kJ/mol$$

Notice that the second ionization energy is not the energy required to remove *two* electrons from sodium (that quantity is the sum of IE_1 and IE_2), but rather the energy required to remove one electron from Na^+. We look at trends in IE_1 and IE_2 separately.

Trends in First Ionization Energy

The first ionization energies of the elements through Xe are shown in **Figure 3.18 ▼**. 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

First Ionization Energies
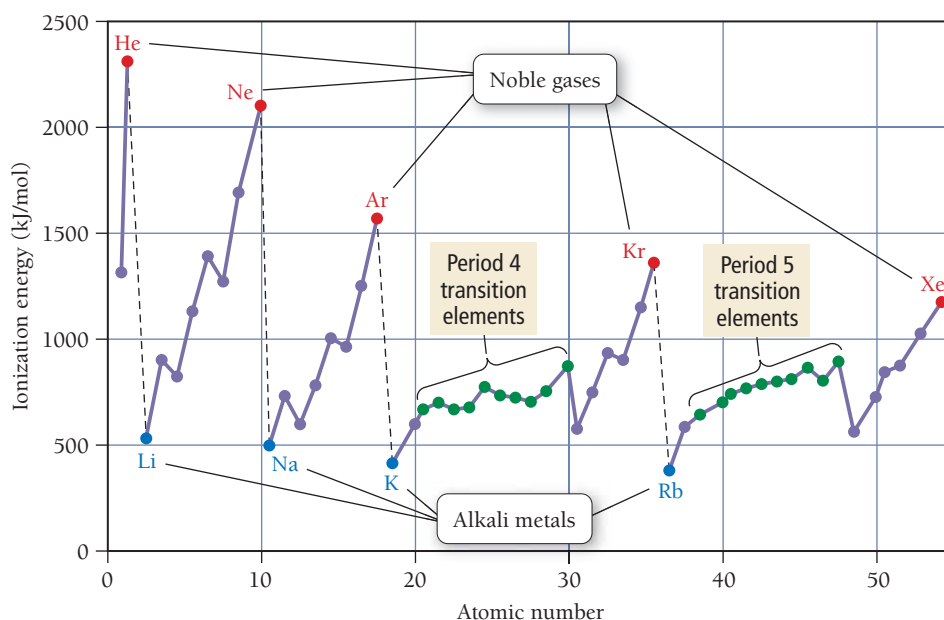
▶ **FIGURE 3.18 First Ionization Energy versus Atomic Number for the Elements through Xenon**
First ionization energy starts at a minimum with each alkali metal and rises to a peak with each noble gas.

Trends in First Ionization Energy
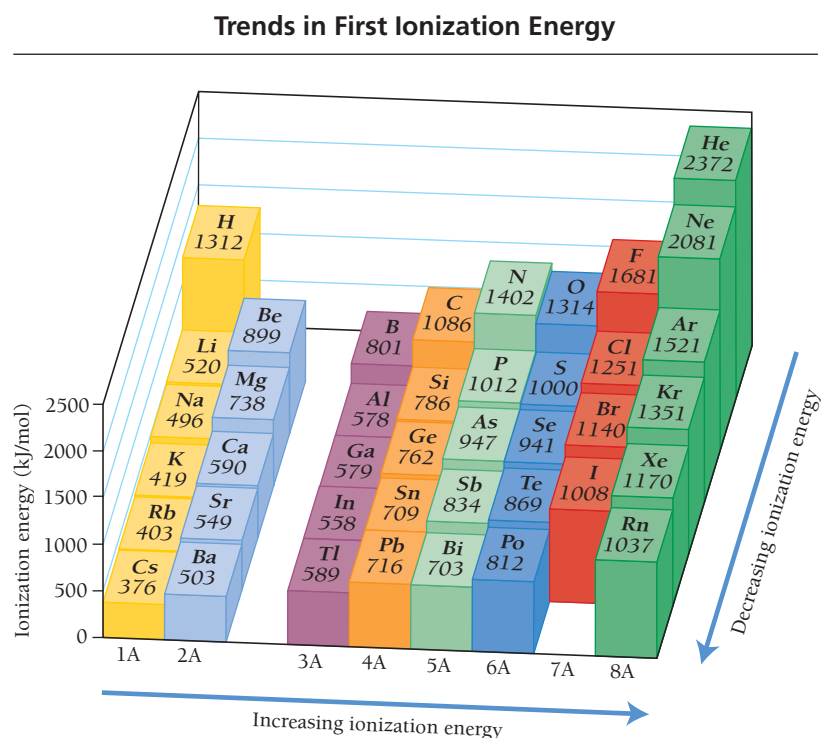
▲ **FIGURE 3.19 Trends in Ionization Energy** Ionization energy increases as we move to the right across a period and decreases as we move down a column in the periodic table.

the observed trend? As we have seen, the principal quantum number, n, increases as we move down a column. For a given sublevel, orbitals with higher principal quantum numbers are larger than orbitals with smaller principal quantum numbers. (For example, a $4s$ orbital is larger than a $3s$ orbital.) 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 lower ionization energies as we move down a column, as shown in **Figure 3.19 ▲**.

What about the trend as we move to the right across a row? For example, does 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 $3s^2 3p^5$. 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 first 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 3.19.

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_{eff}).

EXAMPLE 3.9

First Ionization Energy

Interactive
Worked Example
Video 3.9

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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 first 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. First ionization energy increases as you go to the right due to increasing effective nuclear charge.

(b) As or Sb

As has a higher first ionization energy than Sb because, as you trace the path between As and Sb on the periodic table, you move down a column. First 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 first ionization energy than Si because, as you trace the path between N and Si on the periodic table, you move down a column (first ionization energy decreases due to increasing size of outermost orbitals) and then to the left across a row (first ionization energy decreases due to decreasing effective nuclear charge). 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 first ionization energy because, as you trace the path between O and Cl, you go to the right across a row (first ionization energy increases) and then down a column (first ionization energy decreases). These effects tend to counter each other, and it is not obvious which will dominate.

FOR PRACTICE 3.9

On the basis of periodic trends, determine the element in each pair with the higher first ionization energy (if possible).
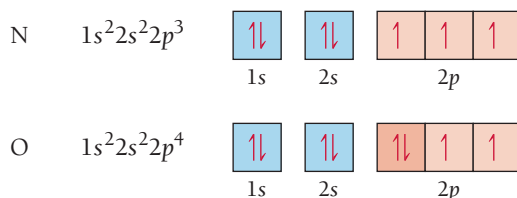(a) Sn or I   (b) Ca or Sr   (c) C or P   (d) F or S

FOR MORE PRACTICE 3.9

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 3.19, 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 change in going from the s block to the p block. Recall from Section 3.3 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 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:

N $1s^2 2s^2 2p^3$

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$	$\uparrow$
1s	2s		2p	

O $1s^2 2s^2 2p^4$

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow$	$\uparrow$
1s	2s		2p	

Nitrogen has three electrons in three p orbitals, while oxygen has four. In nitrogen, the 2p orbitals are half-filled (which makes the configuration particularly stable). Oxygen's fourth electron 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 in the margin. 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:

Na   [Ne] $3s^1$
Mg   [Ne] $3s^2$
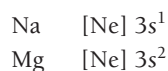
The first ionization of sodium involves removing the valence electron in the 3s orbital. Recall that these valence electrons are held more loosely than the core electrons and that the resulting ion has a noble gas configuration, which is particularly stable. Consequently, the first ionization energy 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 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_{eff} that we discussed earlier (Z_{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 IE_3 very high.
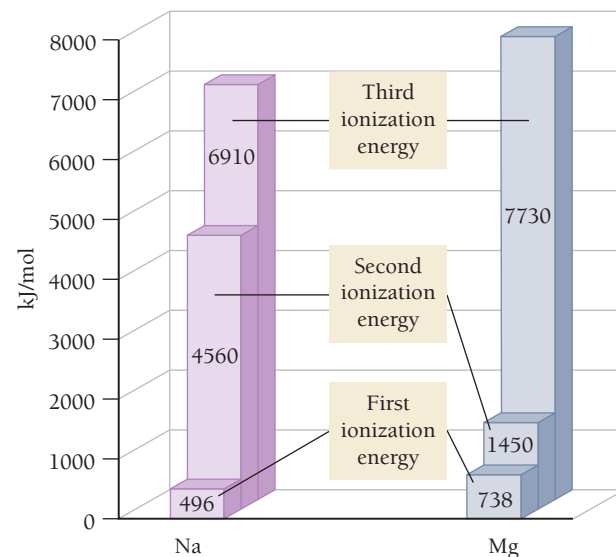
As shown in Table 3.1, similar trends exist for the successive ionization energies of many elements. Ionization energies increase fairly uniformly with each successive removal of an outermost electron but take a large jump with the removal of the first core electron.

TABLE 3.1 Successive Values of Ionization Energies for the Elements Sodium through Argon (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
Na	496	4560			Core electrons		
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

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3.7
Cc
Conceptual Connection

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.

3.8   Electron Affinities and Metallic Character

Electron affinity and metallic character also exhibit periodic trends. Electron affinity is a measure of how easily an atom accepts an additional electron and 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 known 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 exothermic, which, as discussed in Chapter E, gives off heat and therefore carries a negative sign.) 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 can represent the electron affinity of chlorine with the equation:

$$Cl(g) + 1\ e^- \longrightarrow Cl^-(g) \quad EA = -349\ kJ/mol$$
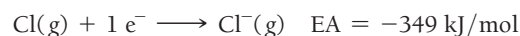
Figure 3.20 ◀ displays the electron affinities for a number of main-group elements. As we can see from this figure, the trends in electron affinity are not as regular as trends in other properties we have examined. For instance, we might expect electron affinities to become relatively more positive (so that the addition of an electron is less exothermic) as we move down a column because the electron is entering orbitals with successively higher principal quantum numbers and will therefore be farther from the nucleus. This trend applies to the group 1A metals but does not hold for the other columns in the periodic table.

Electron Affinities (kJ/mol)

1A	2A	3A	4A	5A	6A	7A	8A
H −73							He >0
Li −60	Be >0	B −27	C −122	N >0	O −141	F −328	Ne >0
Na −53	Mg >0	Al −43	Si −134	P −72	S −200	Cl −349	Ar >0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr >0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe >0

▲ **FIGURE 3.20 Electron Affinities of Selected Main-Group Elements**

A more regular trend in electron affinity, however, occurs as we move to the right across a row. Based on the periodic properties we have learned so far, would you expect more energy to be released when an electron is gained by Na or Cl? We know that Na has an outer electron configuration of $3s^1$ and Cl has an outer electron configuration of $3s^2 3p^5$. Because adding an electron to chlorine gives it a noble gas configuration and adding an electron to sodium does not, and because the outermost electrons in chlorine 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. 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. The halogens (group 7A) therefore 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 $ns^2 np^3$ 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 that 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 the 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 Section 3.5, 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, but 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 of the periodic table (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 3.21 ▼**:

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

Trends in Metallic Character
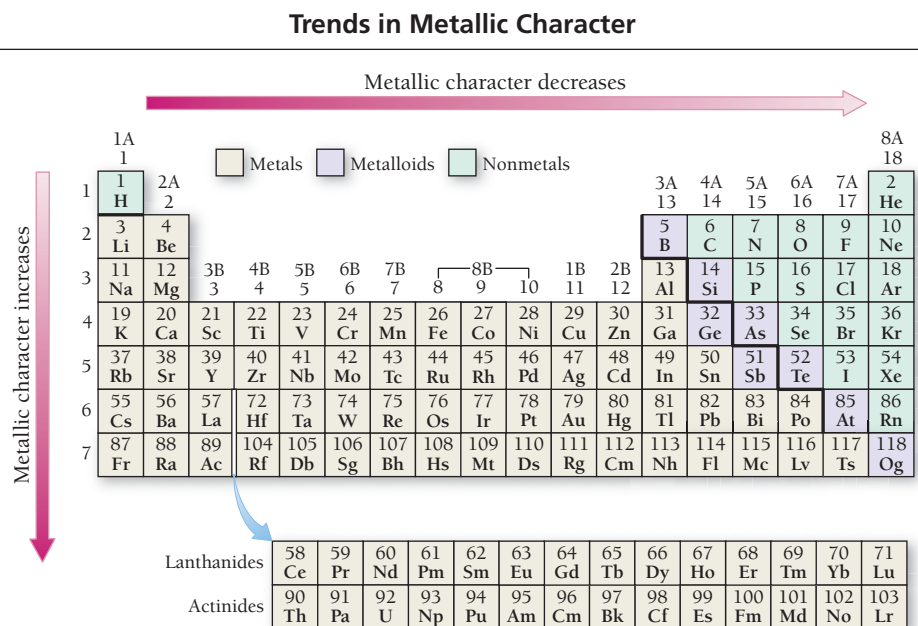
◀ **FIGURE 3.21 Trends in Metallic Character I** Metallic character decreases as we move to the right across a period and increases as we move down a column in the periodic table.

Trends in Metallic Character

▲ **FIGURE 3.22 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.

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

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

These trends explain the overall distribution of metals and nonmetals in the periodic table first discussed in Section 3.5. 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 shown in **Figure 3.22 ▲**.

EXAMPLE 3.10

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 you 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 you 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 go 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 obvious which will predominate.

FOR PRACTICE 3.10

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 3.10

Arrange the following elements in order of increasing metallic character: Si, Cl, Na, Rb.

Periodic Trends

3.8

Cc

Conceptual Connection

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Use the trends in ionization energy and electron affinity to explain why sodium chloride has the formula NaCl and not Na_2Cl or $NaCl_2$.

NEW! This brand-new section, added at the suggestion of first-edition adopting instructors, summarizes periodic trends with a new table so students can review the information learned throughout the chapter in one quick glance.

3.9 Periodic Trends Summary

In this chapter, we have examined various trends in properties that we can understand in terms of electron configurations. Since electron configurations are just a way of specifying electronic structure, the trends in this chapter are a good example of the overall theme of this book: *structure determines properties*. In other words, we have just 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 3.2.

TABLE 3.2 Summary of Periodic Properties

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

Self-Assessment Quizzes at the end of each chapter contain 10–15 questions, similar to those found on the ACS exam and other standardized exams to help students optimize the use of quizzing to improve their understanding and performance. These questions are algorithmically coded into MasteringChemistry™ and include wrong-answer feedback with links to the eText 2.0.
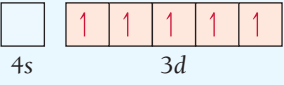
SELF-ASSESSMENT
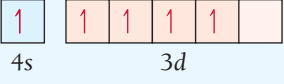
QUIZ

The eText 2.0 icon indicates that this feature is embedded and interactive in the eText.

PEARSON
eText 2.0

1. According to Coulomb's law, if the separation between two particles of the same charge is doubled, the potential energy of the two particles _____.
    a) is twice as high as it was before the distance separation
    b) is one-half as high as it was before the separation
    c) does not change
    d) is one-fourth as high as it was before the separation

2. Which electron in S is most shielded from nuclear charge?
    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.)

3. Choose the correct electron configuration for Se.
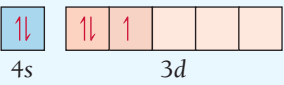   a) $1s^2 2s^2 2p^6 3s^2 3p^4$
    b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$
    c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^4$
    d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

4. Choose the correct orbital diagram for vanadium.

    a) [Ar] [⬆⬇] | [⬆⬇][⬆][ ][ ][ ]
            4s   3d

    b) [Ar] [ ] | [⬆][⬆][⬆][⬆][⬆]
            4s   3d

    c) [Ar] [⬆] | [⬆][⬆][⬆][⬆][ ]
            4s   3d

    d) [Ar] [⬆⬇] | [⬆][⬆][⬆][ ][ ]
            4s

5. Which set of four quantum numbers corresponds to an electron in a 4p orbital?
    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) $n = 4, l = 4, m_l = 3, m_s = -\frac{1}{2}$

6. Which element has the smallest atomic radius?
    a) C   b) Si   c) Be   d) F

7. Which statement is true about electron shielding of nuclear charge?
    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.

8. Which statement is true about effective nuclear charge?
    a) Effective nuclear charge *decreases* as we move to the right across a row in the periodic table.
    b) Effective nuclear charge *increases* as we move to the right across a row in the periodic table.
    c) Effective nuclear charge remains relatively constant as we move to the right across a row in the periodic table.
    d) Effective nuclear charge *increases*, then *decreases*, at regular intervals as we move to the right across a row in the periodic table.

9. What is the electron configuration for Fe^{2+}?
    a) $[Ar]4s^2 3d^6$
    b) $[Ar]4s^2 3d^4$
    c) $[Ar]4s^0 3d^6$
    d) $[Ar]4s^2 3d^8$

10. Which species is diamagnetic?
    a) Cr^{2+} b) Zn
    c) Mn   d) C

11. Arrange these atoms and ions in order of increasing radius: Cs^+, Ba^{2+}, I^-.
    a) $I^- < Ba^{2+} < Cs^+$
    b) $Cs^+ < Ba^{2+} < I^-$
    c) $Ba^{2+} < Cs^+ < I^-$
    d) $I^- < Cs^+ < Ba^{2+}$

12. Arrange these elements in order of increasing first ionization energy: Cl, Sn, Si.
    a) $Cl < Si < Sn$
    b) $Sn < Si < Cl$
    c) $Si < Cl < Sn$
    d) $Sn < Cl < Si$

13. The ionization energies of an unknown third period element are shown here. Identify the element. $IE_1 = 786$ kJ/mol; $IE_2 = 1580$ kJ/mol; $IE_3 = 3230$ kJ/mol; $IE_4 = 4360$ kJ/mol; $IE_5 = 16{,}100$ kJ/mol;
    a) Mg   b) Al
    c) Si   d) P

14. Identify the correct trends in metallic character.
    a) Metallic character *increases* as we move to the right across a row in the periodic table and *increases* as we move down a column.
    b) Metallic character *decreases* as we move to the right across a row in the periodic table and *increases* as we move down a column.
    c) Metallic character *decreases* as we move to the right across a row in the periodic table and *decreases* as we move down a column.
    d) Metallic character *increases* as we move to the right across a row in the periodic table and *decreases* as we move down a column.

15. For which element is the gaining of an electron most exothermic?
    a) Li
    b) N
    c) F
    d) B

16. What is the charge of the ion most commonly formed by S?
    a) 2+
    b) +
    c) −
    d) 2−

Answers: 1. b; 2. c; 3. b; 4. d; 5. a; 6. d; 7. d; 8. b; 9. c; 10. b; 11. c; 12. b; 13. c; 14. b; 15. c; 16. d

CHAPTER SUMMARY 3

REVIEW

MasteringChemistry™ 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.

KEY LEARNING OUTCOMES

Each Key Learning Outcome is correlated to at least one example and practice problem and several end-of-chapter exercises, allowing students to check their mastery of the material.

CHAPTER OBJECTIVES	ASSESSMENT
Write Electron Configurations (3.3)	• Example 3.1 For Practice 3.1 Exercises 45, 46, 49, 50
Write Orbital Diagrams (3.3)	• Example 3.2 For Practice 3.2 Exercises 47, 48
Differentiate Between Valence Electrons and Core Electrons (3.4)	• Example 3.3 For Practice 3.3 Exercises 55–60
Write Electron Configurations from the Periodic Table (3.4)	• Example 3.4 For Practice 3.4 For More Practice 3.4 Exercises 49–52
Predict the Charge of Ions (3.5)	• Example 3.5 For Practice 3.5 Exercises 63, 64
Use Periodic Trends to Predict Atomic Size (3.6)	• Example 3.6 For Practice 3.6 For More Practice 3.6 Exercises 71–74
Write Electron Configurations for Ions (3.7)	• Example 3.7 For Practice 3.7 Exercises 63, 64, 75–78
Apply Periodic Trends to Predict Ion Size (3.7)	• Example 3.8 For Practice 3.8 For More Practice 3.8 Exercises 79–82
Apply Periodic Trends to Predict Relative Ionization Energies (3.7)	• Example 3.9 For Practice 3.9 For More Practice 3.9 Exercises 83–88
Predict Metallic Character Based on Periodic Trends (3.8)	• Example 3.10 For Practice 3.10 For More Practice 3.10 Exercises 89–94

KEY TERMS

Section 3.1
periodic property (114)

Section 3.2
periodic law (115)
main-group elements (116)
transition elements (or transition metals) (116)
family (or group) of elements (116)

Section 3.3
electron configuration (117)
ground state (117)

orbital diagram (117)
Pauli exclusion principle (117)
degenerate (118)
Coulomb's law (118)
shielding (119)
effective nuclear charge (Z_{eff}) (119)
penetration (119)
aufbau principle (121)
Hund's rule (121)

Section 3.4
valence electrons (124)
core electrons (124)

Section 3.5
noble gases (128)
metals (128)
nonmetals (129)
metalloids (129)
semiconductors (129)
alkali metals (130)
alkaline earth metals (130)
halogens (130)

Section 3.6
van der Waals radius (nonbonding atomic radius) (131)

covalent radius (bonding atomic radius) (131)
atomic radius (131)

Section 3.7
paramagnetic (136)
diamagnetic (136)
ionization energy (IE) (140)

Section 3.8
electron affinity (EA) (144)

KEY CONCEPTS

Periodic Properties and the Periodic Table (3.1, 3.2)
- The periodic table was developed primarily by Dmitri Mendeleev in the nineteenth century. Mendeleev arranged the elements in a table so that their atomic masses 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 and ionic radius, ionization energy, electron affinity, density, and metallic character.
- Quantum mechanics explains the periodic table by showing how electrons fill the quantum-mechanical orbitals within the atoms that compose the elements.

Electron Configurations (3.3)
- 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 exist within the $1s$ orbital.
- The order of filling quantum-mechanical orbitals in multi-electron 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 (with opposing spins).
- According to Hund's rule, orbitals of the same energy first fill singly with electrons with parallel spins before pairing.

Electron Configurations and the Periodic Table (3.4)
- An atom's outermost electrons (valence electrons) are most important in determining the atom's properties.
- Because quantum-mechanical orbitals fill sequentially with increasing atomic number, we can predict the electron configuration of an element from its position in the periodic table.

Electron Configurations and the Properties of Elements (3.5)
- The most stable (or chemically unreactive) elements in the periodic table are the noble gases. These elements have completely full principal energy levels, which have particularly low potential energy compared to other possible electron configurations.
- Elements on the left side and in the center of the periodic table are metals and tend to lose electrons when they undergo chemical changes.

- Elements on the upper right side of the periodic table are nonmetals and tend to gain electrons when they undergo chemical changes.
- 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.
- Many main-group elements form ions with noble gas electron configurations.

Effective Nuclear Charge and Periodic Trends in Atomic Size (3.6)
- 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.

Ion Properties (3.7)
- We determine the electron configuration of an ion by adding or subtracting the corresponding number of electrons to the electron configuration of the neutral atom.
- For main-group ions, the order of removing electrons is the same as the order in which they are added in building up the electron configuration.
- For transition metal atoms, ns electrons are removed before $(n - 1)d$ electrons.
- The radius of a cation is much *smaller* than that of the corresponding atom, and the radius of an anion is much *larger* than that of the corresponding atom.
- The first ionization energy—the energy required to remove the first electron from an atom in the gaseous state—generally decreases as we move down a column in the periodic table and increases when we move to the right across a row.

- Successive ionization energies increase smoothly from one valence electron to the next, but the ionization energy increases dramatically for the first core electron.

Electron Affinities and Metallic Character (3.8)

- Electron affinity—the energy associated with an element in its gaseous state gaining an electron—does not show a general

trend as we move down a column in the periodic table, but it generally becomes more negative (more exothermic) to the right across a row.
- Metallic character—the tendency to lose electrons in a chemical reaction—generally increases down a column in the periodic table and decreases to the right across a row.

KEY EQUATIONS AND RELATIONSHIPS

Order of Filling Quantum-Mechanical Orbitals (3.3)

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

EXERCISES

REVIEW QUESTIONS

1. What are periodic properties?
2. Use aluminum as an example to explain how density is a periodic property.
3. Explain the contributions of Döbereiner and Newlands to the organization of elements according to their properties.
4. Who is credited with arranging the periodic table? How are elements arranged in this table?
5. Explain the contributions of Meyer and Moseley to the periodic table.
6. 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?
7. What is an electron configuration? Provide an example.
8. 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.
9. What is shielding? In an atom, which electrons tend to do the most shielding (core electrons or valence electrons)?
10. 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?
11. Why are the sublevels within a principal level split into different energies for multi-electron atoms but not for the hydrogen atom?
12. What is an orbital diagram? Provide an example.
13. Why is electron spin important when writing electron configurations? Explain in terms of the Pauli exclusion principle.
14. What are degenerate orbitals? According to Hund's rule, how are degenerate orbitals occupied?
15. List all orbitals from 1s through 5s according to increasing energy for multi-electron atoms.
16. What are valence electrons? Why are they important?
17. 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 ƒ block.

18. Explain why the s block in the periodic table has only two columns while the p block has six.
19. Explain why the rows in the periodic table become progressively longer as we move down the table. For example, the first row contains two elements, the second and third rows each contain eight elements, and the fourth and fifth rows each contain 18 elements.
20. Explain the relationship between a main-group element's lettered group number (the number of the element's column) and its valence electrons.
21. Explain 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?
22. Which of the transition elements in the first transition series have anomalous electron configurations?
23. Explain how to write the electron configuration for an element based on its position in the periodic table.
24. Explain the relationship between the properties of an element and the number of valence electrons that it contains.
25. List the number of valence electrons for each family in the periodic table, 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

26. Define atomic radius. For main-group elements, describe the observed trends in atomic radius as we:
   a. move across a period in the periodic table
   b. move down a column in the periodic table

27. What is effective nuclear charge? What is shielding?

28. When an alkali metal forms an ion, what is the charge of the ion? What is the charge of an alkaline earth metal ion?

29. When a halogen forms an ion, what is the charge of the ion? When the nonmetals in the oxygen family form ions, what is the charge of the ions? What is the charge of the ions formed by N and Al?

30. Use the concepts of effective nuclear charge, shielding, and n value of the valence orbital to explain the trend in atomic radius as we move across a period in the periodic table.

31. For transition elements, describe the trends in atomic radius as we:
   a. move across a period in the periodic table
   b. move down a column in the periodic table

   Explain the reasons for the trends described in parts a and b.

32. 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?

33. Explain 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?

34. Describe the relationship between:
   a. the radius of a cation and the radius of the atom from which it is formed
   b. the radius of an anion and the radius of the atom from which it is formed

35. What is ionization energy? What is the difference between first ionization energy and second ionization energy?

36. What is the general trend in first ionization energy as we move down a column in the periodic table? As we move across a row?

37. What are the exceptions to the periodic trends in first ionization energy? Why do they occur?

38. 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 we might predict them.

39. What is electron affinity? What are the observed periodic trends in electron affinity?

40. What is metallic character? What are the observed periodic trends in metallic character?

PROBLEMS BY TOPIC

Note: Answers to all odd-numbered Problems, numbered in blue, can be found in Appendix III. Exercises in the Problems by Topic section are paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.

The Periodic Table

41. Write the name of each element and classify it as a metal, nonmetal, or metalloid.
   a. K   b. Ba   c. I   d. O   e. Sb

42. Write the symbol for each element and classify it as a metal, nonmetal, or metalloid.
   a. gold   b. fluorine   c. sodium
   d. tin   e. argon

43. Determine whether each element is a main-group element.
   a. tellurium   b. potassium
   c. vanadium   d. manganese

44. Determine whether each element is a transition element.
   a. Cr   b. Br   c. Mo   d. Cs

Electron Configurations

45. Write the full electron configuration for each element.
   a. Si   b. O   c. K   d. Ne

46. Write the full electron configuration for each element.
   a. C   b. P   c. Ar   d. Na

47. Write the full orbital diagram for each element.
   a. N   b. F   c. Mg   d. Al

48. Write the full orbital diagram for each element.
   a. S   b. Ca   c. Ne   d. He

49. Use the periodic table to write the electron configuration for each element. Represent core electrons with the symbol of the previous noble gas in brackets.
   a. P   b. Ge   c. Zr   d. I

50. Use the periodic table to determine the element corresponding to each electron configuration.
   a. $[Ar]\,4s^2 3d^{10} 4p^6$ b. $[Ar]\,4s^2 3d^2$
   c. $[Kr]\,5s^2 4d^{10} 5p^2$ d. $[Kr]\,5s^2$

51. Use the periodic table to determine each quantity.
   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

52. 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

53. Name an element in the fourth period (row) of the periodic table with:
   a. five valence electrons   b. four $4p$ electrons
   c. three $3d$ electrons   d. a complete outer shell

54. Name an element in the third period (row) of the periodic table with:
   a. three valence electrons   b. four $3p$ electrons
   c. six $3p$ electrons
   d. two $3s$ electrons and zero $3p$ electrons

Valence Electrons and Simple Chemical Behavior from the Periodic Table

55. Determine the number of valence electrons in each element.
    a. Ba   **b.** Cs   **c.** Ni   **d.** S

56. Determine the number of valence electrons in each element. Which elements do you expect to lose electrons in chemical reactions? Which do you expect to gain electrons?
    a. Al   **b.** Sn   **c.** Br   **d.** Se

57. Which outer electron configuration would you expect to correspond to a reactive metal? To a reactive nonmetal?
    a. ns^2 **b.** ns^2np^6
    c. ns^2np^5 **d.** ns^2np^2

58. Which outer electron configuration would you expect to correspond to a noble gas? To a metalloid?
    a. ns^2 **b.** ns^2np^6
    c. ns^2np^5 **d.** ns^2np^2

59. List the number of valence electrons for each element and classify each element as an alkali metal, alkaline earth metal, halogen, or noble gas.
    a. sodium   **b.** iodine   **c.** calcium
    d. barium   **e.** krypton

60. List the number of valence electrons in each element and classify each element as an alkali metal, alkaline earth metal, halogen, or noble gas.
    a. F   **b.** Sr   **c.** K   **d.** Ne   **e.** At

61. Which pair of elements do you expect to be most similar? Why?
    a. N and Ni   **b.** Mo and Sn   **c.** Na and Mg
    d. Cl and F   **e.** Si and P

62. Which pair of elements do you expect to be most similar? Why?
    a. nitrogen and oxygen
    b. titanium and gallium
    c. lithium and sodium
    d. germanium and arsenic
    e. argon and bromine

63. Predict the charge of the ion formed by each element and write the electron configuration of the ion.
    a. O   **b.** K   **c.** Al   **d.** Rb

64. Predict the charge of the ion formed by each element and write the electron configuration of the ion.
    a. Mg   **b.** N   **c.** F   **d.** Na

Coulomb's Law and Effective Nuclear Charge

65. According to Coulomb's law, which pair of charged particles has the lowest potential energy?
    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

66. 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

67. Which electrons experience a greater effective nuclear charge: the valence electrons in beryllium or the valence electrons in nitrogen? Why?

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

69. If core electrons completely shielded valence electrons from nuclear charge (i.e., if each core electron reduced nuclear charge by one 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?
    a. K   **b.** Ca   **c.** O   **d.** C

70. In Section 3.6, we estimated the effective nuclear charge on beryllium's valence electrons to be slightly greater than $2+$. What would a similar treatment 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

71. Choose the larger atom in each pair.
    a. Al or In   **b.** Si or N   **c.** P or Pb   **d.** C or F

72. Choose the larger atom in each pair.
    a. Sn or Si   **b.** Br or Ga   **c.** Sn or Bi   **d.** Se or Sn

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

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

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

75. Write the electron configuration for each ion.
    a. O^{2-} **b.** Br^- **c.** Sr^{2+} **d.** Co^{3+} **e.** Cu^{2+}

76. Write the electron configuration for each ion.
    a. Cl^- **b.** P^{3-} **c.** K^- **d.** Mo^{3+} **e.** V^{3+}

77. Write orbital diagrams for each ion and determine if the ion is diamagnetic or paramagnetic.
    a. V^{5+} **b.** Cr^{3+} **c.** Ni^{2+} **d.** Fe^{3+}

78. Write orbital diagrams for each ion and determine if the ion is diamagnetic or paramagnetic.
    a. Cd^{2+} **b.** Au^+ **c.** Mo^{3+} **d.** Zr^{2+}

79. Which is the larger species in each pair?
    a. Li or Li^+ **b.** I^- or Cs^+
    c. Cr or Cr^{3+} **d.** O or O^{2-}

80. Which is the larger species in each pair?
    a. Sr or Sr^{2+} **b.** N or N^{3-} **c.** Ni or Ni^{2+} **d.** S^{2-} or Ca^{2+}

81. Arrange this isoelectronic series in order of decreasing radius: F^-, O^{2-}, Mg^{2+}, Na^+.

82. Arrange this isoelectronic series in order of increasing atomic radius: Se^{2-}, Sr^{2+}, Rb^+, Br^-.

83. Choose the element with the higher first ionization energy in each pair.
    a. Br or Bi   **b.** Na or Rb   **c.** As or At   **d.** P or Sn

84. Choose the element with the higher first ionization energy in each pair.
    a. P or I   **b.** Si or Cl   **c.** P or Sb   **d.** Ga or Ge

85. Arrange these elements in order of increasing first ionization energy: Si, F, In, N.

86. Arrange these elements in order of decreasing first ionization energy: Cl, S, Sn, Pb.

87. 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?)
    a. Be
    b. N
    c. O
    d. Li

88. Consider this set of successive ionization energies:

    $IE_1 = 578$ kJ/mol $IE_2 = 1820$ kJ/mol

    $IE_3 = 2750$ kJ/mol $IE_4 = 11,600$ kJ/mol

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

Electron Affinities and Metallic Character

89. Choose the element with the more negative (more exothermic) electron affinity in each pair.
    a. Na or Rb
    b. B or S
    c. C or N
    d. Li or F

90. Choose the element with the more negative (more exothermic) electron affinity in each pair.
    a. Mg or S
    b. K or Cs
    c. Si or P
    d. Ga or Br

91. Choose the more metallic element in each pair.
    a. Sr or Sb
    b. As or Bi
    c. Cl or O
    d. S or As

92. Choose the more metallic element in each pair.
    a. Sb or Pb
    b. K or Ge
    c. Ge or Sb
    d. As or Sn

93. Arrange these elements in order of increasing metallic character: Fr, Sb, In, S, Ba, Se.

94. Arrange these elements in order of decreasing metallic character: Sr, N, Si, P, Ga, Al.

CUMULATIVE PROBLEMS

95. Bromine is a highly reactive liquid, whereas krypton is an inert gas. Explain the difference based on their electron configurations.

96. Potassium is a highly reactive metal, whereas argon is an inert gas. Explain the difference based on their electron configurations.

97. Both vanadium and its 3+ ion are paramagnetic. Use electron configurations to explain this statement.

98. Use electron configurations to explain why copper is paramagnetic while its 1+ ion is not.

99. Suppose you were trying to find a substitute for K^+ for some application. Where would you begin your search? Which ions are most like K^+? For each ion you propose, explain the ways in which it is similar to K^+ and the ways it is different. Refer to periodic trends in your discussion.

100. Suppose you were trying to find a substitute for Na^+ for some application. Where would you begin your search? What ions are most like Na^+? For each ion you propose, explain the ways in which it is similar to Na^+ and the ways it is different. Use periodic trends in your discussion.

101. 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?

102. Which pair of elements would you expect to have the most similar atomic radii, and why?
     a. Si and Ga
     b. Si and Ge
     c. Si and As

103. Consider these elements: N, Mg, O, F, 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.

104. Consider these elements: P, Ca, Si, S, 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.

105. Explain why atomic radius decreases as we move to the right across a period for main-group elements but not for transition elements.

106. 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?

107. 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.

108. The lightest halogen is also the most chemically reactive, and reactivity generally decreases as we move down the column of halogens in the periodic table. Explain this trend in terms of periodic properties.

109. 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 this observation.

110. 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 behavior.

111. 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 have these chemical properties.

112. Write the electronic 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.

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

a. 10, 12, 58, 11, 7, 44, 63, 66
b. 9, 99, 30, 95, 19, 47, 79

114. 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.

115. 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 would have sufficient energy to ionize the atom?

116. 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.

CHALLENGE PROBLEMS

117. 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

a. Estimate the densities of argon and xenon by interpolation from the data.
b. Provide an estimate of the density of the yet undiscovered element with atomic number 118 by extrapolation from the data.
c. 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?
d. 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 that occur 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?

118. 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?

119. Consider the metals in the first transition series. Use periodic trends to predict a trend in density as we move to the right across the series.

120. 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:

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

121. A carbon atom can absorb radiation of various wavelengths with resulting changes in its electronic configuration. Write orbital diagrams for the electronic configurations of carbon that result from absorption of the three longest wavelengths of radiation that change its electronic configuration.

122. 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.

123. 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.

124. 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.

125. Unlike the elements in groups 1A and 2A, those in group 3A do not show a regular decrease in first ionization energy in going down the column. Explain the irregularities.

126. Using the data in Figures 3.19 and 3.20, calculate ΔE (the change in energy) for the reaction

$$Na(g) + Cl(g) \longrightarrow Na^+(g) + Cl^-(g)$$

127. 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.

128. In Section 3.5 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.

129. 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.

130. Predict the electronic configurations of the first two excited states (next higher energy states beyond the ground state) of Pd.

CONCEPTUAL PROBLEMS

131. 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:
  a. a noble gas
  b. a reactive nonmetal
  c. a reactive metal

132. 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.

133. Determine whether each statement regarding penetration and shielding is true or false. (Assume that all lower energy orbitals are fully occupied.)

  a. An electron in a 3s orbital is more shielded than an electron in a 2s orbital.
  b. An electron in a 3s orbital penetrates into the region occupied by core electrons more than electrons in a 3p orbital.
  c. An electron in an orbital that penetrates closer to the nucleus will always experience more shielding than an electron in an orbital that does not penetrate as far.
  d. An electron in an orbital that penetrates close to the nucleus will tend to experience a higher effective nuclear charge than one that does not.

134. 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.

135. Use the trends in ionization energy and electron affinity to explain why calcium fluoride has the formula CaF_2 and not Ca_2F or CaF.

## QUESTIONS FOR GROUP WORK

Active Classroom Learning

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

136. In a complete sentence, describe the relationship between shielding and penetration.

137. 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 3.8 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."

138. 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.

139. In complete sentences, explain: a) why Se^{2-} and Br^- are about the same size; b) why Br^- is slightly smaller than Se^{2-}; and c) which singly charged cation you would expect to be approximately the same size as Se^{2-} and Br^- and why.

140. 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.
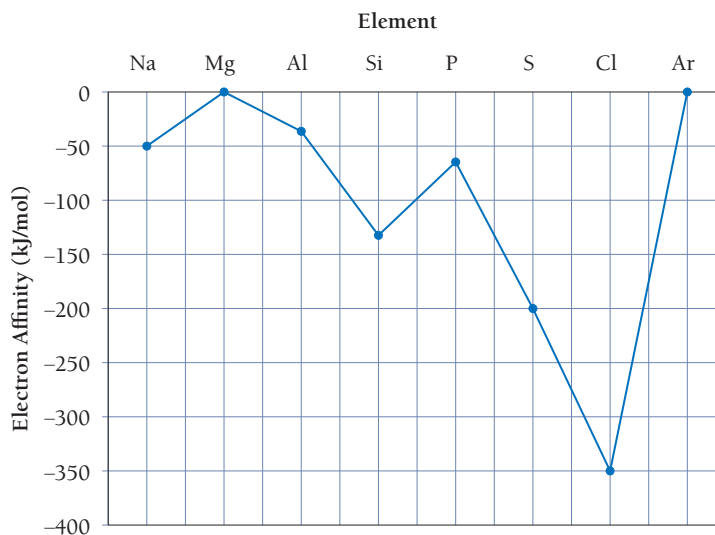
DATA INTERPRETATION AND ANALYSIS

141. The following graphs show the first ionization energies and electron affinities of the period 3 elements. Refer the graphs to answer the questions that follow.
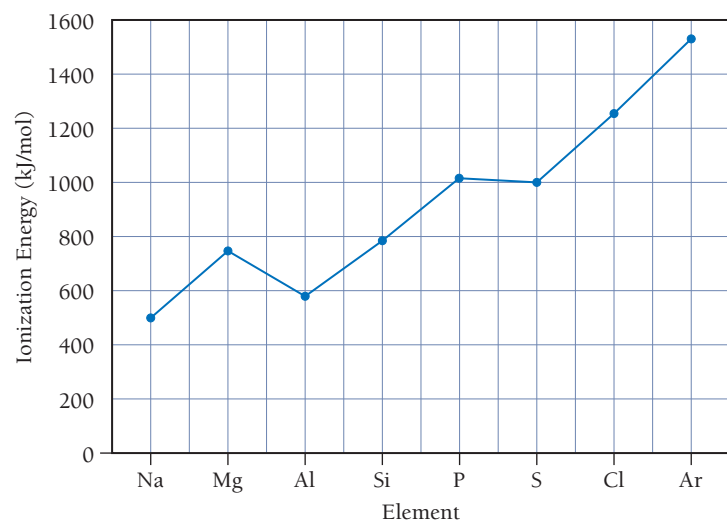
▲ First Ionization Energies of Period 3 Elements

▲ Electron Affinities of Period 3 Elements

a. 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.

b. The trend in first ionization energy has two execptions: one at Al and another 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.

c. 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.

d. 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.

e. 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

Cc 3.1 **(d)** Cr is in the transition elements section of the periodic table (see Figure 3.4).

Cc 3.2 **(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 (it becomes more negative).

Cc 3.3 **(c)** Penetration results in less shielding from nuclear charge and therefore lower energy.

Cc 3.4 $n = 4, l = 0, m_l = 0, m_s = +\frac{1}{2}; n = 4, l = 0, m_l = 0, m_s = -\frac{1}{2}$

Cc 3.5 **(c)** Because Z_{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.

Cc 3.6 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.

Cc 3.7 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, in contrast, are held tightly and are not easily transferred or shared. Consequently, valence electrons play a central role in chemical bonding.

Cc 3.8 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). Similarly, the electron affinity of chlorine to gain one electron (-349 kJ/mol) is highly exothermic since the added electron completes chlorine's valence shell. The gain of a second electron by the negatively charged chlorine anion is not so favorable. Therefore, we expect sodium and chlorine to combine in a 1:1 ratio.