A modern periodic table usually shows the atomic number along with the element symbol. As you already know, the atomic number also indicates the number of electrons in the atoms of an element. Electron configurations of elements help to explain the recurrence of physical and chemical properties. The importance and usefulness of the periodic table lie in the fact that we can use our understanding of the general properties and trends within a group or a period to predict with considerable accuracy the properties of any element, even though that element may be unfamiliar to us.

8.2 Periodic Classification of the Elements

Figure 8.2 shows the periodic table together with the outermost ground-state electron configurations of the elements. (The electron configurations of the elements are also given in Table 7.3.) Starting with hydrogen, we see that subshells are filled in the order shown in Figure 7.24. According to the type of subshell being filled, the elements can be divided into categories—the representative elements, the noble gases, the transition elements (or transition metals), the lanthanides, and the actinides. The ***representative elements*** (also called *main group elements*) are *the elements in Groups 1A through 7A, all of which have incompletely filled s or p subshells of the highest principal quantum number*. With the exception of helium, the *noble gases* (the Group 8A elements) all have a completely filled *p* subshell. (The electron configurations are $1s^2$ for helium and ns^2np^6 for the other noble gases, where n is the principal quantum number for the outermost shell.)

The transition metals are the elements in Groups 1B and 3B through 8B, which have incompletely filled *d* subshells, or readily produce cations with incompletely

Aufbau configurations are shown here and should be reorganized to energy level order.

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

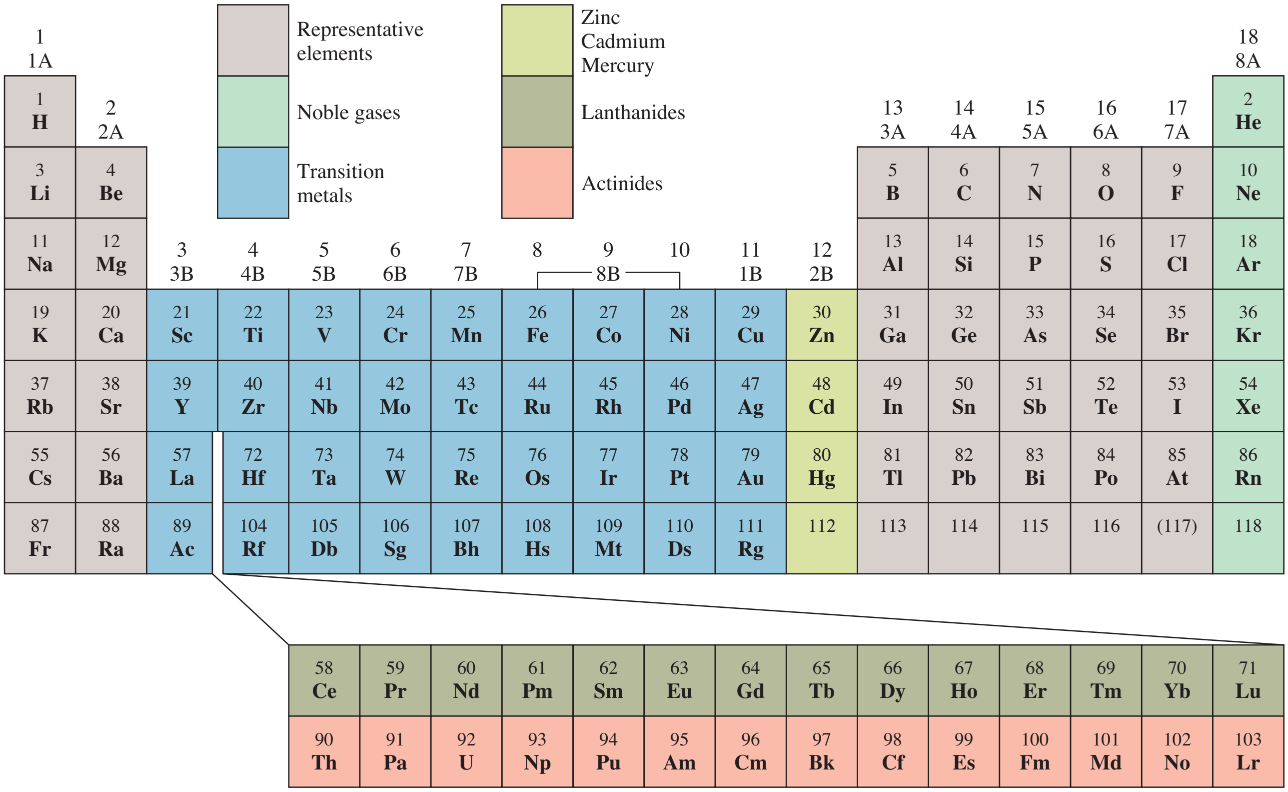
Figure 8.2 *The ground-state electron configurations of the elements. For simplicity, only the configurations of the outer electrons are shown.*

filled *d* subshells. (These metals are sometimes referred to as the *d*-block transition elements.) The nonsequential numbering of the transition metals in the periodic table (that is, 3B–8B, followed by 1B–2B) acknowledges a correspondence between the outer electron configurations of these elements and those of the representative elements. For example, scandium and gallium both have three outer electrons. However, because they are in different types of atomic orbitals, they are placed in different groups (3B and 3A). The metals iron (Fe), cobalt (Co), and nickel (Ni) do not fit this classification and are all placed in Group 8B. The Group 2B elements, Zn, Cd, and Hg, are neither representative elements nor transition metals. There is no special name for this group of metals. It should be noted that the designation of A and B groups is not universal. In Europe the practice is to use B for representative elements and A for transition metals, which is just the opposite of the American convention. The International Union of Pure and Applied Chemistry (IUPAC) has recommended numbering the columns sequentially with Arabic numerals 1 through 18 (see Figure 8.2). The proposal has sparked much controversy in the international chemistry community, and its merits and drawbacks will be deliberated for some time to come. In this text we will adhere to the American designation.

The lanthanides and actinides are sometimes called *f*-block transition elements because they have incompletely filled *f* subshells. Figure 8.3 distinguishes the groups of elements discussed here.

The chemical reactivity of the elements is largely determined by their ***valence electrons,*** which are *the outermost electrons.* For the representative elements, the valence electrons are those in the highest occupied *n* shell. *All nonvalence electrons in an atom* are referred to as ***core electrons.*** Looking at the electron configurations

For the representative elements, the valence electrons are simply those electrons at the highest principal energy level *n*.



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
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**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
55 **Cs**	56 **Ba**	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**
87 **Fr**	88 **Ra**	89 **Ac**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112	113	114	115	116	(117)	118

58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**	71 **Lu**
90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**

Figure 8.3 *Classification of the elements. Note that the Group 2B elements are often classified as transition metals even though they do not exhibit the characteristics of the transition metals.*

of the representative elements once again, a clear pattern emerges: all the elements in a given group have the same number and type of valence electrons. The similarity of the valence electron configurations is what makes the elements in the same group resemble one another in chemical behavior. Thus, for instance, the alkali metals (the Group 1A elements) all have the valence electron configuration of ns^1 (Table 8.1) and they all tend to lose one electron to form the unipositive cations. Similarly, the alkaline earth metals (the Group 2A elements) all have the valence electron configuration of ns^2, and they all tend to lose two electrons to form the dipositive cations. We must be careful, however, in predicting element properties based solely on "group membership." For example, the elements in Group 4A all have the same valence electron configuration ns^2np^2, but there is a notable variation in chemical properties among the elements: carbon is a nonmetal, silicon and germanium are metalloids, and tin and lead are metals.

As a group, the noble gases behave very similarly. Helium and neon are chemically inert, and there are few examples of compounds formed by the other noble gases. This lack of chemical reactivity is due to the completely filled *ns* and *np* subshells, a condition that often correlates with great stability. Although the valence electron configuration of the transition metals is not always the same within a group and there is no regular pattern in the change of the electron configuration from one metal to the next in the same period, all transition metals share many characteristics that set them apart from other elements. The reason is that these metals all have an incompletely filled *d* subshell. Likewise, the lanthanide (and the actinide) elements resemble one another because they have incompletely filled *f* subshells.

TABLE 8.1

Electron Configurations of Group 1A and Group 2A Elements

Group 1A		Group 2A	
Li	[He]$2s^1$	Be	[He]$2s^2$
Na	[Ne]$3s^1$	Mg	[Ne]$3s^2$
K	[Ar]$4s^1$	Ca	[Ar]$4s^2$
Rb	[Kr]$5s^1$	Sr	[Kr]$5s^2$
Cs	[Xe]$6s^1$	Ba	[Xe]$6s^2$
Fr	[Rn]$7s^1$	Ra	[Rn]$7s^2$

EXAMPLE 8.1

An atom of a certain element has 15 electrons. Without consulting a periodic table, answer the following questions: (a) What is the ground-state electron configuration of the element? (b) How should the element be classified? (c) Is the element diamagnetic or paramagnetic?

Strategy (a) We refer to the building-up principle discussed in Section 7.9 and start writing the electron configuration with principal quantum number $n = 1$ and continuing upward until all the electrons are accounted for. (b) What are the electron configuration characteristics of representative elements? transition elements? noble gases? (c) Examine the pairing scheme of the electrons in the outermost shell. What determines whether an element is diamagnetic or paramagnetic?

Solution (a) We know that for $n = 1$ we have a 1*s* orbital (2 electrons); for $n = 2$ we have a 2*s* orbital (2 electrons) and three 2*p* orbitals (6 electrons); for $n = 3$ we have a 3*s* orbital (2 electrons). The number of electrons left is $15 - 12 = 3$ and these three electrons are placed in the 3*p* orbitals. The electron configuration is $1s^22s^22p^63s^23p^3$.

(b) Because the 3*p* subshell is not completely filled, this is a representative element. Based on the information given, we cannot say whether it is a metal, a nonmetal, or a metalloid.

(c) According to Hund's rule, the three electrons in the 3*p* orbitals have parallel spins (three unpaired electrons). Therefore, the element is paramagnetic.

Check For (b), note that a transition metal possesses an incompletely filled *d* subshell and a noble gas has a completely filled outer shell. For (c), recall that if the atoms of an element contain an odd number of electrons, then the element must be paramagnetic.

Representing Free Elements in Chemical Equations

Having classified the elements according to their ground-state electron configurations, we can now look at the way chemists represent metals, metalloids, and nonmetals as free elements in chemical equations. Because metals do not exist in discrete molecular units, we always use their empirical formulas in chemical equations. The empirical formulas are the same as the symbols that represent the elements. For example, the empirical formula for iron is Fe, the same as the symbol for the element.

For nonmetals there is no single rule. Carbon, for example, exists as an extensive three-dimensional network of atoms, and so we use its empirical formula (C) to represent elemental carbon in chemical equations. But hydrogen, nitrogen, oxygen, and the halogens exist as diatomic molecules, and so we use their molecular formulas (H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2) in equations. The stable form of phosphorus is molecular (P_4), and so we use P_4. For sulfur, chemists often use the empirical formula (S) in chemical equations, rather than S_8, which is the stable form. Thus, instead of writing the equation for the combustion of sulfur as

$$S_8(s) + 8O_2(g) \longrightarrow 8SO_2(g)$$

Note that these two equations for the combustion of sulfur have identical stoichiometry. This correspondence should not be surprising, because both equations describe the same chemical system. In both cases, a number of sulfur atoms react with twice as many oxygen atoms.

we usually write

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

All the noble gases are monatomic species; thus we use their symbols: He, Ne, Ar, Kr, Xe, and Rn. The metalloids, like the metals, all have complex three-dimensional networks, and we represent them, too, with their empirical formulas, that is, their symbols: B, Si, Ge, and so on.

Electron Configurations of Cations and Anions

Because many ionic compounds are made up of monatomic anions and cations, it is helpful to know how to write the electron configurations of these ionic species. Just as for neutral atoms, we use the Pauli exclusion principle and Hund's rule in writing the ground-state electron configurations of cations and anions. We will group the ions in two categories for discussion.

Ions Derived from Representative Elements

Ions formed from atoms of most representative elements have the noble-gas outer-electron configuration of ns^2np^6. In the formation of a cation from the atom of a representative element, one or more electrons are removed from the highest occupied n shell. The electron configurations of some atoms and their corresponding cations are as follows:

$$\begin{array}{rlrl} \text{Na:} & [\text{Ne}]3s^1 & \text{Na}^+: & [\text{Ne}] \\ \text{Ca:} & [\text{Ar}]4s^2 & \text{Ca}^{2+}: & [\text{Ar}] \\ \text{Al:} & [\text{Ne}]3s^23p^1 & \text{Al}^{3+}: & [\text{Ne}] \end{array}$$

Note that each ion has a stable noble gas configuration.

In the formation of an anion, one or more electrons are added to the highest partially filled n shell. Consider the following examples:

$$\begin{array}{rlrl} \text{H:} & 1s^1 & \text{H}^-: & 1s^2 \text{ or } [\text{He}] \\ \text{F:} & 1s^22s^22p^5 & \text{F}^-: & 1s^22s^22p^6 \text{ or } [\text{Ne}] \\ \text{O:} & 1s^22s^22p^4 & \text{O}^{2-}: & 1s^22s^22p^6 \text{ or } [\text{Ne}] \\ \text{N:} & 1s^22s^22p^3 & \text{N}^{3-}: & 1s^22s^22p^6 \text{ or } [\text{Ne}] \end{array}$$

All of these anions also have stable noble gas configurations. Notice that F^-, Na^+, and Ne (and Al^{3+}, O^{2-}, and N^{3-}) have the same electron configuration. They are said to be ***isoelectronic*** because they *have the same number of electrons, and hence the same ground-state electron configuration*. Thus, H^- and He are also isoelectronic.

Cations Derived from Transition Metals

In Section 7.9 we saw that in the first-row transition metals (Sc to Cu), the 4*s* orbital is always filled before the 3*d* orbitals. Consider manganese, whose electron configuration is $[Ar]4s^23d^5$. When the Mn^{2+} ion is formed, we might expect the two electrons to be removed from the 3*d* orbitals to yield $[Ar]4s^23d^3$. In fact, the electron configuration of Mn^{2+} is $[Ar]3d^5$! The reason is that the electron-electron and electron-nucleus interactions in a neutral atom can be quite different from those in its ion. Thus, whereas the 4*s* orbital is always filled before the 3*d* orbital in Mn, electrons are removed from the 4*s* orbital in forming Mn^{2+} because the 3*d* orbital is more stable than the 4*s* orbital in transition metal ions. Therefore, when a cation is formed from an atom of a transition metal, electrons are always removed first from the *ns* orbital and then from the $(n - 1)d$ orbitals.

Bear in mind that the order of electron filling does not determine or predict the order of electron removal for transition metals. For these metals, the *ns* electrons are lost before the $(n - 1)d$ electrons.

Keep in mind that most transition metals can form more than one cation and that frequently the cations are not isoelectronic with the preceding noble gases.

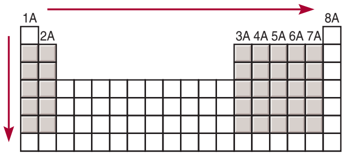
8.3 Periodic Variation in Physical Properties

As we have seen, the electron configurations of the elements show a periodic variation with increasing atomic number. Consequently, there are also periodic variations in physical and chemical behavior. In this section and the next two, we will examine some physical properties of elements that are in the same group or period and additional properties that influence the chemical behavior of the elements. First, let's look at the concept of effective nuclear charge, which has a direct bearing on many atomic properties.

Effective Nuclear Charge

In Chapter 7 we discussed the shielding effect that electrons close to the nucleus have on outer-shell electrons in many-electron atoms. The presence of other electrons in an atom reduces the electrostatic attraction between a given electron and the positively charged protons in the nucleus. The ***effective nuclear charge*** **(Z_{eff})** is *the nuclear charge felt by an electron when both the actual nuclear charge* (Z) *and the repulsive effects (shielding) of the other electrons are taken into account.* In general, Z_{eff} is given by

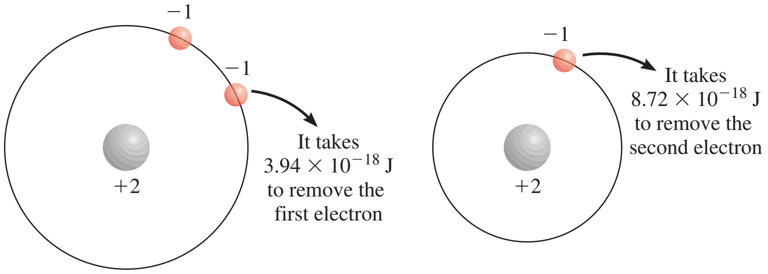
$$Z_{eff} = Z - \sigma \tag{8.2}$$



The increase in effective nuclear charge from left to right across a period and from top to bottom in a group for representative elements.

where σ (sigma) is called the *shielding constant* (also called the *screening constant*). The shielding constant is greater than zero but smaller than Z.

One way to illustrate how electrons in an atom shield one another is to consider the amounts of energy required to remove the two electrons from a helium atom. Experiments show that it takes 3.94×10^{-18} J to remove the first electron and 8.72×10^{-18} J to remove the second electron. There is no shielding once the first electron is removed, so the second electron feels the full effect of the $+2$ nuclear charge.



Because the core electrons are, on average, closer to the nucleus than valence electrons, core electrons shield valence electrons much more than valence electrons shield one another. Consider the second-period elements from Li to Ne. Moving from left to right, we find the number of core electrons ($1s^2$) remains constant while the nuclear charge increases. However, because the added electron is a valence electron and valence electrons do not shield each other well, the net effect of moving across the period is a greater effective nuclear charge felt by the valence electrons, as shown here.

See Figure 7.27 for radial probability plots of 1*s* and 2*s* orbitals.

	Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Z	3	4	5	6	7	8	9	10
Z_{eff}	1.28	1.91	2.42	3.14	3.83	4.45	5.10	5.76

The effective nuclear charge also increases as we go down a particular periodic group. However, because the valence electrons are now added to increasingly large shells as n increases, the electrostatic attraction between the nucleus and the valence electrons actually decreases.

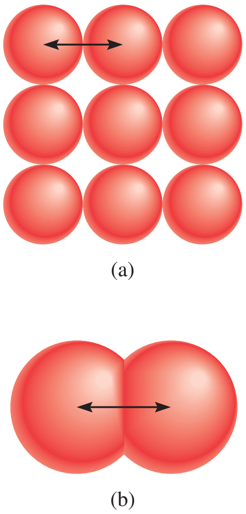
Animation
Atomic and Ionic Radius

Atomic Radius

A number of physical properties, including density, melting point, and boiling point, are related to the sizes of atoms, but atomic size is difficult to define. As we saw in Chapter 7, the electron density in an atom extends far beyond the nucleus, but we normally think of atomic size as the volume containing about 90 percent of the total electron density around the nucleus. When we must be even more specific, we define the size of an atom in terms of its ***atomic radius,*** which is *one-half the distance between the two nuclei in two adjacent metal atoms or in a diatomic molecule*.

For atoms linked together to form an extensive three-dimensional network, atomic radius is simply one-half the distance between the nuclei in two neighboring atoms [Figure 8.4(a)]. For elements that exist as simple diatomic molecules, the atomic radius is one-half the distance between the nuclei of the two atoms in a particular molecule [Figure 8.4(b)].

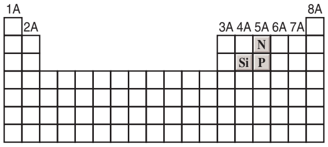
Figure 8.5 shows the atomic radius of many elements according to their positions in the periodic table, and Figure 8.6 plots the atomic radii of these elements against their atomic numbers. Periodic trends are clearly evident. Consider the second-period elements. Because the effective nuclear charge increases from left to right, the added valence electron at each step is more strongly attracted by the nucleus than the one before. Therefore, we expect and indeed find the atomic radius decreases from Li to Ne. Within a group we find that atomic radius increases with atomic number. For the alkali metals in Group 1A, the valence electron resides in the *ns* orbital. Because orbital size increases with the increasing principal quantum number n, the size of the atomic radius increases even though the effective nuclear charge also increases from Li to Cs.


(a)

(b)

Figure 8.4 *(a) In metals such as beryllium, the atomic radius is defined as one-half the distance between the centers of two adjacent atoms. (b) For elements that exist as diatomic molecules, such as iodine, the radius of the atom is defined as one-half the distance between the centers of the atoms in the molecule.*

Figure 8.5 *Atomic radii (in picometers) of representative elements according to their positions in the periodic table. Note that there is no general agreement on the size of atomic radii. We focus only on the trends in atomic radii, not on their precise values.*



EXAMPLE 8.2

Referring to a periodic table, arrange the following atoms in order of increasing atomic radius: P, Si, N.

Strategy What are the trends in atomic radii in a periodic group and in a particular period? Which of the preceding elements are in the same group? in the same period?

Solution From Figure 8.1 we see that N and P are in the same group (Group 5A). Therefore, the radius of N is smaller than that of P (atomic radius increases as we go down a group). Both Si and P are in the third period, and Si is to the left of P. Therefore, the radius of P is smaller than that of Si (atomic radius decreases as we move from left to right across a period). Thus, the order of increasing radius is $N < P < Si$.

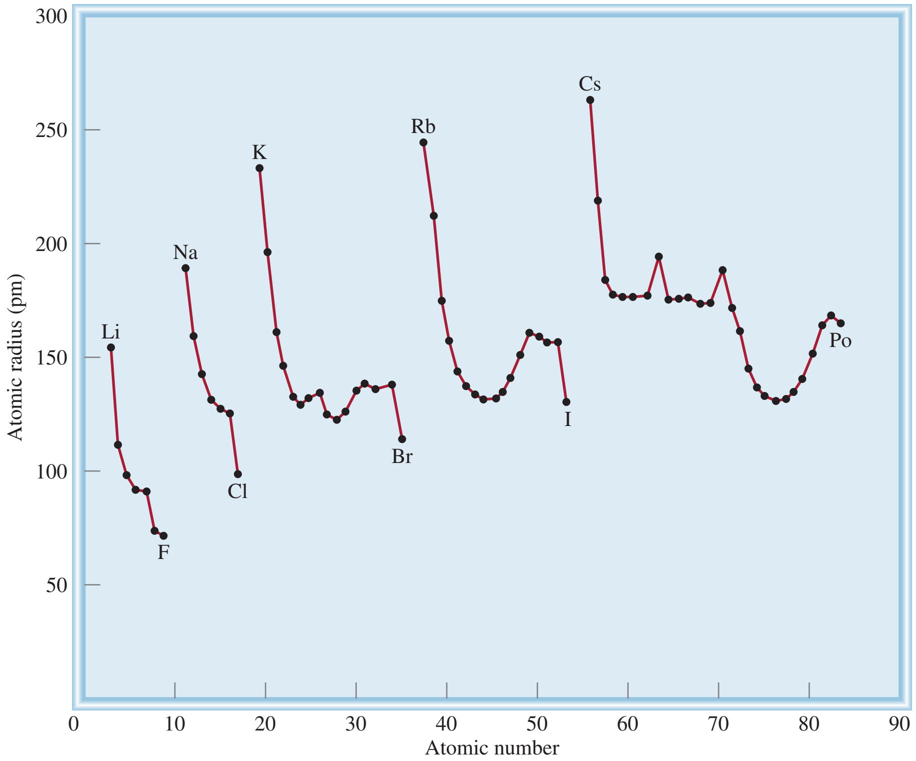


Figure 8.6 *Plot of atomic radii (in picometers) of elements against their atomic numbers.*

Ionic Radius

Ionic radius is *the radius of a cation or an anion*. It can be measured by X-ray diffraction (see Chapter 11). Ionic radius affects the physical and chemical properties of an ionic compound. For example, the three-dimensional structure of an ionic compound depends on the relative sizes of its cations and anions.

When a neutral atom is converted to an ion, we expect a change in size. If the atom forms an anion, its size (or radius) increases, because the nuclear charge remains the same but the repulsion resulting from the additional electron(s) enlarges the domain of the electron cloud. On the other hand, removing one or more electrons from an atom reduces electron-electron repulsion but the nuclear charge remains the same, so the electron cloud shrinks, and the cation is smaller than the atom. Figure 8.7 shows the changes in size that result when alkali metals are converted to cations and halogens are converted to anions; Figure 8.8 shows the changes in size that occur when a lithium atom reacts with a fluorine atom to form a LiF unit.

Figure 8.9 shows the radii of ions derived from the familiar elements, arranged according to the elements' positions in the periodic table. We can see parallel trends between atomic radii and ionic radii. For example, from top to bottom both the atomic radius and the ionic radius increase within a group. For ions derived from elements in different groups, a size comparison is meaningful only if the ions are isoelectronic. If we examine isoelectronic ions, we find that cations are smaller than anions. For example, Na^+ is smaller than F^-. Both ions have the same number of electrons, but Na ($Z = 11$) has more protons than F ($Z = 9$). The larger effective nuclear charge of Na^+ results in a smaller radius.

For isoelectronic ions, the size of the ion is based on the size of the electron cloud, not on the number of protons in the nucleus.

Focusing on isoelectronic cations, we see that the radii of *tripositive ions* (ions that bear three positive charges) are smaller than those of *dipositive ions* (ions that bear two positive charges), which in turn are smaller than *unipositive ions* (ions

Figure 8.7 *Comparison of atomic radii with ionic radii. (a) Alkali metals and alkali metal cations. (b) Halogens and halide ions.*

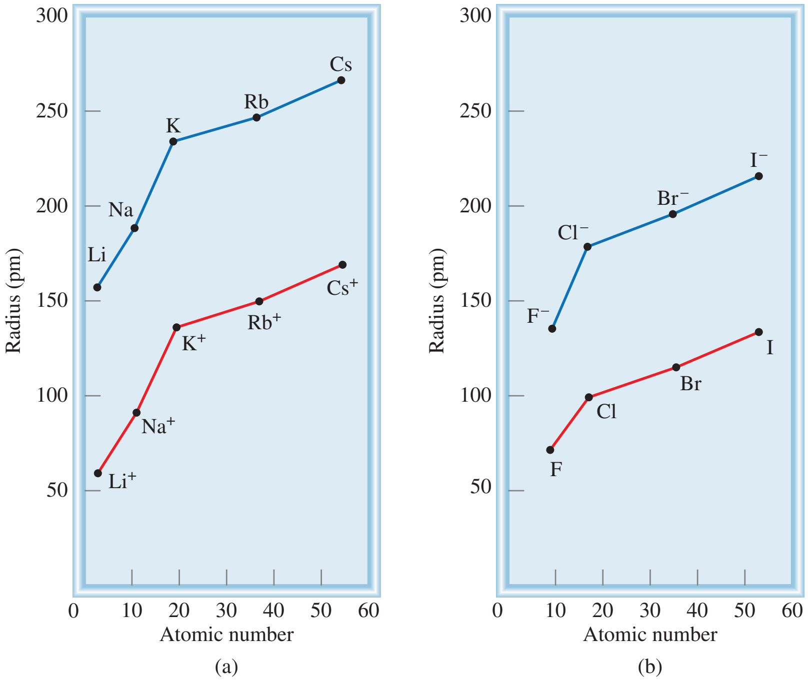
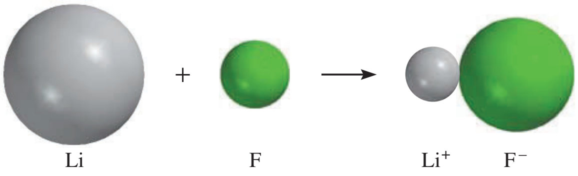


Figure 8.8 *Changes in the sizes of Li and F when they react to form LiF.*



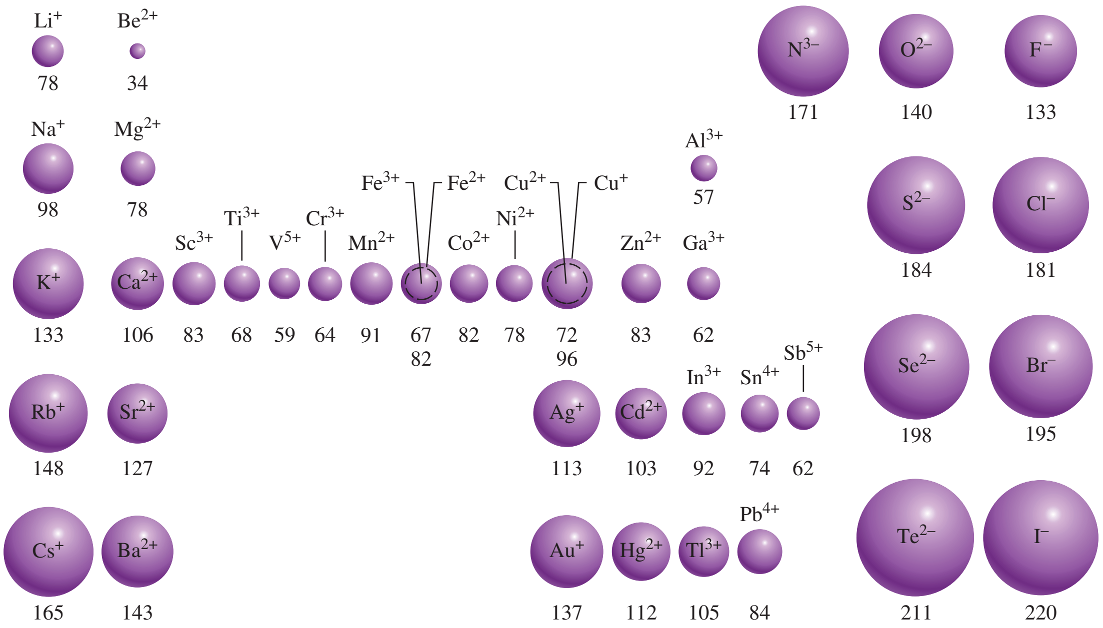


Figure 8.9 *The radii (in picometers) of ions of familiar elements arranged according to the elements' positions in the periodic table.*

that bear one positive charge). This trend is nicely illustrated by the sizes of three isoelectronic ions in the third period: Al^{3+}, Mg^{2+}, and Na^{+} (see Figure 8.9). The Al^{3+} ion has the same number of electrons as Mg^{2+}, but it has one more proton. Thus, the electron cloud in Al^{3+} is pulled inward more than that in Mg^{2+}. The smaller radius of Mg^{2+} compared with that of Na^{+} can be similarly explained. Turning to isoelectronic anions, we find that the radius increases as we go from ions with uninegative charge ($-$) to those with dinegative charge ($2-$), and so on. Thus, the oxide ion is larger than the fluoride ion because oxygen has one fewer proton than fluorine; the electron cloud is spread out more in O^{2-}.

EXAMPLE 8.3

For each of the following pairs, indicate which one of the two species is larger: (a) N^{3-} or F^{-}; (b) Mg^{2+} or Ca^{2+}; (c) Fe^{2+} or Fe^{3+}.

Strategy In comparing ionic radii, it is useful to classify the ions into three categories: (1) isoelectronic ions, (2) ions that carry the same charges and are generated from atoms of the same periodic group, and (3) ions carry different charges but are generated from the same atom. In case (1), ions carrying a greater negative charge are always larger; in case (2), ions from atoms having a greater atomic number are always larger; in case (3), ions having a smaller positive charge are always larger.

Solution (a) N^{3-} and F^{-} are isoelectronic anions, both containing 10 electrons. Because N^{3-} has only seven protons and F^{-} has nine, the smaller attraction exerted by the nucleus on the electrons results in a larger N^{3-} ion.

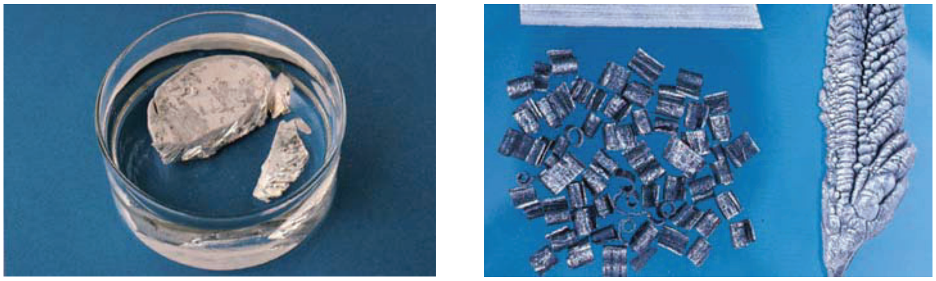
(b) Both Mg and Ca belong to Group 2A (the alkaline earth metals). Thus, Ca^{2+} ion is larger than Mg^{2+} because Ca's valence electrons are in a larger shell ($n = 4$) than are Mg's ($n = 3$).

(c) Both ions have the same nuclear charge, but Fe^{2+} has one more electron (24 electrons compared to 23 electrons for Fe^{3+}) and hence greater electron-electron repulsion. The radius of Fe^{2+} is larger.

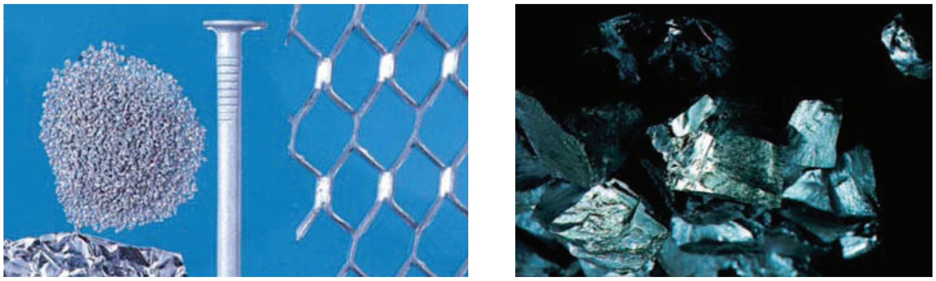
Variation of Physical Properties Across a Period and Within a Group

From left to right across a period there is a transition from metals to metalloids to nonmetals. Consider the third-period elements from sodium to argon (Figure 8.10). Sodium, the first element in the third period, is a very reactive metal, whereas chlorine,

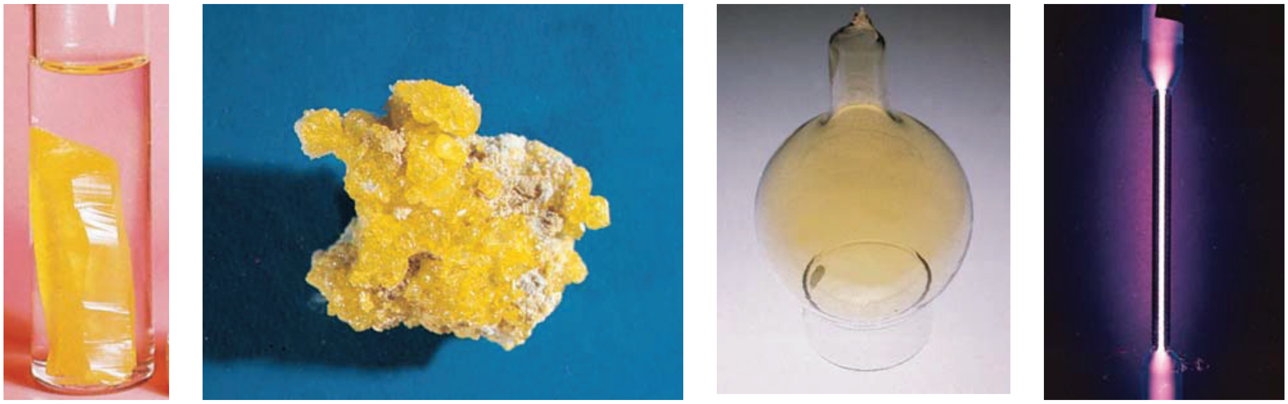
Figure 8.10 *The third-period elements. The photograph of argon, which is a colorless, odorless gas, shows the color emitted by the gas from a discharge tube.*



Sodium (Na) Magnesium (Mg)



Aluminum (Al) Silicon (Si)



Phosphorus (P_4) Sulfur (S_8) Chlorine (Cl_2) Argon (Ar)

the second-to-last element of that period, is a very reactive nonmetal. In between, the elements show a gradual transition from metallic properties to nonmetallic properties. Sodium, magnesium, and aluminum all have extensive three-dimensional atomic networks, which are held together by forces characteristic of the metallic state. Silicon is a metalloid; it has a giant three-dimensional structure in which the Si atoms are held together very strongly. Starting with phosphorus, the elements exist in simple, discrete molecular units (P_4, S_8, Cl_2, and Ar) that have low melting points and boiling points.

Ionization Energy

Not only is there a correlation between electron configuration and physical properties, but a close correlation also exists between electron configuration (a microscopic property) and chemical behavior (a macroscopic property). As we will see throughout this book, the chemical properties of any atom are determined by the configuration of the atom's valence electrons. The stability of these outermost electrons is reflected directly in the atom's ionization energies. ***Ionization energy*** is *the minimum energy (in kJ/mol) required to remove an electron from a gaseous atom in its ground state*. In other words, ionization energy is the amount of energy in kilojoules needed to strip 1 mole of electrons from 1 mole of gaseous atoms. Gaseous atoms are specified in this definition because an atom in the gas phase is virtually uninfluenced by its neighbors and so there are no intermolecular forces (that is, forces between molecules) to take into account when measuring ionization energy.

Note that while valence electrons are relatively easy to remove from the atom, core electrons are much harder to remove. Thus, there is a large jump in ionization energy between the last valence electron and the first core electron.

The magnitude of ionization energy is a measure of how "tightly" the electron is held in the atom. The higher the ionization energy, the more difficult it is to remove the electron. For a many-electron atom, the amount of energy required to remove the first electron from the atom in its ground state,

$$\text{energy} + \text{X}(g) \longrightarrow \text{X}^{+}(g) + e^{-} \tag{8.3}$$

is called the *first ionization energy* (I_1). In Equation (8.3), X represents an atom of any element and e^- is an electron. The second ionization energy (I_2) and the third ionization energy (I_3) are shown in the following equations:

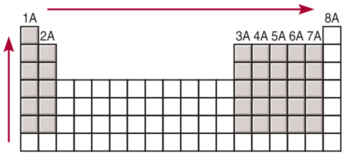
$$\begin{aligned} \text{energy} + \text{X}^{+}(g) &\longrightarrow \text{X}^{2+}(g) + e^{-} \qquad \text{second ionization} \\ \text{energy} + \text{X}^{2+}(g) &\longrightarrow \text{X}^{3+}(g) + e^{-} \qquad \text{third ionization} \end{aligned}$$

The pattern continues for the removal of subsequent electrons.

When an electron is removed from an atom, the repulsion among the remaining electrons decreases. Because the nuclear charge remains constant, more energy is needed to remove another electron from the positively charged ion. Thus, ionization energies always increase in the following order:

$$I_1 < I_2 < I_3 < \cdots$$

Table 8.2 lists the ionization energies of the first 20 elements. Ionization is always an endothermic process. By convention, energy absorbed by atoms (or ions) in the ionization process has a positive value. Thus, ionization energies are all positive quantities. Figure 8.11 shows the variation of the first ionization energy with atomic number. The



The increase in first ionization energy from left to right across a period and from bottom to top in a group for representative elements.

TABLE 8.2 **The Ionization Energies (kJ/mol) of the First 20 Elements**

Z	Element	First	Second	Third	Fourth	Fifth	Sixth
1	H	1,312					
2	He	2,373	5,251				
3	Li	520	7,300	11,815			
4	Be	899	1,757	14,850	21,005		
5	B	801	2,430	3,660	25,000	32,820	
6	C	1,086	2,350	4,620	6,220	38,000	47,261
7	N	1,400	2,860	4,580	7,500	9,400	53,000
8	O	1,314	3,390	5,300	7,470	11,000	13,000
9	F	1,680	3,370	6,050	8,400	11,000	15,200
10	Ne	2,080	3,950	6,120	9,370	12,200	15,000
11	Na	495.9	4,560	6,900	9,540	13,400	16,600
12	Mg	738.1	1,450	7,730	10,500	13,600	18,000
13	Al	577.9	1,820	2,750	11,600	14,800	18,400
14	Si	786.3	1,580	3,230	4,360	16,000	20,000
15	P	1,012	1,904	2,910	4,960	6,240	21,000
16	S	999.5	2,250	3,360	4,660	6,990	8,500
17	Cl	1,251	2,297	3,820	5,160	6,540	9,300
18	Ar	1,521	2,666	3,900	5,770	7,240	8,800
19	K	418.7	3,052	4,410	5,900	8,000	9,600
20	Ca	589.5	1,145	4,900	6,500	8,100	11,000

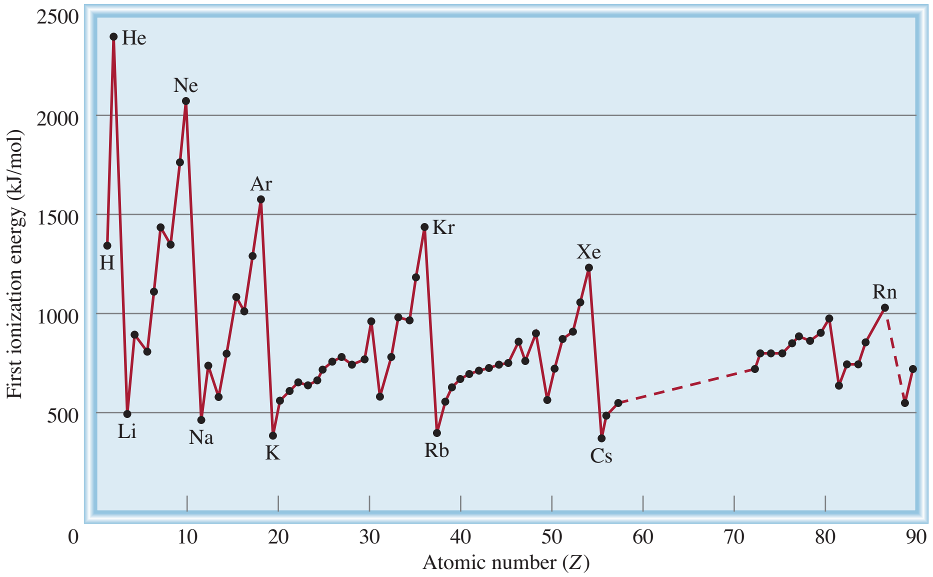


Figure 8.11 *Variation of the first ionization energy with atomic number. Note that the noble gases have high ionization energies, whereas the alkali metals and alkaline earth metals have low ionization energies.*

plot clearly exhibits the periodicity in the stability of the most loosely held electron. Note that, apart from small irregularities, the first ionization energies of elements in a period increase with increasing atomic number. This trend is due to the increase in effective nuclear charge from left to right (as in the case of atomic radii variation). A larger effective nuclear charge means a more tightly held valence electron, and hence a higher first ionization energy. A notable feature of Figure 8.11 is the peaks, which correspond to the noble gases. We tend to associate full valence-shell electron configurations with an inherent degree of chemical stability. The high ionization energies of the noble gases, stemming from their large effective nuclear charge, comprise one of the reasons for this stability. In fact, helium ($1s^2$) has the highest first ionization energy of all the elements.

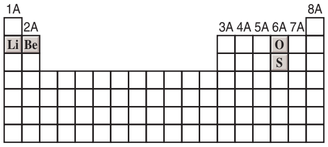
At the bottom of the graph in Figure 8.11 are the Group 1A elements (the alkali metals), which have the lowest first ionization energies. Each of these metals has one valence electron (the outermost electron configuration is ns^1), which is effectively shielded by the completely filled inner shells. Consequently, it is energetically easy to remove an electron from the atom of an alkali metal to form a unipositive ion (Li^+, Na^+, K^+, . . .). Significantly, the electron configurations of these cations are isoelectronic with those noble gases just preceding them in the periodic table.

The Group 2A elements (the alkaline earth metals) have higher first ionization energies than the alkali metals do. The alkaline earth metals have two valence electrons (the outermost electron configuration is ns^2). Because these two *s* electrons do not shield each other well, the effective nuclear charge for an alkaline earth metal atom is larger than that for the preceding alkali metal. Most alkaline earth compounds contain dipositive ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). The Be^{2+} ion is isoelectronic with Li^+ and with He, Mg^{2+} is isoelectronic with Na^+ and with Ne, and so on.

As Figure 8.11 shows, metals have relatively low ionization energies compared to nonmetals. The ionization energies of the metalloids generally fall between those of metals and nonmetals. The difference in ionization energies suggests why metals always form cations and nonmetals form anions in ionic compounds. (The only important nonmetallic cation is the ammonium ion, NH_4^+.) For a given group, ionization energy decreases with increasing atomic number (that is, as we move down the group). Elements in the same group have similar outer electron configurations. However, as the principal quantum number *n* increases, so does the average distance of a valence electron from the nucleus. A greater separation between the electron and the nucleus means a weaker attraction, so that it becomes easier to remove the first electron as we go from element to element down a group even though the effective nuclear charge also increases in the same direction. Thus, the metallic character of the elements within a group increases from top to bottom. This trend is particularly noticeable for elements in Groups 3A to 7A. For example, in Group 4A, carbon is a nonmetal, silicon and germanium are metalloids, and tin and lead are metals.

Although the general trend in the periodic table is for first ionization energies to increase from left to right, some irregularities do exist. The first exception occurs between Group 2A and 3A elements in the same period (for example, between Be and B and between Mg and Al). The Group 3A elements have lower first ionization energies than 2A elements because they all have a single electron in the outermost *p* subshell (ns^2np^1), which is well shielded by the inner electrons and the ns^2 electrons. Therefore, less energy is needed to remove a single *p* electron than to remove an *s* electron from the same principal energy level. The second irregularity occurs between Groups 5A and 6A (for example, between N and O and between P and S). In the Group 5A elements (ns^2np^3), the *p* electrons are in three separate orbitals according to Hund's rule. In Group 6A (ns^2np^4), the additional electron must be paired with one of the three *p* electrons. The proximity of two electrons in the same orbital results in greater electrostatic repulsion, which makes it easier to ionize an atom of the Group 6A element, even though the nuclear charge has increased by one unit. Thus, the ionization energies for Group 6A elements are lower than those for Group 5A elements in the same period.

Example 8.4 compares the ionization energies of some elements.



EXAMPLE 8.4

(a) Which atom should have a smaller first ionization energy: oxygen or sulfur? (b) Which atom should have a higher second ionization energy: lithium or beryllium?

Strategy (a) First ionization energy decreases as we go down a group because the outermost electron is farther away from the nucleus and feels less attraction. (b) Removal of the outermost electron requires less energy if it is shielded by a filled inner shell.

Solution (a) Oxygen and sulfur are members of Group 6A. They have the same valence electron configuration (ns^2np^4), but the 3*p* electron in sulfur is farther from the nucleus and experiences less nuclear attraction than the 2*p* electron in oxygen. Thus, we predict that sulfur should have a smaller first ionization energy.

(b) The electron configurations of Li and Be are $1s^22s^1$ and $1s^22s^2$, respectively. The second ionization energy is the minimum energy required to remove an electron from a gaseous unipositive ion in its ground state. For the second ionization process, we write

$$\begin{array}{lll} \mathrm{Li}^+(g) & \longrightarrow & \mathrm{Li}^{2+}(g) + e^- \\ 1s^2 & & 1s^1 \\ \mathrm{Be}^+(g) & \longrightarrow & \mathrm{Be}^{2+}(g) + e^- \\ 1s^22s^1 & & 1s^2 \end{array}$$

Because 1*s* electrons shield 2*s* electrons much more effectively than they shield each other, we predict that it should be easier to remove a 2*s* electron from Be^+ than to remove a 1*s* electron from Li^+.

(Continued)

Check Compare your result with the data shown in Table 8.2. In (a), is your prediction consistent with the fact that the metallic character of the elements increases as we move down a periodic group? In (b), does your prediction account for the fact that alkali metals form +1 ions while alkaline earth metals form +2 ions?

8.5 Electron Affinity

Another property that greatly influences the chemical behavior of atoms is their ability to accept one or more electrons. This property is called ***electron affinity,*** which is *the negative of the energy change that occurs when an electron is accepted by an atom in the gaseous state to form an anion.*

$$X(g) + e^- \longrightarrow X^-(g) \qquad (8.4)$$

Consider the process in which a gaseous fluorine atom accepts an electron:

$$F(g) + e^- \longrightarrow F^-(g) \qquad \Delta H = -328 \text{ kJ/mol}$$

The electron affinity of fluorine is therefore assigned a value of +328 kJ/mol. The more positive is the electron affinity of an element, the greater is the affinity of an atom of the element to accept an electron. Another way of viewing electron affinity is to think of it as the energy that must be supplied to remove an electron from the anion. For fluorine, we write

Electron affinity is positive if the reaction is exothermic and negative if the reaction is endothermic.

$$F^-(g) \longrightarrow F(g) + e^- \qquad \Delta H = +328 \text{ kJ/mol}$$

Thus, a large positive electron affinity means that the negative ion is very stable (that is, the atom has a great tendency to accept an electron), just as a high ionization energy of an atom means that the electron in the atom is very stable.

TABLE 8.3 Electron Affinities (kJ/mol) of Some Representative Elements and the Noble Gases*

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 44	Si 134	P 72	S 200	Cl 349	Ar < 0
K 48	Ca 2.4	Ga 29	Ge 118	As 77	Se 195	Br 325	Kr < 0
Rb 47	Sr 4.7	In 29	Sn 121	Sb 101	Te 190	I 295	Xe < 0
Cs 45	Ba 14	Tl 30	Pb 110	Bi 110	Po ?	At ?	Rn < 0

*The electron affinities of the noble gases, Be, and Mg have not been determined experimentally, but are believed to be close to zero or negative.

Experimentally, electron affinity is determined by removing the additional electron from an anion. In contrast to ionization energies, however, electron affinities are difficult to measure because the anions of many elements are unstable. Table 8.3 shows the electron affinities of some representative elements and the noble gases, and Figure 8.12 plots the electron affinities of the first 56 elements versus atomic number. The overall trend is an increase in the tendency to accept electrons (electron affinity

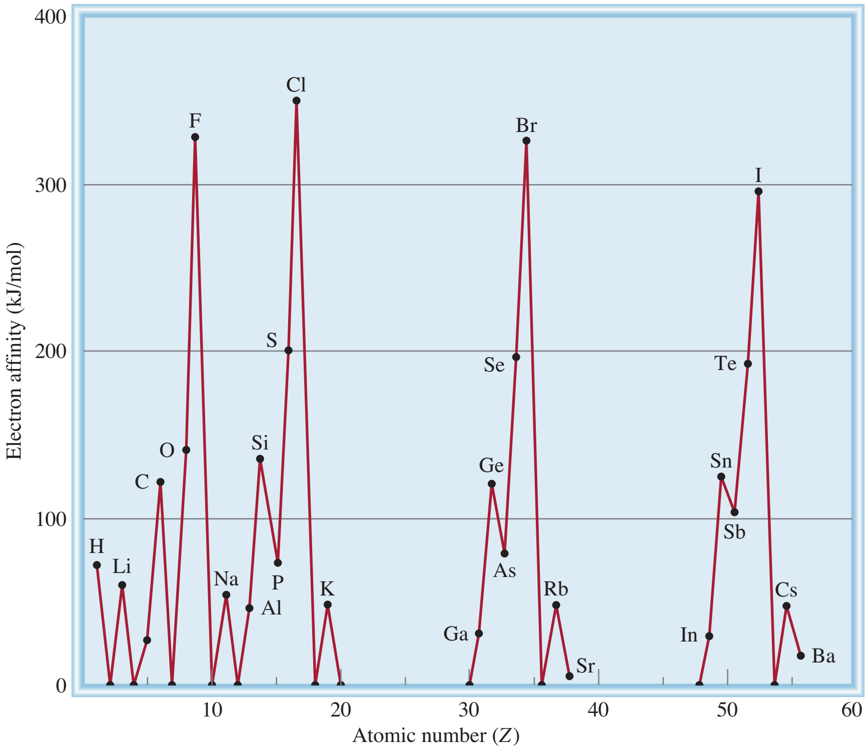


Figure 8.12 *A plot of electron affinity against atomic number from hydrogen to barium.*

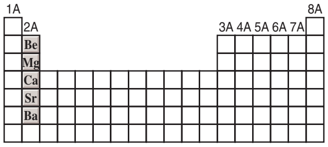
values become more positive) from left to right across a period. The electron affinities of metals are generally lower than those of nonmetals. The values vary little within a given group. The halogens (Group 7A) have the highest electron affinity values.

There is a general correlation between electron affinity and effective nuclear charge, which also increases from left to right in a given period (see p. 331). However, as in the case of ionization energies, there are some irregularities. For example, the electron affinity of a Group 2A element is lower than that for the corresponding Group 1A element, and the electron affinity of a Group 5A element is lower than that for the corresponding Group 4A element. These exceptions are due to the valence electron configurations of the elements involved. An electron added to a Group 2A element must end up in a higher-energy *np* orbital, where it is effectively shielded by the ns^2 electrons and therefore experiences a weaker attraction to the nucleus. Therefore, it has a lower electron affinity than the corresponding Group 1A element. Likewise, it is harder to add an electron to a Group 5A element (ns^2np^3) than to the corresponding Group 4A element (ns^2np^2) because the electron added to the Group 5A element must be placed in a *np* orbital that already contains an electron and will therefore experience a greater electrostatic repulsion. Finally, in spite of the fact that noble gases have high effective nuclear charge, they have extremely low electron affinities (zero or negative values). The reason is that an electron added to an atom with an ns^2np^6 configuration has to enter an $(n + 1)s$ orbital, where it is well shielded by the core electrons and will only be very weakly attracted by the nucleus. This analysis also explains why species with complete valence shells tend to be chemically stable.

There is a much less regular variation in electron affinities from top to bottom within a group (see Table 8.3).

Example 8.5 shows why the alkaline earth metals do not have a great tendency to accept electrons.

EXAMPLE 8.5



Why are the electron affinities of the alkaline earth metals, shown in Table 8.3, either negative or small positive values?

Strategy What are the electron configurations of alkaline earth metals? Would the added electron to such an atom be held strongly by the nucleus?

Solution The valence electron configuration of the alkaline earth metals is ns^2, where n is the highest principal quantum number. For the process

$$\underset{ns^2}{\mathrm{M}(g)} + e^- \longrightarrow \underset{ns^2np^1}{\mathrm{M}^-(g)}$$

where M denotes a member of the Group 2A family, the extra electron must enter the *np* subshell, which is effectively shielded by the two *ns* electrons (the *ns* electrons are more penetrating than the *np* electrons) and the inner electrons. Consequently, alkaline earth metals have little tendency to pick up an extra electron.

8.6 Variation in Chemical Properties of the Representative Elements

Ionization energy and electron affinity help chemists understand the types of reactions that elements undergo and the nature of the elements' compounds. On a conceptual level, these two measures are related in a simple way: Ionization energy measures the attraction of an atom for its own electrons, whereas electron affinity expresses the attraction of an atom for an additional electron from some other source. Together they give us insight into the general attraction of an atom for electrons. With these concepts we can survey the chemical behavior of the elements systematically, paying particular attention to the relationship between their chemical properties and their electron configurations.

We have seen that the metallic character of the elements *decreases* from left to right across a period and *increases* from top to bottom within a group. On the basis of these trends and the knowledge that metals usually have low ionization energies while nonmetals usually have high electron affinities, we can frequently predict the outcome of a reaction involving some of these elements.

General Trends in Chemical Properties

Before we study the elements in individual groups, let us look at some overall trends. We have said that elements in the same group resemble one another in chemical behavior because they have similar valence electron configurations. This statement, although correct in the general sense, must be applied with caution. Chemists have long known that the first member of each group (the element in the second period from lithium to fluorine) differs from the rest of the members of the same group. Lithium, for example, exhibits many, but not all, of the properties characteristic of the alkali metals. Similarly, beryllium is a somewhat atypical member of Group 2A, and so on. The difference can be attributed to the unusually small size of the first element in each group (see Figure 8.5).

Bear in mind that a comparison of the properties of elements in the same group is most valid if we are dealing with elements of the same type with respect to their metallic character. This guideline applies to the elements in Groups 1A and 2A, which are all metals, and to the elements in Groups 7A and 8A, which are all nonmet-als. In Groups 3A through 6A, where the elements change either from nonmetals to metals or from nonmetals to metalloids, it is natural to expect greater variation in chemical properties even though the members of the same group have similar outer electron configurations.

Now let us take a closer look at the chemical properties of the representative elements and the noble gases. (We will consider the chemistry of the transition met-als in Chapter 22.)

Hydrogen ($1s^1$)

There is no totally suitable position for hydrogen in the periodic table. Traditionally hydrogen is shown in Group 1A, but it really could be a class by itself. Like the alkali metals, it has a single *s* valence electron and forms a unipositive ion (H^+), which is hydrated in solution. On the other hand, hydrogen also forms the hydride ion (H^-) in ionic compounds such as NaH and CaH_2. In this respect, hydrogen resembles the halogens, all of which form uninegative ions (F^-, Cl^-, Br^-, and I^-) in ionic compounds. Ionic hydrides react with water to produce hydrogen gas and the corresponding metal hydroxides:

$$\begin{aligned} 2NaH(s) + 2H_2O(l) &\longrightarrow 2NaOH(aq) + H_2(g) \\ CaH_2(s) + 2H_2O(l) &\longrightarrow Ca(OH)_2(s) + 2H_2(g) \end{aligned}$$

Of course, the most important compound of hydrogen is water, which forms when hydrogen burns in air:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Group 1A Elements (ns^1, $n \geq 2$)

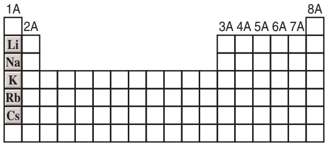
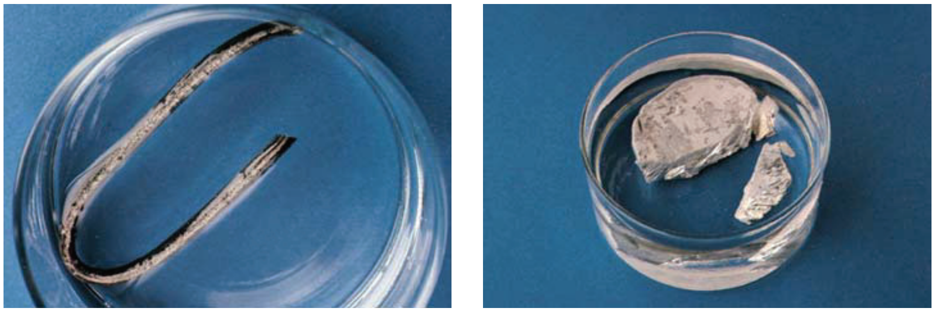
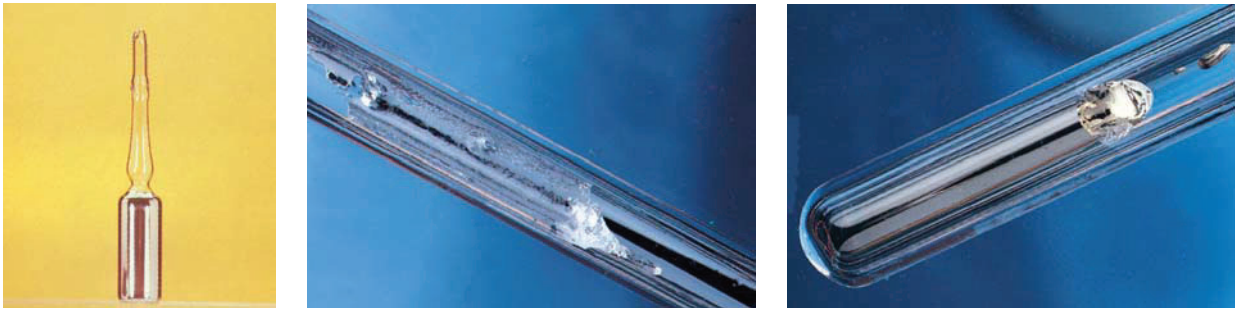


Figure 8.14 shows the Group 1A elements, the alkali metals. All of these elements have low ionization energies and therefore a great tendency to lose the single valence electron. In fact, in the vast majority of their compounds they are unipositive ions. These metals are so reactive that they are never found in the pure state in nature. They react with water to produce hydrogen gas and the corresponding metal hydroxide:

$$2M(s) + 2H_2O(l) \longrightarrow 2MOH(aq) + H_2(g)$$



Lithium (Li) Sodium (Na)



Potassium (K) Rubidium (Rb) Cesium (Cs)

Figure 8.14 *The Group 1A elements: the alkali metals. Francium (not shown) is radioactive.*

where M denotes an alkali metal. When exposed to air, they gradually lose their shiny appearance as they combine with oxygen gas to form oxides. Lithium forms lithium oxide (containing the O^{2-} ion):

$$4\mathrm{Li}(s) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{Li}_2\mathrm{O}(s)$$

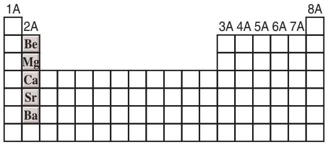
The other alkali metals all form oxides and *peroxides* (containing the O_2^{2-} ion). For example,

$$2\mathrm{Na}(s) + \mathrm{O}_2(g) \longrightarrow \mathrm{Na}_2\mathrm{O}_2(s)$$

Potassium, rubidium, and cesium also form *superoxides* (containing the O_2^- ion):

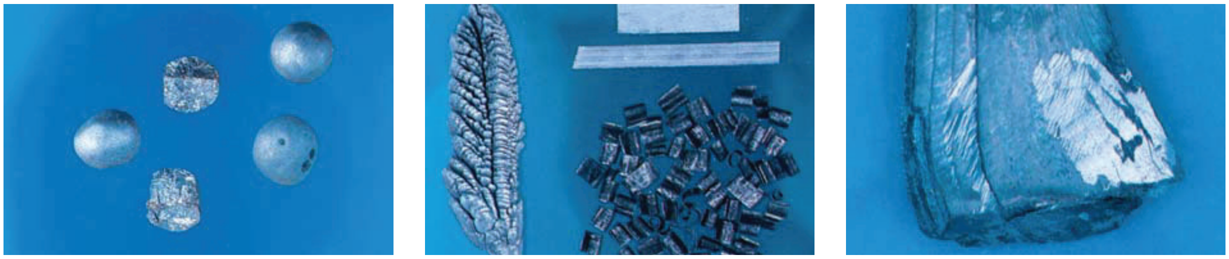
$$\mathrm{K}(s) + \mathrm{O}_2(g) \longrightarrow \mathrm{KO}_2(s)$$

The reason that different types of oxides are formed when alkali metals react with oxygen has to do with the stability of the oxides in the solid state. Because these oxides are all ionic compounds, their stability depends on how strongly the cations and anions attract one another. Lithium tends to form predominantly lithium oxide because this compound is more stable than lithium peroxide. The formation of other alkali metal oxides can be explained similarly.

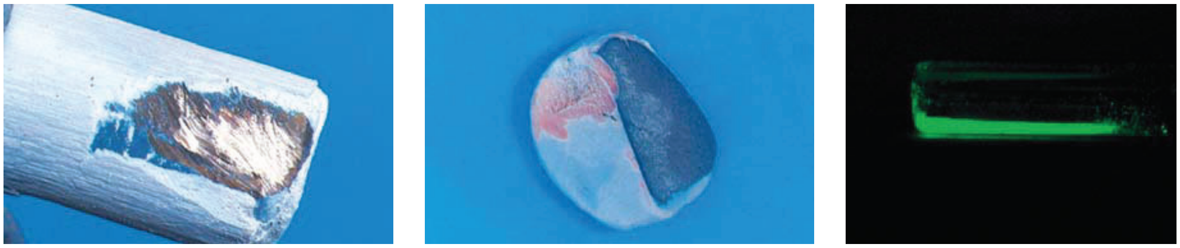


Group 2A Elements (ns^2, $n \geq 2$)

Figure 8.15 shows the Group 2A elements. As a group, the alkaline earth metals are somewhat less reactive than the alkali metals. Both the first and the second ionization energies decrease from beryllium to barium. Thus, the tendency is to form M^{2+} ions (where M denotes an alkaline earth metal atom), and hence the metallic character increases from top to bottom. Most beryllium compounds (BeH_2 and beryllium halides, such as $BeCl_2$) and some magnesium compounds (MgH_2, for example) are molecular rather than ionic in nature.



Beryllium (Be) Magnesium (Mg) Calcium (Ca)



Strontium (Sr) Barium (Ba) Radium (Ra)

Figure 8.15 *The Group 2A elements: the alkaline earth metals.*

The reactivities of alkaline earth metals with water vary quite markedly. Beryllium does not react with water; magnesium reacts slowly with steam; calcium, strontium, and barium are reactive enough to attack cold water:

$$\mathrm{Ba}(s) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{Ba(OH)_2}(aq) + \mathrm{H_2}(g)$$

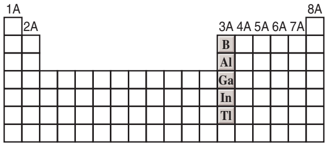
The reactivities of the alkaline earth metals toward oxygen also increase from Be to Ba. Beryllium and magnesium form oxides (BeO and MgO) only at elevated temperatures, whereas CaO, SrO, and BaO form at room temperature.

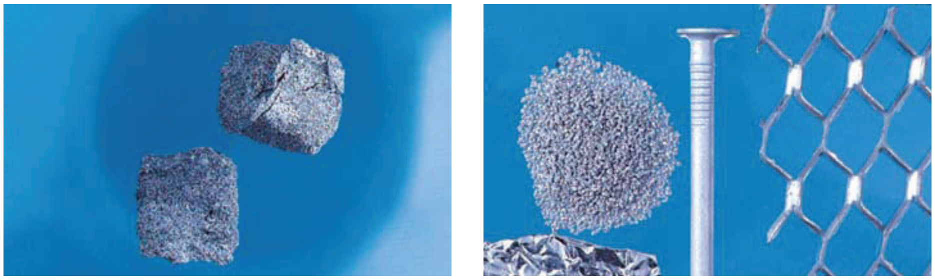
Magnesium reacts with acids in aqueous solution, liberating hydrogen gas:

$$\mathrm{Mg}(s) + 2\mathrm{H}^+(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) + \mathrm{H_2}(g)$$

Calcium, strontium, and barium also react with aqueous acid solutions to produce hydrogen gas. However, because these metals also attack water, two different reactions will occur simultaneously.

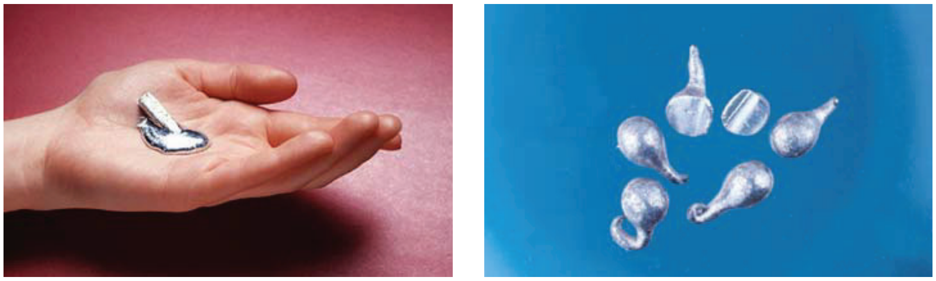
The chemical properties of calcium and strontium provide an interesting example of periodic group similarity. Strontium-90, a radioactive isotope, is a major product of an atomic bomb explosion. If an atomic bomb is exploded in the atmosphere, the strontium-90 formed will eventually settle on land and water, and it will reach our bodies via a relatively short food chain. For example, if cows eat contaminated grass and drink contaminated water, they will pass along strontium-90 in their milk. Because calcium and strontium are chemically similar, Sr^{2+} ions can replace Ca^{2+} ions in our bones. Constant exposure of the body to the high-energy radiation emitted by the strontium-90 isotopes can lead to anemia, leukemia, and other chronic illnesses.





Boron (B)

Aluminum (Al)



Gallium (Ga)

Indium (In)

Figure 8.16 *The Group 3A elements. The low melting point of gallium (29.8°C) causes it to melt when held in hand.*

Sulfur (S_8) Selenium (Se_8) Tellurium (Te)

Figure 8.19 *The Group 6A elements sulfur, selenium, and tellurium. Molecular oxygen is a colorless, odorless gas. Polonium (not shown) is radioactive.*

Group 7A Elements (ns^2np^5, $n \geq 2$)

All the halogens are nonmetals with the general formula X_2, where X denotes a halogen element (Figure 8.20). Because of their great reactivity, the halogens are never found in the elemental form in nature. (The last member of Group 7A, astatine, is a

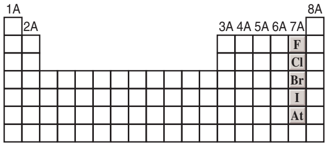


Figure 8.20 *The Group 7A elements chlorine, bromine, and iodine. Fluorine is a greenish-yellow gas that attacks ordinary glassware. Astatine is radioactive.*

radioactive element. Little is known about its properties.) Fluorine is so reactive that it attacks water to generate oxygen:

$$2F_2(g) + 2H_2O(l) \longrightarrow 4HF(aq) + O_2(g)$$

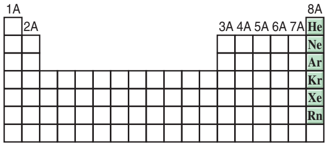
Actually the reaction between molecular fluorine and water is quite complex; the products formed depend on reaction conditions. The reaction shown above is one of several possible changes.

The halogens have high ionization energies and large positive electron affinities. Anions derived from the halogens (F^-, Cl^-, Br^-, and I^-) are called *halides*. They are isoelectronic with the noble gases immediately to their right in the periodic table. For example, F^- is isoelectronic with Ne, Cl^- with Ar, and so on. The vast majority of the alkali metal halides and alkaline earth metal halides are ionic compounds. The halogens also form many molecular compounds among themselves (such as ICl and BrF_3) and with nonmetallic elements in other groups (such as NF_3, PCl_5, and SF_6). The halogens react with hydrogen to form hydrogen halides:

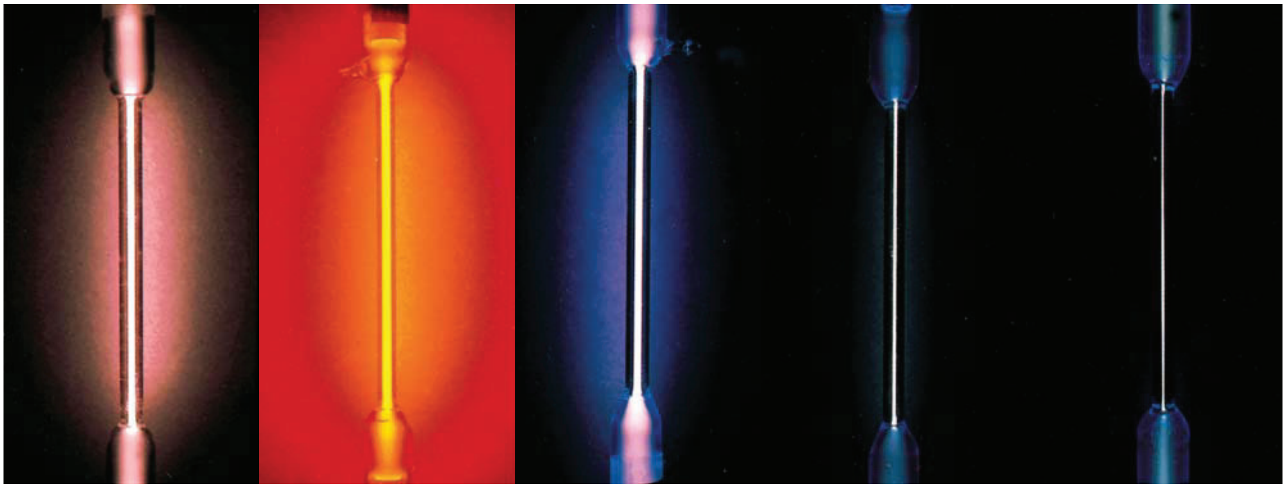
$$H_2(g) + X_2(g) \longrightarrow 2HX(g)$$

When this reaction involves fluorine, it is explosive, but it becomes less and less violent as we substitute chlorine, bromine, and iodine. The hydrogen halides dissolve in water to form hydrohalic acids. Hydrofluoric acid (HF) is a weak acid (that is, it is a weak electrolyte), but the other hydrohalic acids (HCl, HBr, and HI) are all strong acids (strong electrolytes).

Group 8A Elements (ns^2np^6, $n \geq 2$)

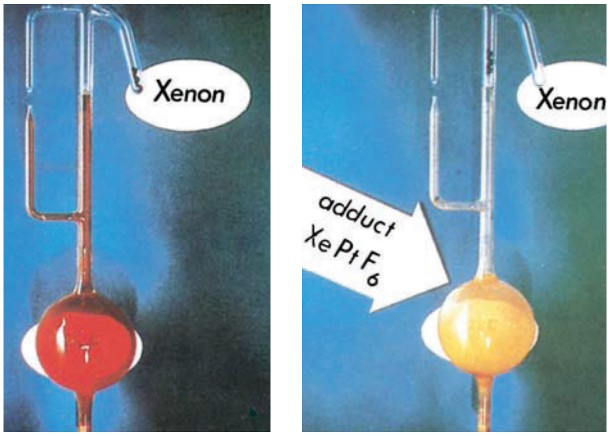


All noble gases exist as monatomic species (Figure 8.21). Their atoms have completely filled outer *ns* and *np* subshells, which give them great stability. (Helium is $1s^2$.) The Group 8A ionization energies are among the highest of all elements, and these gases have no tendency to accept extra electrons. For years these elements were called inert gases, and rightly so. Until 1963 no one had been able to prepare a



Helium (He) Neon (Ne) Argon (Ar) Krypton (Kr) Xenon (Xe)

Figure 8.21 *All noble gases are colorless and odorless. These pictures show the colors emitted by the gases from a discharge tube.*



(a) (b)

Figure 8.22 *(a) Xenon gas (colorless) and PtF_6 (red gas) separated from each other. (b) When the two gases are allowed to mix, a yellow-orange solid compound is formed. Note that the product was initially given the incorrect formula $XePtF_6$.*

compound containing any of these elements. The British chemist Neil Bartlett[†] shattered chemists' long-held views of these elements when he exposed xenon to platinum hexafluoride, a strong oxidizing agent, and brought about the following reaction (Figure 8.22):

$$\mathrm{Xe}(g) + 2\mathrm{PtF_6}(g) \longrightarrow \mathrm{XeF^+Pt_2F_{11}^-}(s)$$

In 2000, chemists prepared a compound containing argon (HArF) that is stable only at very low temperatures.

Since then, a number of xenon compounds (XeF_4, XeO_3, XeO_4, $XeOF_4$) and a few krypton compounds (KrF_2, for example) have been prepared (Figure 8.23). Despite the immense interest in the chemistry of the noble gases, however, their compounds do not have any major commercial applications, and they are not involved in natural biological processes. No compounds of helium and neon are known.

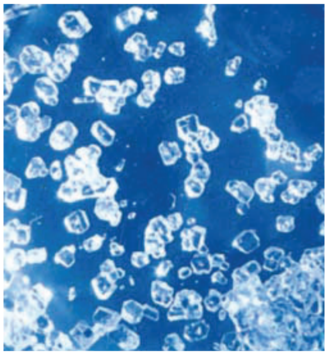
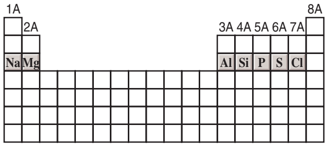


Figure 8.23 *Crystals of xenon tetrafluoride (XeF_4).*

[†] Neil Bartlett (1932–2008). English chemist. Bartlett's work was mainly in the preparation and study of compounds with unusual oxidation states and in solid-state chemistry.

Properties of Oxides Across a Period



One way to compare the properties of the representative elements across a period is to examine the properties of a series of similar compounds. Because oxygen combines with almost all elements, we will compare the properties of oxides of the third-period elements to see how metals differ from metalloids and nonmetals. Some elements in the third period (P, S, and Cl) form several types of oxides, but for simplicity we will consider only those oxides in which the elements have the highest oxidation number. Table 8.4 lists a few general characteristics of these oxides. We observed earlier that oxygen has a tendency to form the oxide ion. This tendency is greatly favored when oxygen combines with metals that have low ionization energies, namely, those in Groups 1A and 2A, plus aluminum. Thus, Na_2O, MgO, and Al_2O_3 are ionic compounds, as indicated by their high melting points and boiling points. They have extensive three-dimensional structures in which each cation is surrounded by a specific number of anions, and vice versa. As the ionization energies of the elements increase from left to right, so does the molecular nature of the oxides that are formed. Silicon is a metalloid; its oxide (SiO_2) also has a huge three-dimensional network, although no ions are present. The oxides of phosphorus, sulfur, and chlorine are molecular compounds composed of small discrete units. The weak attractions among these molecules result in relatively low melting points and boiling points.

Most oxides can be classified as acidic or basic depending on whether they produce acids or bases when dissolved in water or react as acids or bases in certain processes. Some oxides are ***amphoteric,*** which means that they *display both acidic and basic properties*. The first two oxides of the third period, Na_2O and MgO, are basic oxides. For example, Na_2O reacts with water to form the base sodium hydroxide:

$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$$

Magnesium oxide is quite insoluble; it does not react with water to any appreciable extent. However, it does react with acids in a manner that resembles an acid-base reaction:

$$MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$$

Note that the products of this reaction are a salt ($MgCl_2$) and water, the usual products of an acid-base neutralization.

Aluminum oxide is even less soluble than magnesium oxide; it too does not react with water. However, it shows basic properties by reacting with acids:

$$Al_2O_3(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O(l)$$

TABLE 8.4 Some Properties of Oxides of the Third-Period Elements

	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Type of compound	← Ionic →			← Molecular →			
Structure	← Extensive three-dimensional →				← Discrete molecular units →		
Melting point (°C)	1275	2800	2045	1610	580	16.8	−91.5
Boiling point (°C)	?	3600	2980	2230	?	44.8	82
Acid-base nature	Basic	Basic	Amphoteric	← Acidic →			

It also exhibits acidic properties by reacting with bases:

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2NaAl(OH)_4(aq)$$

Thus, Al_2O_3 is classified as an amphoteric oxide because it has properties of both acids and bases. Other amphoteric oxides are ZnO, BeO, and Bi_2O_3.

Silicon dioxide is insoluble and does not react with water. It has acidic properties, however, because it reacts with very concentrated bases:

$$SiO_2(s) + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$

For this reason, concentrated aqueous, strong bases such as NaOH(*aq*) should not be stored in Pyrex glassware, which is made of SiO_2.

The remaining third-period oxides are acidic. They react with water to form phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), and perchloric acid ($HClO_4$):

$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$
$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$
$$Cl_2O_7(l) + H_2O(l) \longrightarrow 2HClO_4(aq)$$