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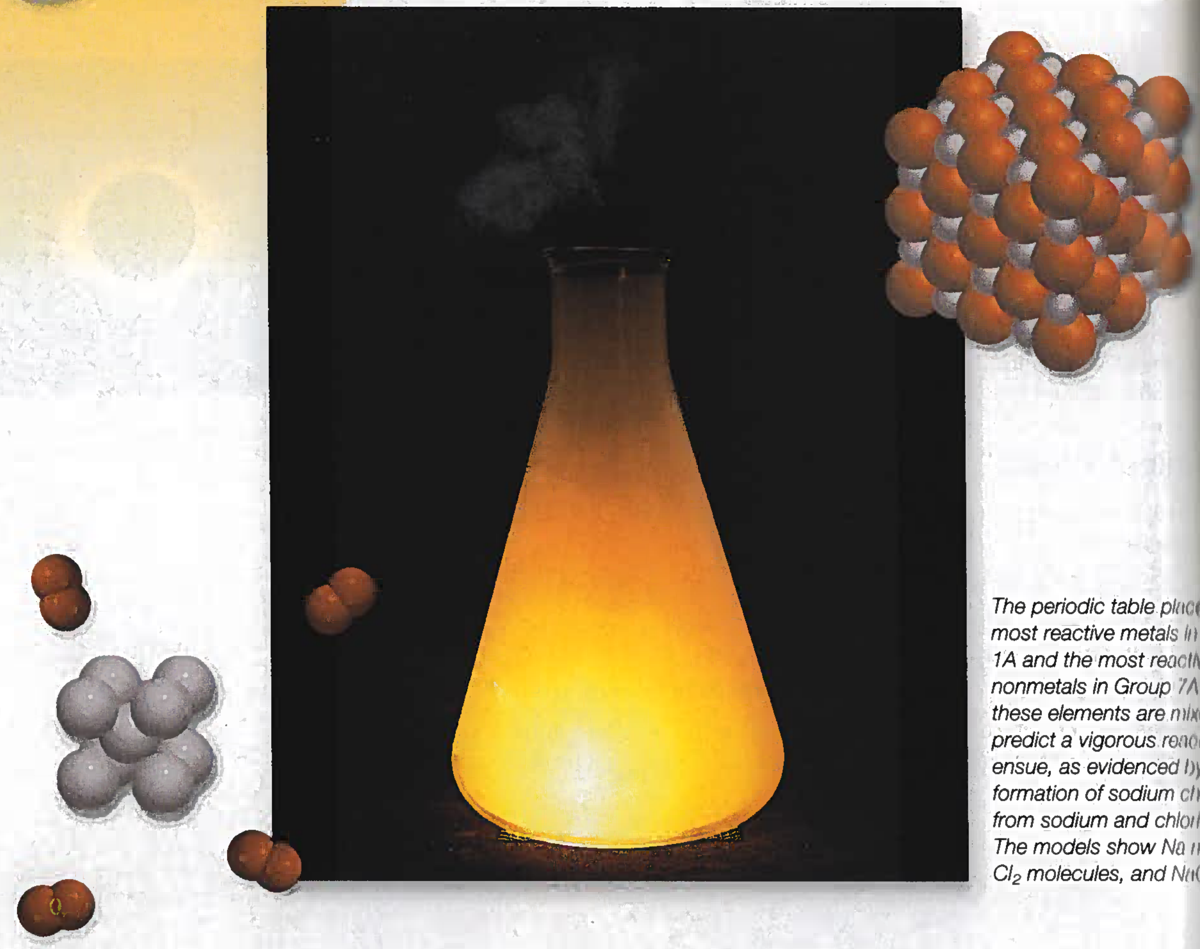
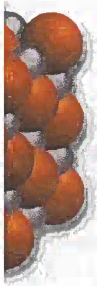


The periodic table places most reactive metals in 1A and the most reactive nonmetals in Group 7A. these elements are mixed predict a vigorous reaction ensue, as evidenced by the formation of sodium chl from sodium and chlorine The models show Na m Cl_2 molecules, and NaCl

Periodic Relationships Among the Elements



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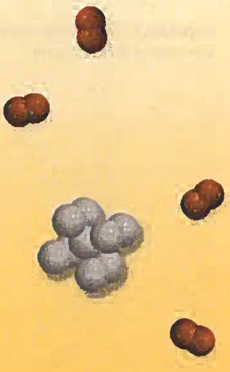
A LOOK AHEAD

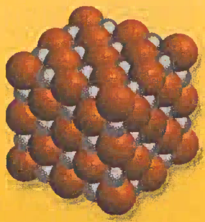
- We start with the development of the periodic table and the contributions made by nineteenth-century scientists, in particular Mendeleev. (8.1)
- We see that electron configuration is the logical way to build up the periodic table, which explains some of the early anomalies. We also learn the rules for writing the electron configurations of cations and anions. (8.2)
- Next, we examine the periodic trends in physical properties, such as the size of atoms and ions in terms of effective nuclear charge. (8.3)
- We continue our study of periodic trends by examining chemical properties like ionization energy and electron affinity. (8.4 and 8.5)
- We then apply the knowledge acquired in the chapter to systematically study the properties of the representative elements as individual groups and also across a given period. (8.6)

Interactive Activity Summary

1. Interactivity: Attraction of Nucleus (8.3)
2. Animation: Atomic and Ionic Radius (8.3)
3. Interactivity: Atomic Radii (8.3)
4. Interactivity: Ionic Radii (8.3)
5. Interactivity: Ionization Energy (8.4)

Many of the chemical properties of the elements can be understood in terms of their electron configurations. Because electrons fill atomic orbitals in a fairly regular fashion, it is not surprising that elements with similar electron configurations, such as sodium and potassium, behave similarly in many respects and that, in general, the properties of the elements exhibit observable trends. Chemists in the nineteenth century recognized periodic trends in the physical and chemical properties of elements, long before quantum theory came onto the scene. Although these chemists were not aware of the existence of electrons and protons, their efforts to systematize the chemistry of the elements were remarkably successful. Their main sources of information were the atomic masses of the elements and other known physical and chemical properties.





8.1 Development of the Periodic Table

In the nineteenth century, when chemists had only a vague idea of atoms and mo cules and did not know of the existence of electrons and protons, they devised t periodic table using their knowledge of atomic masses. Accurate measurements of th atomic masses of many elements had already been made. Arranging elements acc ing to their atomic masses in a periodic table seemed logical to those chemists, wh felt that chemical behavior should somehow be related to atomic mass.

In 1864 the English chemist John Newlands[†] noticed that when the elements w arranged in order of atomic mass, every eighth element had similar properties. Ne lands referred to this peculiar relationship as the *law of octaves*. However, this "l turned out to be inadequate for elements beyond calcium, and Newlands's work w not accepted by the scientific community.

In 1869 the Russian chemist Dmitri Mendeleev[‡] and the German chemist Loth Meyer[§] independently proposed a much more extensive tabulation of the elem based on the regular, periodic recurrence of properties. Mendeleev's classification sy tem was a great improvement over Newlands's for two reasons. First, it grouped th elements together more accurately, according to their properties. Equally import it made possible the prediction of the properties of several elements that had not y been discovered. For example, Mendeleev proposed the existence of an unknown e ment that he called eka-aluminum and predicted a number of its properties. (*Eka* i Sanskrit word meaning "first"; thus eka-aluminum would be the first element und aluminum in the same group.) When gallium was discovered four years later, its pro erties matched the predicted properties of eka-aluminum remarkably well:

Gallium melts in a person's hand (body temperature is about 37°C).

Appendix 1 explains the names and symbols of the elements.

	Eka-Aluminum (Ea)	Gallium (Ga)
Atomic mass	68 amu	69.9 amu
Melting point	Low	29.78°C
Density	5.9 g/cm^3	5.94 g/cm^3
Formula of oxide	Ea_2O_3	Ga_2O_3

Mendeleev's periodic table included 66 known elements. By 1900, some 30 more h been added to the list, filling in some of the empty spaces. Figure 8.1 charts the di covery of the elements chronologically.

Although this periodic table was a celebrated success, the early versions had so glaring inconsistencies. For example, the atomic mass of argon (39.95 amu) is great than that of potassium (39.10 amu). If elements were arranged solely according t increasing atomic mass, argon would appear in the position occupied by potassium i our modern periodic table (see the inside front cover). But no chemist would pla argon, an inert gas, in the same group as lithium and sodium, two very reactive me als. This and other discrepancies suggested that some fundamental property other th atomic mass must be the basis of periodicity. This property turned out to be asso ated with atomic number, a concept unknown to Mendeleev and his contemporari

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[†] John Alexander Reina Newlands (1838–1898). English chemist. Newlands's work was a step in the ri direction in the classification of the elements. Unfortunately, because of its shortcomings, he was subje to much criticism, and even ridicule. At one meeting he was asked if he had ever examined the eleme according to the order of their initial letters! Nevertheless, in 1887 Newlands was honored by the Ro Society of London for his contribution.

[‡] Dmitri Ivanovich Mendeleev (1836–1907). Russian chemist. His work on the periodic classification of e ments is regarded by many as the most significant achievement in chemistry in the nineteenth centu

[§] Julius Lothar Meyer (1830–1895). German chemist. In addition to his contribution to the periodic ta Meyer also discovered the chemical affinity of hemoglobin for oxygen.

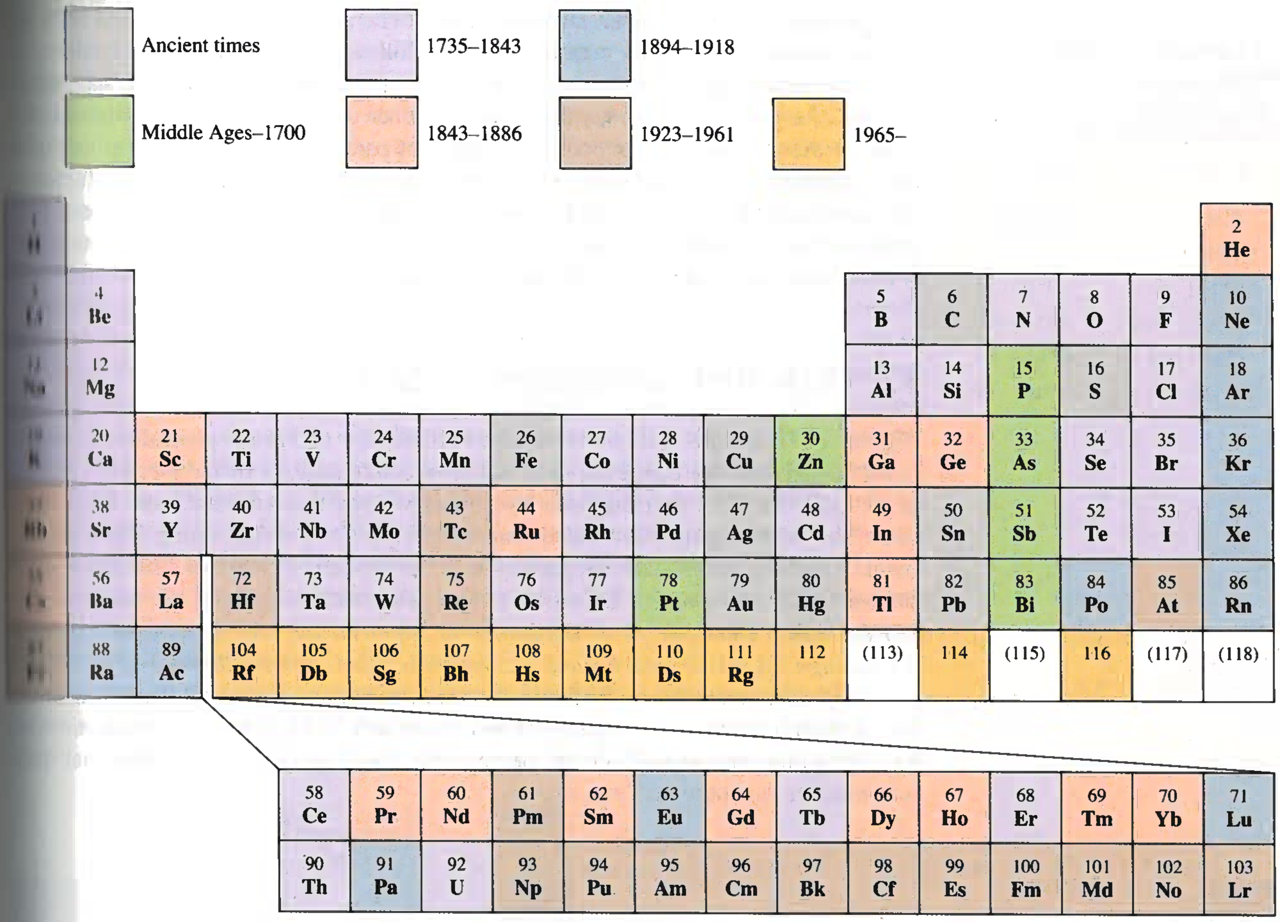

Figure 8.1 *A chronological chart of the discovery of the elements. To date, 114 elements have been identified.*

Using data from α-scattering experiments (see Section 2.2), Rutherford estimated the number of positive charges in the nucleus of a few elements, but the significance of these numbers was overlooked for several more years. In 1913 a young English physicist, Henry Moseley,† discovered a correlation between what he called *atomic number* and the frequency of X rays generated by bombarding an element with high-energy electrons. Moseley noticed that the frequencies of X rays emitted from the elements could be correlated by the equation

$$\sqrt{\nu} = a(Z - b)$$

where ν is the frequency of the emitted X rays and a and b are constants that are the same for all the elements. Thus, from the square root of the measured frequency of the X rays emitted, we can determine the atomic number of the element.

With a few exceptions, Moseley found that atomic number increases in the same order as atomic mass. For example, calcium is the twentieth element in order of increasing atomic mass, and it has an atomic number of 20. The discrepancies that

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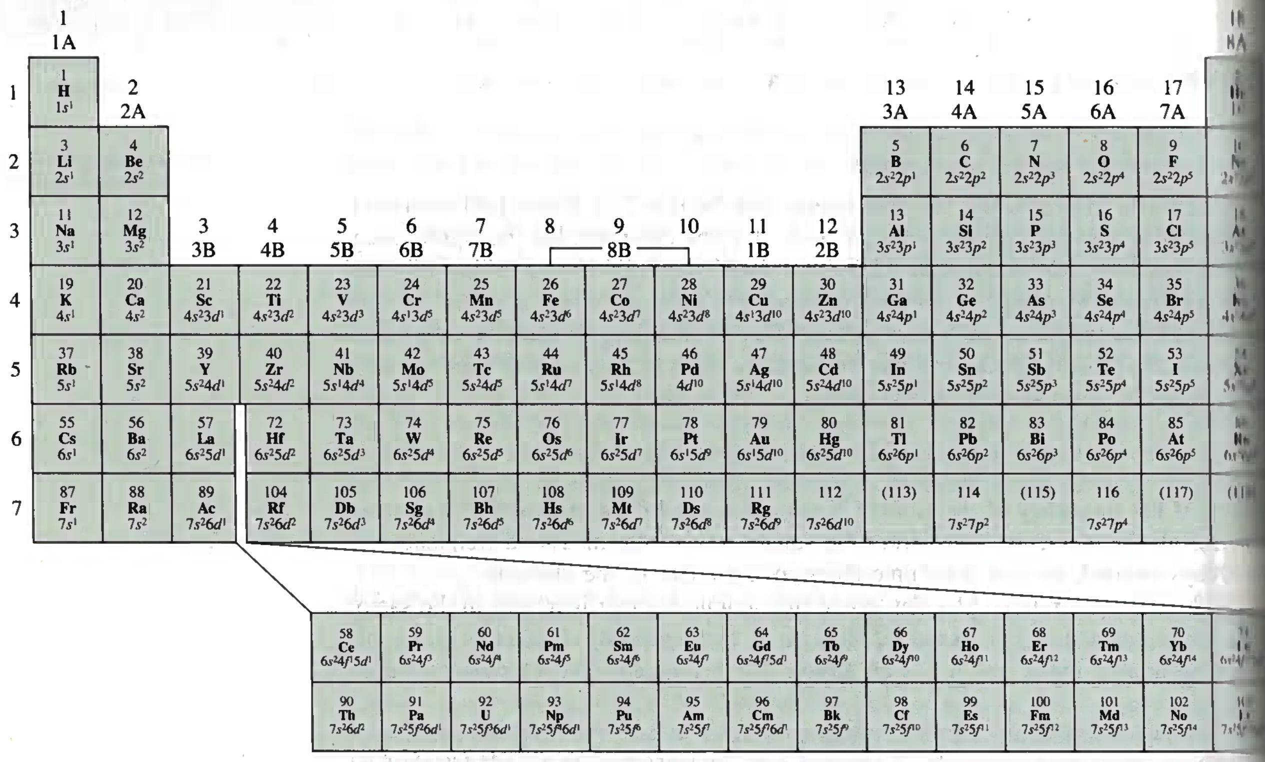
† Henry Gwyn-Jeffreys Moseley (1887–1915). English physicist. Moseley discovered the relationship between X-ray spectra and atomic number. A lieutenant in the Royal Engineers, he was killed in action at the age of 28 during the British campaign in Gallipoli, Turkey.

had puzzled earlier scientists now made sense. The atomic number of argon is 18 that of potassium is 19, so potassium should follow argon in the periodic table.

A modern periodic table usually shows the atomic number along with the ele symbol. As you already know, the atomic number also indicates the number of el trons in the atoms of an element. Electron configurations of elements help to expl the recurrence of physical and chemical properties. The importance and usefulne the periodic table lie in the fact that we can use our understanding of the general pr erties and trends within a group or a period to predict with considerable accuracy 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 elec configurations of the elements. (The electron configurations of the elements are given in Table 7.3.) Starting with hydrogen, we see that subshells are filled in order shown in Figure 7.24. According to the type of subshell being filled, the ments can be divided into categories—the representative elements, the noble g the transition elements (or transition metals), the lanthanides, and the actinides. **representative elements** (also called *main group elements*) are *the elements in Gr 1A through 7A, all of which have incompletely filled s or p subshells of the hig principal quantum number.* With the exception of helium, the *noble gases* (the 8A elements) all have a completely filled *p* subshell. (The electron configuratio $1s^2$ for helium and ns^2np^6 for the other noble gases, where *n* is the principal tum number for the outermost shell.)



	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
1	1 **H** $1s^1$																
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** $2s^22p^5$
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** $3s^23p^5$
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** $4s^24p^5$
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** $5s^25p^5$
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** $6s^26p^5$
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)	114 $7s^27p^2$	(115)	116 $7s^27p^4$	(117)

58 **Ce** $6s^24f^15d^1$	59 **Pr** $6s^24f^3$	60 **Nd** $6s^24f^4$	61 **Pm** $6s^24f^5$	62 **Sm** $6s^24f^6$	63 **Eu** $6s^24f^7$	64 **Gd** $6s^24f^75d^1$	65 **Tb** $6s^24f^9$	66 **Dy** $6s^24f^{10}$	67 **Ho** $6s^24f^{11}$	68 **Er** $6s^24f^{12}$	69 **Tm** $6s^24f^{13}$	70 **Yb** $6s^24f^{14}$
90 **Th** $7s^26d^2$	91 **Pa** $7s^25f^26d^1$	92 **U** $7s^25f^36d^1$	93 **Np** $7s^25f^46d^1$	94 **Pu** $7s^25f^6$	95 **Am** $7s^25f^7$	96 **Cm** $7s^25f^76d^1$	97 **Bk** $7s^25f^9$	98 **Cf** $7s^25f^{10}$	99 **Es** $7s^25f^{11}$	100 **Fm** $7s^25f^{12}$	101 **Md** $7s^25f^{13}$	102 **No** $7s^25f^{14}$

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

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 $[Rn]7s^2$

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 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.

A clear pattern emerges when we examine the electron configurations of the elements in a particular group. The electron configurations for Groups 1A and 2A are shown in Table 8.1. All members of the Group 1A alkali metals have similar outer

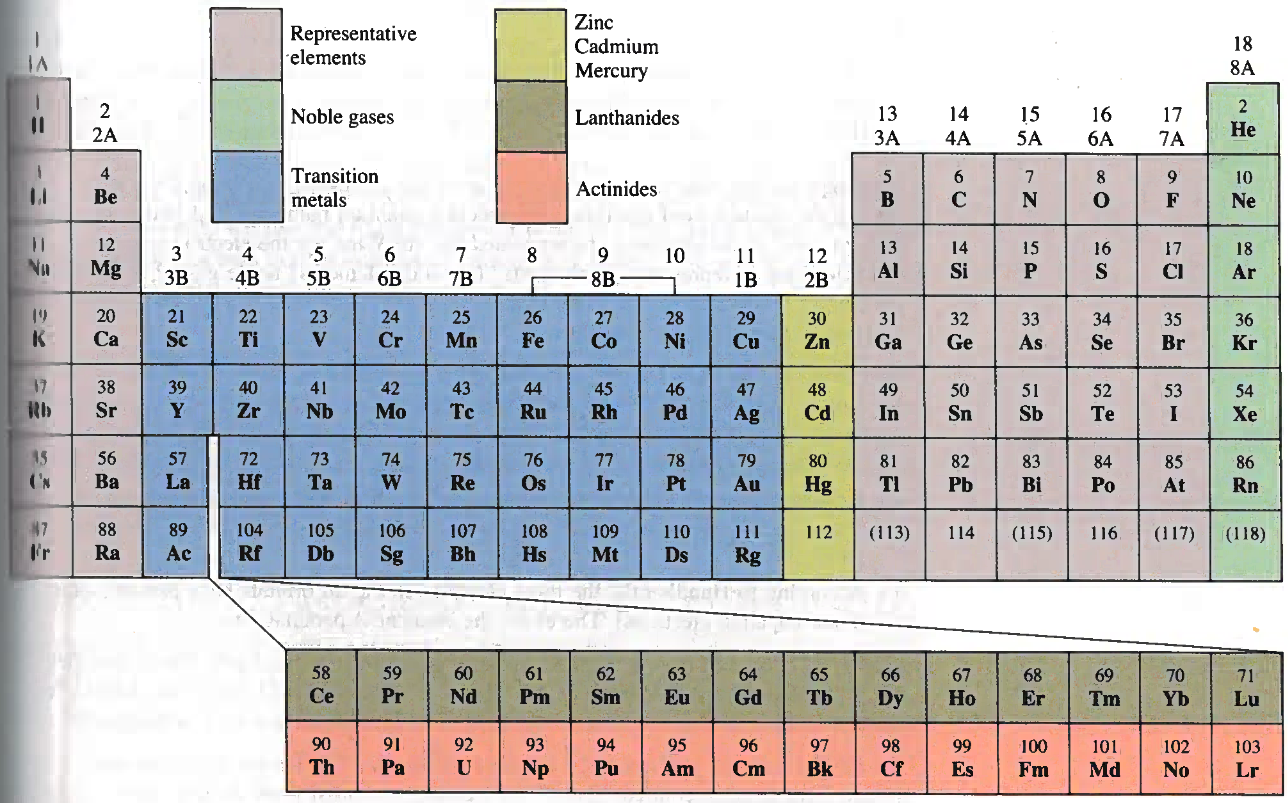


Figure 8.3 *Classification of the elements. Note that the Group 2B elements are often classified as transition metals even though they do not exhibit the characteristics of the transition metals.*

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

electron configurations; each has a noble gas core and an ns^1 outer electron. Similarly, the Group 2A alkaline earth metals have a noble gas core and an outer electron configuration of ns^2. *The outer electrons of an atom, which are the ones involved in chemical bonding,* are often called ***valence electrons.*** The similarity of the outer electron configurations (that is, they have the same number and type of valence electrons) is what makes the elements in the same group resemble one another in chemical behavior. This observation holds true for the other representative elements. Thus, for instance, the halogens (the Group 7A elements) all have outer electron configurations of ns^2np^5, and they have very similar properties. We must be careful, however, in predicting properties for Groups 3A through 7A. For example, the elements in Group 4A all have the same outer electron configuration, ns^2np^2, but there is some variation in chemical properties among these 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. With the exception of krypton and xenon, the rest of these elements are totally inert chemically. The reason is that these elements all have completely filled outer *ns* and *np* subshells, a condition that represents great stability. Although the outer 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.

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.

Similar problem: 8.20.

Practice Exercise An atom of a certain element has 20 electrons. (a) Write the ground-state electron configuration of the element, (b) classify the element, (c) determine whether the element is diamagnetic or 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

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

we usually write

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

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.

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. Following are the electron configurations of some atoms and their corresponding cations:

Na: $[\mathrm{Ne}]3s^1$ $\quad$ Na^+: [Ne]
Ca: $[\mathrm{Ar}]4s^2$ $\quad$ Ca^{2+}: [Ar]
Al: $[\mathrm{Ne}]3s^23p^1$ $\quad$ Al^{3+}: [Ne]

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:

H: $1s^1$ $\quad$ H^-: $1s^2$ or [He]
F: $1s^22s^22p^5$ $\quad$ F^-: $1s^22s^22p^6$ or [Ne]
O: $1s^22s^22p^4$ $\quad$ O^{2-}: $1s^22s^22p^6$ or [Ne]
N: $1s^22s^22p^3$ $\quad$ N^{3-}: $1s^22s^22p^6$ or [Ne]

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

Bear in mind that the order of electron filling does not determine or predict the order of electron removal for transition metals.

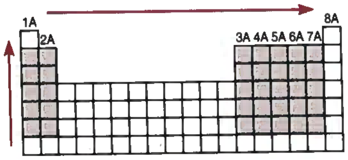
In Section 7.9 we saw that in the first-row transition metals (Sc to Cu), the 4*s* orbital is always filled before the 3*d* orbitals. Consider manganese, whose electron configuration is $[Ar]4s^23d^5$. When the Mn^{2+} ion is formed, we might expect the two electrons to be removed from the 3*d* orbitals 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.

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 atomic size and on the tendency for ionization.

Effective Nuclear Charge



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

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 shielding electrons reduces the electrostatic attraction between the positively charged protons in the nucleus and the outer electrons. Moreover, the repulsive forces between electrons in a many-electron atom further offset the attractive force exerted by the nucleus. The concept of effective nuclear charge enables us to account for the effects of shielding on periodic properties.

Consider, for example, the helium atom, which has the ground-state electron configuration $1s^2$. Helium's two protons give the nucleus a charge of +2, but the full attractive force of this charge on the two 1*s* electrons is partially offset by electron-electron repulsion. Consequently, we say that the 1*s* electrons shield each other from the nucleus. The effective nuclear charge (Z_{eff}), which is the charge felt by an electron, is given by

$$Z_{eff} = Z - \sigma \quad (8.1)$$

where Z is the actual nuclear charge (that is, the atomic number of the element) and σ (sigma) is called the *shielding constant* (also called the *screening constant*). The shielding constant is greater than zero but smaller than Z.

Interactivity:
Attraction of Nucleus
ARIS, Interactives

One way to illustrate electron shielding is to consider the amounts of energy required to remove the two electrons from a helium atom. Measurements show that it takes 2373 kJ of energy to remove the first electron from 1 mole of He atoms and 5251 kJ of energy to remove the remaining electron from 1 mole of He^+ ions. The reason it takes so much more energy to remove the second electron is that with only one electron present, there is no shielding, and the electron feels the full effect of the +2 nuclear charge.

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

For atoms with three or more electrons, the electrons in a given shell are shielded by electrons in inner shells (that is, shells closer to the nucleus) but not by electrons in outer shells. Thus, in a lithium atom, whose electron configuration is $1s^22s^1$, the $2s$ electron is shielded by the two $1s$ electrons, but the $2s$ electron does not have a shielding effect on the $1s$ electrons. In addition, filled inner shells shield outer electrons more effectively than electrons in the same subshell shield each other.

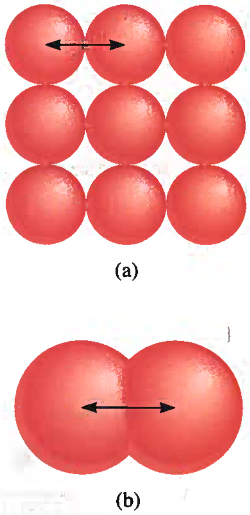
Atomic Radius

Animation:
Atomic and Ionic Radius
ARIS, Animations

Interactivity:
Atomic Radii
ARIS, Interactives

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)].

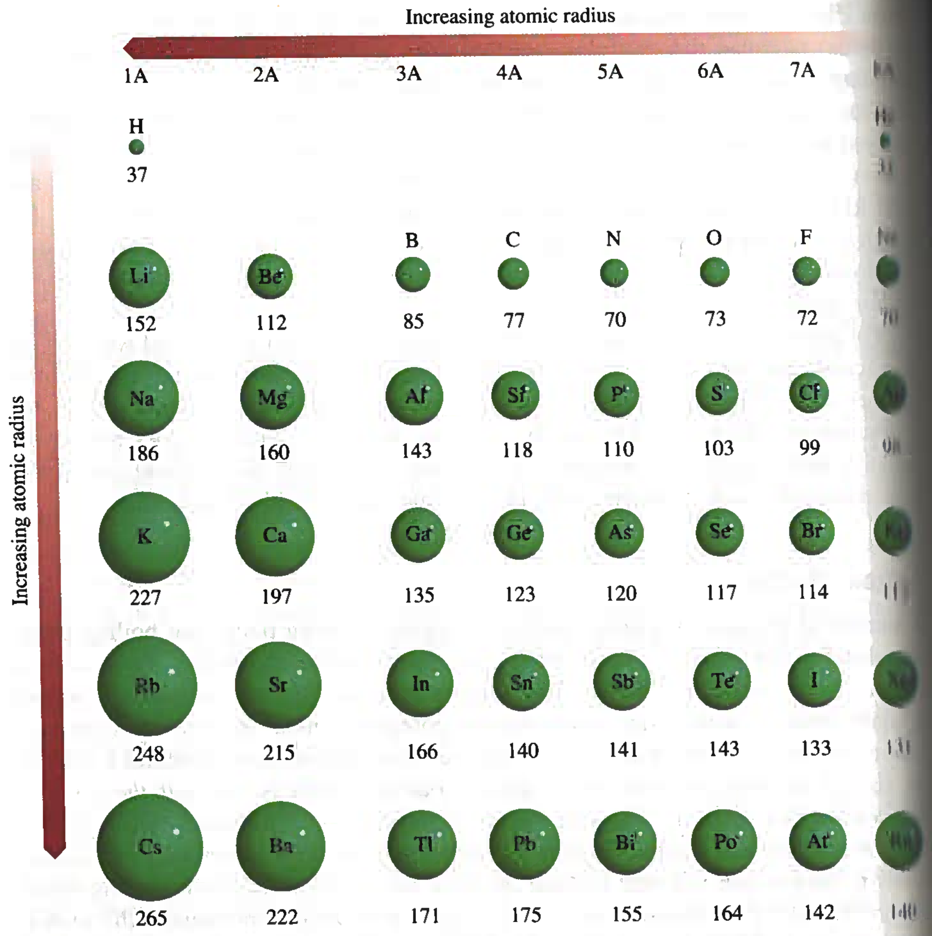

(a)

(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.*

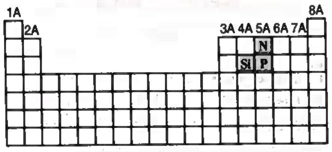
Figure 8.5 shows the atomic radii of many elements according to their positions in the periodic table, and Figure 8.6 plots the atomic radii of these elements against their atomic numbers. Periodic trends are clearly evident. In studying the trends, bear in mind that the atomic radius is determined to a large extent by the strength of the attraction between the nucleus and the outer-shell electrons. The larger the effective nuclear charge, the stronger the hold of the nucleus on these electrons, and the smaller the atomic radius. Consider the second-period elements from Li to F, for example. Moving from left to right, we find that the number of electrons in the inner shell ($1s^2$) remains constant while the nuclear charge increases. The electrons that are added to counterbalance the increasing nuclear charge are ineffective in shielding one another. Consequently, the effective nuclear charge increases steadily while the principal quantum number remains constant ($n = 2$). For example, the outer $2s$ electron in lithium is shielded from the nucleus (which has three protons) by the two $1s$ electrons. As an approximation, we assume that the shielding effect of the two $1s$ electrons is to cancel two positive charges in the nucleus. Thus, the $2s$ electron only feels the attraction of one proton in the nucleus; the effective nuclear charge is +1. In beryllium ($1s^22s^2$), each of the $2s$ electrons is shielded by the inner two $1s$ electrons, which cancel two of the four positive charges in the nucleus. Because the $2s$ electrons do not shield each other as effectively, the net result is that the effective nuclear charge of each $2s$ electron

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.*



is greater than +1. Thus, as the effective nuclear charge increases, the ato radius decreases steadily from lithium to fluorine.

Within a group of elements we find that atomic radius increases with increas atomic number. For the alkali metals in Group 1A, the outermost electron resides i the *ns* orbital. Because orbital size increases with the increasing principal quantu number *n*, the size of the metal atoms increases from Li to Cs. We can apply the sam reasoning to the elements in other groups.



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?

(Continued)

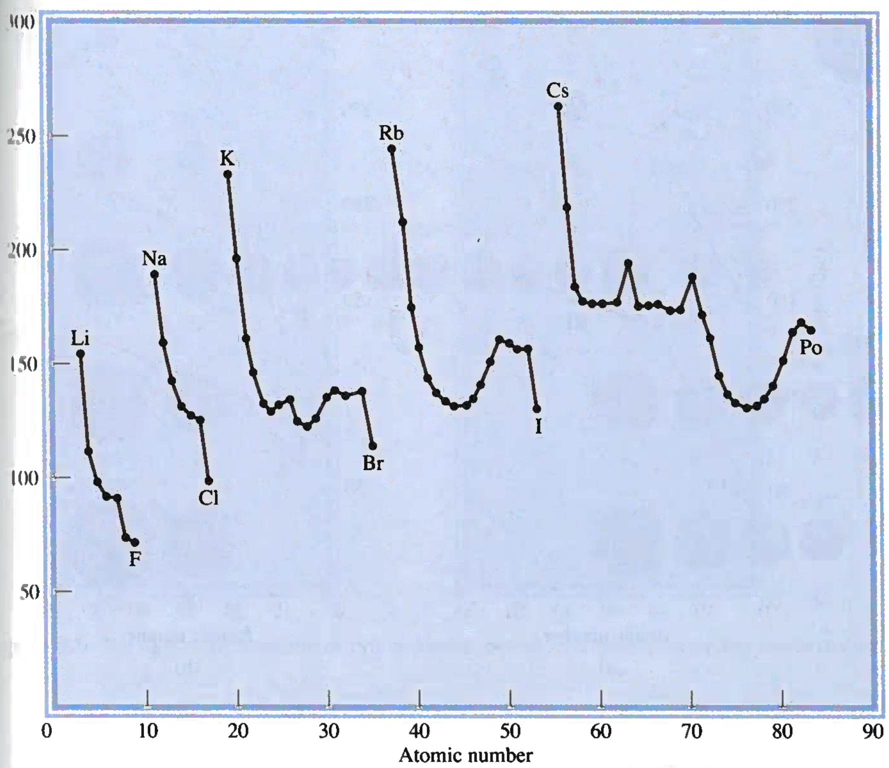


Figure 8.6 *Plot of atomic radii (in picometers) of elements against their atomic numbers.*

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 $\boxed{N < P < Si}$.

Practice Exercise Arrange the following atoms in order of decreasing radius: C, Li, Be.

Similar problems: 8.37, 8.38.

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.

Interactivity:
Ionic Radii
ARIS, Interactives

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

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

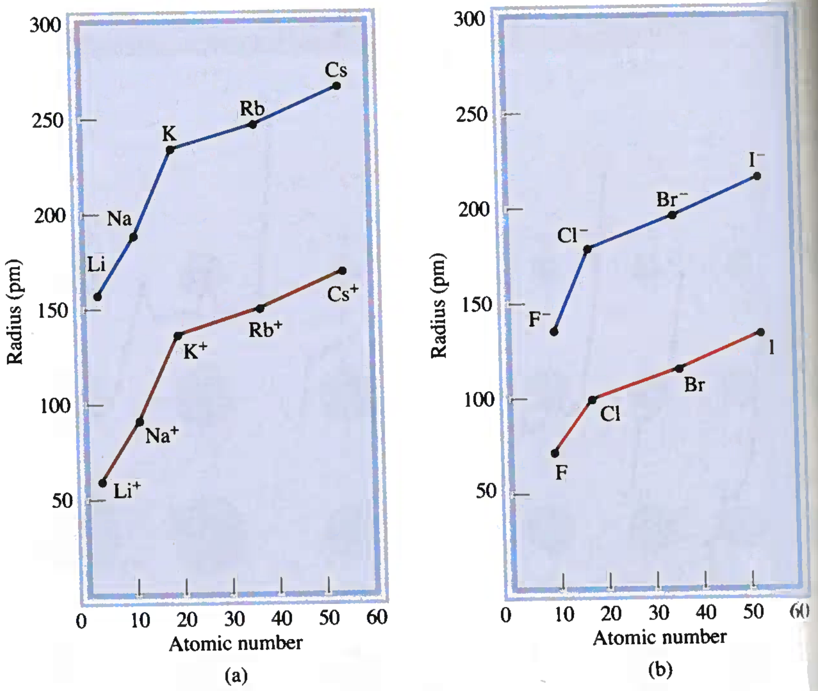
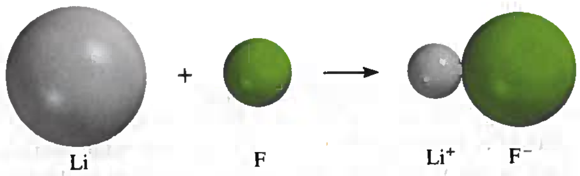


Figure 8.8 *Changes in the sizes of Li and F when they react to form LiF.*



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 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.

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 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

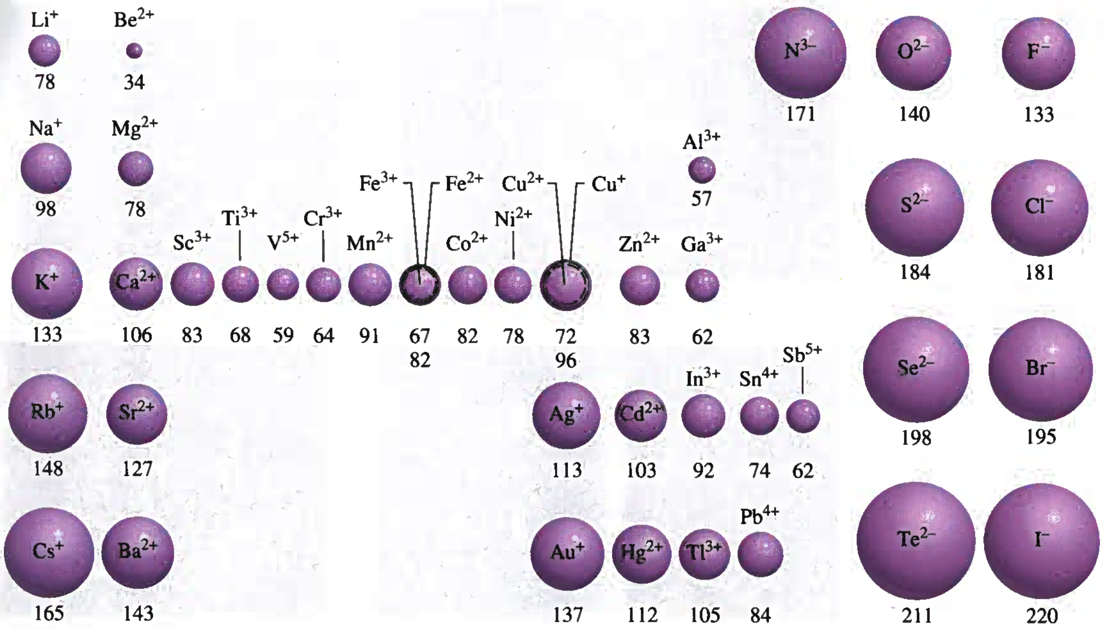


Figure 8.9 *The radii (in picometers) of ions of familiar elements arranged according to the elements' positions in the periodic table.*

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.

Similar problems: 8.43, 8.45.

Practice Exercise Select the smaller ion in each of the following pairs: (a) K^+, Li^+; (b) Au^+, Au^{3+}; (c) P^{3-}, N^{3-}.

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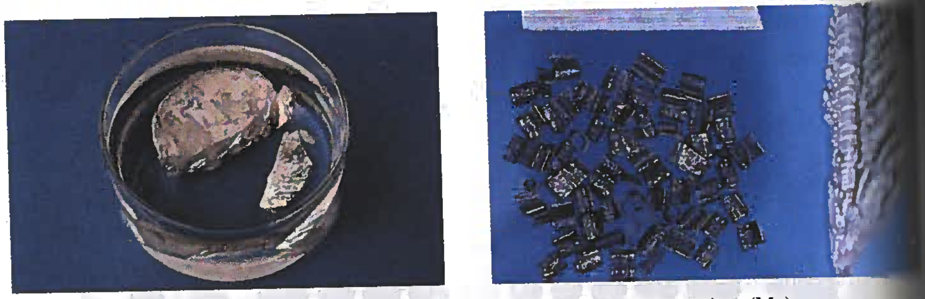
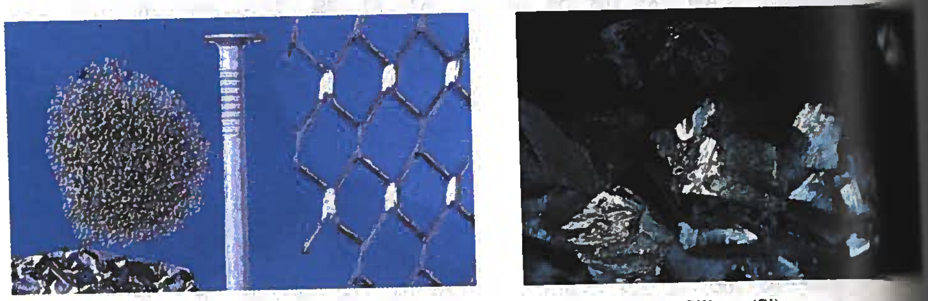
Figure 8.10 *The third-period elements. The photograph of argon, which is a colorless, odorless gas, shows the color emitted by the gas from a discharge tube.*



Sodium (Na)

Magnesium (Mg)



Aluminum (Al)

Silicon (Si)

Phosphorus (P_4)

Sulfur (S_8)

Chlorine (Cl_2)

Argon (Ar)

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 no metals. 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 chl rine, the second-to-last element of that period, is a very reactive nonmetal. In betwee the elements show a gradual transition from metallic properties to nonmetallic prope ties. Sodium, magnesium, and aluminum all have extensive three-dimensional atom networks, which are held together by forces characteristic of the metallic state. Silic is a metalloid; it has a giant three-dimensional structure in which the Si atoms are he together very strongly. Starting with phosphorus, the elements exist in simple, discre molecular units (P_4, S_8, Cl_2, and Ar) that have low melting points and boiling poin

Within a periodic group the physical properties vary more predictably, especiall if the elements are in the same physical state. For example, the melting points of arg and xenon are −189.2°C and −111.9°C, respectively. We can estimate the melti

CHEMISTRY *in Action*

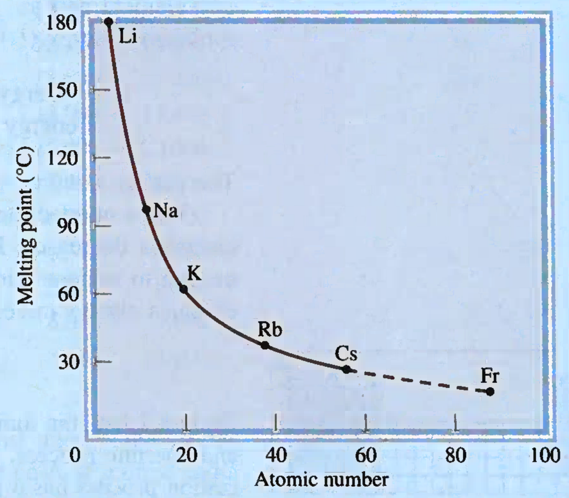
The Third Liquid Element?

Of the 114 known elements, 11 are gases under atmospheric conditions. Six of these are the Group 8A elements (the noble gases He, Ne, Ar, Kr, Xe, and Rn), and the other five are hydrogen (H_2), nitrogen (N_2), oxygen (O_2), fluorine (F_2), and chlorine (Cl_2). Curiously, only two elements are liquids at 25°C: mercury (Hg) and bromine (Br_2).

We do not know the properties of all the known elements because some of them have never been prepared in quantities large enough for investigation. In these cases, we must rely on periodic trends to predict their properties. What are the chances, then, of discovering a third liquid element?

Let us look at francium (Fr), the last member of Group 1A, to see if it might be a liquid at 25°C. All of francium's isotopes are radioactive. The most stable isotope is francium-223, which has a half-life of 21 minutes. (*Half-life* is the time it takes for one-half of the nuclei in any given amount of a radioactive substance to disintegrate.) This short half-life means that only very small traces of francium could possibly exist on Earth. And although it is feasible to prepare francium in the laboratory, no weighable quantity of the element has been prepared or isolated. Thus, we know very little about francium's physical and chemical properties. Yet we can use the group periodic trends to predict some of those properties.

Take francium's melting point as an example. The plot shows how the melting points of the alkali metals vary with atomic number. From lithium to sodium, the melting point drops 81.4°; from sodium to potassium, 34.6°; from potassium to rubidium, 24°; from rubidium to cesium, 11°. On the basis of this trend, we can predict that the change from cesium to francium would be about 5°. If so, the melting point of francium would be about 23°C, which would make it a liquid under atmospheric conditions.



A plot of the melting points of the alkali metals versus their atomic numbers. By extrapolation, the melting point of francium should be 23°C.

point of the intermediate element krypton by taking the average of these two values as follows:

$$\text{melting point of Kr} = \frac{[(-189.2°\text{C}) + (-111.9°\text{C})]}{2} = -150.6°\text{C}$$

This value is quite close to the actual melting point of −156.6°C.

The Chemistry in Action essay above illustrates one interesting application of periodic group properties.

8.4 Ionization Energy

Interactivity:
Ionization Energy
ARIS, Interactives

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.

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,

$$\text{energy} + \mathrm{X}(g) \longrightarrow \mathrm{X}^{+}(g) + e^{-} \qquad (8.2)$$

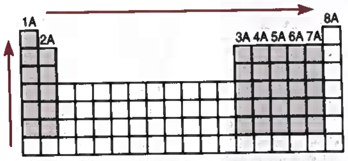
is called the *first ionization energy* (I_1). In Equation (8.2), X represents an atom of any element and e^- is an electron. The second ionization energy (I_2) and the third ionization energy (I_3) are shown in the following equations:

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

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:

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



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 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 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

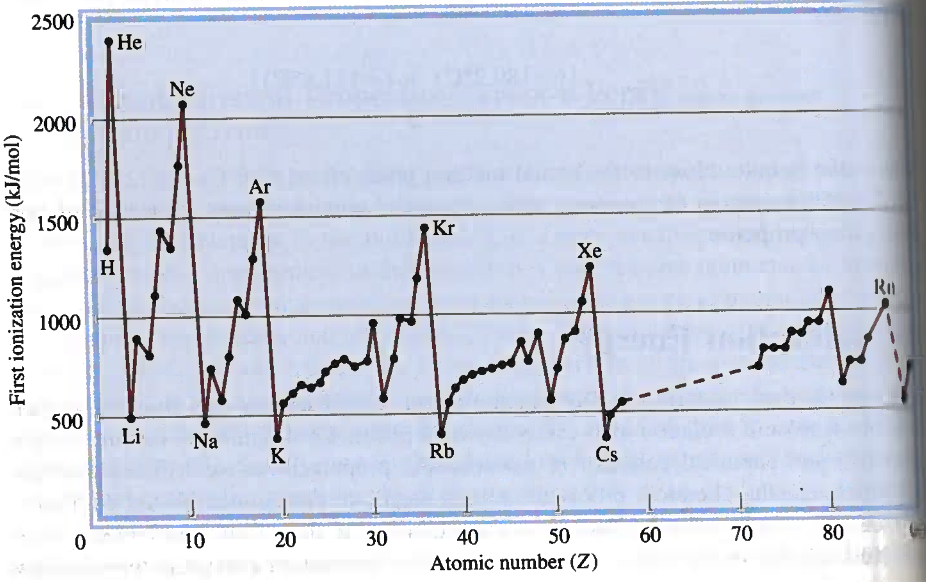


Figure 8.11 *Variation of the first ionization energy with atomic number. Note that the noble gases have high ionization energies, whereas the alkali metals and alkaline earth metals have low ionization energies.*

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

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 outer electron, and hence a higher first ionization energy. A notable feature of Figure 8.11 is the peaks, which correspond to the noble gases. The high ionization energies of the noble gases, stemming from their stable ground-state electron configurations, account for the fact that most of them are chemically unreactive. In fact, helium ($1s^2$) has the highest first ionization energy of all the elements.

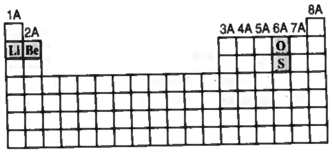
At the bottom of the graph in Figure 8.11 are the Group 1A elements (the alkali metals) which have the lowest first ionization energies. Each of these metals has one valence electron (the outermost electron configuration is ns^1), which is effectively shielded by the completely filled inner shells. Consequently, 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 increasingly easier to remove the first electron as we go from element to element down a group. 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 a paired *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?

Similar problem: 8.55.

Practice Exercise (a) Which of the following atoms should have a larger first ionization energy: N or P? (b) Which of the following atoms should have a smaller second ionization energy: Na or Mg?

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.*

$$X(g) + e^- \longrightarrow X^-(g) \qquad (8.3)$$

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.

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 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. This is not surprising when we realize that by accepting an electron, each halogen atom assumes the stable electron configuration of the noble gas immediately to its right. For example, the electron configuration of F^- is $1s^22s^22p^6$, or [Ne]; for Cl^- it is $[Ne]3s^23p^6$ or [Ar]; and so on. Calculations show that the noble gases all have electron affinities of less than zero. Thus, the anions of these gases, if formed, would be inherently unstable.

The electron affinity of oxygen has a positive value (141 kJ/mol), which means that the process

$$O(g) + e^- \longrightarrow O^-(g) \qquad \Delta H = -141 \text{ kJ/mol}$$

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

1A	2A	3A	4A	5A	6A	7A	8A
H							He
73							<0
Li	Be	B	C	N	O	F	Ne
60	≤ 0	27	122	0	141	328	<0
Na	Mg	Al	Si	P	S	Cl	Ar
53	≤ 0	44	134	72	200	349	<0
K	Ca	Ga	Ge	As	Se	Br	Kr
48	2.4	29	118	77	195	325	<0
Rb	Sr	In	Sn	Sb	Te	I	Xe
47	4.7	29	121	101	190	295	<0
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
45	14	30	110	110	?	?	<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.

is favorable (exothermic). On the other hand, the electron affinity of the O^- ion is highly negative (−780 kJ/mol), which means the process

$$O^-(g) + e^- \longrightarrow O^{2-}(g) \qquad \Delta H = 780\ \text{kJ/mol}$$

is endothermic even though the O^{2-} ion is isoelectronic with the noble gas Ne. Th process is unfavorable in the gas phase because the resulting increase in electron-electron

J
was
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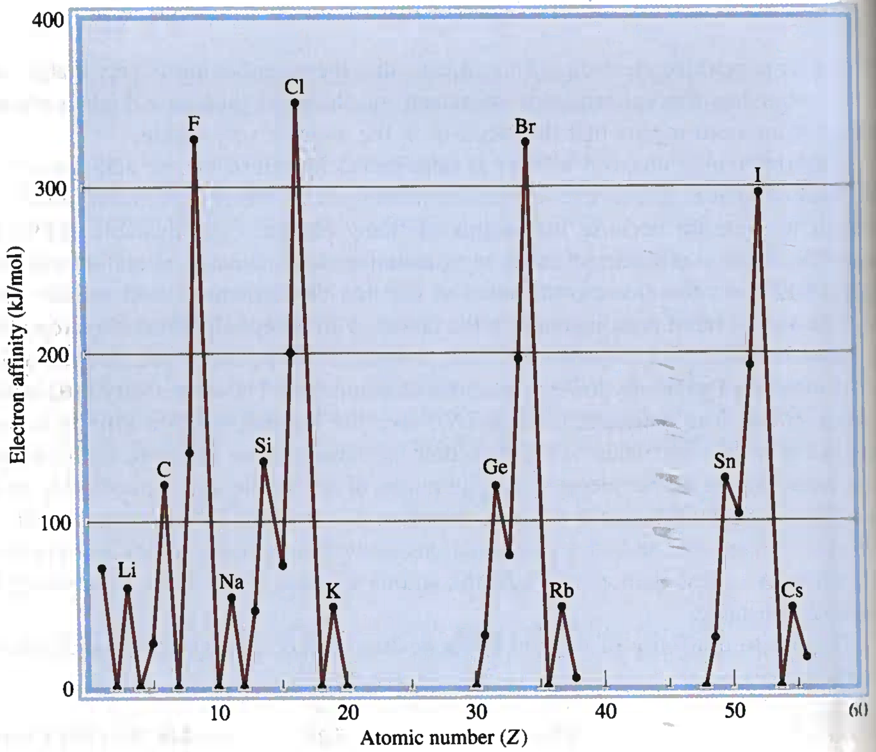


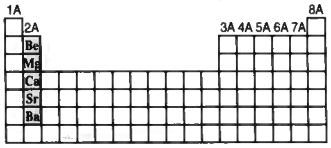
Figure 8.12 *A plot of electron affinity against atomic number from hydrogen to barium.*

repulsion outweighs the stability gained by achieving a noble gas configuration. However, note that O^{2-} is common in ionic compounds (for example, Li_2O and MgO); in solids, the O^{2-} ion is stabilized by the neighboring cations. We will study the stability of ionic compounds in Chapter 9.

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

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

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.

Similar problem: 8.63.

Practice Exercise Is it likely that Ar will form the anion Ar^-?

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 outer electron configurations. This statement, although correct in the general sense, must be applied with caution. Chemists have

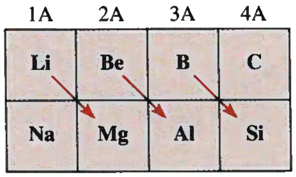


Figure 8.13 *Diagonal relationships in the periodic table.*

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).

Another trend in the chemical behavior of the representative elements is the diagonal relationship. ***Diagonal relationships*** are *similarities between pairs of elements in different groups and periods of the periodic table.* Specifically, the first three members of the second period (Li, Be, and B) exhibit many similarities to those elements located diagonally below them in the periodic table (Figure 8.13). The reason for this phenomenon is the closeness of the charge densities of their cations. (*Charge density* is the charge of an ion divided by its volume.) Cations with comparable charge densities react similarly with anions and therefore form the same type of compounds. Thus, the chemistry of lithium resembles that of magnesium in some ways; the same holds for beryllium and aluminum and for boron and silicon. Each of these pairs is said to exhibit a diagonal relationship. We will see a number of examples of this relationship later.

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 nonmetals. 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 metals in Chapter 22.)

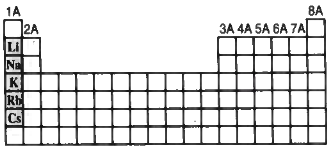
Hydrogen ($1s^1$)

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:

$$2NaH(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$
$$CaH_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + 2H_2(g)$$

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.

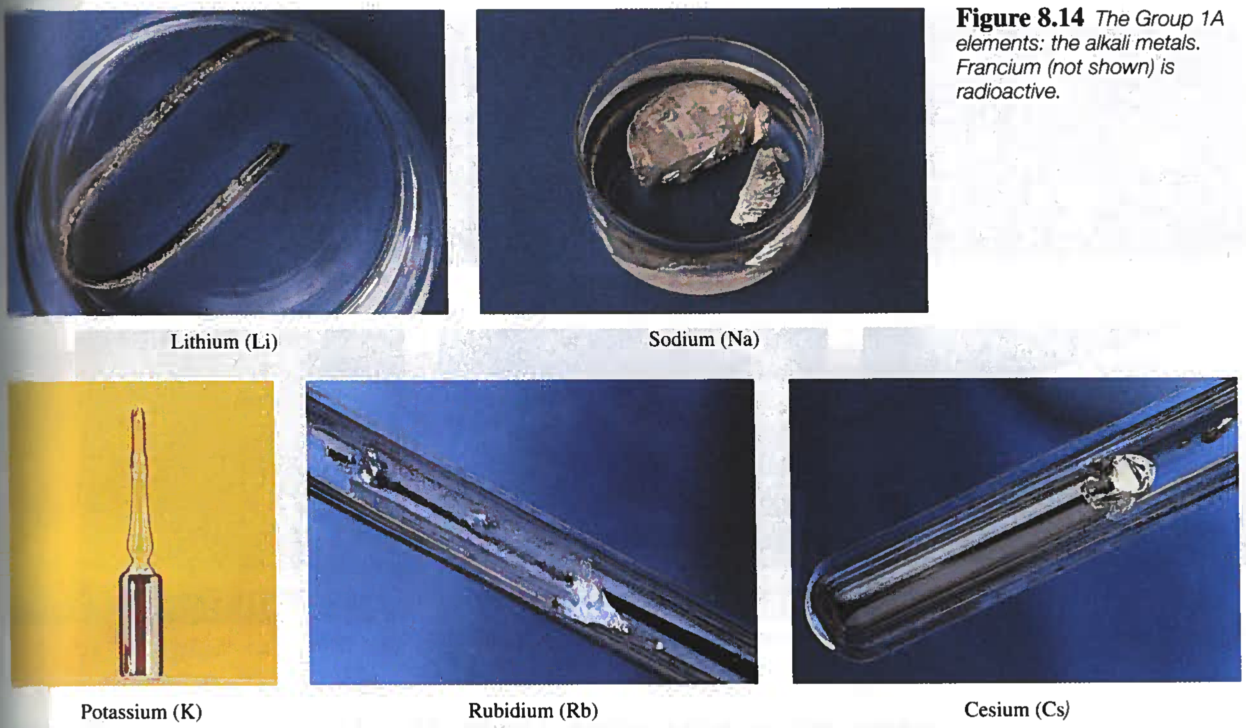


Figure 8.14 *The Group 1A elements: the alkali metals. Francium (not shown) is radioactive.*

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:

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

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):

$$4Li(s) + O_2(g) \longrightarrow 2Li_2O(s)$$

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

$$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$

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

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

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, $n \geq 2$)

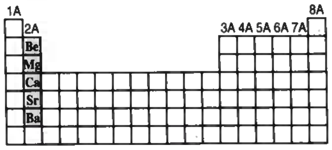
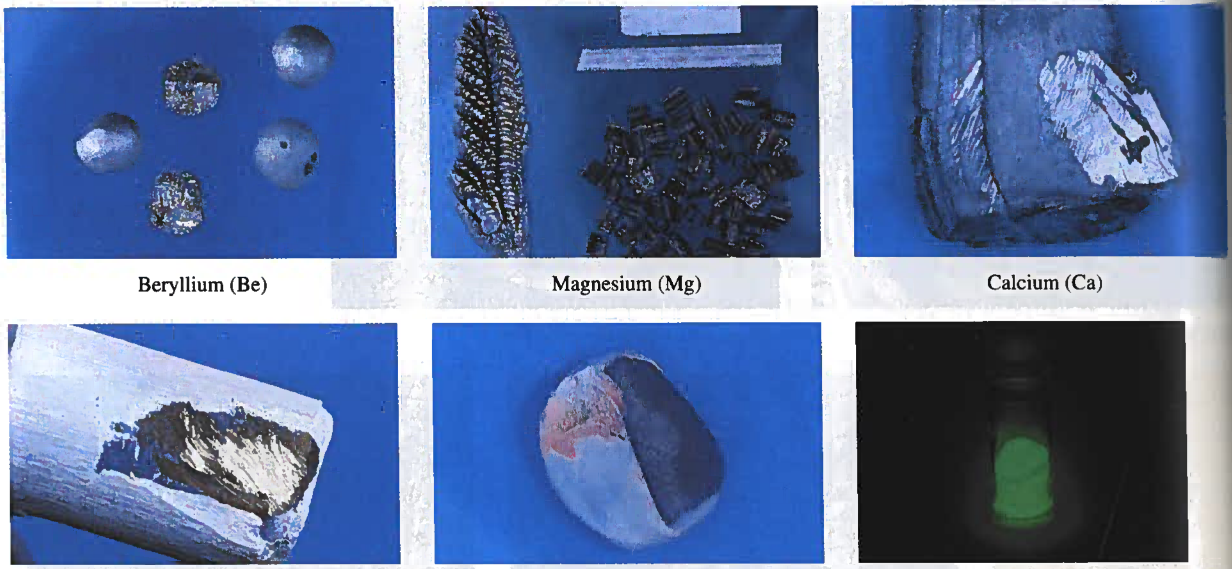


Figure 8.15 shows the Group 2A elements. As a group, the alkaline earth metals are somewhat less reactive than the alkali metals. Both the first and the second ionization



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

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

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

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.

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:

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

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:

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

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.

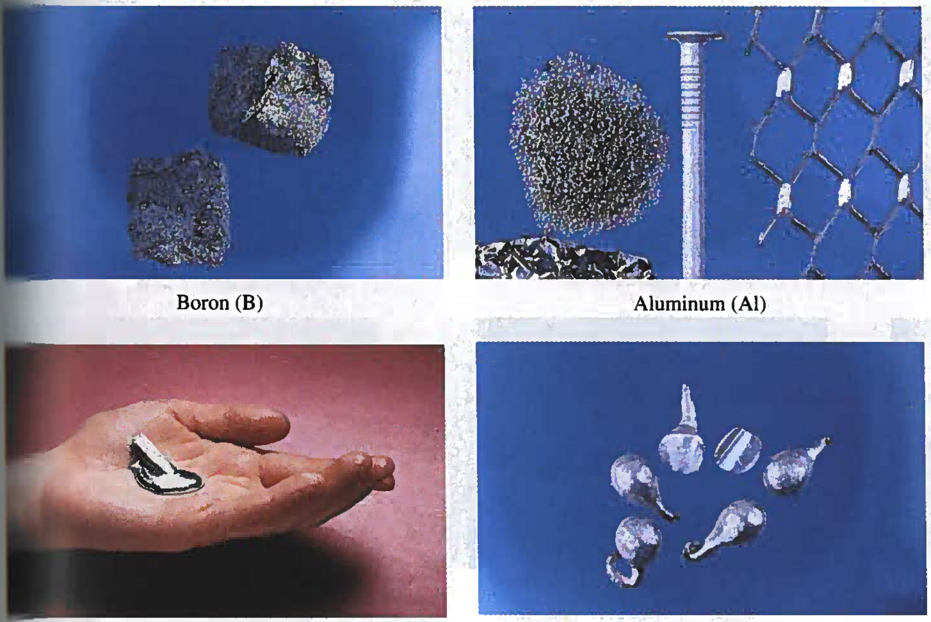
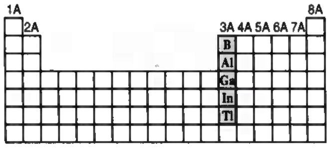

Boron (B)
Aluminum (Al)
Gallium (Ga)
Indium (In)

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

Group 3A Elements (ns^2np^1, $n \geq 2$)



The first member of Group 3A, boron, is a metalloid; the rest are metals (Figure 8.16). Boron does not form binary ionic compounds and is unreactive toward oxygen gas and water. The next element, aluminum, readily forms aluminum oxide when exposed to air:

$$4\text{Al}(s) + 3\text{O}_2(g) \longrightarrow 2\text{Al}_2\text{O}_3(s)$$

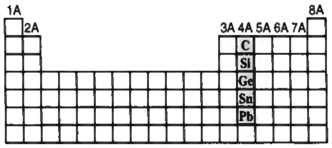
Aluminum that has a protective coating of aluminum oxide is less reactive than elemental aluminum. Aluminum forms only tripositive ions. It reacts with hydrochloric acid as follows:

$$2\text{Al}(s) + 6\text{H}^+(aq) \longrightarrow 2\text{Al}^{3+}(aq) + 3\text{H}_2(g)$$

The other Group 3A metallic elements form both unipositive and tripositive ions. Moving down the group, we find that the unipositive ion becomes more stable than the tripositive ion.

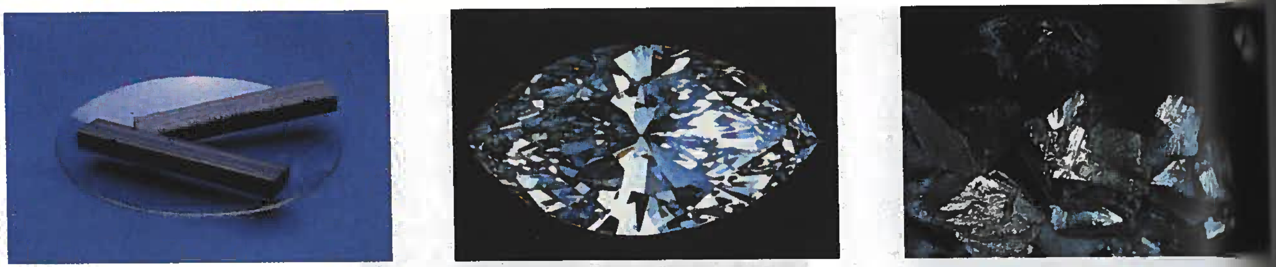
The metallic elements in Group 3A also form many molecular compounds. For example, aluminum reacts with hydrogen to form AlH_3, which resembles BeH_2 in its properties. (Here is an example of the diagonal relationship.) Thus, from left to right across the periodic table, we are seeing a gradual shift from metallic to nonmetallic character in the representative elements.

Group 4A Elements (ns^2np^2, $n \geq 2$)



The first member of Group 4A, carbon, is a nonmetal, and the next two members, silicon and germanium, are metalloids (Figure 8.17). The metallic elements of this group, tin and lead, do not react with water, but they do react with acids (hydrochloric acid, for example) to liberate hydrogen gas:

$$\text{Sn}(s) + 2\text{H}^+(aq) \longrightarrow \text{Sn}^{2+}(aq) + \text{H}_2(g)$$
$$\text{Pb}(s) + 2\text{H}^+(aq) \longrightarrow \text{Pb}^{2+}(aq) + \text{H}_2(g)$$

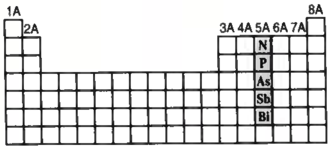


Carbon (graphite) Carbon (diamond) Silicon (Si)

Germanium (Ge) Tin (Sn) Lead (Pb)

Figure 8.17 *The Group 4A elements.*

The Group 4A elements form compounds in both the +2 and +4 oxidation states. For carbon and silicon, the +4 oxidation state is the more stable one. For example, CO_2 is more stable than CO, and SiO_2 is a stable compound, but SiO does not exist under normal conditions. As we move down the group, however, the trend in stability is reversed. In tin compounds the +4 oxidation state is only slightly more stable than the +2 oxidation state. In lead compounds the +2 oxidation state is unquestionably the more stable one. The outer electron configuration of lead is $6s^26p^2$, and lead tends to lose only the $6p$ electrons (to form Pb^{2+}) rather than both the $6p$ and $6s$ electrons (to form Pb^{4+}).



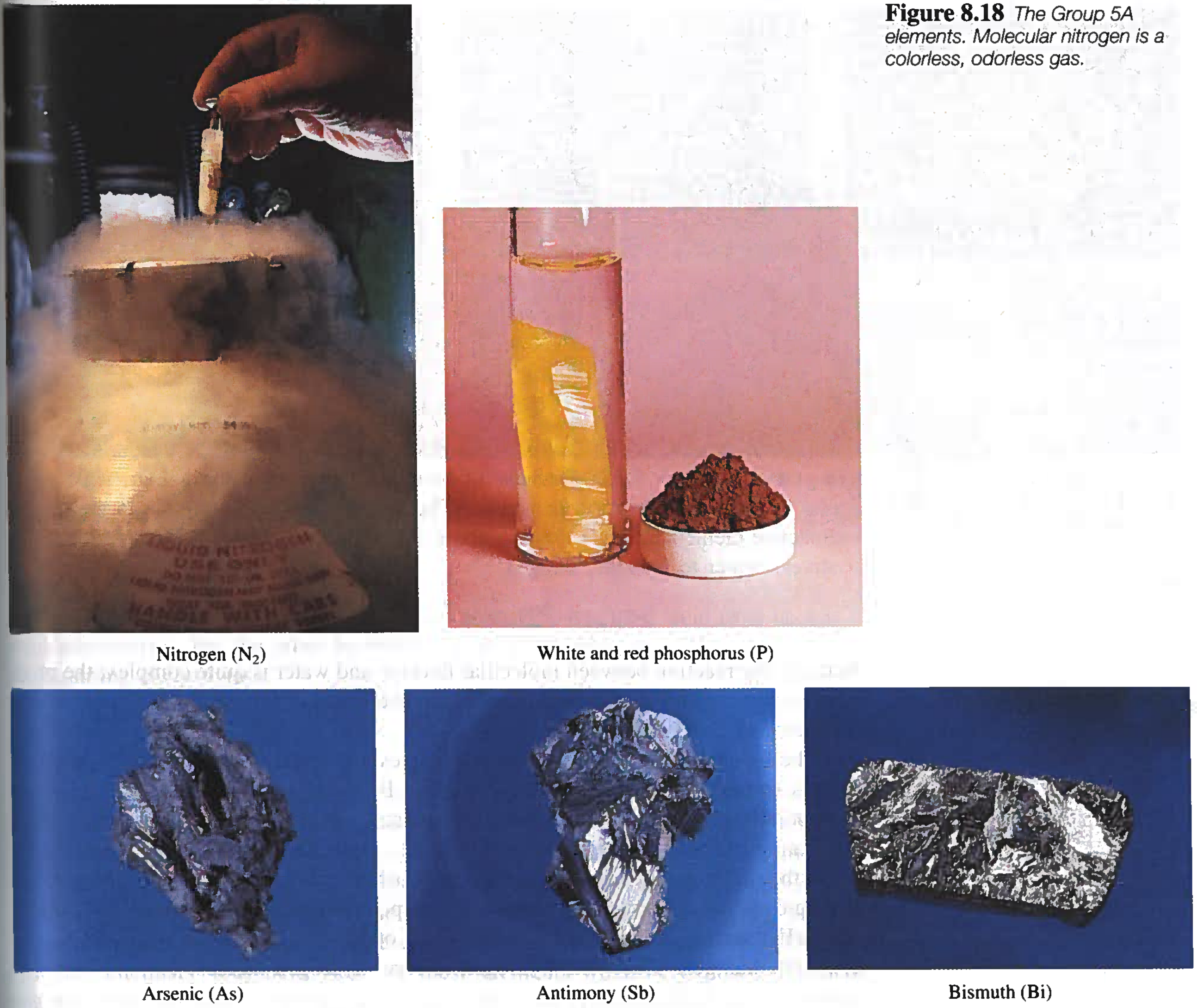
Group 5A Elements (ns^2np^3, $n \geq 2$)

In Group 5A, nitrogen and phosphorus are nonmetals, arsenic and antimony are metalloids, and bismuth is a metal (Figure 8.18). Thus, we expect a greater variation in properties within the group.

Elemental nitrogen is a diatomic gas (N_2). It forms a number of oxides (NO, N_2O, NO_2, N_2O_4, and N_2O_5), of which only N_2O_5 is a solid; the others are gases. Nitrogen has a tendency to accept three electrons to form the nitride ion, N^{3-} (thus achieving the electron configuration $1s^22s^22p^6$, which is isoelectronic with neon). Most metallic nitrides (Li_3N and Mg_3N_2, for example) are ionic compounds. Phosphorus exists as P_4 molecules. It forms two solid oxides with the formulas P_4O_6 and P_4O_{10}. The important oxoacids HNO_3 and H_3PO_4 are formed when the following oxides react with water:

$$N_2O_5(s) + H_2O(l) \longrightarrow 2HNO_3(aq)$$
$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$

Arsenic, antimony, and bismuth have extensive three-dimensional structures. Bismuth is a far less reactive metal than those in the preceding groups.


Nitrogen (N_2)

White and red phosphorus (P)

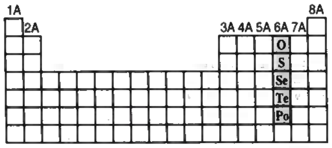
Arsenic (As)

Antimony (Sb)

Bismuth (Bi)

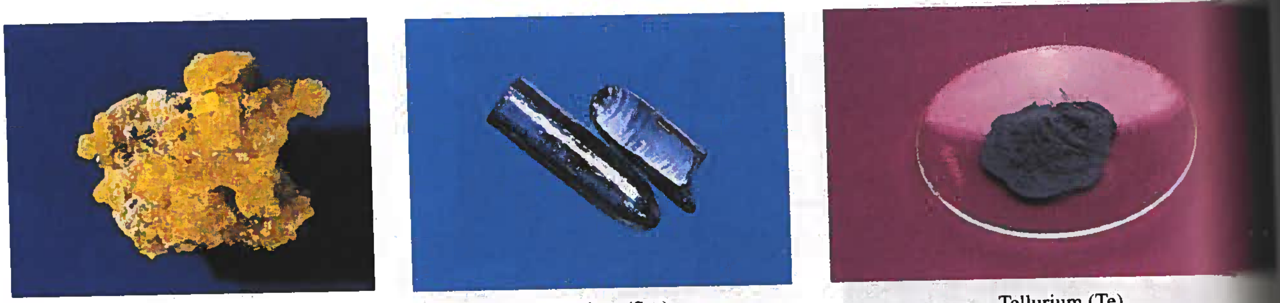
Figure 8.18 *The Group 5A elements. Molecular nitrogen is a colorless, odorless gas.*

Group 6A Elements (ns^2np^4, $n \geq 2$)



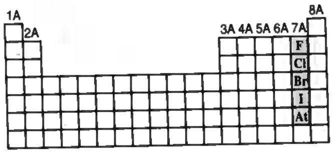
The first three members of Group 6A (oxygen, sulfur, and selenium) are nonmetals, and the last two (tellurium and polonium) are metalloids (Figure 8.19). Oxygen is a diatomic gas; elemental sulfur and selenium have the molecular formulas S_8 and Se_8, respectively; tellurium and polonium have more extensive three-dimensional structures. (Polonium, the last member, is a radioactive element that is difficult to study in the laboratory.) Oxygen has a tendency to accept two electrons to form the oxide ion (O^{2-}) in many ionic compounds. Sulfur, selenium, and tellurium also form dinegative anions (S^{2-}, Se^{2-}, and Te^{2-}). The elements in this group (especially oxygen) form a large number of molecular compounds with nonmetals. The important compounds of sulfur are SO_2, SO_3, and H_2S. Sulfuric acid is formed when sulfur trioxide reacts with water:

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$



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

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

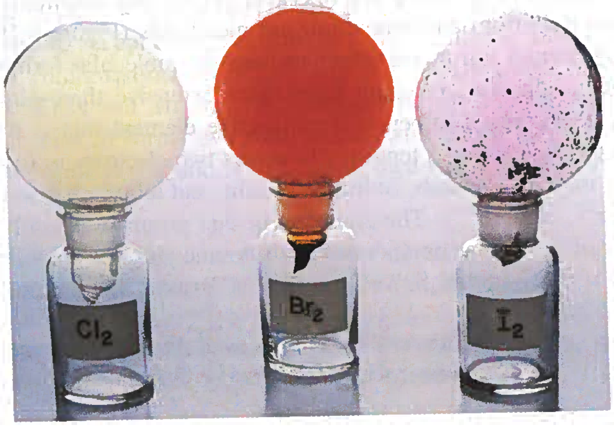
Actually the reaction between molecular fluorine and water is quite complex; the products formed depend on reaction conditions. The reaction shown above is one of several possible changes.

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

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



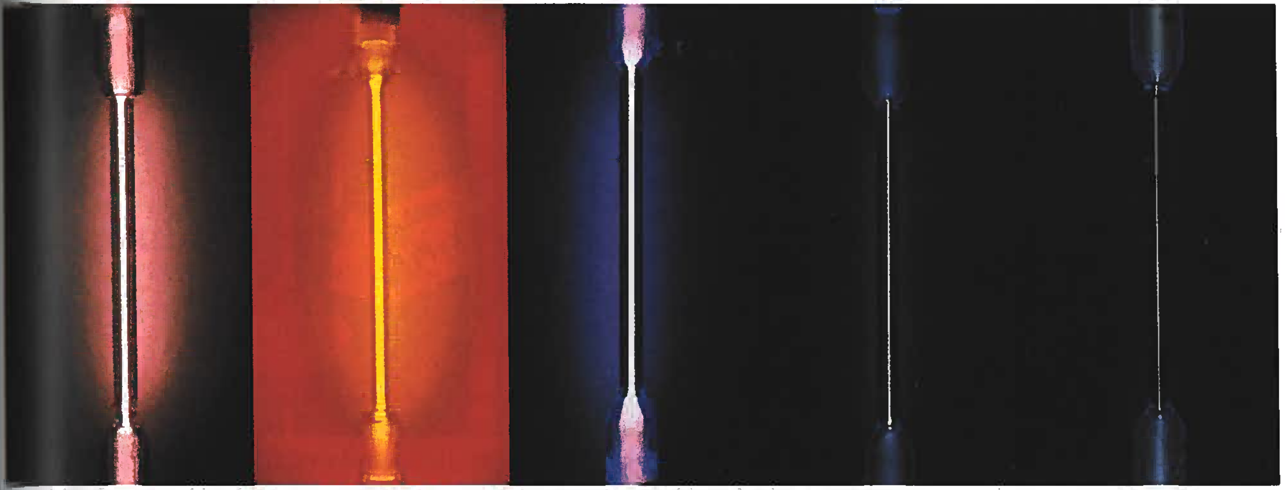
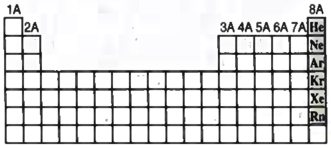


Figure 8.21 *All noble gases are colorless and odorless. These pictures show the colors emitted by the gases from a discharge tube.*

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, $n \geq 2$)



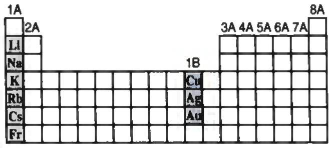
All noble gases exist as monatomic species (Figure 8.21). Their atoms have completely filled outer *ns* and *np* subshells, which give them great stability. (Helium is $1s^2$.) The Group 8A ionization energies are among the highest of all elements, and these gases have no tendency to accept extra electrons.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

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

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.

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

Comparison of Group 1A and Group 1B Elements



When we compare the Group 1A elements (alkali metals) and the Group 1B elements (copper, silver, and gold), we arrive at an interesting conclusion. Although the metals

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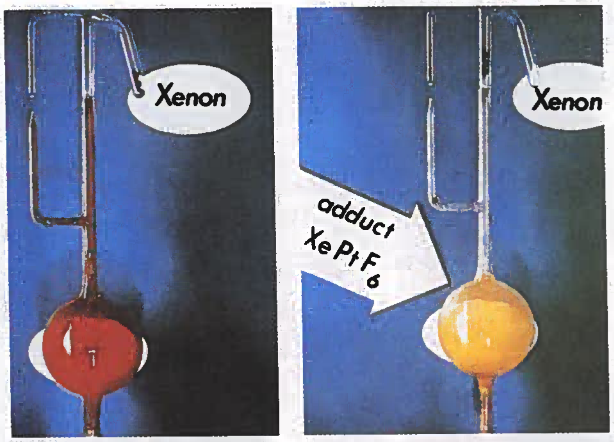
[†] Neil Bartlett (1932–). English chemist. Bartlett's work is mainly in the preparation and study of compounds with unusual oxidation states and in solid-state chemistry.



(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 $XePtF_6$.*

in these two groups have similar outer electron configurations, with one electron in the outermost *s* orbital, their chemical properties are quite different.

The first ionization energies of Cu, Ag, and Au are 745 kJ/mol, 731 kJ/mol, and 890 kJ/mol, respectively. Because these values are considerably larger than those of the alkali metals (see Table 8.2), the Group 1B elements are much less reactive. The higher ionization energies of the Group 1B elements result from incomplete shielding of the nucleus by the inner *d* electrons (compared with the more effective shielding of the completely filled noble gas cores). Consequently the outer *s* electrons of these elements are more strongly attracted by the nucleus. In fact, copper, silver, and gold are so unreactive that they are usually found in the uncombined state in nature. The inertness and rarity of these metals make them valuable in the manufacture of coins and in jewelry. For this reason, these metals are also called "coinage metals." The difference in chemical properties between the Group 2A elements (the alkaline earth metals) and the Group 2B metals (zinc, cadmium, and mercury) can be explained in a similar way.

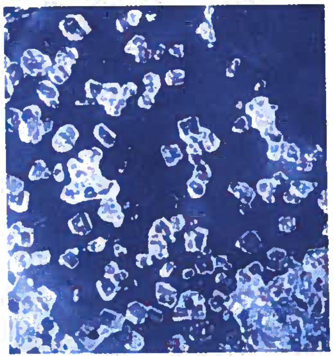
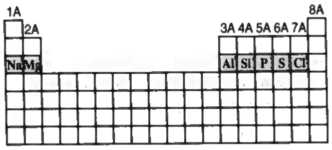


Figure 8.23 *Crystals of xenon tetrafluoride (XeF_4).*

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.

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 →			

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:

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

It also exhibits acidic properties by reacting with bases:

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

Note that this acid-base neutralization produces a salt but no water.

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:

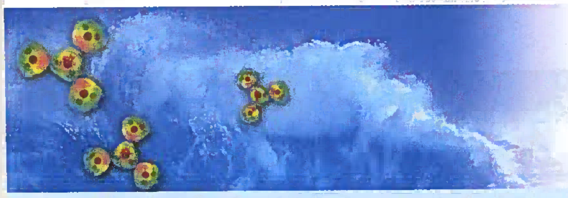
$$SiO_2(s) + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$

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 ($HClO_4$):

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

Certain oxides such as CO and NO are neutral; that is, they do not react with water to produce an acidic or basic solution. In general, oxides containing nonmetallic elements are not basic.



CHEMISTRY *in Action*

Discovery of the Noble Gases

In the late 1800s John William Strutt, Third Baron of Rayleigh, who was a professor of physics at the Cavendish Laboratory in Cambridge, England, accurately determined the atomic masses of a number of elements, but he obtained a puzzling result with nitrogen. One of his methods of preparing nitrogen was by the thermal decomposition of ammonia:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

Another method was to start with air and remove from it oxygen, carbon dioxide, and water vapor. Invariably, the nitrogen from air was a little denser (by about 0.5 percent) than the nitrogen from ammonia.

Lord Rayleigh's work caught the attention of Sir William Ramsay, a professor of chemistry at the University College, London. In 1898 Ramsay passed nitrogen, which he had obtained from air by Rayleigh's procedure, over red-hot magnesium to convert it to magnesium nitride:

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

After all of the nitrogen had reacted with magnesium, Ramsay was left with an unknown gas that would not combine with anything.

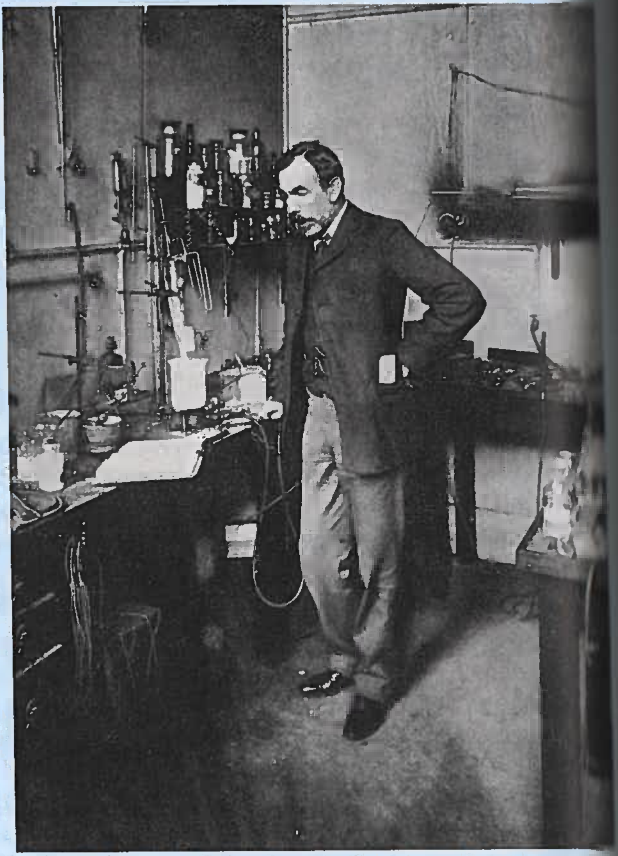
With the help of Sir William Crookes, the inventor of the discharge tube, Ramsay and Lord Rayleigh found that the emission spectrum of the gas did not match any of the known elements. The gas was a new element! They determined its atomic mass to be 39.95 amu and called it argon, which means "the lazy one" in Greek.

Once argon had been discovered, other noble gases were quickly identified. Also in 1898 Ramsay isolated helium from uranium ores (see Chemical Mystery essay on p. 311). From the atomic masses of helium and argon, their lack of chemical reactivity, and what was then known about the periodic table, Ramsay was convinced that there were other unreactive gases and that they were all members of one periodic group. He and his student Morris Travers set out to find the unknown gases. They used a refrigeration machine to first produce liquid air. Applying a technique called *fractional distillation,* they then allowed the liquid air to warm up gradually and collected components that boiled off at different temperatures. In this manner, they analyzed and identified three new elements—neon, krypton, and xenon—in only three months. Three new elements in three months is a record that may never be broken!

The discovery of the noble gases helped to complete the periodic table. Their atomic masses suggested that these elements should be placed to the right of the halogens. The ap ent discrepancy with the position of argon was resolved Moseley, as discussed in the chapter.

Finally, the last member of the noble gases, radon, was covered by the German chemist Frederick Dorn in 1900. A dioactive element and the heaviest elemental gas kno radon's discovery not only completed the Group 8A elem but also advanced our understanding about the nature of dioactive decay and transmutation of elements.

Lord Rayleigh and Ramsay both won Nobel Prizes in 1 for the discovery of argon. Lord Rayleigh received the pri physics and Ramsay's award was in chemistry.



Sir William Ramsay (1852–1916).

This brief examination of oxides of the third-period elements shows that as the metallic character of the elements decreases from left to right across the period, their oxides change from basic to amphoteric to acidic. Metallic oxides are usually basic, and most oxides of nonmetals are acidic. The intermediate properties of the oxides (as shown by the amphoteric oxides) are exhibited by elements whose positions are intermediate within the period. Note also that because the metallic character of the elements increases from top to bottom within a group of representative elements, we would expect oxides of elements with higher atomic numbers to be more basic than the lighter elements. This is indeed the case.

Example 8.6

Classify the following oxides as acidic, basic, or amphoteric: (a) Rb_2O, (b) BeO, (c) As_2O_5.

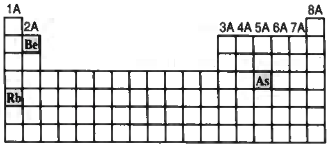
Strategy What type of elements form acidic oxides? basic oxides? amphoteric oxides?

Solution (a) Because rubidium is an alkali metal, we would expect Rb_2O to be a basic oxide.

(b) Beryllium is an alkaline earth metal. However, because it is the first member of Group 2A, we expect that it may differ somewhat from the other members of the group. In the text we saw that Al_2O_3 is amphoteric. Because beryllium and aluminum exhibit a diagonal relationship, BeO may resemble Al_2O_3 in properties. It turns out that BeO is also an amphoteric oxide.

(c) Because arsenic is a nonmetal, we expect As_2O_5 to be an acidic oxide.

Practice Exercise Classify the following oxides as acidic, basic, or amphoteric: (a) ZnO, (b) P_4O_{10}, (c) CaO.



Similar problem: 8.72.

Summary of Facts and Concepts

1. Nineteenth-century chemists developed the periodic table by arranging elements in the increasing order of their atomic masses. Discrepancies in early versions of the periodic table were resolved by arranging the elements in order of their atomic numbers.
2. Electron configuration determines the properties of an element. The modern periodic table classifies the elements according to their atomic numbers, and thus also by their electron configurations. The configuration of the valence electrons directly affects the properties of the atoms of the representative elements.
3. Periodic variations in the physical properties of the elements reflect differences in atomic structure. The metallic character of elements decreases across a period from metals through the metalloids to nonmetals and increases from top to bottom within a particular group of representative elements.
4. Atomic radius varies periodically with the arrangement of the elements in the periodic table. It decreases from left to right and increases from top to bottom.
5. Ionization energy is a measure of the tendency of an atom to resist the loss of an electron. The higher the ionization energy, the stronger the attraction between the nucleus and an electron. Electron affinity is a measure of the tendency of an atom to gain an electron. The more positive the electron affinity, the greater the tendency for the atom to gain an electron. Metals usually have low ionization energies, and nonmetals usually have high electron affinities.
6. Noble gases are very stable because their outer *ns* and *np* subshells are completely filled. The metals among the representative elements (in Groups 1A, 2A, and 3A) tend to lose electrons until their cations become isoelectronic with the noble gases that precede them in the periodic table. The nonmetals in Groups 5A, 6A, and 7A tend to accept electrons until their anions become isoelectronic with the noble gases that follow them in the periodic table.

Key Words

Amphoteric oxide, p. 345
Atomic radius, p. 323
Diagonal relationship, p. 336
Electron affinity, p. 333
Ionic radius, p. 325
Ionization energy, p. 329
Isoelectronic, p. 322
Representative elements, p. 318
Valence electrons, p. 320

Questions and Problems

Development of the Periodic Table

Review Questions

8.1 Briefly describe the significance of Mendeleev's periodic table.

8.2 What is Moseley's contribution to the modern periodic table?

8.3 Describe the general layout of a modern periodic table.

8.4 What is the most important relationship among elements in the same group in the periodic table?

Periodic Classification of the Elements

Review Questions

8.5 Which of the following elements are metals, nonmetals, or metalloids? As, Xe, Fe, Li, B, Cl, Ba, P, I, Si.

8.6 Compare the physical and chemical properties of metals and nonmetals.

8.7 Draw a rough sketch of a periodic table (no details are required). Indicate regions where metals, nonmetals, and metalloids are located.

8.8 What is a representative element? Give names and symbols of four representative elements.

8.9 Without referring to a periodic table, write the name and give the symbol for an element in each of the following groups: 1A, 2A, 3A, 4A, 5A, 6A, 7A, 8A, transition metals.

8.10 Indicate whether the following elements exist as atomic species, molecular species, or extensive three-dimensional structures in their most stable states at 25°C and 1 atm and write the molecular or empirical formula for each one: phosphorus, iodine, magnesium, neon, carbon, sulfur, cesium, and oxygen.

8.11 You are given a dark shiny solid and asked to determine whether it is iodine or a metallic element. Suggest a nondestructive test that would enable you to arrive at the correct answer.

8.12 What are valence electrons? For representative elements, the number of valence electrons of an element is equal to its group number. Show that this is true for the following elements: Al, Sr, K, Br, P, S, C.

8.13 Write the outer electron configurations for the (a) al kali metals, (b) alkaline earth metals, (c) halog (d) noble gases.

8.14 Use the first-row transition metals (Sc to Cu) as an ample to illustrate the characteristics of the elec configurations of transition metals.

8.15 How does the electron configuration of ions deri from representative elements give them stability?

8.16 What do we mean when we say that two ions or atom and an ion are isoelectronic?

8.17 What is wrong with the statement "The atoms of el ment X are isoelectronic with the atoms of element Y

8.18 Give three examples of first-row transition metal (to Cu) ions whose electron configurations are rep sented by the argon core.

Problems

8.19 In the periodic table, the element hydrogen is sometim grouped with the alkali metals (as in this book) an sometimes with the halogens. Explain why hydrog can resemble the Group 1A and the Group 7A elemen

8.20 A neutral atom of a certain element has 17 electron Without consulting a periodic table, (a) write th ground-state electron configuration of the element, (b classify the element, (c) determine whether this el ment is diamagnetic or paramagnetic.

8.21 Group the following electron configurations in pai that would represent similar chemical properties o their atoms:

(a) $1s^22s^22p^63s^2$
(b) $1s^22s^22p^3$
(c) $1s^22s^22p^63s^23p^64s^23d^{10}4p^6$
(d) $1s^22s^2$
(e) $1s^22s^22p^6$
(f) $1s^22s^22p^63s^23p^3$

8.22 Group the following electron configurations in pai that would represent similar chemical properties of their atoms:

(a) $1s^22s^22p^5$
(b) $1s^22s^1$

(c) $1s^22s^22p^6$
(d) $1s^22s^22p^63s^23p^5$
(e) $1s^22s^22p^63s^23p^64s^1$
(f) $1s^22s^22p^63s^23p^64s^23d^{10}4p^6$

8.23 Without referring to a periodic table, write the electron configuration of elements with the following atomic numbers: (a) 9, (b) 20, (c) 26, (d) 33. Classify the elements.

8.24 Specify the group of the periodic table in which each of the following elements is found: (a) $[\mathrm{Ne}]3s^1$, (b) $[\mathrm{Ne}]3s^23p^3$, (c) $[\mathrm{Ne}]3s^23p^6$, (d) $[\mathrm{Ar}]4s^23d^8$.

8.25 A M^{2+} ion derived from a metal in the first transition metal series has four electrons in the 3*d* subshell. What element might M be?

8.26 A metal ion with a net +3 charge has five electrons in the 3*d* subshell. Identify the metal.

8.27 Write the ground-state electron configurations of the following ions: (a) Li^+, (b) H^-, (c) N^{3-}, (d) F^-, (e) S^{2-}, (f) Al^{3+}, (g) Se^{2-}, (h) Br^-, (i) Rb^+, (j) Sr^{2+}, (k) Sn^{2+}, (l) Te^{2-}, (m) Ba^{2+}, (n) Pb^{2+}, (o) In^{3+}, (p) Tl^+, (q) Tl^{3+}.

8.28 Write the ground-state electron configurations of the following ions, which play important roles in biochemical processes in our bodies: (a) Na^+, (b) Mg^{2+}, (c) Cl^-, (d) K^+, (e) Ca^{2+}, (f) Fe^{2+}, (g) Cu^{2+}, (h) Zn^{2+}.

8.29 Write the ground-state electron configurations of the following transition metal ions: (a) Sc^{3+}, (b) Ti^{4+}, (c) V^{5+}, (d) Cr^{3+}, (e) Mn^{2+}, (f) Fe^{2+}, (g) Fe^{3+}, (h) Co^{2+}, (i) Ni^{2+}, (j) Cu^+, (k) Cu^{2+}, (l) Ag^+, (m) Au^+, (n) Au^{3+}, (o) Pt^{2+}.

8.30 Name the ions with +3 charges that have the following electron configurations: (a) $[\mathrm{Ar}]3d^3$, (b) [Ar], (c) $[\mathrm{Kr}]4d^6$, (d) $[\mathrm{Xe}]4f^{14}5d^6$.

8.31 Which of the following species are isoelectronic with each other? C, Cl^-, Mn^{2+}, B^-, Ar, Zn, Fe^{3+}, Ge^{2+}.

8.32 Group the species that are isoelectronic: Be^{2+}, F^-, Fe^{2+}, N^{3-}, He, S^{2-}, Co^{3+}, Ar.

Periodic Variation in Physical Properties

Review Questions

8.33 Define atomic radius. Does the size of an atom have a precise meaning?

8.34 How does atomic radius change (a) from left to right across a period and (b) from top to bottom in a group?

8.35 Define ionic radius. How does the size of an atom change when it is converted to (a) an anion and (b) a cation?

8.36 Explain why, for isoelectronic ions, the anions are larger than the cations.

Problems

8.37 On the basis of their positions in the periodic table, select the atom with the larger atomic radius in each of the following pairs: (a) Na, Cs; (b) Be, Ba; (c) N, Sb; (d) F, Br; (e) Ne, Xe.

8.38 Arrange the following atoms in order of decreasing atomic radius: Na, Al, P, Cl, Mg.

8.39 Which is the largest atom in Group 4A?

8.40 Which is the smallest atom in Group 7A?

8.41 Why is the radius of the lithium atom considerably larger than the radius of the hydrogen atom?

8.42 Use the second period of the periodic table as an example to show that the size of atoms decreases as we move from left to right. Explain the trend.

8.43 Indicate which one of the two species in each of the following pairs is smaller: (a) Cl or Cl^-; (b) Na or Na^+; (c) O^{2-} or S^{2-}; (d) Mg^{2+} or Al^{3+}; (e) Au^+ or Au^{3+}.

8.44 List the following ions in order of increasing ionic radius: N^{3-}, Na^+, F^-, Mg^{2+}, O^{2-}.

8.45 Explain which of the following cations is larger, and why: Cu^+ or Cu^{2+}.

8.46 Explain which of the following anions is larger, and why: Se^{2-} or Te^{2-}.

8.47 Give the physical states (gas, liquid, or solid) of the representative elements in the fourth period (K, Ca, Ga, Ge, As, Se, Br) at 1 atm and 25°C.

8.48 The boiling points of neon and krypton are −245.9°C and −152.9°C, respectively. Using these data, estimate the boiling point of argon.

Ionization Energy

Review Questions

8.49 Define ionization energy. Ionization energy measurements are usually made when atoms are in the gaseous state. Why? Why is the second ionization energy always greater than the first ionization energy for any element?

8.50 Sketch the outline of the periodic table and show group and period trends in the first ionization energy of the elements. What types of elements have the highest ionization energies and what types the lowest ionization energies?

Problems

8.51 Arrange the following in order of increasing first ionization energy: Na, Cl, Al, S, and Cs.

8.52 Arrange the following in order of increasing first ionization energy: F, K, P, Ca, and Ne.

8.53 Use the third period of the periodic table as an example to illustrate the change in first ionization energies of the elements as we move from left to right. Explain the trend.

8.54 In general, ionization energy increases from left to right across a given period. Aluminum, however, has a lower ionization energy than magnesium. Explain.

8.55 The first and second ionization energies of K are 419 kJ/mol and 3052 kJ/mol, and those of Ca are 590 kJ/mol and 1145 kJ/mol, respectively. Compare their values and comment on the differences.

8.56 Two atoms have the electron configurations $1s^22s^22p^6$ and $1s^22s^22p^63s^1$. The first ionization energy of one is 2080 kJ/mol, and that of the other is 496 kJ/mol. Match each ionization energy with one of the given electron configurations. Justify your choice.

8.57 A hydrogenlike ion is an ion containing only one electron. The energies of the electron in a hydrogenlike ion are given by

$$E_n = -(2.18 \times 10^{-18}\ \text{J})Z^2\left(\frac{1}{n^2}\right)$$

where n is the principal quantum number and Z is the atomic number of the element. Calculate the ionization energy (in kJ/mol) of the He^+ ion.

8.58 Plasma is a state of matter consisting of positive gaseous ions and electrons. In the plasma state, a mercury atom could be stripped of its 80 electrons and therefore would exist as Hg^{80+}. Use the equation in Problem 8.57 to calculate the energy required for the last ionization step, that is,

$$Hg^{79+}(g) \longrightarrow Hg^{80+}(g) + e^-$$

Electron Affinity

Review Questions

8.59 (a) Define electron affinity. (b) Electron affinity measurements are made with gaseous atoms. Why? (c) Ionization energy is always a positive quantity, whereas electron affinity may be either positive or negative. Explain.

8.60 Explain the trends in electron affinity from aluminum to chlorine (see Table 8.3).

Problems

8.61 Arrange the elements in each of the following groups in increasing order of the most positive electron affinity: (a) Li, Na, K; (b) F, Cl, Br, I.

8.62 Specify which of the following elements you would expect to have the greatest electron affinity: He, K, Co, S, Cl.

8.63 Considering their electron affinities, do you think it is possible for the alkali metals to form an anion like M^-, where M represents an alkali metal?

8.64 Explain why alkali metals have a greater affinity for electrons than alkaline earth metals.

Variation in Chemical Properties of the Representative Elements

Review Questions

8.65 What is meant by the diagonal relationship? Name two pairs of elements that show this relationship.

8.66 Which elements are more likely to form acidi
ides? Basic oxides? Amphoteric oxides?

Problems

8.67 Use the alkali metals and alkaline earth metals as
amples to show how we can predict the chemi
properties of elements simply from their elec
configurations.

8.68 Based on your knowledge of the chemistry of th
kali metals, predict some of the chemical propertie
francium, the last member of the group.

8.69 As a group, the noble gases are very stable chemi
(only Kr and Xe are known to form compounds). Wh

8.70 Why are Group 1B elements more stable than Gr
1A elements even though they seem to have the sa
outer electron configuration, ns^1, where n is the pr
cipal quantum number of the outermost shell?

8.71 How do the chemical properties of oxides ch
from left to right across a period? From top to bo
within a particular group?

8.72 Write balanced equations for the reactions be
tween each of the following oxides and water: (a) L
(b) CaO, (c) SO_3.

8.73 Write formulas for and name the binary hydrogen co
pounds of the second-period elements (Li to F). D
scribe how the physical and chemical properties of th
compounds change from left to right across the peri

8.74 Which oxide is more basic, MgO or BaO? Why?

Additional Problems

8.75 State whether each of the following properties of th
representative elements generally increases or d
creases (a) from left to right across a period and
from top to bottom within a group: metallic chara
atomic size, ionization energy, acidity of oxides.

8.76 With reference to the periodic table, name (a) a h
gen element in the fourth period, (b) an element si
lar to phosphorus in chemical properties, (c) the m
reactive metal in the fifth period, (d) an element th
has an atomic number smaller than 20 and is simil
strontium.

8.77 Write equations representing the following proce

(a) The electron affinity of S^-.

(b) The third ionization energy of titanium.

(c) The electron affinity of Mg^{2+}.

(d) The ionization energy of O^{2-}.

8.78 Arrange the following isoelectronic species in or
of (a) increasing ionic radius and (b) increasing io
ization energy: O^{2-}, F^-, Na^+, Mg^{2+}.

8.79 Write the empirical (or molecular) formulas of co
pounds that the elements in the third period (sodium
chlorine) should form with (a) molecular oxygen
(b) molecular chlorine. In each case indicate wheth

you would expect the compound to be ionic or molecular in character.

8.80 Element M is a shiny and highly reactive metal (melting point 63°C), and element X is a highly reactive nonmetal (melting point −7.2°C). They react to form a compound with the empirical formula MX, a colorless, brittle white solid that melts at 734°C. When dissolved in water or when in the molten state, the substance conducts electricity. When chlorine gas is bubbled through an aqueous solution containing MX, a reddish-brown liquid appears and Cl^- ions are formed. From these observations, identify M and X. (You may need to consult a handbook of chemistry for the melting-point values.)

8.81 Match each of the elements on the right with its description on the left:

(a) A dark-red liquid	Calcium (Ca)
(b) A colorless gas that burns in oxygen gas	Gold (Au)
	Hydrogen (H_2)
(c) A reactive metal that attacks water	Argon (Ar)
	Bromine (Br_2)
(d) A shiny metal that is used in jewelry	
(e) An inert gas	

8.82 Arrange the following species in isoelectronic pairs: O^+, Ar, S^{2-}, Ne, Zn, Cs^+, N^{3-}, As^{3+}, N, Xe.

8.83 In which of the following are the species written in decreasing order by size of radius? (a) Be, Mg, Ba, (b) N^{3-}, O^{2-}, F^-, (c) Tl^{3+}, Tl^{2+}, Tl^+.

8.84 Which of the following properties show a clear periodic variation? (a) first ionization energy, (b) molar mass of the elements, (c) number of isotopes of an element, (d) atomic radius.

8.85 When carbon dioxide is bubbled through a clear calcium hydroxide solution, the solution appears milky. Write an equation for the reaction and explain how this reaction illustrates that CO_2 is an acidic oxide.

8.86 You are given four substances: a fuming red liquid, a dark metallic-looking solid, a pale-yellow gas, and a yellow-green gas that attacks glass. You are told that these substances are the first four members of Group 7A, the halogens. Name each one.

8.87 For each pair of elements listed below, give three properties that show their chemical similarity: (a) sodium and potassium and (b) chlorine and bromine.

8.88 Name the element that forms compounds, under appropriate conditions, with every other element in the periodic table except He, Ne, and Ar.

8.89 Explain why the first electron affinity of sulfur is 200 kJ/mol but the second electron affinity is −649 kJ/mol.

8.90 The H^- ion and the He atom have two 1*s* electrons each. Which of the two species is larger? Explain.

8.91 Predict the products of the following oxides with water: Na_2O, BaO, CO_2, N_2O_5, P_4O_{10}, SO_3. Write an equation for each of the reactions. Specify whether the oxides are acidic, basic, or amphoteric.

8.92 Write the formulas and names of the oxides of the second-period elements (Li to N). Identify the oxides as acidic, basic, or amphoteric.

8.93 State whether each of the following elements is a gas, a liquid, or a solid under atmospheric conditions. Also state whether it exists in the elemental form as atoms, as molecules, or as a three-dimensional network: Mg, Cl, Si, Kr, O, I, Hg, Br.

8.94 What factors account for the unique nature of hydrogen?

8.95 The air in a manned spacecraft or submarine needs to be purified of exhaled carbon dioxide. Write equations for the reactions between carbon dioxide and (a) lithium oxide (Li_2O), (b) sodium peroxide (Na_2O_2), and (c) potassium superoxide (KO_2).

8.96 The formula for calculating the energies of an electron in a hydrogenlike ion is given in Problem 8.57. This equation cannot be applied to many-electron atoms. One way to modify it for the more complex atoms is to replace Z with $(Z - \sigma)$, where Z is the atomic number and σ is a positive dimensionless quantity called the shielding constant. Consider the helium atom as an example. The physical significance of σ is that it represents the extent of shielding that the two 1*s* electrons exert on each other. Thus, the quantity $(Z - \sigma)$ is appropriately called the "effective nuclear charge." Calculate the value of σ if the first ionization energy of helium is 3.94×10^{-18} J per atom. (Ignore the minus sign in the given equation in your calculation.)

8.97 Why do noble gases have negative electron affinity values?

8.98 The atomic radius of K is 216 pm and that of K^+ is 133 pm. Calculate the percent decrease in volume that occurs when $K(g)$ is converted to $K^+(g)$. [The volume of a sphere is $(\frac{4}{3})\pi r^3$, where r is the radius of the sphere.]

8.99 The atomic radius of F is 72 pm and that of F^- is 136 pm. Calculate the percent increase in volume that occurs when $F(g)$ is converted to $F^-(g)$. (See Problem 8.98 for the volume of a sphere.)

8.100 A technique called photoelectron spectroscopy is used to measure the ionization energy of atoms. A sample is irradiated with UV light, and electrons are ejected from the valence shell. The kinetic energies of the ejected electrons are measured. Because the energy of the UV photon and the kinetic energy of the ejected electron are known, we can write

$$h\nu = \text{IE} + \tfrac{1}{2}mu^2$$

where ν is the frequency of the UV light, and m and u are the mass and velocity of the electron, respectively. In one experiment the kinetic energy of the ejected electron from potassium is found to be 5.34×10^{-19} J using a UV source of wavelength 162 nm. Calculate the ionization energy of potassium. How can you be sure that this ionization energy corresponds to the electron in the valence shell (that is, the most loosely held electron)?

8.101 Referring to the Chemistry in Action essay on p. 346, answer the following questions. (a) Why did it take so long to discover the first noble gas (argon) on Earth? (b) Once argon had been discovered, why did it take relatively little time to discover the rest of the noble gases? (c) Why was helium not isolated by the fractional distillation of liquid air?

8.102 The energy needed for the following process is 1.96×10^4 kJ/mol:

$$\text{Li}(g) \longrightarrow \text{Li}^{3+}(g) + 3e^-$$

If the first ionization energy of lithium is 520 kJ/mol, calculate the second ionization energy of lithium, that is, the energy required for the process

$$\text{Li}^{+}(g) \longrightarrow \text{Li}^{2+}(g) + e^-$$

(*Hint:* You need the equation in Problem 8.57.)

8.103 An element X reacts with hydrogen gas at 200°C to form compound Y. When Y is heated to a higher temperature, it decomposes to the element X and hydrogen gas in the ratio of 559 mL of H_2 (measured at STP) for 1.00 g of X reacted. X also combines with chlorine to form a compound Z, which contains 63.89 percent by mass of chlorine. Deduce the identity of X.

8.104 A student is given samples of three elements, X, Y, and Z, which could be an alkali metal, a member of Group 4A, and a member of Group 5A. She makes the following observations: Element X has a metallic luster and conducts electricity. It reacts slowly with hydrochloric acid to produce hydrogen gas. Element Y is a light-yellow solid that does not conduct electricity. Element Z has a metallic luster and conducts electricity. When exposed to air, it slowly forms a white powder. A solution of the white powder in water is basic. What can you conclude about the elements from these observations?

8.105 Using the following boiling-point data and the procedure in the Chemistry in Action essay on p. 329, estimate the boiling point of francium:

metal	Li	Na	K	Rb	Cs
boiling point (°C)	1347	882.9	774	688	678.4

8.106 What is the electron affinity of the Na^+ ion?

8.107 The ionization energies of sodium (in kJ/mol), starting with the first and ending with the eleventh, are 495.9, 4560, 6900, 9540, 13,400, 16,600, 20,120, 28,930, 141,360, 170,000. Plot the log of ion energy (y axis) versus the number of ioniz axis); for example, log 495.9 is plotted vers beled I_1, the first ionization energy), log 4560 ted versus 2 (labeled I_2, the second ionization and so on. (a) Label I_1 through I_{11} with the elec orbitals such as 1s, 2s, 2p, and 3s. (b) What deduce about electron shells from the breaks curve?

8.108 Experimentally, the electron affinity of an elem be determined by using a laser light to ionize the of the element in the gas phase:

$$\text{X}^-(g) + h\nu \longrightarrow \text{X}(g) + e^-$$

Referring to Table 8.3, calculate the photon length (in nanometers) corresponding to the el affinity for chlorine. In what region of the electro netic spectrum does this wavelength fall?

8.109 Explain, in terms of their electron configuration Fe^{2+} is more easily oxidized to Fe^{3+} than Mn Mn^{3+}.

8.110 The standard enthalpy of atomization of an elem the energy required to convert one mole of an ele in its most stable form at 25°C to one mol monatomic gas. Given that the standard enthalp atomization for sodium is 108.4 kJ/mol, calcula energy in kilojoules required to convert one mol sodium metal at 25°C to one mole of gaseous ions.

8.111 Write the formulas and names of the hydrides of following second-period elements: Li, C, N, O, dict their reactions with water.

8.112 Based on knowledge of the electronic configuratio titanium, state which of the following compound titanium is unlikely to exist: K_3TiF_6, $K_2Ti_2O_5$, K_2TiO_4, K_2TiF_6.

8.113 Name an element in Group 1A or Group 2A that important constituent of each of the following stances: (a) remedy for acid indigestion, (b) coolant nuclear reactors, (c) Epsom salt, (d) baking pow (e) gunpowder, (f) a light alloy, (g) fertilizer that neutralizes acid rain, (h) cement, and (i) grit for roads. You may need to ask your instructor about so of the items.

8.114 In halogen displacement reactions a halogen eleme can be generated by oxidizing its anions with a hal gen element that lies above it in the periodic tabl This means that there is no way to prepare element fluorine, because it is the first member of Group 7 Indeed, for years the only way to prepare element fluorine was to oxidize F^- ions by electrolytic mean Then, in 1986, a chemist reported that by reacti potassium hexafluoromanganate(IV) (K_2MnF_6) wi antimony pentafluoride (SbF_5) at 150°C, he h generated elemental fluorine. Balance the following equation representing the reaction:

$$K_2MnF_6 + SbF_5 \longrightarrow KSbF_6 + MnF_3 + F_2$$

8.115 Write a balanced equation for the preparation of (a) molecular oxygen, (b) ammonia, (c) carbon dioxide, (d) molecular hydrogen, (e) calcium oxide. Indicate the physical state of the reactants and products in each equation.

8.116 Write chemical formulas for oxides of nitrogen with the following oxidation numbers: +1, +2, +3, +4, +5. (*Hint:* There are *two* oxides of nitrogen with +4 oxidation number.)

8.117 Most transition metal ions are colored. For example, a solution of $CuSO_4$ is blue. How would you show that the blue color is due to the hydrated Cu^{2+} ions and not the SO_4^{2-} ions?

8.118 In general, atomic radius and ionization energy have opposite periodic trends. Why?

8.119 Explain why the electron affinity of nitrogen is approximately zero, while the elements on either side, carbon and oxygen, have substantial positive electron affinities.

8.120 Consider the halogens chlorine, bromine, and iodine. The melting point and boiling point of chlorine are −101.0°C and −34.6°C while those of iodine are 113.5°C and 184.4°C, respectively. Thus, chlorine is a gas and iodine is a solid under room conditions. Estimate the melting point and boiling point of bromine. Compare your values with those from a handbook of chemistry.

8.121 While it is possible to determine the second, third, and higher ionization energies of an element, the same cannot usually be done with the electron affinities of an element. Explain.

8.122 The only confirmed compound of radon is radon fluoride, RnF. One reason that it is difficult to study the chemistry of radon is that all isotopes of radon are radioactive so it is dangerous to handle the substance. Can you suggest another reason why there are so few known radon compounds? (*Hint:* Radioactive decays are exothermic processes.)

8.123 Little is known of the chemistry of astatine, the last member of Group 7A. Describe the physical characteristics that you would expect this halogen to have. Predict the products of the reaction between sodium astatide (NaAt) and sulfuric acid. (*Hint:* Sulfuric acid is an oxidizing agent.)

8.124 As discussed in the chapter, the atomic mass of argon is greater than that of potassium. This observation created a problem in the early development of the periodic table because it meant that argon should be placed after potassium. (a) How was this difficulty resolved? (b) From the following data, calculate the average atomic masses of argon and potassium: Ar-36 (35.9675 amu; 0.337 percent), Ar-38 (37.9627 amu; 0.063 percent), Ar-40 (39.9624 amu; 99.60 percent); K-39 (38.9637 amu; 93.258 percent), K-40 (39.9640 amu; 0.0117 percent), K-41 (40.9618 amu; 6.730 percent).

8.125 Calculate the maximum wavelength of light (in nanometers) required to ionize a single sodium atom.

8.126 Predict the atomic number and ground-state electron configuration of the next member of the alkali metals after francium.

8.127 Why do elements that have high ionization energies also have more positive electron affinities? Which group of elements would be an exception to this generalization?

8.128 The first four ionization energies of an element are approximately 738 kJ/mol, 1450 kJ/mol, 7.7×10^3 kJ/mol, and 1.1×10^4 kJ/mol. To which periodic group does this element belong? Why?

8.129 Some chemists think that helium should properly be called "helon." Why? What does the ending in helium (-ium) suggest?

8.130 (a) The formula of the simplest hydrocarbon is CH_4 (methane). Predict the formulas of the simplest compounds formed between hydrogen and the following elements: silicon, germanium, tin, and lead. (b) Sodium hydride (NaH) is an ionic compound. Would you expect rubidium hydride (RbH) to be more or less ionic than NaH? (c) Predict the reaction between radium (Ra) and water. (d) When exposed to air, aluminum forms a tenacious oxide (Al_2O_3) coating that protects the metal from corrosion. Which metal in Group 2A would you expect to exhibit similar properties? Why?

8.131 Match each of the elements on the right with its description on the left:

(a) A pale yellow gas that reacts with water.
(b) A soft metal that reacts with water to produce hydrogen.
(c) A metalloid that is hard and has a high melting point.
(d) A colorless, odorless gas.
(e) A metal that is more reactive than iron, but does not corrode in air.

Nitrogen (N_2)
Boron (B)
Aluminum (Al)
Fluorine (F_2)
Sodium (Na)

8.132 Write an account on the importance of the periodic table. Pay particular attention to the significance of the position of an element in the table and how the position relates to the chemical and physical properties of the element.

8.133 On the same graph, plot the effective nuclear charge (shown in parentheses) and atomic radius (see Figure 8.5) versus atomic number for the second-period elements: Li(1.30), Be(1.95), B(2.60), C(3.25), N(3.90), O(4.55), F(5.20), Ne(5.85). Comment on the trends.

8.134 One allotropic form of an element X is a colorless crystalline solid. The reaction of X with an excess amount of oxygen produces a colorless gas. This gas dissolves in water to yield an acidic solution. Choose one of the following elements that matches X: (a) sulfur, (b) phosphorus, (c) carbon, (d) boron, and (e) silicon.

8.135 When magnesium metal is burned in air, it form
products A and B. A reacts with water to form a
solution. B reacts with water to form a similar sol
as that of A plus a gas with a pungent odor. Ident
and B and write equations for the reactions. (*Hint*
Chemistry in Action on p. 346.)

Special Problems

8.136 The ionization energy of a certain element is 412 kJ/mol. When the atoms of this element are in the first excited state, however, the ionization energy is only 126 kJ/mol. Based on this information, calculate the wavelength of light emitted in a transition from the first excited state to the ground state.

8.137 Potassium superoxide (see p. 337) is used in breathing equipment because it produces oxygen when reacted with water vapor and carbon dioxide in exhaled air. (a) Write equations for the reactions. (b) Calculate the pressure (in atm) at which oxygen gas stored at 20°C would have the same density as the oxygen gas provided by KO_2. The density of KO_2 at 20°C is 2.15 g/cm^3.

8.138 Referring to Table 8.2, explain why the first ionization energy of helium is less than twice the ionization energy of hydrogen, but the second ionization energy of helium is greater than twice the ionization energy of hydrogen. [*Hint*: According to Coulomb's law,
energy between two charges Q_1 and Q_2 separated
distance r is proportional to (Q_1Q_2/r).]

8.139 As mentioned in Chapter 3 (p. 104), ammoni
nitrate (NH_4NO_3) is the most important nitro
containing fertilizer in the world. Describe how
would prepare this compound, given only air and
ter as the starting materials. You may have any dev
at your disposal for this task.

8.140 One way to estimate the effective charge (Z_{eff})
a many-electron atom is to use the equation I_1
(1312 kJ/mol)(Z_{eff}^2/n^2), where I_1 is the first ioniza
energy and n is the principal quantum number of
shell in which the electron resides. Use this equat
to calculate the effective charges of Li, Na, and
Also calculate Z_{eff}/n for each metal. Comment on y
results.

Answers to Practice Exercises

8.1 (a) $1s^22s^22p^63s^23p^64s^2$, (b) it is a representative element, (c) diamagnetic. **8.2** Li > Be > C. **8.3** (a) Li^+, (b) Au^{3+}, (c) N^{3-}. **8.4** (a) N, (b) Mg. **8.5** No. **8.6** (a) amphoteric, (b) acidic, (c) basic.