

6

Chemical Periodicity



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Oxygen and Ozone

Reactions of Oxygen and the Oxides

Combustion Reactions

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The bright colors in fireworks displays are produced when various metals react with oxygen.

OBJECTIVES

After you have studied this chapter, you should be able to

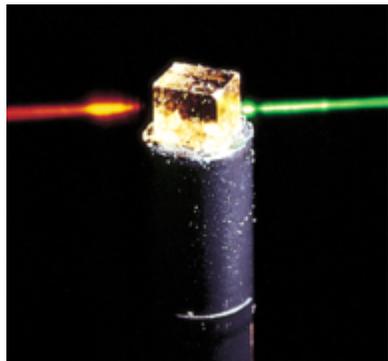
- *More effectively use the periodic table*
- *Discuss chemical periodicity of the following physical properties:*
 - Atomic radii*
 - Ionization energy*
 - Electron affinity*
 - Ionic radii*
 - Electronegativity*
- *Describe chemical periodicity in the reactions of*
 - Hydrogen*
 - Oxygen*
- *Describe chemical periodicity in the compounds of*
 - Hydrogen*
 - Oxygen*

6-1 MORE ABOUT THE PERIODIC TABLE

In Chapter 4 we described the development of the periodic table, some terminology for it, and its guiding principle, the *periodic law*.

The properties of the elements are periodic functions of their atomic numbers.

In Chapter 5 we described electron configurations of the elements. In the long form of the periodic table, elements are arranged in blocks based on the kinds of atomic orbitals being filled. (Please review Table 5-5 and Figure 5-31 carefully.) We saw that electron



The properties of elements are correlated with their positions in the periodic table. Chemists use the periodic table as an invaluable guide in their search for new, useful materials. A barium sodium niobate crystal can convert infrared laser light into visible green light. This harmonic generation or “frequency doubling” is very important in chemical research using lasers and in the telecommunications industry.

$[\text{He}] = 1s^2$



Some transition metals (*left to right*): Ti, V, Cr, Mn, Fe, Co, Ni, Cu.

configurations of elements in the A groups are entirely predictable from their positions in the periodic table. We also noted, however, that some irregularities occur within the B groups.

Now we classify the elements according to their electron configurations, which is a very useful system.

Noble Gases. For many years the Group VIIIA elements—the noble gases—were called inert gases because no chemical reactions were known for them. We now know that the heavier members do form compounds, mostly with fluorine and oxygen. Except for helium, each of these elements has eight electrons in its outermost occupied shell. Their outer shell may be represented as having the electron configuration $\dots ns^2np^6$.

Representative Elements. The A group elements in the periodic table are called representative elements. Their “last” electron is assigned to an outer shell s or p orbital. These elements show distinct and fairly regular variations in their properties with changes in atomic number.

d -Transition Elements. Elements in the B groups in the periodic table are known as the d -transition elements or, more simply, as transition elements or transition metals. The elements of four transition series are all metals and are characterized by electrons being assigned to d orbitals. Stated differently, the d -transition elements contain electrons in both the ns and $(n - 1)d$ orbitals, but not in the np orbitals. The first transition series, Sc through Zn, has electrons in the $4s$ and $3d$ orbitals, but not in the $4p$ orbitals. They are referred to as

First transition series:	${}_{21}\text{Sc}$ through ${}_{30}\text{Zn}$
Second transition series:	${}_{39}\text{Y}$ through ${}_{48}\text{Cd}$
Third transition series:	${}_{57}\text{La}$ and ${}_{72}\text{Hf}$ through ${}_{80}\text{Hg}$
Fourth transition series:	${}_{89}\text{Ac}$ and ${}_{104}\text{Rf}$ through element 112



CHEMISTRY IN USE

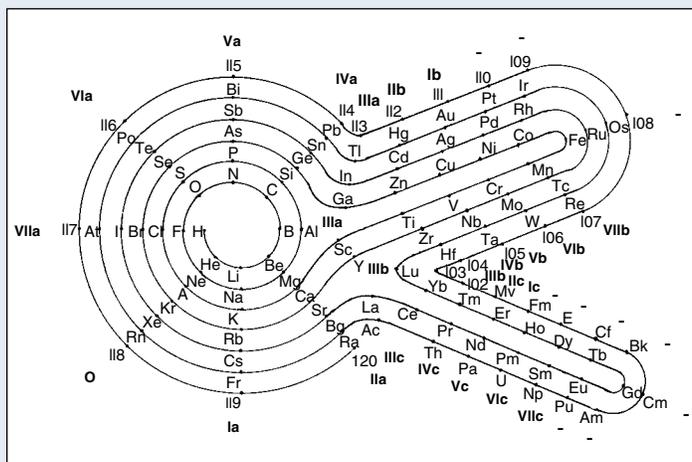
The Development of Science

The Periodic Table

The periodic table is one of the first things a student of chemistry encounters. It appears invariably in textbooks, in lecture halls, and in laboratories. Scientists consider it an indispensable reference. And yet, less than 150 years ago, the idea of arranging the elements by atomic weight or number was considered absurd. At an 1866 meeting of the Chemical Society at Burlington House, England, J. A. R. Newlands (1837–1898) presented a theory he called the law of octaves. It stated that when the known elements were listed by increasing atomic weights, those that were eight places apart would be similar, much like notes on a piano keyboard. His colleagues' reactions are probably summed up best by the remark of a Professor Foster: "Have you thought of arranging the elements according to their initial letters? Maybe some better connections would come to light that way."

It is not surprising that poor Newlands was not taken seriously. In the 1860s, little information was available to illustrate relationships among the elements. Only 62 of them had been distinguished from more complex substances when Mendeleev first announced his discovery of the periodic law in 1869. As advances in atomic theory were made, however, and as new experiments contributed to the understanding of chemical behavior, some scientists had begun to see similarities and patterns among the elements. In 1869, Lothar Meyer and Dmitri Mendeleev independently published similar versions of the now-famous periodic table.

Mendeleev's discovery was the result of many years of hard work. He gathered information on the elements from all corners of the earth—by corresponding with colleagues, studying books and papers, and redoing experiments to confirm data. He put the statistics of each element on a small card and pinned the cards to his laboratory wall, where he arranged and rearranged them many times until he was sure that they were in the right order. One especially farsighted feature of Mendeleev's accomplishment was his realization that some elements were missing from the table. He predicted the properties of these substances (gallium, scandium, and germanium). (It is important to remember that Mendeleev's periodic table organization was devised more than 50 years before the discovery and characterization of subatomic particles.)



An alternative representation of the periodic table, as proposed by Charles Janet, 1928.

Since its birth in 1869, the periodic table has been discussed and revised many times. Spectroscopic and other discoveries have filled in the blanks left by Mendeleev and added a new column consisting of the noble gases. As scientists learned more about atomic structure, the basis for ordering was changed from atomic weight to atomic number. The perplexing rare earths were sorted out and given a special place, along with many of the elements created by atomic bombardment. Even the form of the table has been experimented with, resulting in everything from spiral and circular tables to exotic shapes such as the one suggested by Charles Janet. A three-dimensional periodic table that takes into account valence-shell energies has been proposed by Professor Leland C. Allen of Princeton University.

During the past century, chemistry has become a fast-moving science in which methods and instruments are often outdated within a few years. But it is doubtful that our old friend, the periodic table, will ever become obsolete. It may be modified, but it will always stand as a statement of basic relationships in chemistry and as a monument to the wisdom and insight of its creator, Dmitri Mendeleev.

Lisa Saunders Boffa
Senior Chemist
Exxon Corporation

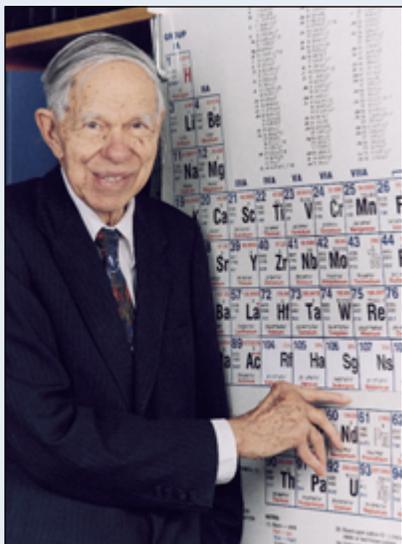


The Development of Science

Glenn Seaborg: A Human Side to the Modern Periodic Table

If it were possible to associate a human face with the modern periodic table, that face would most likely belong to Glenn Seaborg (1912–1999), the codiscoverer of ten transuranium elements and the name behind Element 106. Seaborg's contributions to heavy-element chemistry began in 1940, when he and coworkers at the University of California at Berkeley produced the first sample of plutonium by bombarding uranium with deuterons (${}^2_1\text{H}$ nuclei) in a particle accelerator. They found that the isotope plutonium-239 undergoes nuclear fission (see Chapter 26), making it a potential energy source for nuclear power or nuclear weapons.

As American involvement in World War II grew, President Franklin Roosevelt called Seaborg and other eminent scientists to the Wartime Metallurgical Laboratory at the University of Chicago, where they figured out how to prepare and purify plutonium-239 in useful quantities for the Manhattan Project, the making of the atom bomb. In 1945, Seaborg was one of the signers of the Franck Report, a document recommending that a safe demonstration test of the atomic bomb might persuade Japan to surrender without the bomb actually being used. Professor Seaborg served as a scientific advisor for nine other presidents following Roosevelt and was chairman of the U.S. Atomic Energy



Commission under Kennedy, Johnson, and Nixon.

Seaborg's contributions illustrate how certain areas of science can be highly influenced by a particular institution or even a national tradition over time. His discovery of plutonium at the University of California at Berkeley followed the 1940 synthesis of neptunium at the same site by Edwin

McMillan, who shared the 1951 Nobel Prize in chemistry with Seaborg for these accomplishments. Since that time, Seaborg and other teams involving Berkeley researchers at the University's Lawrence Berkeley Laboratory have prepared nine more heavy elements. He and coworkers hold the world's only patents on chemical elements, for americium and curium. The original location of the first transuranium laboratory on the Berkeley campus (a few yards from the later site of Professor Seaborg's reserved "Nobel Laureate" parking space) is now a national historic landmark.

Laboratories in the United States, Russia, and Germany have been the most active in the synthesis of new elements. In 1994, nationalistic feelings invaded what should have been impartial decisions by the International Union of Pure and Applied Chemistry (IUPAC) regarding the official names for elements 101 and 109. In some cases, researchers from different countries had proposed different names for these elements based on where credit for their discovery was felt to be deserved. For example, the name "hahnium" was proposed for element 105 by American researchers, while the Russians preferred the more snappy "nielsbohrium." The American Chemical Society proposed to name element 106 seaborgium (Sg), but the IUPAC's nomenclature committee rejected the choice, objecting to the fact that Seaborg was still alive ("and they can prove it," he quipped). Outrage at this and some of the other naming decisions prompted many scientists to ignore the IUPAC's recommended name for 106, rutherfordium, and to continue to use seaborgium. In 1997, the IUPAC reversed its decision and endorsed Sg, saving the chemical literature from future confusion caused by different naming practices in the scientific journals and conferences of different countries.

If Professor Seaborg had been nominated for a different honor—appearance on a U.S. postage stamp—the story would have had an unhappier ending. Although surely not as rare a commodity as the names of new chemical elements, United States stamps are not permitted to honor living individuals. Seaborg would have been the only person in the world who could have received mail addressed entirely in elements: Seaborgium, Lawrencium (for the Lawrence Berkeley Laboratory), Berkelium, Californium, Americium—and don't forget the ZIP code, 94720.

Additional information about Seaborg and his research is available through the Web site for this textbook.

*Lisa Saunders Boffa
Senior Chemist
Exxon Corporation*



The elements of Period 3. Properties progress (*left to right*) from solids (Na, Mg, Al, Si, P, S) to gases (Cl, Ar) and from the most metallic (Na) to the most nonmetallic (Ar).

***f*-Transition Elements.** Sometimes known as *inner transition elements*, these are elements in which electrons are being added to *f* orbitals. In these elements, the second from the outermost occupied shell is building from 18 to 32 electrons. All are metals. The *f*-transition elements are located between Groups IIIB and IVB in the periodic table. They are

First *f*-transition series (lanthanides): $_{58}\text{Ce}$ through $_{71}\text{Lu}$

Second *f*-transition series (actinides): $_{90}\text{Th}$ through $_{103}\text{Lr}$

The A and B designations for groups of elements in the periodic table are somewhat arbitrary, and they are reversed in some periodic tables. In another designation, the groups are numbered 1 through 18. The system used in this text is the one commonly used in the United States. Elements with the same group numbers, but with different letters, have relatively few similar properties. The origin of the A and B designations is the fact that some compounds of elements with the same group numbers have similar formulas but quite different properties, for example, NaCl (IA) and AgCl (IB), MgCl_2 (IIA) and ZnCl_2 (IIB). As we shall see, variations in the properties of the B groups across a row are not nearly as regular and dramatic as the variations observed across a row of A group elements.

The *outermost* electrons have the greatest influence on the properties of elements. Adding an electron to an *inner d* orbital results in less striking changes in properties than adding an electron to an *outer s* or *p* orbital.

In any atom the *outermost* electrons are those that have the highest value of the principal quantum number, *n*.

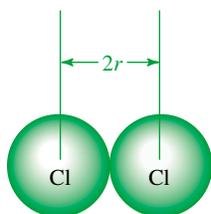
PERIODIC PROPERTIES OF THE ELEMENTS

Now we investigate the nature of periodicity. Knowledge of periodicity is valuable in understanding bonding in simple compounds. Many physical properties, such as melting points, boiling points, and atomic volumes, show periodic variations. For now, we describe the variations that are most useful in predicting chemical behavior. The variations in these properties depend on electron configurations, especially the configurations in the outermost occupied shell, and on how far away that shell is from the nucleus.

[www http://webbook.nist.gov](http://webbook.nist.gov)

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 8.9, Atomic Properties and Periodic Trends.

See the *Saunders Interactive General Chemistry CD-ROM*, Screen 8.10, Atomic Properties and periodic Trends: Size.



The radius of an atom, r , is taken as half of the distance between nuclei in *homonuclear* molecules such as Cl_2 .

6-2 ATOMIC RADII

In Section 5-16 we described individual atomic orbitals in terms of probabilities of distributions of electrons over certain regions in space. Similarly, we can visualize the total electron cloud that surrounds an atomic nucleus as somewhat indefinite. We cannot isolate a single atom and measure its diameter the way we can measure the diameter of a golf ball. For all practical purposes, the size of an individual atom cannot be uniquely defined. An indirect approach is required. The size of an atom is determined by its immediate environment, especially its interaction with surrounding atoms. By analogy, suppose we arrange some golf balls in an orderly array in a box. If we know how the balls are positioned, the number of balls, and the dimensions of the box, we can calculate the diameter of an individual ball. Application of this reasoning to solids and their densities leads us to values for the atomic sizes of many elements. In other cases, we derive atomic radii from the observed distances between atoms that are combined with one another. For example, the distance between atomic centers (nuclei) in the Cl_2 molecule is measured to be 2.00 \AA . This suggests that the radius of *each* Cl atom is half the interatomic distance, or 1.00 \AA . We collect the data obtained from many such measurements to indicate the *relative* sizes of individual atoms.

The top of Figure 6-1 displays the relative sizes of atoms of the representative elements and the noble gases. It shows the periodicity in atomic radii. (The ionic radii at the bottom of Figure 6-1 are discussed in Section 6-5.)

The **effective nuclear charge**, Z_{eff} , experienced by an electron in an outer shell is less than the actual nuclear charge, Z . This is because the *attraction* of outer-shell electrons by the nucleus is partly counterbalanced by the repulsion of these outer-shell electrons by electrons in inner shells. We say that the electrons in inner shells *screen*, or *shield*, electrons in outer shells from the full effect of the nuclear charge. This concept of a **screening**, or **shielding**, **effect** helps us understand many periodic trends in atomic properties.

Consider an atom of lithium; it has two electrons in a filled shell, $1s^2$, and one electron in the $2s$ orbital, $2s^1$. The electron in the $2s$ orbital is fairly effectively screened from the nucleus by the two electrons in the filled $1s$ orbital, so the $2s$ electron does not “feel” the full $3+$ charge of the nucleus. The effective nuclear charge, Z_{eff} , experienced by the electron in the $2s$ orbital, however, is not 1 (3 minus 2) either. The electron in the outer shell of lithium has some probability of being found close to the nucleus (see Figure 5-20). We say that, to some extent, it *penetrates* the region of the $1s$ electrons; that is, the $1s$ electrons do not completely shield the outer-shell electrons from the nucleus. The electron in the $2s$ shell “feels” an effective nuclear charge a little larger than $1+$. Sodium, element number 11, has ten electrons in inner shells, $1s^2 2s^2 2p^6$, and one electron in an outer shell, $3s^1$. The ten inner-shell electrons of the sodium atom screen (shield) the outer-shell electron somewhat from the nucleus, counteracting some of the $11+$ nuclear charge. But the $3s$ electron of sodium penetrates the inner shells to a significant extent, so the effective nuclear charge felt by the outermost ($3s$) electron is actually greater than it is for lithium ($2s$). The somewhat increased attraction for the outermost electron in sodium is outweighed, however, by the fact that the “outer” electron in a sodium atom is in the third shell, whereas in lithium it is in the second shell. Recall from Chapter 5 that the third shell ($n = 3$) is farther from the nucleus than the second shell ($n = 2$). Thus, we see why sodium atoms are larger than lithium atoms. Similar reasoning explains why potassium atoms are larger than sodium atoms and why the sizes of the elements in each column of the periodic table are related in a similar way.

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
Atomic radii							
H 0.37							He 0.31
Li 1.52	Be 1.12	B 0.85	C 0.77	N 0.75	O 0.73	F 0.72	Ne 0.71
Na 1.86	Mg 1.60	Al 1.43	Si 1.18	P 1.10	S 1.03	Cl 1.00	Ar 0.98
K 2.27	Ca 1.97	Ga 1.35	Ge 1.22	As 1.20	Se 1.19	Br 1.14	Kr 1.12
Rb 2.48	Sr 2.15	In 1.67	Sn 1.40	Sb 1.40	Te 1.42	I 1.33	Xe 1.31
Cs 2.65	Ba 2.22	Tl 1.70	Pb 1.46	Bi 1.50	Po 1.68	At 1.40	Rn 1.41

Atomic radii are often stated in **angstroms** ($1 \text{ \AA} = 10^{-10} \text{ m}$) or in the SI units **nanometers** ($1 \text{ nm} = 10^{-9} \text{ m}$) or **picometers** ($1 \text{ pm} = 10^{-12} \text{ m}$). To convert from \AA to nm, move the decimal point to the left one place ($1 \text{ \AA} = 0.1 \text{ nm}$). For example, the atomic radius of Li is 1.52 \AA , or 0.152 nm .

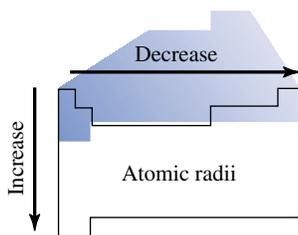
Ionic radii							
Li ⁺ 0.90	Be ²⁺ 0.59			N ³⁻ 1.71	O ²⁻ 1.26	F ⁻ 1.19	
Na ⁺ 1.16	Mg ²⁺ 0.85	Al ³⁺ 0.68			S ²⁻ 1.70	Cl ⁻ 1.67	
K ⁺ 1.52	Ca ²⁺ 1.14	Ga ³⁺ 0.76			Se ²⁻ 1.84	Br ⁻ 1.82	
Rb ⁺ 1.66	Sr ²⁺ 1.32	In ³⁺ 0.94			Te ²⁻ 2.07	I ⁻ 2.06	
Cs ⁺ 1.81	Ba ²⁺ 1.49	Tl ³⁺ 1.03					



 2 \AA

Figure 6-1 (Top) Atomic radii of the A group (representative) elements and the noble gases, in angstroms, \AA (Section 6-2). Atomic radii *increase going down a group* because electrons are being added to shells farther from the nucleus. Atomic radii *decrease from left to right within a given period* owing to increasing effective nuclear charge. Hydrogen atoms are the smallest and cesium atoms are the largest naturally occurring atoms.

(Bottom) Sizes of ions of the A group elements, in angstroms (Section 6-5). Positive ions (cations) are always *smaller* than the neutral atoms from which they are formed. Negative ions (anions) are always *larger* than the neutral atoms from which they are formed.



General trends in atomic radii of A group elements with position in the periodic table.

Within a family (vertical group on the periodic table) of representative elements, atomic radii increase from top to bottom as electrons are added to shells farther from the nucleus.

As we move *across* the periodic table, atoms become smaller due to increasing effective nuclear charges. Consider the elements B ($Z = 5$, $1s^2 2s^2 2p^1$) to F ($Z = 9$, $1s^2 2s^2 2p^5$). In B there are two electrons in a noble gas configuration, $1s^2$, and three electrons in the second shell, $2s^2 2p^1$. The two electrons in the noble gas configuration fairly effectively screen out the effect of two protons in the nucleus. So the electrons in the second shell of B “feel” a greater effective nuclear charge than do those of Be. By similar arguments, we see that in carbon ($Z = 6$, $1s^2 2s^2 2p^2$) the electrons in the second shell “feel” an effective nuclear charge greater than those of B. So we expect C atoms to be smaller than B atoms, and they are. In nitrogen ($Z = 7$, $1s^2 2s^2 2p^3$), the electrons in the second shell “feel” an even greater effective nuclear charge, and so N atoms are smaller than C atoms.

As we move from left to right *across a period* in the periodic table, atomic radii of representative elements *decrease* as a proton is added to the nucleus and an electron is added to a particular shell.

For the transition elements, the variations are not so regular because electrons are being added to an inner shell. All transition elements have smaller radii than the preceding Group IA and IIA elements in the same period.

EXAMPLE 6-1 Trends in Atomic Radii

Arrange the following elements in order of increasing atomic radii. Justify your order.

Cs, F, K, Cl

Plan

Both K and Cs are Group IA metals, whereas F and Cl are halogens (VIIA nonmetals). Figure 6-1 shows that atomic radii increase as we descend a group, so $K < Cs$ and $F < Cl$. Atomic radii decrease from left to right.

Solution

The order of increasing atomic radii is $F < Cl < K < Cs$.

You should now work Exercise 18.

6-3 IONIZATION ENERGY

The **first ionization energy** (IE_1), also called *first ionization potential*, is

the minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom to form an ion with a $1+$ charge.

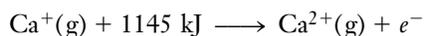
TABLE 6-1 First Ionization Energies (kJ/mol of atoms) of Some Elements

H 1312																He 2372	
Li 520	Be 899											B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
Na 496	Mg 738											Al 578	Si 786	P 1012	S 1000	Cl 1251	Ar 1521
K 419	Ca 599	Sc 631	Ti 658	V 650	Cr 652	Mn 717	Fe 759	Co 758	Ni 757	Cu 745	Zn 906	Ga 579	Ge 762	As 947	Se 941	Br 1140	Kr 1351
Rb 403	Sr 550	Y 617	Zr 661	Nb 664	Mo 685	Tc 702	Ru 711	Rh 720	Pd 804	Ag 731	Cd 868	In 558	Sn 709	Sb 834	Te 869	I 1008	Xe 1170
Cs 377	Ba 503	La 538	Hf 681	Ta 761	W 770	Re 760	Os 840	Ir 880	Pt 870	Au 890	Hg 1007	Tl 589	Pb 715	Bi 703	Po 812	At 890	Rn 1037

For calcium, for example, the first ionization energy, IE_1 , is 590 kJ/mol:



The **second ionization energy** (IE_2) is the amount of energy required to remove the second electron. For calcium, it may be represented as



For a given element, IE_2 is *always greater than* IE_1 because it is always more difficult to remove an electron from a positively charged ion than from the corresponding neutral atom. Table 6-1 gives first ionization energies.

Ionization energies measure how tightly electrons are bound to atoms. Ionization always requires energy to remove an electron from the attractive force of the nucleus. Low ionization energies indicate ease of removal of electrons, and hence ease of positive ion (cation) formation. Figure 6-2 shows a plot of first ionization energy versus atomic number for several elements.

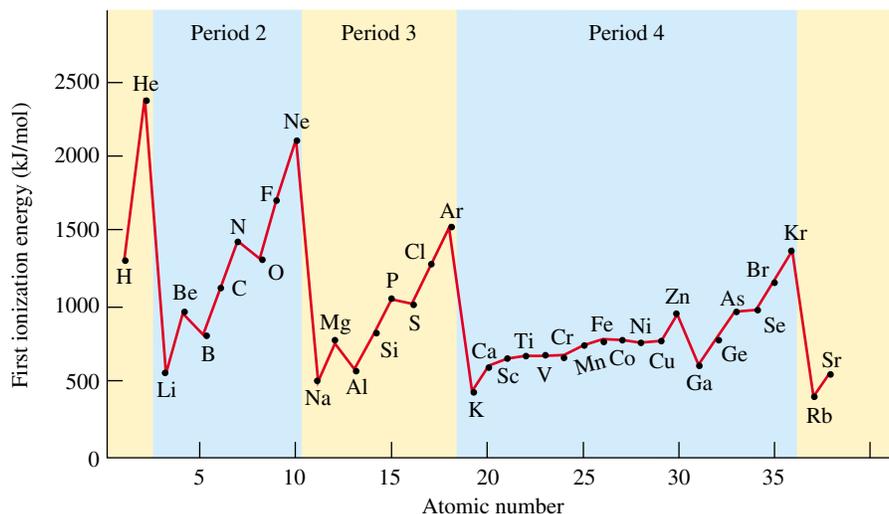
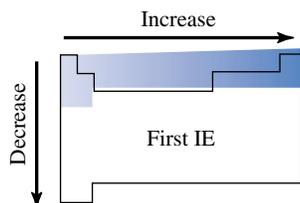


Figure 6-2 A plot of first ionization energies for the first 38 elements versus atomic number. The noble gases have very high first ionization energies, and the IA metals have low first ionization energies. Note the similarities in the variations for the Period 2 elements, 3 through 10, to those for the Period 3 elements, 11 through 18, as well as for the later A group elements. Variations for B group elements are not nearly so pronounced as those for A group elements.



General trends in first ionization energies of A group elements with position in the periodic table. Exceptions occur at Groups IIIA and VIA.

By Coulomb's Law, $F \propto \frac{(q^+)(q^-)}{d^2}$,

the attraction for the outer shell electrons is directly proportional to the *effective* charges and inversely proportional to the *square* of the distance between the charges. Even though the effective nuclear charge increases going down a group, the greatly increased size results in a weaker net attraction for the outer electrons and thus in a lower first ionization energy.

As one goes across a period on the periodic table, the slight breaks in the increasing ionization energies occur between Groups IIA and IIIA (electrons first enter the np subshell) and again between Groups VA and VIA (electrons are first paired in the np subshell).

Elements with low ionization energies (IE) lose electrons easily to form cations.

We see that in each period of Figure 6-2, the noble gases have the highest first ionization energies. This should not be surprising, because the noble gases are known to be very unreactive elements. It requires more energy to remove an electron from a helium atom (slightly less than 4.0×10^{-18} J/atom, or 2372 kJ/mol) than to remove one from a neutral atom of any other element.



The Group IA metals (Li, Na, K, Rb, Cs) have very low first ionization energies. Each of these elements has only one electron in its outermost shell ($. . . ns^1$), and they are the largest atoms in their periods. The first electron added to a shell is easily removed to form a noble gas configuration. As we move down the group, the first ionization energies become smaller. The force of attraction of the positively charged nucleus for electrons decreases as the square of the distance between them increases. So as atomic radii increase in a given group, first ionization energies decrease because the outermost electrons are farther from the nucleus.

Effective nuclear charge, Z_{eff} , increases going from left to right across a period. The increase in effective nuclear charge causes the outermost electrons to be held more tightly, making them harder to remove. The first ionization energies therefore generally *increase* from left to right across the periodic table. The reason for the trend in first ionization energies is the same as that used in Section 6-2 to explain trends in atomic radii. The first ionization energies of the Group IIA elements (Be, Mg, Ca, Sr, Ba) are significantly higher than those of the Group IA elements in the same periods. This is because the Group IIA elements have higher Z_{eff} values and smaller atomic radii. Thus, their outermost electrons are held more tightly than those of the neighboring IA metals. It is harder to remove an electron from a pair in the filled outermost s orbitals of the Group IIA elements than to remove the single electron from the half-filled outermost s orbitals of the Group IA elements.

The first ionization energies for the Group IIIA elements (B, Al, Ga, In, Tl) are exceptions to the general horizontal trends. They are *lower* than those of the IIA elements in the same periods because the IIIA elements have only a single electron in their outermost p orbitals. Less energy is required to remove the first p electron than the second s electron from the outermost shell, because the p orbital is at a higher energy (less stable) than an s orbital within the same shell (n value).

Going from Groups IIIA to VA, electrons are going singly into separate np orbitals, where they do not shield one another significantly. The general left-to-right increase in IE_1 for each period is interrupted by a dip between Groups VA (N, P, As, Sb, Bi) and VIA elements (O, S, Se, Te, Po). Presumably, this behavior is because the fourth np electron in the Group VIA elements is paired with another electron in the same orbital, so it experiences greater repulsion than it would in an orbital by itself. This increased repulsion apparently outweighs the increase in Z_{eff} , so the fourth np electron in an outer shell (Group VIA elements) is somewhat easier to remove (lower ionization energy) than is the third np electron in an outer shell (Group VA elements). After the dip between Groups VA and VIA, the importance of the increasing Z_{eff} outweighs the repulsion of electrons needing to be paired, and the general left-to-right increases in first ionization energies resume.

Knowledge of the relative values of ionization energies assists us in predicting whether an element is likely to form ionic or molecular (covalent) compounds. Elements with low ionization energies form ionic compounds by losing electrons to form **cations** (positively

charged ions). Elements with intermediate ionization energies generally form molecular compounds by sharing electrons with other elements. Elements with very high ionization energies, such as Groups VIA and VIIA, often gain electrons to form **anions** (negatively charged ions).

One factor that favors an atom of a *representative* element forming a monatomic ion in a compound is the formation of a stable noble gas electron configuration. Energy considerations are consistent with this observation. For example, as one mole of Li from Group IA forms one mole of Li^+ ions, it absorbs 520 kJ per mole of Li atoms. The IE_2 value is 14 times greater, 7298 kJ/mol, and is prohibitively large for the formation of Li^{2+} ions under ordinary conditions. For Li^{2+} ions to form, an electron would have to be removed from the filled first shell. We recognize that this is unlikely. The other alkali metals behave in the same way, for similar reasons.

The first two ionization energies of Be (Group IIA) are 899 and 1757 kJ/mol, but IE_3 is more than eight times larger, 14,849 kJ/mol. So Be forms Be^{2+} ions, but not Be^{3+} ions. The other alkaline earth metals—Mg, Ca, Sr, Ba, and Ra—behave in a similar way. Only the lower members of Group IIIA, beginning with Al, form 3+ ions. Bi and some *d*- and *f*-transition metals do so, too. We see that the magnitudes of successive ionization energies support the ideas of electron configurations discussed in Chapter 5.

Due to the high energy required, *simple monatomic cations with charges greater than 3+ do not form under ordinary circumstances.*

EXAMPLE 6-2 Trends in First IEs

Arrange the following elements in order of increasing first ionization energy. Justify your order.

Na, Mg, Al, Si

Plan

Table 6-1 shows that first ionization energies generally increase from left to right in the same period, but there are exceptions at Groups IIIA and VIA. Al is a IIIA element with only one electron in its outer *p* orbitals, $1s^2 2s^2 2p^6 3s^2 3p^1$.

Solution

There is a slight dip at Group IIIA in the plot of first IE versus atomic number (see Figure 6-2). The order of increasing first ionization energy is $\text{Na} < \text{Al} < \text{Mg} < \text{Si}$.

You should now work Exercise 26.

6-4 ELECTRON AFFINITY

The **electron affinity (EA)** of an element may be defined as

the amount of energy *absorbed* when an electron is added to an isolated gaseous atom to form an ion with a 1− charge.

The convention is to assign a positive value when energy is absorbed and a negative value when energy is released. Most elements have no affinity for an additional electron and

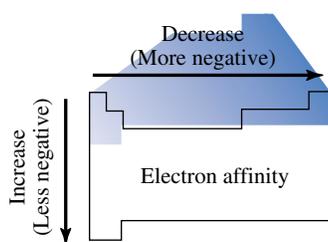
Here is one reason why trends in ionization energies are important.

Noble gas electron configurations are stable only for ions in *compounds*. In fact, $\text{Li}^+(\text{g})$ is less stable than $\text{Li}(\text{g})$ by 520 kJ/mol.

 See the Saunders Interactive General Chemistry CD-ROM, Screen 8.13, Electron Affinity.

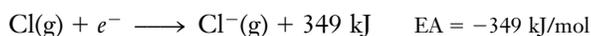
This is consistent with thermodynamic convention.

The value of EA for Cl can also be represented as -5.79×10^{-19} J/atom or -3.61 eV/atom. The electron volt (eV) is a unit of energy ($1 \text{ eV} = 1.6022 \times 10^{-19}$ J).



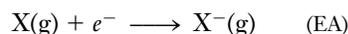
General trends in electron affinities of A group elements with position in the periodic table. There are many exceptions.

thus have an electron affinity (EA) equal to zero. We can represent the electron affinities of helium and chlorine as

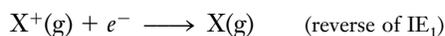


The first equation tells us that helium will not add an electron. The second equation tells us that when one mole of gaseous chlorine atoms gain one electron each to form gaseous chloride ions, 349 kJ of energy is *released* (*exothermic*). Figure 6-3 shows a plot of electron affinity versus atomic number for several elements.

Electron affinity involves the *addition* of an electron to a neutral gaseous atom. The process by which a neutral atom X gains an electron (EA),



is *not* the reverse of the ionization process,



The first process begins with a neutral atom, whereas the second begins with a positive ion. Thus, IE_1 and EA are *not* simply equal in value with the signs reversed. We see from Figure 6-3 that electron affinities generally become more negative from left to right across a row in the periodic table (excluding the noble gases). This means that most representative elements in Groups IA to VIIA show a greater attraction for an extra electron from left to right. Halogen atoms, which have the outer electron configuration ns^2np^5 , have the most negative electron affinities. They form stable anions with noble gas configurations, $\dots ns^2np^6$, by gaining one electron.

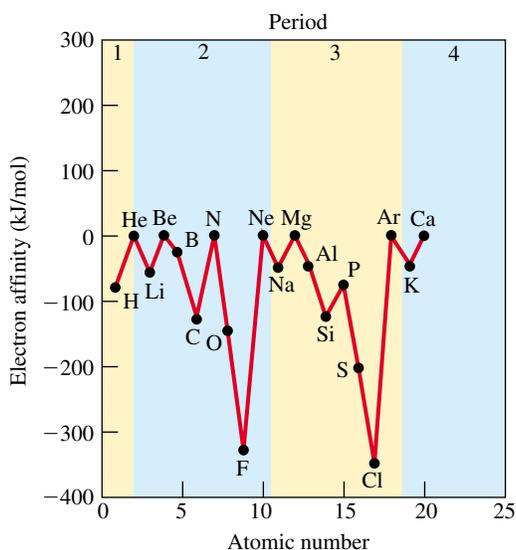


Figure 6-3 A plot of electron affinity versus atomic number for the first 20 elements. The *general* horizontal trend is that electron affinities become more negative (more energy is released as an extra electron is added) from Group IA through Group VIIA for a given period. Exceptions occur at the IIA and VA elements.

TABLE 6-2 *Electron Affinity Values (kJ/mol) of Some Elements**

1	H -73								He 0
2	Li -60	Be (-0)		B -29	C -122	N 0	O -141	F -328	Ne 0
3	Na -53	Mg (-0)	Cu -118	Al -43	Si -134	P -72	S -200	Cl -349	Ar 0
4	K -48	Ca (-0)	Ag -125	Ga -29	Ge -119	As -78	Se -195	Br -324	Kr 0
5	Rb -47	Sr (-0)	Au -282	In -29	Sn -107	Sb -101	Te -190	I -295	Xe 0
6	Cs -45	Ba (-0)		Tl -19	Pb -35	Bi -91			

*Estimated values are in parentheses.

Elements with very negative electron affinities gain electrons easily to form negative ions (anions).

“Electron affinity” is a precise and quantitative term, like “ionization energy,” but it is difficult to measure. Table 6-2 shows electron affinities for several elements.

For many reasons, the variations in electron affinities are not regular across a period. The general trend is: the electron affinities of the elements become more negative from left to right in each period. Noteworthy exceptions are the elements of Groups IIA and VA, which have less negative values than the trends suggest (see Figure 6-3). It is very difficult to add an electron to a IIA metal atom because its outer s subshell is filled. The values for the VA elements are slightly less negative than expected because they apply to the addition of an electron to a half-filled set of np orbitals ($ns^2np^3 \rightarrow ns^2np^4$), which requires pairing. The resulting repulsion overcomes the increased attractive force of the nucleus.

Energy is always required to bring a negative charge (electron) closer to another negative charge (anion). So the addition of a second electron to a $1-$ anion to form an ion with a $2-$ charge is always endothermic. Thus, electron affinities of *anions* are always positive.

This reasoning is similar to that used to explain the low IE_1 values for Group VIA elements.

EXAMPLE 6-3 Trends in EAs

Arrange the following elements in order of increasing values of electron affinity, that is, from most negative to least negative.

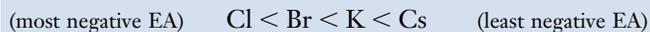


Plan

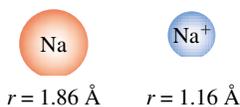
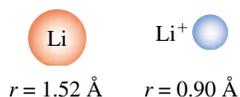
Table 6-2 shows that electron affinity values generally become more negative from left to right across a period, with major exceptions at Groups IIA (Be) and VA (N). They generally become more negative from bottom to top.

Solution

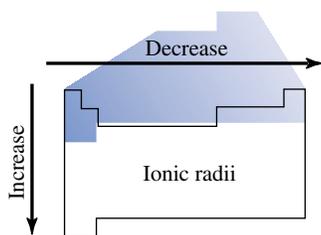
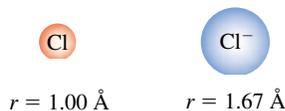
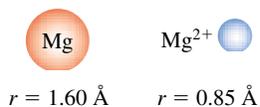
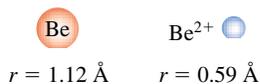
The order of increasing values of electron affinity is



You should now work Exercises 32 and 33.



The nuclear charge remains constant when the ion is formed.

**6-5 IONIC RADII**

Many elements on the left side of the periodic table react with other elements by *losing* electrons to form positively charged ions. Each of the Group IA elements (Li, Na, K, Rb, Cs) has only one electron in its outermost shell (electron configuration . . . ns^1). These elements react with other elements by losing one electron to attain noble gas configurations. They form the ions Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺. A neutral lithium atom, Li, contains three protons in its nucleus and three electrons, with its outermost electron in the $2s$ orbital. A lithium ion, Li⁺, however, contains three protons in its nucleus but only two electrons, both in the $1s$ orbital. So a Li⁺ ion is much smaller than a neutral Li atom (see figure in the margin). Likewise, a sodium ion, Na⁺, is considerably smaller than a sodium atom, Na. The relative sizes of atoms and common ions of some representative elements are shown in Figure 6-1.

Isoelectronic species have the same number of electrons. We see that the ions formed by the Group IIA elements (Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺) are significantly smaller than the *isoelectronic* ions formed by the Group IA elements in the same period. The radius of the Li⁺ ion is 0.90 Å, whereas the radius of the Be²⁺ ion is only 0.59 Å. This is what we should expect. A beryllium ion, Be²⁺, is formed when a beryllium atom, Be, loses both of its $2s$ electrons while the $4+$ nuclear charge remains constant. We expect the $4+$ nuclear charge in Be²⁺ to attract the remaining two electrons quite strongly. Comparison of the ionic radii of the IIA elements with their atomic radii indicates the validity of our reasoning. Similar reasoning indicates that the ions of the Group IIIA metals (Al³⁺, Ga³⁺, In³⁺, Tl³⁺) should be even smaller than the ions of Group IA and Group IIA elements in the same periods.

Now consider the Group VIIA elements (F, Cl, Br, I). These have the outermost electron configuration . . . ns^2np^5 . These elements can completely fill their outermost p orbitals by *gaining* one electron to attain noble gas configurations. Thus, when a fluorine atom (with seven electrons in its outer shell) gains one electron, it becomes a fluoride ion, F⁻, with eight electrons in its outer shell. These eight electrons repel one another more strongly than the original seven, so the electron cloud expands. The F⁻ ion is much larger than the neutral F atom (see figure in the margin). Similar reasoning indicates that a chloride ion, Cl⁻, should be larger than a neutral chlorine atom, Cl. Observed ionic radii (see Figure 6-1) verify this prediction.

Comparing the sizes of an oxygen atom (Group VIA) and an oxide ion, O²⁻, again we find that the negatively charged ion is larger than the neutral atom. The oxide ion is also larger than the isoelectronic fluoride ion because the oxide ion contains ten electrons held

◀ General trends in ionic radii of A group elements with position in the periodic table.

by a nuclear charge of only 8+, whereas the fluoride ion has ten electrons held by a nuclear charge of 9+. Comparison of radii is not a simple issue when we try to compare atoms, positive and negative ions, and ions with varying charge. Sometimes we compare atoms to their ions, atoms or ions that are vertically or horizontally positioned on the periodic table, or isoelectronic species. The following guidelines are often considered in the order given.

1. Simple positively charged ions (cations) are always smaller than the neutral atoms from which they are formed.
2. Simple negatively charged ions (anions) are always larger than the neutral atoms from which they are formed.
3. The sizes of cations decrease from left to right across a period.
4. The sizes of anions decrease from left to right across a period.
5. Within an isoelectronic series, radii decrease with increasing atomic number because of increasing nuclear charge.
6. Both cation and anion sizes increase going down a group.

Large ring compounds can selectively trap ions based on the ability of various ions to fit within a cavity in the large compound. This results in selectivity such as occurs in transport across membranes in biological systems.

 See the *Saunders Interactive General Chemistry CD-ROM*, Screen 8.11, Atomic Properties and Periodic Trends: Ion Sizes.

An isoelectronic series of ions

						
Ionic radius (Å)	1.71	1.26	1.19	1.16	0.85	0.68
No. of electrons	10	10	10	10	10	10
Nuclear charge	+7	+8	+9	+11	+12	+13

EXAMPLE 6-4 Trends in Ionic Radii

Arrange the following ions in order of increasing ionic radii: (a) Ca^{2+} , K^+ , Al^{3+} ; (b) Se^{2-} , Br^- , Te^{2-} .

Plan

Some of the pairs of ions are isoelectronic, so we can compare their sizes on the basis of nuclear charges. Other comparisons can be made based on the outermost occupied shell (highest value of n).

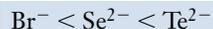
Solution

(a) Ca^{2+} and K^+ are isoelectronic (18 electrons each) with an outer-shell electron configuration of $3s^23p^6$. Because Ca^{2+} has a higher nuclear charge (20+) than K^+ (19+), Ca^{2+} holds its 18 electrons more tightly, and Ca^{2+} is smaller than K^+ . Al^{3+} has electrons only in the second main shell (outer-shell electron configuration of $2s^22p^6$), so it is smaller than either of the other two ions.



(b) Br^- and Se^{2-} are isoelectronic (36 electrons each) with an outer-shell electron configuration of $4s^24p^6$. Because Br^- has a higher nuclear charge (35+) than Se^{2-} (34+), Br^- holds its

36 electrons more tightly, and Br^- is smaller than Se^{2-} . Te^{2-} has electrons in the fifth main shell (outer configuration of $5s^25p^6$), so it is larger than either of the other two ions.



You should now work Exercises 38 and 40.

6-6 ELECTRONEGATIVITY

Because the noble gases form few compounds, they are not included in this discussion.

The **electronegativity (EN)** of an element is a measure of the relative tendency of an atom to attract electrons to itself *when it is chemically combined with another atom*.

Elements with high electronegativities (nonmetals) often gain electrons to form anions. Elements with low electronegativities (metals) often lose electrons to form cations.

Electronegativities of the elements are expressed on a somewhat arbitrary scale, called the Pauling scale (Table 6-3). The electronegativity of fluorine (4.0) is higher than that of any other element. This tells us that when fluorine is chemically bonded to other elements,

TABLE 6-3 *Electronegativity Values of the Elements^a*

IA																		VIIIA						
1	1 H 2.1																	2 He						
2	3 Li 1.0	4 Be 1.5																	5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0	10 Ne
3	11 Na 1.0	12 Mg 1.2																	13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3.0	18 Ar
4	19 K 0.9	20 Ca 1.0	21 Sc 1.3	22 Ti 1.4	23 V 1.5	24 Cr 1.6	25 Mn 1.6	26 Fe 1.7	27 Co 1.7	28 Ni 1.8	29 Cu 1.8	30 Zn 1.6	31 Ga 1.7	32 Ge 1.9	33 As 2.1	34 Se 2.4	35 Br 2.8	36 Kr						
5	37 Rb 0.9	38 Sr 1.0	39 Y 1.2	40 Zr 1.3	41 Nb 1.5	42 Mo 1.6	43 Tc 1.7	44 Ru 1.8	45 Rh 1.8	46 Pd 1.8	47 Ag 1.6	48 Cd 1.6	49 In 1.6	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5	54 Xe						
6	55 Cs 0.8	56 Ba 1.0	57 La 1.1	72 Hf 1.3	73 Ta 1.4	74 W 1.5	75 Re 1.7	76 Os 1.9	77 Ir 1.9	78 Pt 1.8	79 Au 1.9	80 Hg 1.7	81 Tl 1.6	82 Pb 1.7	83 Bi 1.8	84 Po 1.9	85 At 2.1	86 Rn						
7	87 Fr 0.8	88 Ra 1.0	89 Ac 1.1																					
				58 Ce 1.1	59 Pr 1.1	60 Nd 1.1	61 Pm 1.1	62 Sm 1.1	63 Eu 1.1	64 Gd 1.1	65 Tb 1.1	66 Dy 1.1	67 Ho 1.1	68 Er 1.1	69 Tm 1.1	70 Yb 1.0	71 Lu 1.2							
				90 Th 1.2	91 Pa 1.3	92 U 1.5	93 Np 1.3	94 Pu 1.3	95 Am 1.3	96 Cm 1.3	97 Bk 1.3	98 Cf 1.3	99 Es 1.3	100 Fm 1.3	101 Md 1.3	102 No 1.3	103 Lr 1.5							

^aElectronegativity values are given at the bottoms of the boxes.

it has a greater tendency to attract electron density to itself than does any other element. Oxygen is the second most electronegative element.

For the representative elements, electronegativities usually increase from left to right across periods and decrease from top to bottom within groups.

Variations among the transition metals are not as regular. In general, both ionization energies and electronegativities are low for elements at the lower left of the periodic table and high for those at the upper right.

EXAMPLE 6-5 Trends in ENs

Arrange the following elements in order of increasing electronegativity.

B, Na, F, O

Plan

Table 6-3 shows that electronegativities increase from left to right across a period and decrease from top to bottom within a group.

Solution

The order of increasing electronegativity is $\text{Na} < \text{B} < \text{O} < \text{F}$.

You should now work Exercise 44.

Although the electronegativity scale is somewhat arbitrary, we can use it with reasonable confidence to make predictions about bonding. Two elements with quite different electronegativities (a metal and a nonmetal) tend to react with each other to form ionic compounds. The less electronegative element gives up its electron(s) to the more electronegative element. Two nonmetals with similar electronegativities tend to form covalent bonds with each other. That is, they share their electrons. In this sharing, the more electronegative element attains a greater share. This is discussed in detail in Chapters 7 and 8.

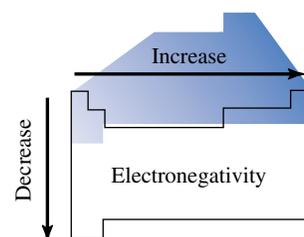
CHEMICAL REACTIONS AND PERIODICITY

Now we will illustrate the periodicity of chemical properties by considering some reactions of hydrogen, oxygen, and their compounds. We choose to discuss hydrogen and oxygen because, of all the elements, they form the most kinds of compounds with other elements. Additionally, compounds of hydrogen and oxygen are very important in such diverse phenomena as all life processes and most corrosion processes.

6-7 HYDROGEN AND THE HYDRIDES

Hydrogen

Elemental hydrogen is a colorless, odorless, tasteless diatomic gas with the lowest molecular weight and density of any known substance. Discovery of the element is attributed to the Englishman Henry Cavendish (1731–1810), who prepared it in 1766 by passing steam through a red-hot gun barrel (mostly iron) and by the reaction of acids with active

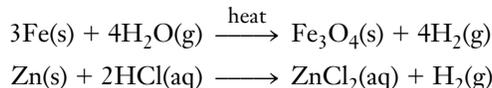


General trends in electronegativities of A group elements with position in the periodic table.

Ionization energy (Section 6-3) and electron affinity (Section 6-4) are precise quantitative concepts. We find, however, that the more qualitative concept of *electronegativity* is more useful in describing chemical bonding.

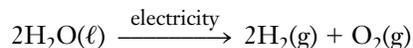
The name “hydrogen” means “water former.”

metals. The latter is still the method commonly used for the preparation of small amounts of H_2 in the laboratory. In each case, H_2 is liberated by a displacement (and redox) reaction, of the kind described in Section 4-8. (See the activity series, Table 4-12.)

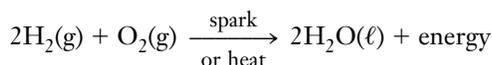


Can you write the net ionic equation for the reaction of Zn with HCl(aq)?

Hydrogen also can be prepared by electrolysis of water.



In the future, if it becomes economical to convert solar energy into electrical energy that can be used to electrolyze water, H_2 could become an important fuel (although the dangers of storage and transportation would have to be overcome). The *combustion* of H_2 liberates a great deal of heat. **Combustion** is the highly exothermic combination of a substance with oxygen, usually with a flame. (See Section 6-8, Combustion Reactions.)

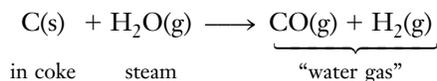


This is the reverse of the decomposition of H_2O .

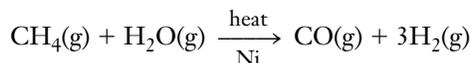
Hydrogen is no longer used in blimps and dirigibles. It has been replaced by helium, which is slightly denser, nonflammable, and much safer.

Hydrogen is very flammable; it was responsible for the Hindenburg airship disaster in 1937. A spark is all it takes to initiate the **combustion reaction**, which is exothermic enough to provide the heat necessary to sustain the reaction.

Hydrogen is prepared by the “water gas reaction,” which results from the passage of steam over white-hot coke (impure carbon, a nonmetal) at 1500°C . The mixture of products commonly called “water gas” is used industrially as a fuel. Both components, CO and H_2 , undergo combustion.



Vast quantities of hydrogen are produced commercially each year by a process called *steam cracking*. Methane reacts with steam at 830°C in the presence of a nickel catalyst.

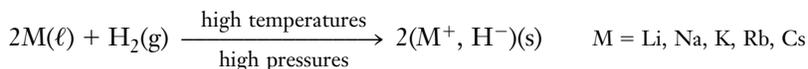


Reactions of Hydrogen and Hydrides

The use of the term “hydride” does not necessarily imply the presence of the hydride ion, H^- .

Atomic hydrogen has the $1s^1$ electron configuration. It reacts with metals and with other nonmetals to form binary compounds called **hydrides**. These can be (a) **ionic hydrides**, which contain hydride ions, H^- , formed when hydrogen gains one electron per atom from an active metal; or (2) **molecular hydrides**, in which hydrogen shares electrons with an atom of another nonmetal.

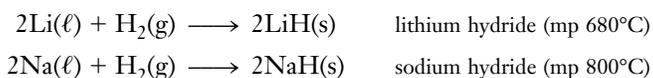
The ionic or molecular character of the binary compounds of hydrogen depends on the position of the other element in the periodic table (Figure 6-4). The reactions of H_2 with the *alkali* (IA) and the heavier (more active) *alkaline earth* (IIA) *metals* result in solid *ionic hydrides*. The reaction with the molten (liquid) IA metals may be represented in general terms as



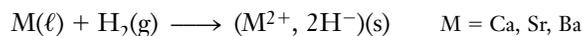
IA	IIA	IIIA	IVA	VA	VIA	VIIA
LiH	BeH ₂	B ₂ H ₆	CH ₄	NH ₃	H ₂ O	HF
NaH	MgH ₂	(AlH ₃) _x	SiH ₄	PH ₃	H ₂ S	HCl
KH	CaH ₂	Ga ₂ H ₆	GeH ₄	AsH ₃	H ₂ Se	HBr
RbH	SrH ₂	InH ₃	SnH ₄	SbH ₃	H ₂ Te	HI
CsH	BaH ₂	TlH	PbH ₄	BiH ₃	H ₂ Po	HAt

Figure 6-4 Common hydrides of the representative elements. The ionic hydrides are shaded blue, molecular hydrides are shaded red, and those of intermediate character are shaded purple.

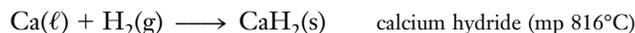
Thus, hydrogen combines with lithium to form lithium hydride and with sodium to form sodium hydride.



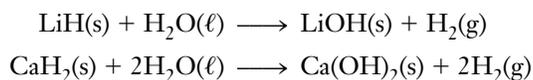
In general terms, the reactions of the heavier (more active) IIA metals may be represented as



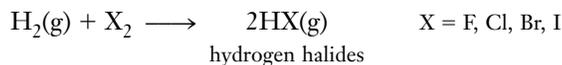
Thus, calcium combines with hydrogen to form calcium hydride:



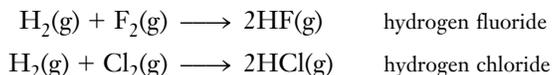
These *ionic hydrides are all basic* because they react with water to form hydroxide ions. When water is added by drops to lithium hydride, for example, lithium hydroxide and hydrogen are produced. The reaction of calcium hydride is similar.



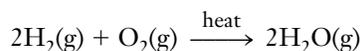
Hydrogen reacts with *nonmetals* to form binary *molecular hydrides*. For example, H₂ combines with the halogens to form colorless, gaseous hydrogen halides (Figure 6-5):



Specifically, hydrogen reacts with fluorine to form hydrogen fluoride and with chlorine to form hydrogen chloride:



Hydrogen combines with Group VIA elements to form molecular compounds:



The heavier members of this family also combine with hydrogen to form binary compounds that are gases at room temperature. Their formulas resemble that of water.

The ionic hydrides are named by naming the metal first, followed by “hydride.”

Ionic hydrides can serve as sources of hydrogen. They must be stored in environments free of moisture and O₂.

We show LiOH and Ca(OH)₂ as solids here because not enough water is available to act as a solvent.

The hydrogen halides are named by the word “hydrogen” followed by the stem for the halogen with an “-ide” ending.

These compounds are named:
 H₂O, hydrogen oxide (water)
 H₂S, hydrogen sulfide
 H₂Se, hydrogen selenide
 H₂Te, hydrogen telluride
 All except H₂O are *very* toxic.



Figure 6-5 Hydrogen, H_2 , burns in an atmosphere of pure chlorine, Cl_2 , to produce hydrogen chloride.

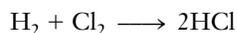
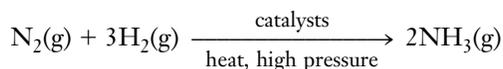


Figure 6-6 Ammonia may be applied directly to the soil as a fertilizer.

The primary industrial use of H_2 is in the synthesis of ammonia, a molecular hydride, by the Haber process (Section 17-7). Most of the NH_3 is used in liquid form as a fertilizer (Figure 6-6) or to make other fertilizers, such as ammonium nitrate, NH_4NO_3 , and ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$:



Many of the molecular (nonmetal) hydrides are acidic; their aqueous solutions contain hydrogen ions. These include HF, HCl, HBr, HI, H_2S , H_2Se , and H_2Te .

EXAMPLE 6-6 Predicting Products of Reactions

Predict the products of the reactions involving the reactants shown. Write a balanced formula unit equation for each.

- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \xrightarrow{\text{heat}}$
- $\text{K}(\ell) + \text{H}_2(\text{g}) \xrightarrow{\text{heat}}$
- $\text{NaH}(\text{s}) + \text{H}_2\text{O}(\ell)$ (excess) \longrightarrow

Plan

- Hydrogen reacts with the halogens (Group VIIA) to form hydrogen halides—in this example, HI.
- Hydrogen reacts with active metals to produce hydrides—in this case, KH.
- Active metal hydrides react with water to produce a metal hydroxide and H_2 .

Solution

- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \xrightarrow{\text{heat}} 2\text{HI}(\text{g})$
- $2\text{K}(\ell) + \text{H}_2(\text{g}) \xrightarrow{\text{heat}} 2\text{KH}(\text{s})$
- $\text{NaH}(\text{s}) + \text{H}_2\text{O}(\ell) \longrightarrow \text{NaOH}(\text{aq}) + \text{H}_2(\text{g})$

Remember that hydride ions, H^- , react with (reduce) water to produce OH^- ions and $\text{H}_2(\text{g})$.

EXAMPLE 6-7 *Ionic and Molecular Properties*

Predict the ionic or molecular character of the products in Example 6-6.

Plan

We refer to Figure 6-4, which displays the nature of hydrides.

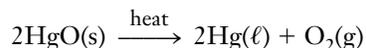
Solution

Reaction (a) is a reaction between hydrogen and another nonmetal. The product, HI, must be molecular. Reaction (b) is the reaction of hydrogen with an active Group IA metal. Thus, KH must be ionic. The products of reaction (c) are molecular $\text{H}_2(\text{g})$ and the strong base, NaOH, which is ionic.

You should now work Exercises 58 and 59.

6-8 OXYGEN AND THE OXIDES**Oxygen and Ozone**

Oxygen was discovered in 1774 by an English minister and scientist, Joseph Priestley (1733–1804). He observed the thermal decomposition of mercury(II) oxide, a red powder:



That part of the earth we see—land, water, and air—is approximately 50% oxygen by mass. About two thirds of the mass of the human body is due to oxygen in H_2O . Elemental oxygen, O_2 , is an odorless and colorless gas that makes up about 21% by volume of dry air. In the liquid and solid states it is pale blue. Oxygen is only slightly soluble in water; only about 0.04 gram dissolves in 1 liter of water at 25°C. This is sufficient to sustain fish and other marine organisms. Oxygen is obtained commercially by the fractional distillation of liquid air. The greatest single industrial use of O_2 is for oxygen-enrichment in blast furnaces for the conversion of pig iron (reduced, high-carbon iron) to steel.

Oxygen also exists in a second allotropic form, ozone, O_3 . Ozone is an unstable, pale blue gas at room temperature. It is formed by passing an electrical discharge through gaseous oxygen. Its unique, pungent odor is often noticed during electrical storms and in the vicinity of electrical equipment. Not surprisingly, its density is about $1\frac{1}{2}$ times that of O_2 . At -112°C it condenses to a deep blue liquid. It is a very strong oxidizing agent. As a concentrated gas or a liquid, ozone can easily decompose explosively:



Oxygen atoms, or **radicals**, are intermediates in this exothermic decomposition of O_3 to O_2 . They act as strong oxidizing agents in such applications as destroying bacteria in water purification.

The ozone molecule is angular (page 51). The two oxygen–oxygen bond lengths (1.28 Å) are identical and are intermediate between typical single and double bond lengths.

Reactions of Oxygen and the Oxides

Oxygen forms oxides by direct combination with all other elements except the noble gases and noble (unreactive) metals (Au, Pd, Pt). **Oxides** are binary compounds that contain oxygen. Although such reactions are generally very exothermic, many proceed quite slowly

The name “oxygen” means “acid former.”

Liquid O_2 is used as an oxidizer for rocket fuels. O_2 also is used in the health fields for oxygen-enriched air.

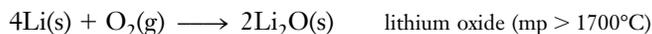
Allotropes are different forms of the same element in the same physical state (Section 2-2).

A *radical* is a species containing one or more unpaired electrons; many radicals are very reactive.

and require heating to supply the energy necessary to break the strong bonds in O_2 molecules. Once these reactions are initiated, most release more than enough energy to be self-sustaining and sometimes become “red hot.”

Reactions of O_2 with Metals

In general, metallic oxides (including peroxides and superoxides) are ionic solids. The Group IA metals combine with oxygen to form three kinds of solid ionic products called oxides, peroxides, and superoxides. Lithium combines with oxygen to form lithium oxide.



By contrast, sodium reacts with an excess of oxygen to form sodium peroxide, Na_2O_2 , rather than sodium oxide, Na_2O , as the *major* product.



Peroxides contain the $\text{O}-\text{O}^{2-}$, O_2^{2-} group, in which the oxidation number of each oxygen is -1 , whereas *normal oxides* such as lithium oxide, Li_2O , contain oxide ions, O^{2-} . The heavier members of the family (K, Rb, Cs) react with excess oxygen to form **superoxides**. These contain the superoxide ion, O_2^- , in which the oxidation number of each oxygen is $-\frac{1}{2}$. The reaction with K is



The tendency of the Group IA metals to form oxygen-rich compounds increases going down the group. This is because cation radii increase going down the group. You can recognize these classes of compounds as

Class	Contains Ions	Oxidation No. of Oxygen
normal oxides	O^{2-}	-2
peroxides	O_2^{2-}	-1
superoxides	O_2^-	$-\frac{1}{2}$

Beryllium reacts with oxygen only at elevated temperatures and forms only the normal oxide, BeO . The other Group IIA metals form normal oxides at moderate temperatures.

The Group IIA metals react with oxygen to form normal ionic oxides, MO , but at high pressures of oxygen the heavier ones form ionic peroxides, MO_2 (Table 6-4).

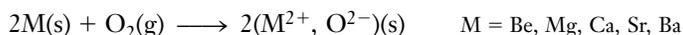
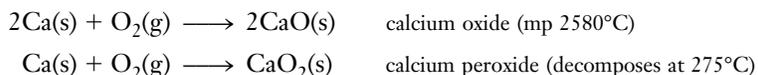


TABLE 6-4 Oxygen Compounds of the IA and IIA Metals*

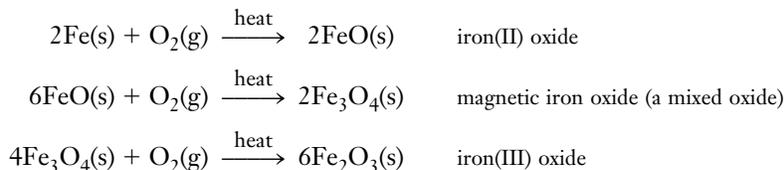
	IA					IIA				
	Li	Na	K	Rb	Cs	Be	Mg	Ca	Sr	Ba
normal oxides	Li ₂ O	Na ₂ O	K ₂ O	Rb ₂ O	Cs ₂ O	BeO	MgO	CaO	SrO	BaO
peroxides	Li ₂ O ₂	Na ₂ O ₂	K ₂ O ₂	Rb ₂ O ₂	Cs ₂ O ₂			CaO ₂	SrO ₂	BaO ₂
superoxides		NaO ₂	KO ₂	RbO ₂	CsO ₂					

*The shaded compounds represent the principal products of the direct reaction of the metal with oxygen.

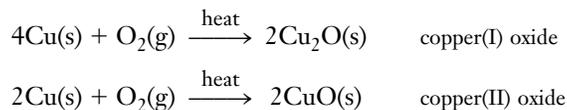
For example, the equations for the reactions of calcium and oxygen are



The other metals, with the exceptions noted previously (Au, Pd, and Pt), react with oxygen to form solid metal oxides. Many metals to the right of Group IIA show variable oxidation states, so they may form several oxides. For example, iron combines with oxygen in the following series of reactions to form three different oxides (Figure 6-7).



Copper reacts with a limited amount of oxygen to form red Cu_2O , whereas with excess oxygen it forms black CuO .



Metals that exhibit variable oxidation states react with a limited amount of oxygen to give oxides with lower oxidation states (such as FeO and Cu_2O). They react with an excess of oxygen to give oxides with higher oxidation states (such as Fe_2O_3 and CuO).



Figure 6-7 Iron powder burns brilliantly to form iron(III) oxide, Fe_2O_3 .

Reactions of Metal Oxides with Water

Oxides of metals are called **basic anhydrides** (or **basic oxides**) because many of them combine with water to form bases with no change in oxidation state of the metal (Figure 6-8). “Anhydride” means “without water”; in a sense, the metal oxide is a hydroxide base with the water “removed.” Metal oxides that are soluble in water react to produce the corresponding hydroxides.

		Increasing acidic character →						
		IA	IIA	IIIA	IVA	VA	VIA	VIIA
Increasing base character ↓		Li_2O	BeO	B_2O_3	CO_2	N_2O_5		OF_2
		Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
		K_2O	CaO	Ga_2O_3	GeO_2	As_2O_5	SeO_3	Br_2O_7
		Rb_2O	SrO	In_2O_3	SnO_2	Sb_2O_5	TeO_3	I_2O_7
		Cs_2O	BaO	Tl_2O_3	PbO_2	Bi_2O_5	PoO_3	At_2O_7

Figure 6-8 The normal oxides of the representative elements in their maximum oxidation states. Acidic oxides (acid anhydrides) are shaded red, amphoteric oxides are shaded purple, and basic oxides (basic anhydrides) are shaded blue. An **amphoteric** oxide is one that shows some acidic and some basic properties.

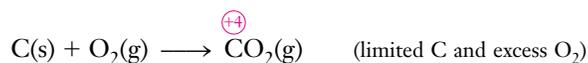
	Metal Oxide + Water		→	Metal Hydroxide (base)	
sodium oxide	Na ₂ O(s)	+ H ₂ O(l)	→	2 NaOH(aq)	sodium hydroxide
calcium oxide	CaO(s)	+ H ₂ O(l)	→	Ca(OH) ₂ (aq)	calcium hydroxide
barium oxide	BaO(s)	+ H ₂ O(l)	→	Ba(OH) ₂ (aq)	barium hydroxide

The oxides of the Group IA metals and the heavier Group IIA metals dissolve in water to give solutions of strong bases. Most other metal oxides are relatively insoluble in water.

Reactions of O₂ with Nonmetals

Oxygen combines with many nonmetals to form molecular oxides. For example, carbon burns in oxygen to form carbon monoxide or carbon dioxide, depending on the relative amounts of carbon and oxygen.

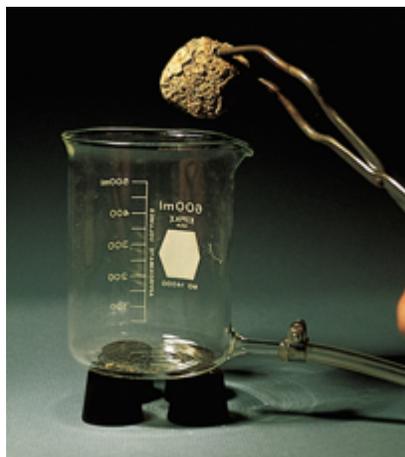
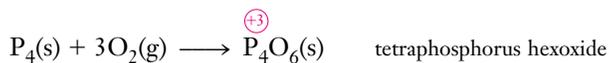
Recall that oxidation states are indicated by red numbers in red circles.



Carbon monoxide is a very poisonous gas because it forms a stronger bond with the iron atom in hemoglobin than does an oxygen molecule. Attachment of the CO molecule to the iron atom destroys the ability of hemoglobin to pick up oxygen in the lungs and carry it to the brain and muscle tissue. Carbon monoxide poisoning is particularly insidious because the gas has no odor and because the victim first becomes drowsy.

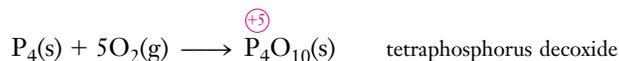
Unlike carbon monoxide, carbon dioxide is not toxic. It is one of the products of the respiratory process. It is used to make carbonated beverages, which are mostly saturated solutions of carbon dioxide in water; a small amount of the carbon dioxide combines with the water to form carbonic acid (H₂CO₃), a very weak acid.

Phosphorus reacts with a limited amount of oxygen to form tetraphosphorus hexoxide, P₄O₆:

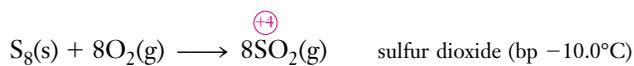


Carbon burns brilliantly in pure O₂ to form CO₂.

whereas reaction with an excess of oxygen gives tetraphosphorus decoxide, P_4O_{10} :



Sulfur burns in oxygen to form primarily sulfur dioxide (Figure 6-9) and only very small amounts of sulfur trioxide.



The production of SO_3 at a reasonable rate requires the presence of a catalyst.

OXIDATION STATES OF NONMETALS

Nearly all nonmetals exhibit more than one oxidation state in their compounds. In general, the *most common* oxidation states of a nonmetal are (1) its periodic group number, (2) its periodic group number minus two, and (3) its periodic group number minus eight. The reactions of nonmetals with a limited amount of oxygen usually give products that contain the nonmetals (other than oxygen) in lower oxidation states, usually case (2). Reactions with excess oxygen give products in which the nonmetals exhibit higher oxidation states, case (1). The examples we have cited are CO and CO_2 , P_4O_6 and P_4O_{10} , and SO_2 and SO_3 . The molecular formulas of the oxides are sometimes not easily predictable, but the *simplest* formulas are. For example, the two most common oxidation states of phosphorus in molecular compounds are +3 and +5. The simplest formulas for the corresponding phosphorus oxides therefore are P_2O_3 and P_2O_5 , respectively. The molecular (true) formulas are twice these, P_4O_6 and P_4O_{10} .

Reactions of Nonmetal Oxides with Water

Nonmetal oxides are called **acid anhydrides** (or **acidic oxides**) because many of them dissolve in water to form acids *with no change in oxidation state of the nonmetal* (see Figure 6-8). Several **ternary acids** can be prepared by reaction of the appropriate nonmetal oxides with water. Ternary acids contain three elements, usually H, O, and another nonmetal.

	Nonmetal Oxide	+ Water	→ Ternary Acid	
carbon dioxide	$CO_2(g)$	$+ H_2O(\ell)$	$\longrightarrow H_2CO_3(aq)$	carbonic acid
sulfur dioxide	$SO_2(g)$	$+ H_2O(\ell)$	$\longrightarrow H_2SO_3(aq)$	sulfurous acid
sulfur trioxide	$SO_3(\ell)$	$+ H_2O(\ell)$	$\longrightarrow H_2SO_4(aq)$	sulfuric acid
dinitrogen pentoxide	$N_2O_5(s)$	$+ H_2O(\ell)$	$\longrightarrow 2HNO_3(aq)$	nitric acid
tetraphosphorus decoxide	$P_4O_{10}(s)$	$+ 6H_2O(\ell)$	$\longrightarrow 4H_3PO_4(aq)$	phosphoric acid

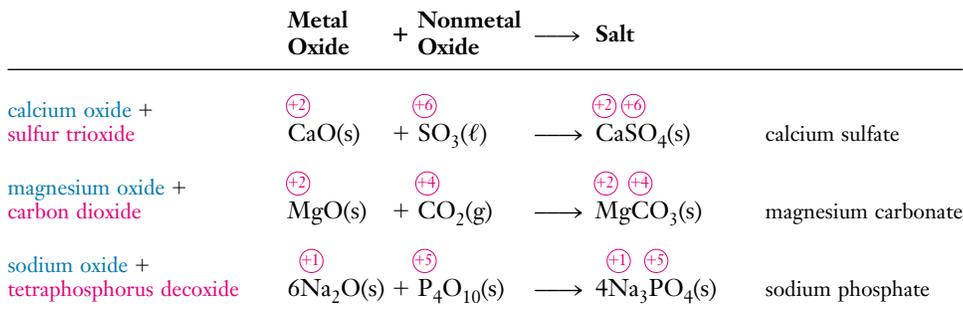
Nearly all oxides of nonmetals react with water to give solutions of ternary acids. The oxides of boron and silicon, which are insoluble, are two exceptions.



Figure 6-9 Sulfur burns in oxygen to form sulfur dioxide.

Reactions of Metal Oxides with Nonmetal Oxides

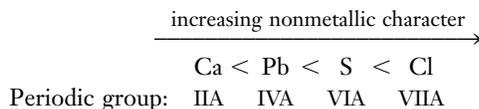
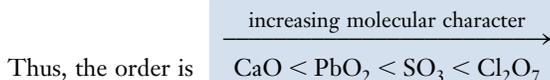
Another common kind of reaction of oxides is the *combination of metal oxides (basic anhydrides) with nonmetal oxides (acid anhydrides), with no change in oxidation states, to form salts.*

**EXAMPLE 6-8 Acidic Character of Oxides**

Arrange the following oxides in order of increasing molecular (acidic) character: SO_3 , Cl_2O_7 , CaO , and PbO_2 .

Plan

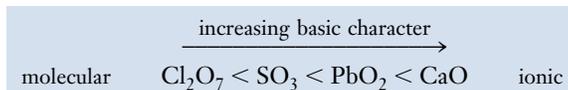
Molecular (acidic) character of oxides increases as nonmetallic character of the element that is combined with oxygen increases (see Figure 6-8).

**Solution****EXAMPLE 6-9 Basic Character of Oxides**

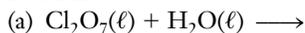
Arrange the oxides in Example 6-8 in order of increasing basicity.

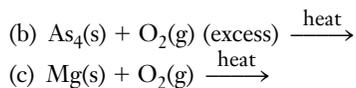
Plan

The greater the molecular character of an oxide, the more acidic it is. Thus, the most basic oxides have the least molecular (most ionic) character (see Figure 6-8).

Solution**EXAMPLE 6-10 Predicting Reaction Products**

Predict the products of the following pairs of reactants. Write a balanced equation for each reaction.

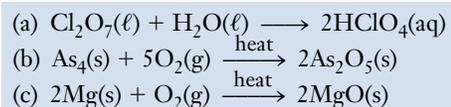


**Plan**

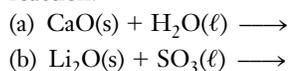
(a) The reaction of a nonmetal oxide (acid anhydride) with water forms a ternary acid in which the nonmetal (Cl) has the same oxidation state (+7) as in the oxide. Thus, the acid is perchloric acid, HClO_4 .

(b) Arsenic, a Group VA nonmetal, exhibits common oxidation states of +5 and $+5 - 2 = +3$. Reaction of arsenic with *excess* oxygen produces the higher-oxidation-state oxide, As_2O_5 . By analogy with the oxide of phosphorus in the +5 oxidation state, P_4O_{10} , we might write the formula as As_4O_{10} , but this oxide exists as As_2O_5 .

(c) The reaction of a Group IIA metal with oxygen produces the normal metal oxide— MgO in this case.

Solution**EXAMPLE 6-11** *Predicting Reaction Products*

Predict the products of the following pairs of reactants. Write a balanced equation for each reaction.

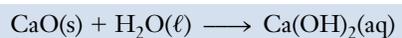
**Plan**

(a) The reaction of a metal oxide with water produces the metal hydroxide.

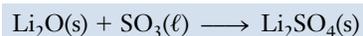
(b) The reaction of a metal oxide with a nonmetal oxide produces a salt containing the cation of the metal oxide and the anion of the acid for which the nonmetal oxide is the anhydride. SO_3 is the acid anhydride of sulfuric acid, H_2SO_4 .

Solution

(a) Calcium oxide reacts with water to form calcium hydroxide.



(b) Lithium oxide reacts with sulfur trioxide to form lithium sulfate.



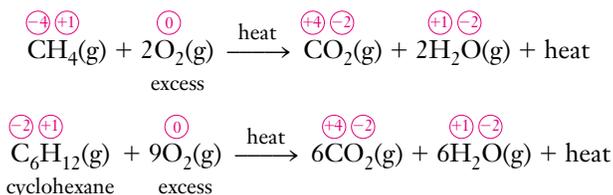
You should now work Exercises 70–73.

CaO is called quicklime. $\text{Ca}(\text{OH})_2$ is called slaked lime.

Combustion Reactions

Combustion, or burning, is an oxidation–reduction reaction in which oxygen combines rapidly with oxidizable materials in highly exothermic reactions, usually with a visible flame. The complete combustion of **hydrocarbons**, in fossil fuels for example, produces carbon dioxide and water (steam) as the major products:

Hydrocarbons are compounds that contain only hydrogen and carbon.



As we have seen, the origin of the term “oxidation” lies in just such reactions, in which oxygen “oxidizes” another species.



Figure 6-10 Georgia Power Company's Plant Bowen at Taylorsville, Georgia. Plants such as this one burn more than 10^7 tons of coal and produce over 2×10^8 megawatt-hours of electricity each year.

“White smoke” from auto exhaust systems is tiny droplets of water condensing in the cooler air.

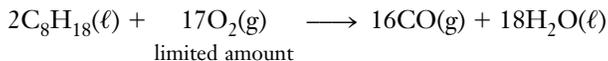
Carbon in the form of soot is one of the many kinds of *particulate matter* in polluted air.

Combustion of Fossil Fuels and Air Pollution

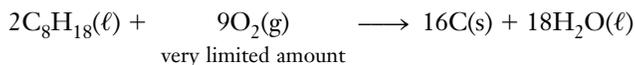
Fossil fuels are mixtures of variable composition that consist primarily of hydrocarbons. We burn them to use the energy that is released rather than to obtain chemical products (Figure 6-10). For example, burning octane, C_8H_{18} , in an excess of oxygen (plenty of air) produces carbon dioxide and water. There are many similar compounds in gasoline and diesel fuels.



Carbon monoxide is produced by the incomplete burning of carbon-containing compounds in a limited amount of oxygen.



In very limited oxygen, carbon (soot) is produced by partially burning hydrocarbons. For octane, the reaction is

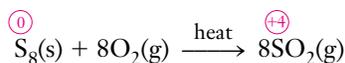


When you see blue or black smoke (carbon) coming from an internal combustion engine, (or smell unburned fuel in the air) you may be quite sure that lots of carbon monoxide is also being produced and released into the air.

We see that the incomplete combustion of hydrocarbons yields undesirable products—carbon monoxide and elemental carbon (soot), which pollute the air. Unfortunately, all fossil fuels—natural gas, coal, gasoline, kerosene, oil, and so on—also have undesirable nonhydrocarbon impurities that burn to produce oxides that act as additional air pollutants. At this time it is not economically feasible to remove all of these impurities from the fuels before burning them.

Fossil fuels result from the decay of animal and vegetable matter (Figure 6-11). All living matter contains some sulfur and nitrogen, so fossil fuels also contain sulfur and nitrogen impurities to varying degrees. Table 6-5 gives composition data for some common kinds of coal.

Combustion of sulfur produces sulfur dioxide, SO_2 , probably the single most harmful pollutant.

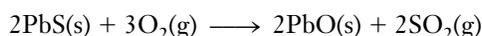


Large amounts of SO_2 are produced by the burning of sulfur-containing coal.

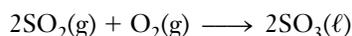
TABLE 6-5 Some Typical Coal Compositions in Percent (dry, ash-free)

	C	H	O	N	S
lignite	70.59	4.47	23.13	1.04	0.74
subbituminous	77.2	5.01	15.92	1.30	0.51
bituminous	80.2	5.80	7.53	1.39	5.11
anthracite	92.7	2.80	2.70	1.00	0.90

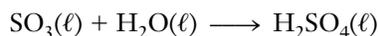
Many metals occur in nature as sulfides. The process of extracting the free (elemental) metals involves **roasting**—heating an ore in the presence of air. For many metal sulfides this produces a metal oxide and SO_2 . The metal oxides are then reduced to the free metals. Consider lead sulfide, PbS , as an example.



Sulfur dioxide is corrosive; it damages plants, structural materials, and humans. It is a nasal, throat, and lung irritant. Sulfur dioxide is slowly oxidized to sulfur trioxide, SO_3 , by oxygen in air:

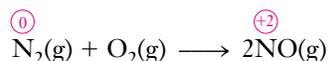


Sulfur trioxide combines with moisture in the air to form the strong, corrosive acid, sulfuric acid:



Oxides of sulfur are the main cause of acid rain.

Compounds of nitrogen are also impurities in fossil fuels; they burn to form nitric oxide, NO . Most of the nitrogen in the NO in exhaust gases from furnaces, automobiles, airplanes, and so on, however, comes from the air that is mixed with the fuel.



NO can be further oxidized by oxygen to nitrogen dioxide, NO_2 ; this reaction is enhanced in the presence of ultraviolet light from the sun.



NO_2 is responsible for the reddish-brown haze that hangs over many cities on sunny afternoons (Figure 6-12) and probably for most of the respiratory problems associated with this kind of air pollution. It can react to produce other oxides of nitrogen and other secondary pollutants.

In addition to being a pollutant itself, nitrogen dioxide reacts with water in the air to form nitric acid, another major contributor to acid rain:

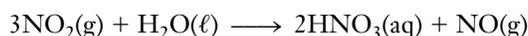


Figure 6-11 The luxuriant growth of vegetation that occurred during the carboniferous age is the source of our coal deposits.

Remember that “clean air” is *about* 80% N_2 and 20% O_2 by mass. This reaction does *not* occur at room temperature but does occur at the high temperatures of furnaces, internal combustion engines, and jet engines.

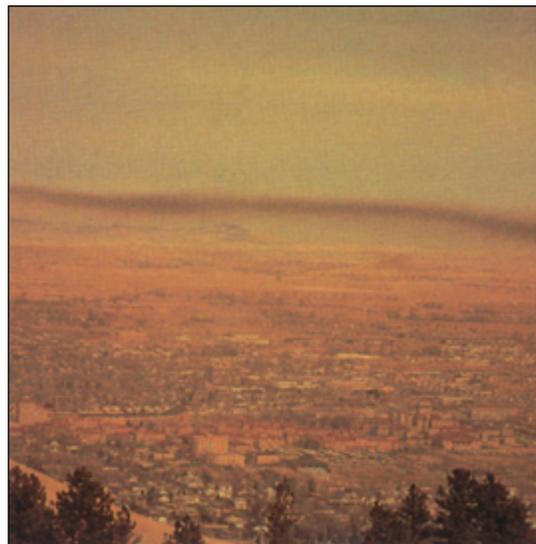


Figure 6-12 Photochemical pollution (a brown haze) enveloping a city.

Key Terms

Acid anhydride A nonmetal oxide that reacts with water to form an acid.

Acidic oxide See *Acid anhydride*.

Actinides Elements 90 through 103 (after *actinium*).

Amphoteric oxide An oxide that shows some acidic and some basic properties.

Amphoterism The ability of a substance to react with both acids and bases.

Angstrom (Å) 10^{-10} meter, 10^{-1} nm, or 10^2 pm.

Atomic radius The radius of an atom.

Basic anhydride A metal oxide that reacts with water to form a base.

Basic oxide See *Basic anhydride*.

Catalyst A substance that speeds up a chemical reaction without itself being consumed in the reaction.

Combustion reaction The reaction of a substance with oxygen in a highly exothermic reaction, usually with a visible flame.

***d*-Transition elements (metals)** The B group elements in the periodic table; sometimes called simply transition elements.

Effective nuclear charge (Z_{eff}) The nuclear charge experienced by the outermost electrons of an atom; the actual nuclear charge minus the effects of shielding due to inner shell electrons.

Electron affinity The amount of energy absorbed in the process in which an electron is added to a neutral isolated gaseous atom to form a gaseous ion with a $1-$ charge; has a negative value if energy is released.

Electronegativity A measure of the relative tendency of an atom to attract electrons to itself when chemically combined with another atom.

***f*-Transition elements (metals)** Elements 58 through 71 and 90 through 103; also called inner transition elements (metals).

Hydride A binary compound of hydrogen.

Inner transition elements See *f-Transition elements*.

Ionic radius The radius of an ion.

Ionization energy The amount of energy required to remove the most loosely held electron of an isolated gaseous atom or ion.

Isoelectronic Having the same number of electrons.

Lanthanides Elements 58 through 71 (after *lanthanum*).

Noble gas configuration The stable electron configuration of a noble gas.

Noble gases Elements of periodic Group VIIIA; also called rare gases; formerly called inert gases.

Normal oxide A metal oxide containing the oxide ion, O^{2-} (oxygen in the -2 oxidation state).

Nuclear shielding See *Shielding effect*.

Oxide A binary compound of oxygen.

Periodicity Regular periodic variations of properties of elements with atomic number and position in the periodic table.

Periodic law The properties of the elements are periodic functions of their atomic numbers.

Peroxide A compound containing oxygen in the -1 oxidation state. Metal peroxides contain the peroxide ion, O_2^{2-} .

Radical A species containing one or more unpaired electrons; many radicals are very reactive.

Rare earths Inner transition elements.

Representative elements The A group elements in the periodic table.

25. Within a group on the periodic table, what is the relationship between shielding and first ionization energy?
26. Arrange the members of each of the following sets of elements in order of increasing first ionization energies: (a) the alkali metals; (b) the halogens; (c) the elements in the second period; (d) Br, F, B, Ga, Cs, and H.
27. The second ionization energy value is generally much larger than the first ionization energy. Explain why this is so.
28. What is the general relationship between the sizes of the atoms of Period 2 and their first ionization energies? Rationalize the relationship.
29. In a plot of first ionization energy versus atomic number for Periods 2 and 3, "dips" occur at the IIIA and VIA elements. Account for these dips.
30. On the basis of electron configurations, would you expect a Na^{2+} ion to exist in compounds? Why or why not? How about Mg^{2+} ?
31. How much energy, in kilojoules, must be absorbed by 1.25 mol of gaseous lithium atoms to convert all of them to gaseous Li^+ ions?

Electron Affinity

32. Arrange the following elements in order of increasing negative values of electron affinity: P, S, Cl, and Br.
33. Arrange the members of each of the following sets of elements in order of increasingly negative electron affinities: (a) the Group IA metals; (b) the Group VIIA elements; (c) the elements in the second period; (d) Li, K, C, F, and Cl.
34. The electron affinities of the halogens are much more negative than those of the Group VIA elements. Why is this so?
35. The addition of a second electron to form an ion with a $2-$ charge is always endothermic. Why is this so?
36. Write the equation for the change described by each of the following, and write the electron configuration for each atom or ion shown: (a) the electron affinity of oxygen; (b) the electron affinity of chlorine; (c) the electron affinity of magnesium.

Ionic Radii

37. Compare the sizes of cations and the neutral atoms from which they are formed by citing three specific examples.
38. Arrange the members of each of the following sets of cations in order of increasing ionic radii: (a) K^+ , Ca^{2+} , Ga^{3+} ; (b) Ca^{2+} , Be^{2+} , Ba^{2+} , Mg^{2+} ; (c) Al^{3+} , Sr^{2+} , Rb^+ , K^+ ; (d) K^+ , Ca^{2+} , Rb^+ .
39. Compare the sizes of anions and the neutral atoms from which they are formed by citing three specific examples.
40. Arrange the following sets of anions in order of increasing ionic radii: (a) Cl^- , S^{2-} , P^{3-} ; (b) O^{2-} , S^{2-} , Se^{2-} ; (c) N^{3-} , S^{2-} , Br^- , P^{3-} ; (d) Cl^- , Br^- , I^- .
41. Explain the trend in size of either the atom or ion as one moves down a group.

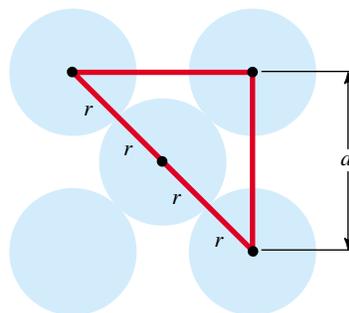
42. Most transition metals can form more than one simple positive ion. For example, iron forms both Fe^{2+} and Fe^{3+} ions, and tin forms both Sn^{2+} and Sn^{4+} ions. Which is the smaller ion of each pair, and why?

Electronegativity

43. What is electronegativity?
44. Arrange the members of each of the following sets of elements in order of increasing electronegativities: (a) Pb, C, Sn, Ge; (b) S, Na, Mg, Cl; (c) P, N, Sb, Bi; (d) Se, Ba, F, Si, Sc.
45. Which of the following statements is better? Why?
 - (a) Magnesium has a weak attraction for electrons in a chemical bond because it has a low electronegativity.
 - (b) The electronegativity of magnesium is low because magnesium has a weak attraction for electrons in a chemical bond.
- *46. Some of the second-period elements show a similarity to the element one column to the right and one row down. For instance, Li is similar in many respects to Mg, and Be is similar to Al. This has been attributed to the charge density on the stable ions (Li^+ vs. Mg^{2+} ; Be^{2+} vs. Al^{3+}). From the values of electronic charge (Chapter 5) and ionic radii (Chapter 6), calculate the charge density for these four ions, in coulombs per cubic angstrom.
47. One element takes on only a negative oxidation number when combined with other elements. From the table of electronegativity values, determine which element this is.
48. Compare the electronegativity values of the metalloids.

Additional Exercises on the Periodic Table

49. The chemical reactivities of carbon and lead are similar, but there are also major differences. Using their electron configurations, explain why these similarities and differences may exist.
50. The bond lengths in F_2 and Cl_2 molecules are 1.42 Å and 1.98 Å, respectively. Calculate the atomic radii for these elements. Predict the Cl—F bond length. (The actual Cl—F bond length is 1.64 Å.)
- *51. The atoms in crystalline nickel are arranged so that they touch one another in a plane as shown in the sketch:



From plane geometry, we can see that $4r = a\sqrt{2}$. Calculate the radius of a nickel atom given that $a = 3.5238 \text{ \AA}$.

52. Compare the respective values of the first ionization energy (see Table 6-1) and electron affinity (see Table 6-2) for several elements. Which energy is greater? Why?
53. Compare the respective values of the first ionization energy (see Table 6-1) and electron affinity (see Table 6-2) for nitrogen to those for carbon and oxygen. Explain why the nitrogen values are considerably different.
- *54. Based on general trends, the electron affinity of fluorine would be expected to be greater than that of chlorine; however, the value is less and is similar to the value for bromine. Explain.
55. Atomic number 91 is the element protactinium, an extremely rare element. There is very little known about protactinium; even the boiling point is unknown. Thorium, atomic number 90, has the boiling point of 4788°C and uranium's boiling point is 4131°C . Predict the boiling point of protactinium, and discuss how close the prediction is likely to be.

Hydrogen and the Hydrides

56. Summarize the physical properties of hydrogen.
57. Write balanced formula unit equations for (a) the reaction of iron with steam, (b) the reaction of calcium with hydrochloric acid, (c) the electrolysis of water, and (d) the "water gas" reaction.
58. Write a balanced formula unit equation for the preparation of (a) an ionic hydride and (b) a molecular hydride.
59. Classify the following hydrides as molecular or ionic: (a) NaH, (b) H_2S , (c) AlH_3 , (d) RbH, (e) NH_3 .
60. Explain why NaH and H_2S are different kinds of hydrides.
61. Write formula unit equations for the reactions of (a) NaH and (b) AlH_3 with water.
62. Name the following (pure) compounds: (a) H_2S , (b) HCl, (c) KH, (d) NH_3 , (e) H_2Se , (f) MgH_2 , (g) CaH_2 .

Oxygen and the Oxides

- *63. How are O_2 and O_3 similar? How are they different?
64. Briefly compare and contrast the properties of oxygen with those of hydrogen.
65. Write molecular equations to show how oxygen can be prepared from (a) mercury(II) oxide, HgO, (b) hydrogen peroxide, H_2O_2 , and (c) potassium chlorate, KClO_3 .
- *66. Which of the following elements form normal oxides as the *major* products of reactions with oxygen? (a) Li, (b) Na, (c) Rb, (d) Mg, (e) Zn (exhibits only one common oxidation state), (f) Al.
67. Oxygen has a positive oxidation number when combined with which element? Compare the electronegativity values of oxygen and that element.

68. Write formula unit equations for the reactions of the following elements with a *limited* amount of oxygen: (a) C, (b) As_4 , (c) Ge.
69. Write formula unit equations for the reactions of the following elements with an *excess* of oxygen: (a) C, (b) As_4 , (c) Ge.
70. Distinguish among normal oxides, peroxides, and superoxides. What is the oxidation state of oxygen in each case?
- *71. Which of the following can be classified as basic anhydrides? (a) CO_2 , (b) Li_2O , (c) SeO_3 , (d) CaO, (e) N_2O_5 .
72. Write balanced formula unit equations for the following reactions and name the products:
 - (a) carbon dioxide, CO_2 , with water
 - (b) sulfur trioxide, SO_3 , with water
 - (c) selenium trioxide, SeO_3 , with water
 - (d) dinitrogen pentoxide, N_2O_5 , with water
 - (e) dichlorine heptoxide, Cl_2O_7 , with water
73. Write balanced formula unit equations for the following reactions and name the products:
 - (a) sodium oxide, Na_2O , with water
 - (b) calcium oxide, CaO, with water
 - (c) lithium oxide, Li_2O , with water
 - (d) magnesium oxide, MgO, with sulfur dioxide, SO_2
 - (e) calcium oxide, CaO, with carbon dioxide, CO_2
- *74. Identify the acid anhydrides of the following ternary acids: (a) H_2SO_4 , (b) H_2CO_3 , (c) H_2SO_3 , (d) H_3PO_4 , (e) HNO_2 .
75. Identify the basic anhydrides of the following metal hydroxides: (a) NaOH, (b) $\text{Mg}(\text{OH})_2$, (c) $\text{Fe}(\text{OH})_2$, (d) $\text{Al}(\text{OH})_3$.

Combustion Reactions

76. Define combustion. Why are all combustion reactions also redox reactions?
77. Write equations for the complete combustion of the following compounds: (a) methane, $\text{CH}_4(\text{g})$; (b) propane, $\text{C}_3\text{H}_8(\text{g})$; (c) ethanol, $\text{C}_2\text{H}_5\text{OH}(\ell)$.
78. Write equations for the *incomplete* combustion of the following compounds to produce carbon monoxide: (a) methane, $\text{CH}_4(\text{g})$; (b) propane, $\text{C}_3\text{H}_8(\text{g})$.

As we have seen, two substances may react to form different products when they are mixed in different proportions under different conditions. In Exercises 79 and 80, write balanced equations for the reactions described. Assign oxidation numbers.

79. (a) Ethane burns in excess air to form carbon dioxide and water.
(b) Ethane burns in a limited amount of air to form carbon monoxide and water.
(c) Ethane burns (poorly) in a very limited amount of air to form elemental carbon and water.
80. (a) Butane (C_4H_{10}) burns in excess air to form carbon dioxide and water.

- (b) Butane burns in a limited amount of air to form carbon monoxide and water.
- (c) When heated in the presence of *very little* air, butane “cracks” to form acetylene, C_2H_2 ; carbon monoxide; and hydrogen.
- *81. (a) How much SO_2 would be formed by burning 1.00 kg of bituminous coal that is 5.15% sulfur by mass? Assume that all of the sulfur is converted to SO_2 .
- (b) If 27.0% of the SO_2 escaped into the atmosphere and 75.0% of the escaped SO_2 were converted to H_2SO_4 , how many grams of H_2SO_4 would be produced in the atmosphere?
- *82. Write equations for the complete combustion of the following compounds. Assume that sulfur is converted to SO_2 and nitrogen is converted to NO . (a) $C_6H_5NH_2(l)$, (b) $C_2H_5SH(l)$, (c) $C_7H_{10}NO_2S(l)$.

CONCEPTUAL EXERCISES

83. Write the electron configuration for the product of the second ionization of the third largest alkaline earth metal.
84. You are given the atomic radii of 110 pm, 118 pm, 120 pm, 122 pm, and 135 pm, but do not know to which element (As, Ga, Ge, P, and Si) these values correspond. Which must be the value of Ge?
85. What compound will most likely form between potassium and element X, if element X has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^4$?
86. Write the electron configurations of beryllium and magnesium. What similarities in their chemical properties can you predict on the basis of their electron configurations?
87. Dolostone is often more porous than limestone. One explanation of the origin of dolostone is that it results from partial replacement of calcium by magnesium in an original limestone sediment. Is this explanation reasonable, given what you know of the ionic radii of magnesium and calcium ions?

BUILDING YOUR KNOWLEDGE

88. Hydrogen can be obtained from water by electrolysis. Hydrogen may someday be an important replacement for current fuels. Describe some of the problems that you would predict if hydrogen were used in today's motor vehicles.
89. The only chemically stable ion of rubidium is Rb^+ . The most stable monatomic ion of bromine is Br^- . Krypton (Kr) is among the least reactive of all elements. Compare the electron configurations of Rb^+ , Br^- , and Kr. Then predict the most stable monatomic ions of strontium (Sr) and selenium (Se).
90. The first ionization energy of potassium, K, is 419 kJ/mol. What is the minimum frequency of light required to ionize gaseous potassium atoms?
91. Potassium and argon would be anomalies in a periodic table in which elements are arranged in order of increasing atomic weights. Identify two other elements among the transition elements whose positions in the periodic table would have been reversed in a “weight-sequence” arrangement. Which pair of elements would most obviously be out of place on the basis of their chemical behavior? Explain your answer in terms of the current atomic model, showing electron configurations for these elements.
92. The second ionization energy for magnesium is 1451 kJ/mol. How much energy, in kilojoules, must be absorbed by 1.50 g of gaseous magnesium atoms to convert them to gaseous Mg^{2+} ions?