



Periodic Properties of the Elements

5

“The Periodic Table is Nature’s Rosetta Stone.”

—Rudy Baum

5.1 THE MODERN PERIODIC TABLE

The modern form of the periodic table is so iconic that almost anyone would recognize the image above simply by looking at its general shape. Nowadays, it is almost impossible to believe that there was ever a time when the periodic nature of the elements was not yet understood. The first primitive form of the periodic table was developed in 1829 by Johann Döbereiner, who noticed a repetitive pattern in the chemical properties of some of the elements, lumping them together in groups of three that he called *triads*. The elements chlorine, bromine, and iodine, for instance, formed a triad. A few years later, in 1865, the Englishman John Newlands recognized that if the elements were listed in order of their increasing atomic weights, they could be arranged into what he called the *law of octaves* (or groups of eight) according to their chemical properties. However, it was not until 1869, when the Russian teacher Dmitri Mendeleev gave a presentation to the Russian Chemical Society called “A Dependence between the Properties of the Atomic Weights of the Elements” that the idea of periodic trends among the various elements began to take hold. Mendeleev wrote out the physical properties of all the known elements on cards and arranged them into groups on the basis of trends in a game that his friends called *Patience*. In Mendeleev’s day, only a third of the elements known today had been discovered. The genius of Mendeleev’s work was that when he arranged the elements in order of increasing atomic mass and the next element did not fit the properties of the next group, he simply left a gap in his deck of cards, assuming that a new element would someday be discovered having the appropriate pattern of trends. It is the predictive capability of Mendeleev’s periodic table that set his above those of his contemporaries.

The modern version of the periodic table, of course, is based on quantum mechanics and the relative energies of the hydrogenic orbitals. When Moeller’s rubric is applied and the orbitals are arranged according to increasing energy, the *Aufbau* (or “building up”) *principle* states that the electrons will fill those orbitals having the lowest energies first. Further, the Pauli exclusion principle states that no more than two electrons can occupy the same orbital and thus each orbital can hold only two electrons. When the elements are arranged in order of increasing atomic number, their physical and chemical properties follow the same periodic pattern as the

Principles of Inorganic Chemistry, First Edition. Brian W. Pfennig.
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PERIODIC TABLE OF THE ELEMENTS
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The periodic table is organized into 7 periods (rows) and 18 groups (columns). The groups are labeled as follows:

- Group 1: IA (Alkali metals)
- Group 2: IIA (Alkaline earth metals)
- Groups 3-10: IIB, IVB, VIB, VIIB, VIIIB, VIIIIB, IX, X, XI, XII (Transition metals)
- Group 11: IB
- Group 12: IIB
- Group 13: IIIA
- Group 14: IVA
- Group 15: VA (Pnictogens)
- Group 16: VIA (Chalcogens)
- Group 17: VIIA (Halogens)
- Group 18: VIIIA (Noble gases)

Below the main table are the Lanthanide and Actinide series:

LANTHANIDE

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LANTHANUM	CERMIUM	PRASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIUM	TERBIUM	DYSPROSIUM	HOLMIUM	ERBIUM	THULIUM	Ytterbium	LUTETIUM

ACTINIDE

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
ACTINIUM	THORIUM	Protactinium	URANIUM	NEPTUNIUM	PLUTONIUM	AMERICIUM	CURMIUM	BERKELIUM	CALIFORNIUM	ENSTENIUM	FERMIUM	Mendelevium	Nobelium	LAWRENCIUM

(1) Pure Appl. Chem., 81, No. 11, 2131-2136 (2009)
Relative atomic masses are expressed with five significant figures. For elements that have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived nuclide of the element. However, these values (Tl, Pa and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

FIGURE 5.1

Modern version of the periodic table. [©E. Generalic, <http://www.periodni.com>, used with permission.]

one predicted based on this ordering of the hydrogenic orbitals. A modern version of the periodic table of the elements is shown in Figure 5.1.

The modern periodic table has 18 columns or groups. It is divided into the metals, which lie on the left-hand side of the red staircase of elements, and the nonmetals, which lie to the right of this staircase. The metals typically lose their valence (or outermost) electrons easily, are malleable and ductile, and are good conductors of heat and electricity. The nonmetals, on the other hand, gain or share their electrons easily, are brittle, lack luster, and are usually poor conductors of heat or electricity. Those elements lying along the staircase (highlighted in red in Figure 5.1) are known as the *metalloids* and have intermediate character between the metals and the nonmetals and are often semiconductors. A number of the different groups have specific names: Group 1 contains the alkali metals, Group 2 contains the alkaline earths, Group 15 contains the pnictogens, Group 16 contains the chalcogens, Group 17 contains the halogens, and Group 18 contains the noble or the inert gases. Furthermore, the *d*-block elements are known as the *transition metals*, the *4f*-block is called the *lanthanide series*, and the *5f*-block is called the *actinides*. A long version of the periodic table, which shows the accurate quantum mechanical placement of the lanthanides and actinides more clearly, is shown in Figure 5.2.

Mendeleev's periodic table was organized according to increasing mass. In some cases, the order of the elements had to be reversed in order to fit the periodic trends more neatly—thus, for instance, Te fell before I even though the atomic mass of Te is heavier. With the discovery of the nucleus in the early 1900s, the modern form of the periodic table is instead organized according to increasing atomic number. We owe this improvement to Henry Moseley, who bombarded the elements with electrons in order to observe their characteristic X-ray fluorescence. The resulting X-ray spectra fit a formula, known as *Moseley's law* that assigned a unique integral number to each element (now known as the *atomic number*). Tragically, Moseley was killed during World War I in the Battle of Gallipoli at the age of 27 and was thus ineligible to win the Nobel Prize he so assuredly deserved.

Long form of the periodic table

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Xe	Rn	Fr	Ra
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo			

FIGURE 5.2

The long version of the periodic table.

In the sections that follow, we will explore some of the more common periodic trends in the physical and chemical properties of the elements. Although it may seem like a daunting task to memorize the descriptive properties of each of the elements, this text aims to highlight the underlying principles that serve as the architecture of the periodic table. Most of these generalizations, including the exceptions to the rule, can be readily understood in terms of only three parameters: (i) the principal quantum number n , (ii) the effective nuclear charge Z^* , and (iii) the element's electron configuration. A fourth property, relativity, also plays a critical role for some of the heavier elements. Most of the periodic trends that follow can be easily rationalized using the above parameters as a basis.

5.2 RADIUS

As a general rule, the radius of an atom will increase down and to the left in the periodic table. The radius of an atom depends on its electron probability. Because of the inherent uncertainty in defining where the end of one atom's sphere of influence over the electron density ends and the next begins, the radius of an atom can be defined in a number of different ways, and the magnitude of an atom's radius will vary from compound to compound. Furthermore, even for the same molecule, the value might depend on the experimental technique employed. For instance, electron diffraction measures the distance between two nuclei, whereas X-ray crystallography measures the distance between peaks of maximum electron density. Other molecules cannot be crystallized and the radius can only be measured in the gas phase, typically using microwave spectroscopy.

The *covalent radius* is defined as exactly one-half the internuclear separation between covalently bonded atoms in a predominantly covalent molecule containing a single bond. This definition can be problematic because not every atom can form a pure covalently bonded molecule containing only single bonds. The lighter noble gas atoms, for instance, do not even form bonds. Selected covalent radii are listed in Table 5.1.

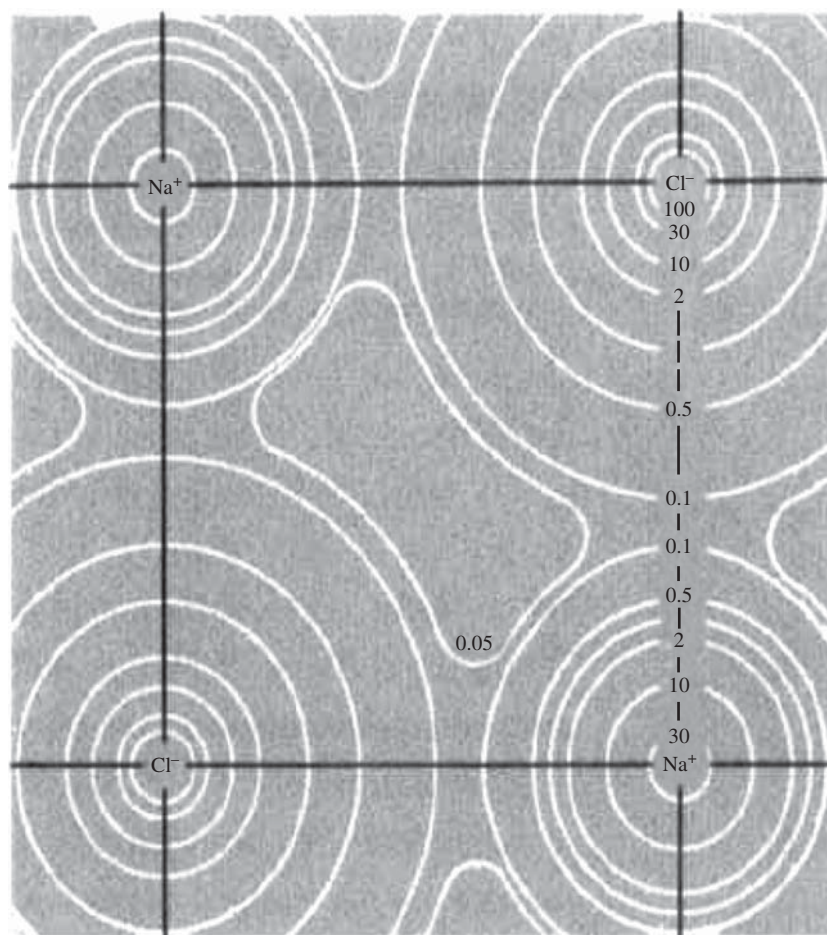
The term *atomic radius* is also sometimes employed to describe the covalent radius of an atom. Atomic radii are based on the internuclear distances measured in a large number of covalently bonded heteronuclear compounds. The covalent radii for N, O, and F (measured using N_2H_4 , H_2O_2 , and F_2 , respectively) are abnormally long because the bonding in these particular compounds is unusually weak. While the covalent radius is half the distance between the nuclei within a single molecule, the *van der Waals radius* is defined as half the distance between the nuclei of two atoms in neighboring molecules. For metal atoms, the *metallic radius* is defined as one-half the distance between neighboring atoms in the extended metallic solid. The metallic radius will depend on the coordination number (or number of nearest

TABLE 5.1 Covalent radii for selected elements.

Element	<i>r</i> (pm)	Element	<i>r</i> (pm)	Element	<i>r</i> (pm)
H	37	Fe	132	In	142
Li	128	Co	126	Sn	139
Be	96	Ni	124	Sb	139
B	84	Cu	132	Te	138
C	76	Zn	122	I	139
N	71	Ga	122	Xe	140
O	66	Ge	120	Cs	244
F	57	As	119	Ba	215
Na	166	Se	120	La	187
Mg	141	Br	120	Hf	175
Al	121	Kr	116	Ta	170
Si	111	Rb	220	W	162
P	107	Sr	195	Re	151
S	105	Y	190	Os	144
Cl	102	Zr	175	Ir	141
Ar	106	Nb	164	Pt	136
K	203	Mo	154	Au	136
Ca	176	Tc	147	Hg	132
Sc	170	Ru	146	Tl	145
Ti	160	Rh	142	Pb	146
V	153	Pd	139	Bi	148
Cr	139	Ag	145	Po	140
Mn	139	Cd	144	At	150

neighbors) of the metal in its crystalline lattice. Metals that exist in more than one type of allotrope will therefore have different metallic radii. Finally, for ionic solids, the *ionic radius* is defined by an electron density contour map, such as the one shown in Figure 5.3, showing where the sphere of influence of one ion ends and the other begins in that intermediate region between oppositely charged ions in an ionic solid. Selected ionic radii (Shannon's data) are listed in Table 5.2.

The different definitions of the radius are required because of the uncertain nature of exactly where the electron probability density should be cut off in defining the size of an atom. Because the different definitions depend on the type of bonding and the coordination number of the element, their values can be dramatically different from one molecule to another. For sodium, the metallic, covalent, and ionic (six-coordinate) radii are 186, 166, and 116 pm, respectively. For the neutral atom, the metallic radius is the largest because it has the largest coordination number. Sodium crystallizes in a body-centered cubic lattice, where each sodium atom is surrounded by eight nearest neighbor Na atoms. Therefore, to a first approximation, the electron density of each atom in metallic Na is shared over all eight of its neighbors (and to a lesser extent over its more distant neighbors). As a result, the distance between atoms will be larger than in the case of covalently bonded Na, where the electron density is shared with only one other Na atom. There is only so much electron density to go around, so the more atoms that are bonded to the Na, the greater its radius will be. It is for this reason that the metallic radius of Na (186 pm) is larger than its covalent radius (166 pm). Because the Na⁺ ion contains one less electron than the neutral Na atom, there will be less electron–electron repulsions and less screening of the outer-most electrons. Therefore, the ionic radius (118 pm) of Na⁺ is shorter than that of the neutral atom. For anions, the larger number of electrons increases the ionic radius because of increased electron–electron repulsions. Thus,

**FIGURE 5.3**

Definition of the ionic radius as viewed from a hard-spheres ionic crystalline lattice (a) and an electron density contour map (b). [Reproduced from Kittel, C. Introduction to Solid State Physics, 6th ed., John Wiley & Sons, Inc: New York, 1986. This material is reproduced with permission of John Wiley & Sons, Inc.]

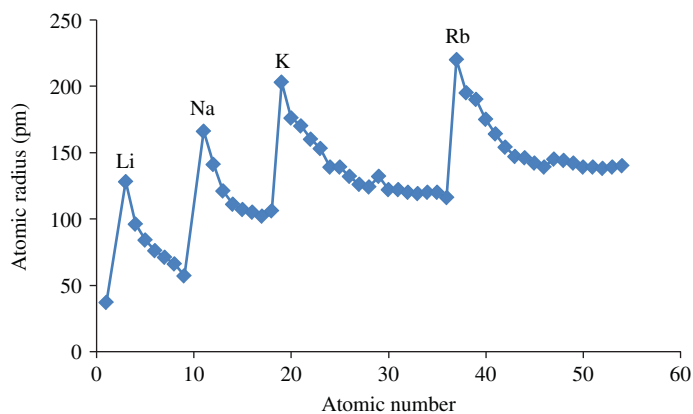
while the covalent radius of Cl is 102 pm, the ionic radius of Cl^- (six-coordinate) is 181 pm. In fact, it is a universal fact that the radius of a cation will always be shorter than that for the neutral atom and the radius of an anion will always be larger than that for the neutral atom.

Across a row or series, the principal quantum number remains essentially the same, whereas the effective nuclear charge is increasing as more and more protons are added to the nucleus. This larger value of Z^* exerts a stronger pull on the electrons, shrinking the atomic radius. Down a column or group in the periodic table, Z^* varies only slightly, while n is increasing. As n increases, the outer-most electron will be added to an orbital having a larger average radial probability. Thus, the atomic radius increases down a column. The periodic trends in atomic radii are illustrated in Figure 5.4. While the trend holds for most of the main group elements, there are a few exceptions. One notable exception (known as the *lanthanide contraction*) is the smaller-than-expected radii of the lanthanides and actinides that result from poor shielding of the f orbitals.

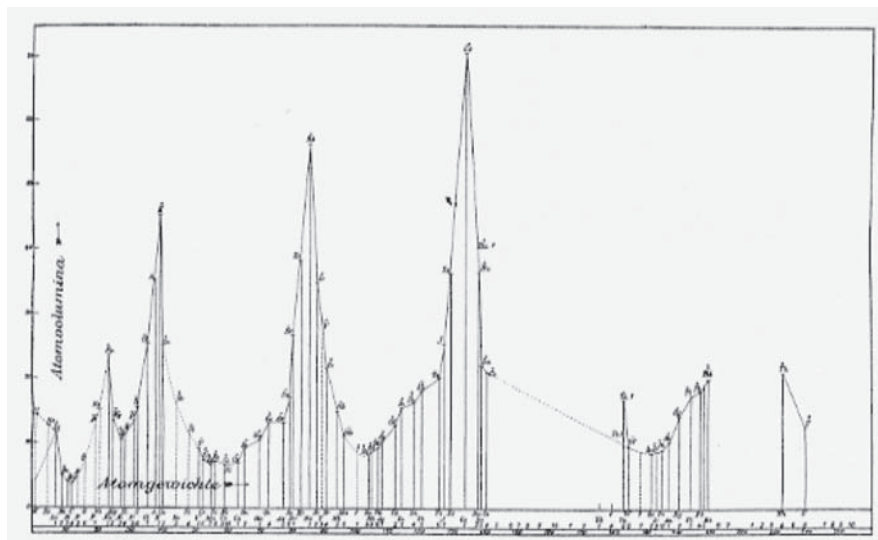
An obvious corollary to the periodic trend for atomic radius is the atomic volume. Because the volume of an atom goes as the cube of the radius, those elements having large atomic radii will have especially large atomic volumes. In fact, Julius Meyer's original graph of atomic volumes, shown in Figure 5.5, makes a strong case for the concept of periodicity. The largest atomic volumes occur for the alkali metals. Because each of these metals has a valence of one, Meyer had already organized them into the same group of the periodic table. While the strength of Mendeleev's

TABLE 5.2 Shannon's ionic radii (pm) for selected ions, according to their coordination number.

Element	2	3	4	6	8
Li ⁺			59	76	92
Be ²⁺		16	27	45	
B ³⁺			11	27	
N ³⁻				146	
O ²⁻	135	136	138	140	
F ⁻	129	130	131	133	
Na ⁺			99	102	118
Mg ²⁺			57	72	89
Al ³⁺			39	54	
P ⁵⁺			17	38	
S ⁶⁺			26	43	
S ²⁻				184	
Cl ⁻				181	
K ⁺			137	138	151
Ca ²⁺				100	112
Ga ³⁺			47	62	
Ge ⁴⁺			39	53	
As ⁵⁺			34	46	
Se ⁶⁺			28	42	
Se ²⁻				198	
Br ⁻				196	
Rb ⁺				152	161
Sr ²⁺				118	126
In ³⁺			62	80	92
Sn ⁴⁺			55	69	81
Sb ⁵⁺				60	
Te ⁶⁺			43	56	
Te ²⁻				221	
I ⁻				220	
Cs ⁺				167	178
Ba ²⁺				135	142
Tl ³⁺			75	89	98
Pb ⁴⁺			65	78	94
Bi ⁵⁺				76	


FIGURE 5.4

Covalent radii as a function of atomic number. The peaks occur for the alkali metals.

**FIGURE 5.5**

Julius Lothar Meyer's original plot of atomic volumes versus increasing atomic mass. The peaks occur for the alkali metals.

work was in its predictive capability, Meyer's research more clearly emphasized the periodicity of elemental properties.

There are a number of other physical properties of the elements that are either directly or indirectly related to the periodic trend for radius. Consider, for example, the melting points of the lithium halides. Because the bonding in these salts is primarily ionic in nature because lithium is a metal and the halogens are nonmetals, the strength of the cation–anion attractive force is expected to have an inverse dependence on the ionic radius of the halide, according to Coulomb's law of electrostatic attraction. The melting point of each crystalline solid depends on the strength of the electrostatic forces holding the ions together. Thus, the melting points for this series of ionic compounds are expected to increase as the ionic radius of the anion decreases, as shown in Table 5.3. One should be careful not to carry such periodic trends to the extreme, however. One of the assumptions in the earlier example is that each of the ionic solids crystallizes in the same type of lattice and therefore has the same number of nearest neighbor ions of the opposite charge. A second assumption is that the solids can be treated as exclusively ionic in nature. In fact, the bonding in lithium iodide has a large amount of covalent character.

There is also a radial trend in the MH_4 boiling points, where M is an element from Group 14. In this case, the bonding is primarily covalent and the species are molecular solids, so that the boiling point depends on the degree of intermolecular forces holding the molecules together in the liquid state. Because the strength of a London dispersion force increases with the polarizability of the element's electron cloud and the polarizability in turn depends on the diffuseness (or size) of the atom,

TABLE 5.3 Melting points of some ionic solids.

Ionic Solid	mp (°C)	Halide Radius (pm)
LiF	842	119
LiCl	614	167
LiBr	547	182
LiI	450	206

TABLE 5.4 Boiling points of MH_4 compounds, where M is an element from Group 14.

Compound	bp ($^{\circ}C$)	Radius of M (pm)
CH_4	-161	70
SiH_4	-112	110
GeH_4	-90	125
SnH_4	-50	145

the boiling points for this series of compounds increase with increasing atomic radius, as shown in Table 5.4.

These two examples should serve as an illustration that the physical properties of a series of compounds from the same column of the periodic table will not only depend on the trend in their atomic radii but also on the different type of forces that hold them together in the condensed state of matter. Thus, periodicity is more than a simple set of rules or trends to memorize. It is actually an exercise in rational thought that uses the periodic table as its scaffold.

The *lattice energy* of an ionic solid is defined as the amount of energy gained when the gaseous ions are brought together from a separation distance of infinity to form the ionic solid, as illustrated in Equation (5.1):



Because the electrostatic attraction between gaseous ions is expected to follow a similar relationship to Coulomb's law, the magnitude of the lattice energy should show an inverse dependence on the distance between the ions in the crystalline solid. This interionic separation will, in turn, depend on the sum of the ionic radii for the two ions. Assuming that each of the magnesium halides crystallizes in the same type of unit cell and that the bonding is primarily ionic in nature, one would therefore expect the magnitude of the lattice energy to increase as the anion is changed from I^- to Br^- to Cl^- to F^- . This is indeed the case. The lattice energies for MgI_2 , $MgBr_2$, $MgCl_2$, and MgF_2 are -2327, -2440, -2526, and -2957 kJ/mol, respectively.

The size of an ion can also influence the *hydration enthalpies* of ionic compounds in water. The smaller the ionic radius, the higher the charge density (Z/r) of the ion will be. Ions with large charge densities can form stronger ion-dipole forces with the polar water molecule. Therefore, the enthalpy of hydration is expected to become more negative (more favorable from a thermodynamic standpoint) as the ionic radius decreases. The hydration enthalpies for the alkali metals, alkaline earths, and halogens are shown in Table 5.5, illustrating the expected periodic trend.

TABLE 5.5 Hydration enthalpies for selected ions (kJ/mol).

Cation	ΔH_{hyd}	Cation	ΔH_{hyd}	Anion	ΔH_{hyd}
Li^+	-520	Mg^{2+}	-1920	F^-	-506
Na^+	-405	Ca^{2+}	-1650	Cl^-	-364
K^+	-321	Sr^{2+}	-1480	Br^-	-337
Rb^+	-300	Ba^{2+}	-1360	I^-	-296
Cs^+	-277				

The solubility of the ions in water, on the other hand, is a tradeoff between the hydration enthalpy and the lattice energy. The solubility product, K_{sp} , for an ionic compound dissolving in water can be calculated from the sum of the hydration enthalpies for the ions and the reverse of the lattice energy for the ionic solid, as shown in Equations (5.2)–(5.5):



As the ionic radii decrease, the negative lattice energy term in Equation (5.4) becomes more positive. At the same time, the smaller ionic radii increase the magnitude of the hydration enthalpies in Equations (5.3) and (5.4). Thus, the radial trends tend to cancel each other. If the magnitude of the hydration enthalpies is the dominating factor, as is the case for the alkaline earth sulfates, then the solubility will increase as the ionic radius of the cation decreases, as shown in Table 5.6. On the other hand, if the lattice energy term is more important, as is the case for the alkaline earth hydroxides, then the solubility will decrease as the ionic radius of the cation decreases.

Example 5-1. Given that the lattice energy of CsF is -724 kJ/mol, use the hydration enthalpies in Table 5.3 to calculate the enthalpy of solution for CsF.

Solution. As shown in Equations (5.2)–(5.5), the enthalpy of solution is the sum of the individual hydration enthalpies for the ions minus the lattice energy of the salt. The sum is given by $-277 - 506 + 724 = -59$ kJ/mol. A graphical representation of this thermodynamic cycle is shown below.

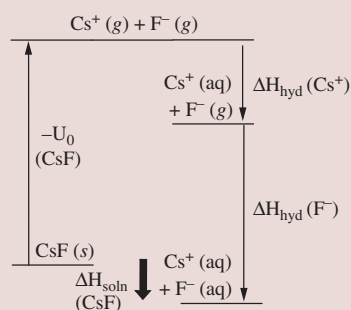


TABLE 5.6 Solubility product (K_{sp}) for selected compounds of the alkaline earths.

Compound	K_{sp}	Compound	K_{sp}
MgSO ₄	Soluble	Mg(OH) ₂	9×10^{-12}
CaSO ₄	6×10^{-5}	Ca(OH) ₂	1×10^{-6}
SrSO ₄	3×10^{-7}	Sr(OH) ₂	3×10^{-4}
BaSO ₄	2×10^{-9}	Ba(OH) ₂	5×10^{-3}

5.3 IONIZATION ENERGY

The ionization energy is defined as the amount of energy required to remove an electron from an atom in the gas phase to a distance of infinity away from the nucleus. The first ionization energy for an atom is shown in Equation (5.6) and is the one that removes the outer-most (or valence) electron from the electrostatic attraction of the nucleus. The second ionization energy is the additional amount of energy required to remove the second electron, and so on. Because it will always take energy to remove an electron, ionization energies are always positive. Theoretical ionization energies can be calculated from the negative of the energy of an electron using Koopman's theorem. Using the Bohr model, the first ionization energy can be calculated using Equation (5.7), where the Rydberg constant is expressed as 2.179×10^{-18} J. Experimentally, ionization energies are measured using photoelectron spectroscopy (PES). This technique employs either soft X-ray or vacuum UV radiation to knock the core and valence electrons, respectively, out of their atomic orbitals. The kinetic energies of the ejected electrons are then measured, and the ionization energy (or work function) is calculated according to Einstein's equation for the photoelectric effect, Equation (3.8):



$$\text{I.E.} = -E_{\text{el}} = -R_{\infty} N_A \left(\frac{Z^*}{n^2} \right) \quad (5.7)$$

The general periodic trend for the first ionization energy is that it increases up and to the right in the periodic table. Progressing down a column, n is increasing, while Z^* remains essentially constant. Owing to the inverse dependence of the ionization energy on n^2 given by Equation (5.7), the first ionization energy is expected to decrease down a column. Moving across a series, the principal quantum number is constant while Z^* is increasing. As a result, the first ionization energy increases across a row. A plot of the first ionization energy as a function of atomic number is shown in Figure 5.6.

As a general rule, I.E. increases across each row until a noble gas atom is reached and then it drops off rapidly as the next row begins. There are some notable exceptions. For instance, the first ionization energy of Be is larger than that of B and that of N is greater than that for O. The same exceptions to the rule occur for the group congeners of subsequent rows in the periodic table: Mg > Al, P > S, Ca > Ga, and As > Se. The exceptions can be rationalized on the basis of the third major factor that affects periodic trends: the electron configuration. The electron configuration of Be is [He] $2s^2$, whereas that of B is [He] $2s^2 2p^1$. The removal of the valence

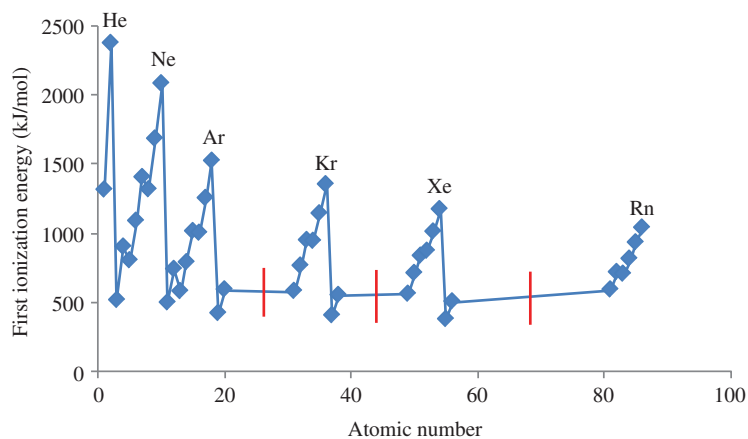


FIGURE 5.6

A plot of the first ionization energies for selected elements as a function of increasing atomic number. The peaks occur for the noble gases.

electron in B leaves the filled 2s subshell, which is a fairly stable electron configuration. Removal of a valence electron in Be, on the other hand, has to occur from a filled 2s subshell. Likewise, the electron configuration of N is $[\text{He}] 2s^2 2p^3$, whereas that of O is $[\text{He}] 2s^2 2p^4$. It is easier to remove the valence electron in O (despite its greater effective nuclear charge) because it yields a half-filled 2p subshell that is stabilized as a result of its large exchange energy. Removal of a 2p electron in N from this half-filled subshell decreases the magnitude of the exchange energy and is therefore less favorable. Exceptions to the general trend also occur at the end of the row of transition metals. The first ionization energy for Zn is considerably larger than that for Ga. For one, the valence electron in Zn is in a 3d subshell ($n = 3$) instead of the 4p level ($n = 4$). More significantly, however, the electron configuration of Zn is $[\text{Ar}] 4s^2 3d^{10}$ as compared with that of Ga, which is $[\text{Ar}] 4s^2 3d^{10} 4p^1$. The valence electron in Zn would need to be removed from a stable filled 3d subshell, whereas removal of the 4p electron from Ga leads to a stable electron configuration. The numerous exceptions to the general trend highlight the fact that it is far better to understand the factors that influence the periodic trends than it is to memorize simple generalizations.

For any given element, the second and third ionization energies are always larger than the first ionization energy. Table 5.7 lists the first several ionization energies for the more common elements.

An atom's ionization energy will strongly affect its chemical reactivity. The noble gases, which have the largest first ionization energies of all the elements, are generally unreactive. Hence, they are also known as the *inert gases*. The first noble gas compound was not discovered until 1962 when Neil Bartlett synthesized the salt $\text{Xe}[\text{PtF}_6]$. Other noble gas compounds include XeF_2 , XeF_4 , XeF_6 , XeF_8^{2-} , XeOF_4 , XeO_3 , KrF^+ , and KrF_2 . The heavier noble gases have lower first ionization energies and are therefore more reactive than the lighter ones. They also have more room to accept ligands around them because of their larger atomic radii. On the other

TABLE 5.7 Ionization energies (kJ/mol) for selected elements.

Element	1st IE	2nd IE	3rd IE	Element	1st IE	2nd IE	3rd IE
H	1312.0			Ge	762.1	1537	2735
He	2372.3	5250.4		As	947.0	1798	
Li	513.3	7298.0		Se	940.9	2044	
Be	899.4	1757.1		Br	1139.9	2104	
B	800.6	2427		Kr	1350.7	2350	
C	1086.2	2352		Rb	403.0	2632	
N	1402.3	2856.1		Sr	549.5	1064.2	
O	1313.9	3388.2		In	558.3	1820.6	2704
F	1681	3374		Sn	708.6	1411.8	2943.0
Ne	2080.6	3952.2		Sb	833.7	1794	2443
Na	495.8	4562.4		Te	869.2	1795	
Mg	737.7	1450.7		I	1008.4	1845.9	
Al	577.4	1816.6	2744.6	Xe	1170.4	2046	
Si	786.5	1577.1		Cs	375.5	2420	
P	1011.7	1903.2	2912	Ba	502.8	965.1	
S	999.6	2251		Tl	589.3	1971.0	2878
Cl	1251.1	2297		Pb	715.5	1450.4	3081.5
Ar	1520.4	2665.2		Bi	703.2	1610	2466
K	418.8	3051.4		Po	812		
Ca	589.7	1145		At	930		
Ga	578.8	1979	2963	Rn	1037		

end of the spectrum, the alkali metals, as a group, have the lowest first ionization energies and are extremely reactive. Oxidation by one electron occurs quite readily and leads to a stable electron configuration that is isoelectronic with the noble gases. Therefore, the second and third ionization energies of the alkali metals are extremely large. Both K and Na will burst into flame if enough solid is added to water. Sodium is oxidized by water according to Equation (5.8) to make sodium hydroxide and hydrogen gas. The reaction is very exothermic and the hydrogen will ignite if sufficient quantities are used. The alkali metals will also ionize in liquid ammonia to make a blue solution containing solvated electrons, as shown in Equation (5.9). They will also react readily with Lewis bases such as OH^- or SO_4^{2-} and atoms from the right-hand side of the periodic table to make a wide variety of ionic salts.



It is the ionization energy that is largely responsible for the staircase-shaped, metal–nonmetal line that divides the periodic table into two parts, as shown in Figure 5.7. The general periodic trend for ionization energy is that it increases up and to the right in the periodic table. Thus, the metal–nonmetal line is diagonal in nature. Metals lie to the left of the staircase, whereas nonmetals lie to its right. Those elements that actually border the staircase are called the *metalloids* because they often exhibit properties that are intermediate between those of a nonmetal and those of a true metal. Because of the low first ionization energies of the metals, these atoms hold their valence electrons only loosely and are easily oxidized. As a result, metallic bonding can be thought of as a crystalline array of metal atoms that have each lost one or more valence electrons to become cations that are surrounded by a “sea” of mobile electrons. The lower the ionization energy, the more readily the metal atom will lose its valence electron(s). The resistivity

Metals		Metalloids		Nonmetals		Noble gases											
H							He										
Li	Be			B	C	N	O	F	Ne								
Na	Mg			Al	Si	P	S	Cl	Ar								
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac*	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

FIGURE 5.7

Representation of the periodic table showing the division line between the metals and the nonmetals.

of a metal, however, has more to do with an atom's size than does its ionization energy. The larger the metallic radius, the more diffuse its electron cloud will be. As metallic bonding occurs as a result of the overlap of atomic orbitals to form delocalized molecular orbitals over the extended structure, there will be less overlap for more diffuse orbitals than for more compact ones. Thus, although the first ionization energy of Na is larger than that of Cs, sodium is the more conductive of the two.

Example 5-2. Use Equation (5.7) to calculate the first ionization energy for each of the following: (a) Na, (b) F, and (c) Kr.

Solution. Using Slater's rules, the values of Z^* for the valence electron Na, F, and Kr are 2.2, 5.2, and 8.3, respectively.

$$(a) \text{ Na} \quad \text{I.E.} = 2.179 \times 10^{-18} \text{ J} (6.022 \times 10^{23} \text{ mol}^{-1}) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) \left(\frac{2.2}{3^2} \right) = 320 \text{ kJ/mol}$$

$$(b) \text{ F} \quad \text{I.E.} = 2.179 \times 10^{-18} \text{ J} (6.022 \times 10^{23} \text{ mol}^{-1}) \left(\frac{1 \text{ MJ}}{10^6 \text{ J}} \right) \left(\frac{5.2}{2^2} \right) = 1.7 \text{ MJ/mol}$$

$$(c) \text{ Kr} \quad \text{I.E.} = 2.179 \times 10^{-18} \text{ J} (6.022 \times 10^{23} \text{ mol}^{-1}) \left(\frac{1 \text{ kJ}}{10^3 \text{ J}} \right) \left(\frac{8.3}{4^2} \right) = 680 \text{ kJ/mol}$$

5.4 ELECTRON AFFINITY

When an electron is added to an atom in the gas phase from a distance of infinity, the energy of this process is known as the *electron gain enthalpy* and is defined in Equation (5.10). Electron gain enthalpies are usually negative because energy is typically released as the electron comes under the influence of the nucleus. For historical reasons, electron affinities are almost always reported as positive numbers. Therefore, electron affinity (E.A.) has the same magnitude but the opposite sign of the electron gain enthalpy.



The periodic trend for electron affinities is that they generally increase up and to the right in the periodic table. As Z^* increases across a series, the larger nuclear charge exerts a stronger attraction on the electron, resulting in a large value for the E.A.. Progressing down a column, the electron is added to a quantum level that is, on average, farther from the nucleus (larger n). Thus, that electron will experience a smaller nuclear attraction, and the atom will have a low E.A. The electron affinities for a number of the main group elements are shown in Table 5.8.

There are quite a few exceptions to the general periodic trend. For instance, in the second series, the E.A. for N is less than that for C and the E.A. for Ne is considerably less than that for F (it is even negative!). As was the case for the ionization energies, exceptions to the trend can usually be explained on the basis of electron configurations. The electron configuration of N contains a half-filled $2p$ subshell. The addition of an electron would decrease the exchange energy and is therefore less favorable than in the case of C, where one more electron will yield the more stable electron configuration. Likewise, the noble gases already have filled np subshells. To decrease their valence would require the addition of an electron into an $(n+1)s$ subshell, which is not a very favorable process. Thus, the noble gases all have negative values for their electron affinities. Because the noble gases have large ionization energies and small electron affinities, they are largely inert. The halogens,

TABLE 5.8 Electron affinities (kJ/mol) for selected elements. For O and S, both the first and second E.A.s are listed.

Element	E.A.	Element	E.A.	Element	E.A.
H	72.8	P	71.7	In	34
He	-21	S	200/-532	Sn	121
Li	59.8	Cl	348.7	Sb	101
Be	≤0	Ar	-35	Te	190.2
B	23	K	48.3	I	295.3
C	122.5	Ca	2.4	Xe	-41
N	-7	Ga	36	Cs	45.5
O	141/-844	Ge	116	Ba	14.0
F	322	As	77	Tl	30
Ne	-29	Se	195.0	Pb	35.2
Na	52.9	Br	324.5	Bi	101
Mg	≤0	Kr	-39	Po	186
Al	44	Rb	46.9	At	270
Si	133.6	Sr	5.0	Rn	-41

on the other hand, have very large electron affinities and are quite reactive. Fluorine gas, for example, will react with almost any other element.

Vertical exceptions within a group also occur. The E.A. for F is less than that for Cl, for example. The smaller-than-expected E.A. for fluorine can be rationalized because of fluorine's extremely small radius. The addition of an electron to its valence shell would therefore increase the magnitude of the electron-electron repulsions. Consequently, the E.A. for fluorine is somewhat less than that for chlorine. Additionally, the bond dissociation enthalpy for F_2 (155 kJ/mol) is considerably less than that expected based on the other members of its group. For comparison, Cl_2 , Br_2 , and I_2 have bond dissociation enthalpies of 242, 193, and 151 kJ/mol. Other anomalies occur for N and O, whose electron affinities are also less than the group trend would have predicted. By analogy with the F-F bond strength, the N-N and O-O bonds are likewise weaker than those for P-P or S-S. In fact, both the hydrazine (N-N) and peroxide (O-O) classes of compounds are particularly reactive. Hydrazine, N_2H_4 , was once used as a rocket fuel, and many peroxides are potentially explosive.

5.5 THE UNIQUENESS PRINCIPLE

In many ways, the anomalies mentioned earlier for the second series elements, such as their smaller-than-expected electron affinities and bond dissociation enthalpies, are more of the rule than the exception. In general, the physical properties of the second series elements are not always representative of their groups, a characteristic that is often referred to as the *uniqueness principle*. Consider, for example, the melting points of the chlorides shown in Table 5.9. The melting points of the second series compounds are very different from the remainder of the group.

One of the proposed reasons for the uniqueness of the second series elements is that their extremely small sizes ensure larger-than-average charge densities (Z/r). The compact and concentrated nature of the charge for second series elements exerts such a strong polarizing effect on the electron cloud of the anion that the orbitals overlap to form a significant percentage of covalent character to the bonding. Because covalent bonds are more directional in nature than ionic bonds, it does

TABLE 5.9 Melting points of selected chlorides, illustrating the second series anomaly known as the *uniqueness principle*.

Compound	mp (°C)	Compound	mp (°C)	Compound	mp (°C)
LiCl	610	BeCl ₂	415	BCl ₃	-107
NaCl	801	MgCl ₂	714	AlCl ₃	193
KCl	771	CaCl ₂	782		
RbCl	718	SrCl ₂	874	InCl ₃	583

TABLE 5.10 Boiling points of the nonmetal hydrides, illustrating the uniqueness principle for the second series elements.

Compound	bp (°C)	Compound	bp (°C)	Compound	bp (°C)
NH ₃	-33	H ₂ O	100	HF	20
PH ₃	-87	H ₂ S	-65	HCl	-85
AsH ₃	-60	H ₂ Se	-45	HBr	-69
SbH ₃	-25	H ₂ Te	-15	HI	-35

not take as much energy to break the ions apart from each other in a covalent bond. Hence, the melting points of the more covalent second series compounds are considerably lower than those for their heavier group congeners.

A similar effect is observed for the boiling points of the nonmetal hydrides, shown in Table 5.10. As a rule, the boiling points increase down a group as a result of the stronger London dispersion forces associated with increased polarizability. The second series elements, however, exhibit a striking exception to the trend, bearing the highest boiling point of any compound in the same group. The larger charge densities of the second row elements (N, O, F) help them form strong hydrogen bonding interactions, which in turn elevates their boiling points.

Another significant difference between the series 2 elements and their heavier group members is that the former are more likely to form multiple bonds. For example, C=C, C≡C, N≡N, C=O, C≡O, O=O, N=O, and N≡O multiple bonds are prevalent, while examples of multiples with Si, P, and S are almost nonexistent (except for P=O and S=O). Nitrogen exists as a triple-bonded diatomic, whereas phosphorous, on the other hand, forms a tetrahedron of singly bonded P₄. Similarly, oxygen exists naturally as a doubly bonded diatomic, but sulfur forms a singly bonded S₈ ring in its natural form. The greater incidence of multiple bonding in the second series elements results from the smaller size of their atomic orbitals, which allows for an enhanced overlap of the *p* orbitals to form pi bonds. The larger and more diffuse *p* orbitals of the third and fourth series elements decrease the amount of overlap so that pi bonds between these atoms will only occur under special circumstances.

A third characteristic of the uniqueness principle is the lack of availability of low-lying *d* orbitals for participation in bonding. Hence, the second series elements cannot violate the octet rule in the formation of compounds. Consider, for example, the mixed halogens with fluorine as the central atom: F₂ and ClF, and BrF compared with those of chlorine, bromine, or iodine, which take higher coordination numbers: ClF₃, ClF₅, BrF₃, BrF₅, IF₃, IF₅, and IF₇. Similarly, the carbon atom in CF₄ is *sp*³ hybridized, while the Si atom in SiF₆²⁻ is *d*²*sp*³ hybridized. The extent to which the

d orbitals actually participate in the bonding in the so-called hypervalent compounds is a matter of contention. However, the lack of low-lying *d* orbitals available for mixing in the second series elements restricts their compounds to the usual group valence.

The decreased solubilities in water of lithium salts are also a direct result of the uniqueness principle. The large charge-to-size ratio of the lithium ion exerts a strong polarizing effect on the anion and increases the degree of covalent character in the bonding. As a result, compounds such as LiOH, LiF, Li₂CO₃, and Li₃PO₄ are not very soluble in water. Instead, they are more soluble in slightly less polar solvents, such as methanol or ethanol. The anomalous solubility of Li⁺ salts is mimicked by those of Mg²⁺, which leads naturally into a discussion of the diagonal effect.

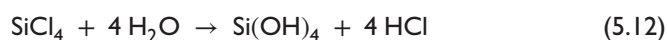
5.6 DIAGONAL PROPERTIES

Diagonal relationships are commonly observed between elements from the second and third series. This periodic trend is especially true for the following pairs of elements: Li/Mg, Be/Al, and B/Si. While vertical periodic trends are still predominant, some properties match better along a diagonal. These diagonal periodic trends are no doubt related to the fact that the radius of an atom increases down and to the left in the periodic table, whereas I.E. and E.A increase up and to the right. The diagonal nature of the metal–nonmetal line has already been discussed.

The solubility of many Li⁺ and Mg²⁺ salts in alcohols is but one example of the way that these two elements are similar. The perchlorate salts of both ions are very hygroscopic. Lithium and magnesium both form organometallic compounds that are soluble in organic solvents because of the covalent nature of their bonding. Organo-lithium reagents, such as LiI, and the Grignards, RMgX, both serve as activating agents in organometallic synthesis. The six-coordinate ionic radius of Li⁺ (76 pm) is much closer in size to Mg²⁺ (72 pm) than it is to Na⁺ (102 pm). Lithium's unusually high enthalpy of vaporization (135 kJ/mol) as compared with its group congeners is also closer to that of Mg (132 kJ/mol) than it is to Na (98 kJ/mol). Both Li and Mg are unique in that they are the only two elements that will react directly with dinitrogen to make a metal nitride.

Beryllium and aluminum also have a number of physical and chemical properties in common. Both metals form compounds that are largely covalent in their bonding and therefore more soluble in organic solvents than other members of their groups. Beryllium and aluminum both form amphoteric oxides, compounds that can act either as acids or bases. The standard reduction potential of Be (−1.85 V) is more similar to that of Al (−1.66 V) than it is to that of Mg (−2.37 V). Their compounds are numerous and usually more stable than those for their other group congeners. Both form stable compounds with oxygen- and nitrogen-based ligands. Beryllium chloride forms polymeric chains of chloride-bridged Be²⁺ ions that are sp³ hybridized, as shown in Figure 5.8, whereas AlCl₃ exists as a dimer having a similar hybridization.

The diagonal elements boron and silicon also have similar properties. The chlorides of both elements form network covalent solids that act as Lewis bases toward water, reacting according to Equations (5.11) and (5.12):



The hydrides of B and Si are volatile and flammable compounds. The boranes, as the boron hydrides are termed, form many interesting hydrogen-bridged structures that are seldom observed with other main group elements. Both boron and silicon form numerous and complex oxygen-containing structures known as the *borates*

and *silicates*. Their ions (B^{3+} and Si^{4+}) also have similar charge densities. Boron is a nonmetal with respect to its chemical reactivity, but it does have semi-metallic properties. Silicon is a semi-conductor and is used in the manufacture of computer chips. Both of these elements lie along the diagonal staircase that separates the metals from the nonmetals.

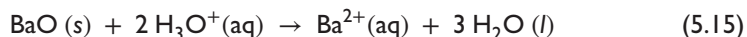
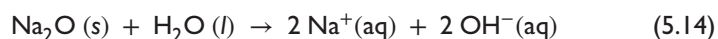
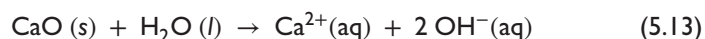
5.7 THE METAL–NONMETAL LINE

The metal–nonmetal line is shown in Figure 5.7. It runs diagonally along a staircase from just left of B to just left of At. Boron is considered to be a nonmetal, whereas Al and Po are metals. The remainder of the elements along this line exhibit both metallic and nonmetallic properties. These elements are called the *metalloids* and include Si, Ge, As, Sb, Te, and At. The metals form infinite lattices with high coordination numbers. Because of their low ionization energies, the metals actually exist in the crystal structure as cations that are surrounded by a mobile sea of electrons. The electrons are free to flow over the entire structure through a delocalized band of molecular orbitals. This is what gives the metals many of their characteristic properties, such as their high electrical and thermal conductivities and their metallic luster. Nonmetals, on the other hand, are poor thermal conductors and electrical insulators. Most metallic solids are malleable (they can be shaped by hammering) and ductile (they can be drawn into wires), while most nonmetals are brittle. Metal atoms tend to form cations, are good reducing agents, and can react with water or acids to form hydrogen gas. The nonmetals tend to form anions, are good oxidizing agents, and never liberate hydrogen from acids.

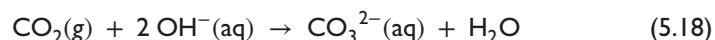
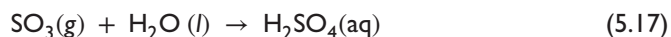
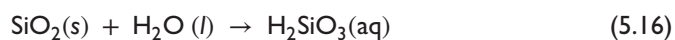
The electrical conductivity, σ , of a metal is measured in $1/\Omega\cdot\text{m}$ and is the current density divided by the electric field strength. The resistivity, ρ , is the inverse of the conductivity. The less tightly the metal atom holds onto its electrons and the greater the overlap between its valence orbitals, the smaller the resistivity will be and the more conductive the metal. Therefore, metals with low first ionization energies and small atomic radii will make the best conductors. Among the transition metals, silver is the most conductive, with a room-temperature resistivity of $1.6 \times 10^{-8} \Omega\cdot\text{m}$.

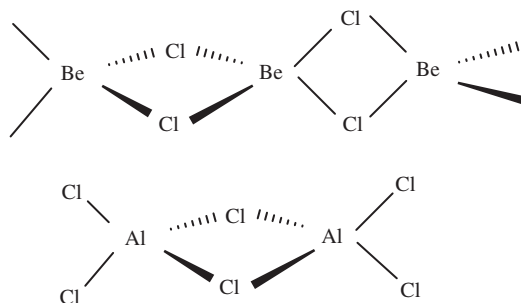
One of the most significant differences between the metals and the nonmetals besides their electrical conductivity is the acid–base properties of their oxides. Metal oxides are basic and react accordingly, as demonstrated by the reactions shown in Equations (5.13)–(5.15). Nonmetal oxides, on the other hand, act as acids, as shown in Equations (5.16)–(5.18). The oxides of the metalloids are amphoteric and can act either as acids or as bases, as shown by Equations (5.19) and (5.20):

Basic oxides: (Li, Na, Mg, K, Ca, Rb, Sr, Cs, Ba, Tl)



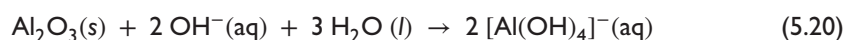
Acidic oxides: (B, C, N, O, F, Si, P, S, Cl, Se, Br, Te, I, Po, At)



**FIGURE 5.8**

Chemical structures of BeCl₂ and AlCl₃, showing how both metal ions have tetrahedral coordinations.

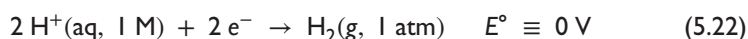
Amphoteric oxides: (Be, Al, Ga, Ge, As, In, Sn, Sb, Pb, Bi)



With few exceptions, the metal oxides are ionic solids and react with water to form aqueous ions, the nonmetal oxides are network covalent solids that react with water to make covalent compounds, and the amphoteric oxides of the metalloids form oligomeric polar-covalent solids. Similar relationships hold for the hydrides and fluorides of each element, with the metal forming an ionic solid and the nonmetal forming a network covalent solid, although the actual demarcation line varies somewhat depending on the anion.

5.8 STANDARD REDUCTION POTENTIALS

One of the few periodic trends of the metals not to show a strong diagonal effect is the standard reduction potential. In fact, this trend follows more of a horizontal rule. The standard reduction potential, E° , is defined in Equation (5.21). The standard reduction potential for the normal hydrogen electrode (N.H.E.), or the half-reaction shown in Equation (5.22), is given a value of zero. Metal atoms with E° 's more negative than the N.H.E. are easier to oxidize and harder to reduce. Metal atoms with E° 's more positive than the N.H.E. are easier to reduce and harder to oxidize:



The standard reduction potential can be calculated using the thermodynamic cycle shown in Equations (5.23)–(5.26):



The periodic trend within a group is a balance between two contributing properties. On one hand, as one proceeds down the group, the decrease in ionization energy makes it easier to oxidize the metal, leading to a negative value for the standard reduction potential. On the other hand, the decrease in the charge density (Z/r) down a column leads to a less negative enthalpy of hydration for the metal ion,

TABLE 5.11 Standard reduction potentials for selected elements at 25 °C.

Half-reaction	E° (V vs NHE)
$\text{Li}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Li} (\text{s})$	-3.05
$\text{K}^+ (\text{aq}) + \text{e}^- \rightarrow \text{K} (\text{s})$	-2.93
$\text{Ba}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Ba} (\text{s})$	-2.90
$\text{Sr}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Sr} (\text{s})$	-2.97
$\text{Ca}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Ca} (\text{s})$	-2.87
$\text{Na}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Na} (\text{s})$	-2.71
$\text{Mg}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Mg} (\text{s})$	-2.37
$\text{Sc}^{3+} (\text{aq}) + 3\text{e}^- \rightarrow \text{Sc} (\text{s})$	-2.08
$\text{Be}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Be} (\text{s})$	-1.85
$\text{Al}^{3+} (\text{aq}) + 3\text{e}^- \rightarrow \text{Al} (\text{s})$	-1.66
$\text{Ti}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Ti} (\text{s})$	-1.63
$\text{V}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{V} (\text{s})$	-1.19
$\text{Mn}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Mn} (\text{s})$	-1.18
$\text{Cr}^{3+} (\text{aq}) + 3\text{e}^- \rightarrow \text{Cr} (\text{s})$	-0.74
$\text{Fe}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Fe} (\text{s})$	-0.44
$\text{Tl}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{Tl} (\text{s})$	-0.33
$\text{Co}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Co} (\text{s})$	-0.28
$\text{Ni}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Ni} (\text{s})$	-0.25
$\text{Sn}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Sn} (\text{s})$	-0.14
$\text{Pb}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Pb} (\text{s})$	-0.13
$2\text{H}^+ (\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2 (\text{g})$	0.00
$\text{Cu}^{2+} (\text{aq}) + 2\text{e}^- \rightarrow \text{Cu} (\text{s})$	0.34
$\text{I}_2 (\text{s}) + 2\text{e}^- \rightarrow 2 \text{I}^- (\text{aq})$	0.54
$\text{Ag}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Ag} (\text{s})$	0.80
$\text{Br}_2 (\text{l}) + 2\text{e}^- \rightarrow 2 \text{Br}^- (\text{aq})$	1.07
$\text{Cl}_2 (\text{g}) + 2\text{e}^- \rightarrow 2 \text{Cl}^- (\text{aq})$	1.36
$\text{F}_2 (\text{g}) + 2\text{e}^- \rightarrow 2 \text{F}^- (\text{aq})$	2.87

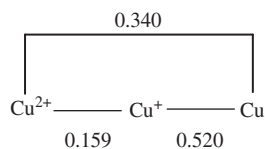
shifting E° more positive. As a result of the opposing trends, there is little variation in the standard reduction potential within a group. There is, however, a fairly steady trend in the E° as one proceeds across a series. Metals on the left-hand side of the periodic table have the lowest ionization energies and the most negative values of E° . The standard reduction potentials of the fourth series elements are as follows (with units of V vs N.H.E.): K^+/K (-2.93), Ca^{2+}/Ca (-2.87), Sc^{3+}/Sc (-2.08), Ti^{2+}/Ti (-1.63), V^{2+}/V (-1.19), Cr^{3+}/Cr (-0.74), Fe^{2+}/Fe (-0.44), Co^{2+}/Co (-0.28), Ni^{2+}/Ni (-0.25), Cu^{2+}/Cu (+0.34), and $\text{Br}_2/2 \text{Br}^-$ (+1.07) (Table 5.11).

Many of the transition metals can take more than one oxidation state. Whenever this occurs, it is useful to show the relationship between the standard reduction potentials graphically using a *Latimer diagram*. Consider the stepwise reduction potentials for Cu^+ and Cu^{2+} shown by Equations (5.27) and (5.28). In order to determine the *skip potential* for the two-electron reduction of Cu^{2+} shown by Equation (5.29), we cannot simply add the two stepwise potentials together to get the final result.



FIGURE 5.9

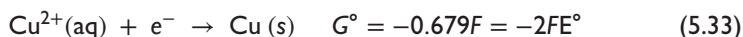
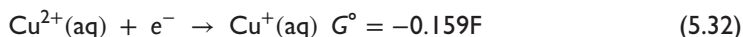
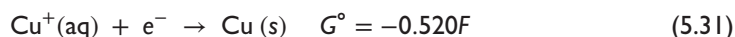
Latimer diagram for copper.



The reason for this becomes apparent when the equation relating the standard reduction potential to the Gibbs free energy is considered, as shown by Equation (5.30), where F is Faraday's constant (96,485 C/mol). While the value of n in Equation (5.30) is 1 for Equations (5.27) and (5.28), it is 2 for Equation (5.29):

$$G^\circ = -n F E^\circ \quad (5.30)$$

The Gibbs free energies are additive, as shown by Equations (5.31)–(5.33), and these can be used to deduce the skip potential for Equation (5.29):



Using the relationship given in Equation (5.33), the skip potential for Equation (5.29) is calculated as 0.340 V. The Latimer diagram for Cu shown in Figure 5.9 summarizes all three potentials in a succinct manner. Arrows are usually omitted from the Latimer diagram because it is assumed that all of the potentials are given for the reduction half-reactions.

It is also sometimes useful to illustrate the Gibbs free energy relationships on a *Frost diagram*. The Frost diagram for Cu is shown in Figure 5.10. The Frost diagram is essentially a plot of the Gibbs free energy (in units of nE°) versus the oxidation state of the metal. The Gibbs free energy for the metal in its elemental form is assigned a value of 0 on the y-axis. From Equation (5.31), the Gibbs free energy difference between Cu(0) and Cu(I) is 0.520. As the Gibbs free energy difference between Cu(I) and Cu(II) is an additional 0.159, the total change in free energy upon going from Cu(0) to Cu(II) is 0.679. Most metals are powerful reducing agents, but Cu is one of the few exceptions because its oxidized forms have a higher free energy than the element. As a result, Cu is not normally oxidized by H^+ unless an oxidizing anion is used. Thus, for instance, HCl will not oxidize copper, but HNO_3 will. Furthermore,

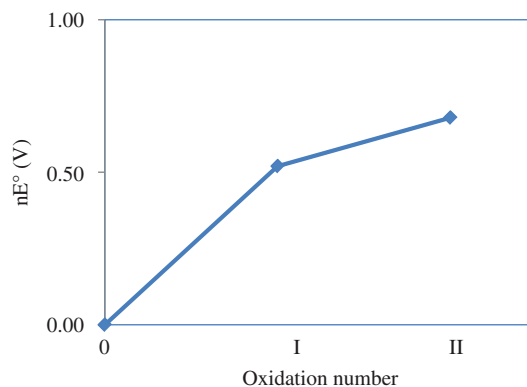
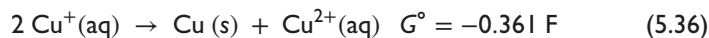


FIGURE 5.10

Frost diagram for copper.

the Frost diagram predicts that when HNO_3 oxidizes Cu metal, the resulting oxidation state will be Cu(II) and not Cu(I). The Cu(I) intermediate is unstable and can disproportionate into Cu(0) and Cu(II), as shown by Equations (5.34)–(5.36):



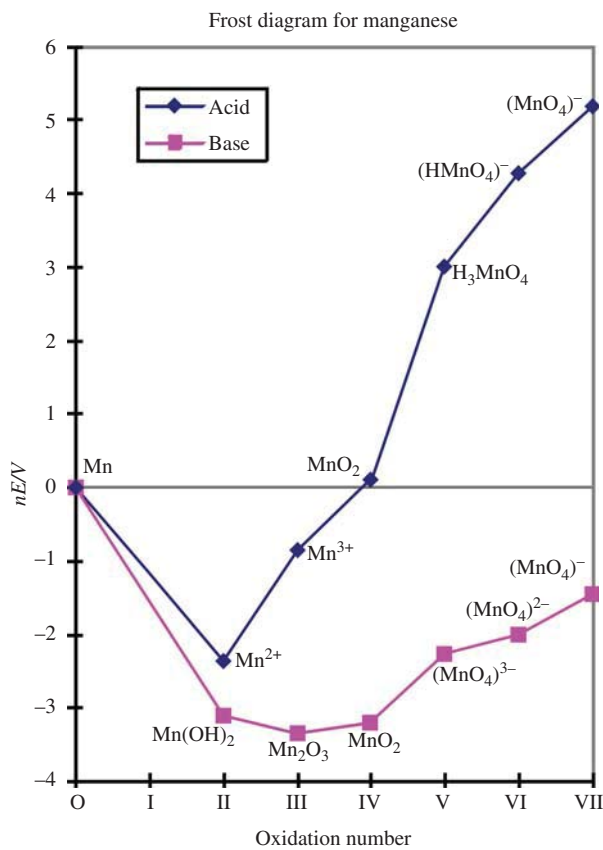
The usefulness of Frost diagrams becomes more apparent as the complexity of the different oxidation numbers increases. Consider the Frost diagram for Mn shown in Figure 5.11. Manganese can take a wide variety of oxidation states and its derivatives also have an acid–base dependence.

Those compounds lying high in the Frost diagram are good oxidizing agents relative to those lying lower on the diagram. Thus, the permanganate ion is the strongest oxidizing agent. Furthermore, the slope of the line determines the relative strength of the compound as an oxidizing agent. Permanganate is a stronger oxidizer in the presence of acid than it is in the presence of base. Those oxidation states that lie above the line connecting their two neighbors in the Frost diagram are unstable with respect to disproportionation, as is the case for MnO_4^{3-} in basic solution. In a similar manner, those species that are likely to undergo comproportionation are those that lie on either side of a substance that sits below the lines connecting its two neighbors. For example, $\text{Mn}(\text{OH})_2$ and MnO_2 can react with each other to form two equivalents of Mn_2O_3 in basic solution. Substances lying on the lower region of the graph have low free energies and are therefore less reactive.

5.9 THE INERT-PAIR EFFECT

One of the more unusual periodic trends is known as the *inert-pair effect*. The elements that immediately follow the 4*d* and 5*d* transition series are considerably less reactive than their group properties might have predicted and they also prefer oxidation states that are two lower than the usual group valence. Consider, for example, the Group IIIA elements. The lighter elements, B, Al, and Ga take only the 3+ oxidation state predicted by their group valence. However, the heavier elements, In and Tl, take both the 3+ and 1+ oxidation states. The same trend is observed for the Group IVA elements. Again, the lighter elements C, Si, and Ge take the 4+ valence predicted by their period. However, Sn and Pb can exist in either the 4+ or the 2+ oxidation state.

The relative stability of the lower oxidation states for the fifth and sixth series post-transition elements (In, Sn, Sb, Tl, Pb, Bi, and Po) has been attributed to the higher-than-expected ionization energies for these seven elements. Consequently, it costs these elements relatively more energy to achieve a higher oxidation state than their lighter group congeners. At the same time, less energy is gained as a result of bond formation because they also exhibit lower-than-predicted bond dissociation enthalpies. Weaker bond enthalpies are expected for the heavier elements as a result of the diffuse nature of orbital overlap with increasing orbital size. The larger-than-expected ionization energies for the post-transition series Group IIIA elements result from the fact that the valence *s* electrons are not shielded from the nucleus very effectively by the intervening *d* electrons. As the two *s* electrons are both held tighter by the nucleus in the post-transition series elements, the ionization energies for these two electrons are unusually large. The end result is that these elements prefer oxidation states that are two lower than their typical group valence. Relativistic effects, which are discussed in the following section, also contribute to the higher-than-expected ionization energies of the valence *s* electrons.

**FIGURE 5.11**

Frost diagram for manganese under acid and base conditions. [Developed by René T. Boéré, University of Lethbridge, Alberta, Canada, copyright (2000, 2013). Used with permission.]

5.10 RELATIVISTIC EFFECTS

For most applications of chemistry, the effect of relativity on electronic motion can largely be ignored. Einstein's theory of relativity states that the mass of a particle becomes infinite as its velocity approaches the speed of light. For the smaller elements, Schrödinger's nonrelativistic model is perfectly appropriate, as the velocities of the electrons in the lighter elements rarely approach the speed of light. However, the larger mass of the heavier elements exerts a stronger electrostatic pull on the inner-most electrons, sometimes accelerating them to speeds in excess of 10^8 m/s. According to Einstein's theory of relativity, particles that are traveling at velocities approaching the speed of light are more massive than they are at rest, as shown by Equation (5.37), where m_{rel} is the relativistic mass of the electron and m_0 is its rest mass. As a result of their relativistic heavier mass, the accelerated electrons have a smaller average radius, as indicated by Equation (5.38), which results from the derivation of the Bohr model of the atom:

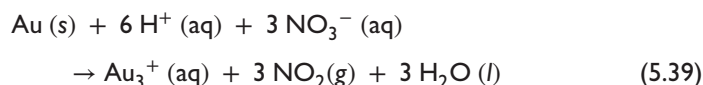
$$m_{rel} = \frac{m_0}{\sqrt{1 - (v/c)^2}} \quad (5.37)$$

$$r = \frac{4\pi\epsilon_0 n^2 \hbar^2}{m_e Z e^2} \quad (5.38)$$

Because the *s* and *p* electrons penetrate the nucleus better than the *d* or *f* electrons do, the *s* and *p* electrons are accelerated to a greater extent. Thus, the

s and p orbitals effectively contract as relativistic effects become more prominent. Furthermore, as the s and p electrons migrate closer to the nucleus, this enhances their ability to shield the d and f electrons from experiencing the full attraction of the nucleus. Thus, the d and f orbitals expand as a result of relativity. The combined effect is to lower the energies of the s and p electrons, as shown in Figure 5.12, while raising the energy of the d and f electrons. The magnitude of the effect increases roughly as the square of the atomic number. Thus, the heavier elements experience considerably larger relativistic effects than do the lighter ones. For a number of elements heavier than Pt, the magnitude of the effect is even comparable to the strength of a chemical bond! The relativistic effect enhances the inert-pair effect mentioned in the preceding section. The smaller radius of the 6s orbital in Tl, for instance, causes the 6s electrons to be held more tightly than they would have been in the absence of relativity and raises their ionization energies. Hence, Tl will commonly prefer the lower 1+ oxidation number over its 3+ state.

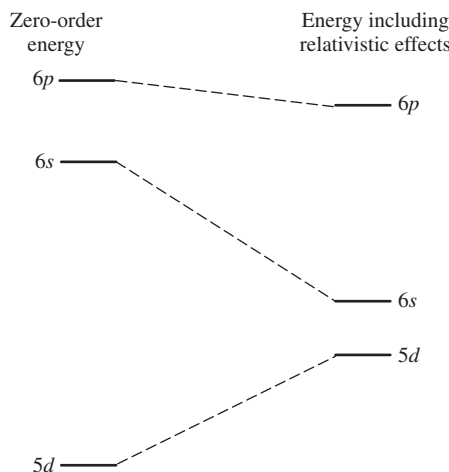
However, unlike the inert-pair effect, any of the heavier elements can experience the relativistic effect. As an example, gold is the least reactive of the coinage metals. This explains why it was one of the first elements to be discovered by ancient civilizations (about 10,000 years ago). Gold exists in nature in its elemental form and is only rarely found in minerals, such as calaverite, AuTe₂, and sylvanite, AuAgTe₄. The electron configuration of Au is [Xe] 4f¹⁴5d¹⁰6s¹. As a result of the relativistic effect, the 6s electron has an unusually large ionization energy (890 kJ/mol, compared with 746 kJ/mol for Cu and 741 kJ/mol for Ag) and is extremely difficult to oxidize. Hence, gold will not rust in air, nor will it react with the oxidizing acid HNO₃. In fact, in order to dissolve gold, a combination of one part nitric acid with three parts HCl must be employed. Nitric acid acts as the oxidizer, while the Cl⁻ ion helps to solubilize the gold as the complex ion AuCl₄⁻, according to Equations (5.39) and (5.40). The mixture is known as *aqua regia* because it is the only acid that can dissolve the “royal” metals Au and Pt:



As a result of relativistic orbital contraction, the atomic radius of Au is less than that expected on the basis of its periodic trends: Cu (135 pm), Ag (160 pm), and Au (135 pm). Because of the small size of its half-filled 6s orbital, the E.A. of Au (223 kJ/mol) is considerably larger than that for Ag (126 kJ/mol) or Cu (118 kJ/mol). In fact, the E.A. of Au is so large that gold exists as the Au⁻ anion in the compound cesium auride (CsAu).

At the same time that the 6s orbital shrinks and is therefore stabilized by the relativistic effect, the 5d orbital expands and is destabilized. Thus, the energy gap between the 5d and 6s orbitals is fairly small, and gold reflects light in the low-energy region of the visible spectrum. This is why gold has a distinctive yellowish color, unlike the silvery reflectance of most of the other metals. Gold is also a fairly soft metal. Pure gold, which is 24 carats, is seldom used in the manufacture of jewelry because it is so soft that ordinary wear and tear will damage the metal. Instead, an alloy of 18k or 14k gold is generally used. A typical piece of 18k jewelry consists of 75.0% Au, 12.5% Ag, and 12.5% Cu, by mass. The presence of the other metals helps harden the alloy.

The unusual differences between Au and Hg, which are neighbors on the periodic table, can also be ascribed to the relativistic energies of the orbitals shown in Figure 5.12. Gold has a melting point of 1064 °C, whereas Hg is a liquid at

**FIGURE 5.12**

Valence orbital energies for Au and Hg in the absence of relativistic effects and with relativistic effects included.

room temperature and has a melting point of -39°C . In many ways, Au acts as a pseudo-halogen, as evidenced by its ability to form the auride anion. The low-lying 6s orbital in Au is singly occupied. Therefore, like the halogens, gold can exist as the diatomic Au_2 . In fact, Au_2 has a gas-phase bond dissociation energy (BDE) of 221 kJ/mol, which is even larger than that for I_2 (151 kJ/mol) and only slightly smaller than that of Cl_2 (242 kJ/mol). Mercury, on the other hand, has two electrons in the low-lying 6s orbital and it behaves as a pseudo-noble gas. Mercury(0) cannot form a diatomic like Au(0) because its electrons are all paired. However, oxidation of Hg by one electron to form Hg(I), which is isoelectronic with Au(0), leads to a stable diatomic cation, Hg_2^{2+} . By analogy with the noble gases, Hg(0) is fairly unreactive. Its unusually low melting point can be ascribed to the fact that Hg atoms can only aggregate together in the condensed phases as a result of weak van der Waals forces. Mercury is unique among the transition metals because it exists in the gas phase almost exclusively as monomeric Hg just like the noble gases do. In comparison with H, whose relativistic mass is 1.00003 times its rest mass and where its 1s electron has an average velocity of $0.0073c$, the relativistic mass of a 1s electron in Hg is 1.23 times its rest mass and its average velocity is $0.58c$, so that its size shrinks by a factor of nearly a quarter.

The spin-orbit coupling of polyelectronic terms is also a consequence of the relativistic effect. For elements with $Z \geq 30$, the L and S quantum numbers in the Russell-Saunders (LS coupling) scheme are no longer valid. Instead, the spin (s) and orbital (l) angular momentum for each electron couple together first to give a new quantum number j . The total angular momentum J is given as the sum of the individual j values for each of the electrons in a process known as jj coupling. This procedure was described in Section 4.5. From a phenomenological point of view, the relativistic approach considers the electron as stationary with the nucleus orbiting it. Because the nucleus is a charged particle, it creates a magnetic moment. The spin and orbital magnetic moments can couple together to mix those states that have the same total angular momenta. The magnitude of spin-orbit coupling depends on the metal, its oxidation state, its ground state term symbol (the values of J , L , and S), and its ligand field, according to Equation (4.27), where λ is the spin-orbit coupling constant. Because the value of λ increases in proportion to Z^4/n^3 , it becomes increasingly important for the heavier atoms. For example, the value of λ for the ground state Cu(II) free ion is -830 cm^{-1} , whereas $\lambda = -1600\text{ cm}^{-1}$ for Rh(III) and -4000 cm^{-1} for Ir(III).

One of the most important consequences of spin–orbit coupling is the mixing of terms in electronic spectroscopy. Electronic transitions between states of different spin multiplicities, such as singlet-to-triplet transitions, are forbidden by the spin selection rule. This explains why phosphorescence ($\Delta S \neq 0$) is a slower process than fluorescence ($\Delta S = 0$). The coupling of the spin and orbital angular momentum relaxes this restraint and allows the different spin states to mix with each other. Hence, the rate of intersystem crossing between states of different multiplicity increases with increasing atomic number. Spin–orbit coupling can also affect the degree of spin–spin coupling in NMR spectroscopy.

5.11 ELECTRONEGATIVITY

The final periodic trend that we shall discuss in this chapter is the important concept of electronegativity. As defined by Linus Pauling, *electronegativity* is the ability of an atom in a molecule to attract the shared electrons closer to itself. Unlike most of the other periodic laws, such as radius, ionization energy, and E.A., electronegativity has no meaning outside the context of a chemical bond. Thus, there is no absolute scale for electronegativity. The Pauling scale of electronegativity was developed in 1932 and is still the most widely used. Pauling arbitrarily assigned the electronegativity of fluorine as 4.00. The electronegativities of the other elements are based on the difference between the experimental bond dissociation energy for a heteronuclear diatomic and the average of the bond dissociation energies for the corresponding homonuclear diatomics. This difference, given by the symbol Δ in Equations (5.41) and (5.42), is known as the *ionic resonance energy*, which is proportional to the percent ionic character in the bonding. The abbreviation BDE stands for the bond dissociation energy. A correction must be made if the diatomic molecule is multiply bonded, as is the case for N_2 or O_2 . The Pauling electronegativities of selected elements are listed in Table 5.12, along the corresponding values for more modern definitions of electronegativity:

$$\Delta = \text{BDE}(A - B) - \frac{\text{BDE}(A - A) + \text{BDE}(B - B)}{2} \quad (5.41)$$

$$\Delta\chi = \chi_A - \chi_B = 0.102\sqrt{\Delta} \quad (5.42)$$

Example 5-3. Calculate the electronegativity of Cl given that the bond dissociation energies for Cl_2 , F_2 , and ClF are 242, 158, and 255 kJ/mol, respectively.

Solution. The ionic resonance energy, Δ , is calculated from Equation (5.41) as follows:

$$\Delta = 255 - \frac{242 + 158}{2} = 55 \text{ kJ/mol}$$

The difference in electronegativity between F and Cl can be calculated from Equation (5.42):

$$\Delta\chi = \chi_F - \chi_{Cl} = 0.102\sqrt{55} = 0.76$$

As the electronegativity of F defined by Pauling is 4.00, the calculated value of χ for Cl is 3.24. The actual values are listed in Table 5.12, where the modern value of χ for F has been corrected to 3.98 instead of 4.00. The tabulated value of 3.16 for Cl is reasonably close to the calculated value of 3.24.

TABLE 5.12 Electronegativities of selected elements using the revised Pauling scale, the Mulliken–Jaffe scale, and Allen’s spectroscopic configuration energies. The latter scales have been converted to the revised Pauling scale. The Mulliken–Jaffe values are listed for the sp^3 valence hybridization, unless otherwise indicated.

Element	χ (Pauling)	χ_{MJ} (Mulliken)	χ_{spec} (Allen)
H	2.20	2.25 (s)	2.30
Li	0.98	0.97 (s)	0.91
Be	1.57	1.54 (sp)	1.58
B	2.04	2.04 (sp^2)	2.05
C	2.55	2.48	2.54
N	3.04	3.04	3.07
O	3.44	3.68	3.61
F	3.98	3.91 (14% s)	4.19
Na	0.93	0.91 (s)	0.87
Mg	1.31	1.37 (sp)	1.29
Al	1.61	1.83 (sp^2)	1.61
Si	1.90	2.28	1.92
P	2.19	2.41	2.25
S	2.58	2.86	2.59
Cl	3.16	3.10 (14% s)	2.87
K	0.82	0.73 (s)	0.73
Ca	1.00	1.08 (sp)	1.03
Ga	1.81	2.01 (sp^2)	1.76
Ge	2.01	2.33	1.99
As	2.18	2.38	2.21
Se	2.55	2.79	2.42
Br	2.96	2.95 (14% s)	2.68
Kr	3.00	3.31	2.97
Rb	0.82	0.82 (s)	0.71
Sr	0.95	1.00 (sp)	0.96
In	1.78	1.76 (sp^2)	1.66
Sn	1.96	2.21	1.82
Sb	2.05	2.22	1.98
Te	2.10	2.57	2.16
I	2.66	2.95	2.36
Xe	2.60	3.01	2.58

Alternative electronegativity scales have been developed by others through the years. The Mulliken–Jaffe scale defines electronegativity on the basis of atomic parameters, namely the average of the valence ionization energy and E.A., as shown in Equation (5.43). The v subscripts indicate that the valence configuration must be used. Thus, for example, boron forms three equivalent bonds by hybridizing its valence $2s$ and $2p$ orbitals to make sp^2 hybrid orbitals. The theoretical ionization energy and E.A. for the sp^2 hybrid orbitals must be used in Equation (5.43) in place of those for an unhybridized $2p$ orbital. Hence, the original Pauling definition of electronegativity as a property of an atom within a molecule still rings true. Mulliken–Jaffe electronegativities are typically expressed in units of electron volts. However, the Pauling scale has been so firmly entrenched that more often than not

the Mulliken–Jaffe scale is converted to the Pauling scale through a simple conversion factor. One advantage of the Mulliken–Jaffe scale is that it correctly predicts the periodic trend for electronegativity. Because the periodic trends for both first ionization energy and E.A. increase up and to the right in the periodic table, the average of these two values should also follow this trend. Indeed, the periodic trend for electronegativity is that it increases toward the upper right-hand corner of the periodic table. When comparing the electronegativities of the elements, there is a very clear demarcation line between the metals and the nonmetals. The metals have only a small difference in energy between their *s* and *p* orbitals, whereas the nonmetals have a much larger gap.

$$\chi_{\text{MJ}} = \frac{\text{I.E.}_v + \text{E.A.}_v}{2} \quad (5.43)$$

More recently, Lee Allen has developed an electronegativity scale that is based on spectroscopic data, namely the average valence electron energies obtained by gas-phase atomic spectroscopy. Allen's spectroscopic electronegativity (χ_{spec}) is based on the configuration energy (C.E.), given by Equation (5.44). In this equation, ϵ_p and ϵ_s are the "one-electron" energies of the valence *p* and *s* orbitals, respectively, and *m* and *n* are the numbers of *p* and *s* electrons occupying those orbitals. More specifically, the energies ϵ_p and ϵ_s are calculated from the average of the $(2L + 1)(2S + 1)$ multiplets of the ground state with those of the singly *s* and singly *p* ionized configurations. The Allen approach has the advantage that it is not based on molecular properties and can be calculated solely from the spectroscopic properties of each atom. Because the formula in Equation (5.44) ignores contributions from the *d* and *f* electrons, it is not at all useful for the transition metals, lanthanides, or actinides. This is not a problem as the chemical properties of the transition metals are dominated by ligand field effects, rather than electronegativities. As was the case for the Mulliken–Jaffe scale, configuration energies can also be converted to the Pauling scale by multiplying the C.E. (in kJ/mol) by 1.75×10^{-3} mol/kJ. The data in Table 5.12 compare the electronegativities of selected atoms using all three definitions. The electronegativities of the lighter noble gases are not included, as these elements tend not to form too many compounds.

$$\chi_{\text{spec}} \propto \text{C.E.} = \frac{m\epsilon_p + n\epsilon_s}{m + n} \quad (5.44)$$

Other definitions have also been proposed through the years. The Allred–Rochow scale is based on the electrostatic force exerted by the nucleus on the valence electrons, whereas the Sanderson scale represents a ratio of the experimental electron density to that predicted by interpolation of the electron densities of the two nearest noble gas atoms. Sanderson is also responsible for the concept of electronegativity equalization. When two or more atoms having different initial electronegativities combine to make a bond, they adjust to have the same intermediate electronegativity in the molecule. The electronegativities of ions and of groups of atoms, such as CF_3 , NH_2 , or COOH , have also been calculated using the principle of electronegativity neutrality. For example, the group electronegativity of CF_3 (3.47) is greater than that of CH_3 (2.31) as a result of the inductive effect of the F atoms. Likewise, the calculated group electronegativity of the electron-withdrawing group COOH (3.04) is greater than that of the electron-donating group NH_2 (2.47).

Example 5-4. Calculate χ_{spec} for N given that $\epsilon_p = 1270$ kJ/mol and $\epsilon_s = 2465$ kJ/mol.

Solution. The electron configuration of N is [He] $2s^2 2p^3$. The C.E. of N can therefore be calculated from Equation (5.44):

$$\text{C.E. (N)} = \frac{3(1270 \text{ kJ/mol}) + 2(2465 \text{ kJ/mol})}{5} = 1750 \text{ kJ/mol}$$

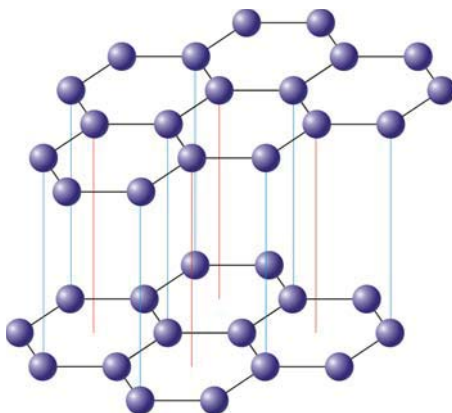
The spectroscopic electronegativity of N is given by

$$\chi_{\text{spec}}(\text{N}) = 1.75 \times 10^{-3} \text{ mol/kJ} (1750 \text{ kJ/mol}) = 3.06$$

The electronegativity of N on the revised Pauling scale is 3.04, in excellent agreement with the calculation.

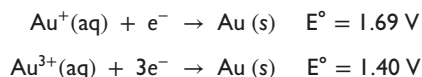
EXERCISES

- 5.1. Explain why the covalent radius of K is considerably smaller than its metallic radius. How are the two different radii defined?
- 5.2. The atomic radius of Cl is 102 pm. Explain why the ionic radius of Cl in the perchlorate ion is 41 pm, whereas the ionic radius of Cl in the chloride ion is 181 pm. Compare both values to the atomic radius.
- 5.3. The ionic radius of Na^+ depends on its coordination number. Rationalize the following trend: 99 pm (four-coordinate), 102 pm (six-coordinate), and 118 pm (eight-coordinate).
- 5.4. Use ionic radii to rationalize why H_2O has a bent molecular geometry while Li_2O is linear.
- 5.5. Although Li^+ has a much smaller ionic radius than K^+ in the gas phase, the solvated radii of the two ions is reversed: Li^+ (aq) = 382 pm, whereas K^+ (aq) = 328 pm. Explain these results in terms of the enthalpy of hydration and the numbers of water molecules that surround each ion in aqueous solution.
- 5.6. Why is Lu^{3+} smaller than Y^{3+} ?
- 5.7. For each pair, circle the species with the larger radius and provide reasoning for your choice: (a) Mg or Mg^{2+} , (b) O or O^{2-} , (c) K^+ or Cl^- , (d) P^{3-} or S^{2-} , (e) N or P, (f) Na or Mg, and (g) Na^+ or Mg^{2+} .
- 5.8. Arrange the following in increasing order of first ionization energy: F, Na, Al, P, S, and Cl.
- 5.9. Which of the alkali metals is the most reactive with water, and why?
- 5.10. Explain why Kr and Xe form more types of noble gas compounds than the lighter noble gases.
- 5.11. Calculate the first ionization energy for the valence electron in O in MJ/mol.
- 5.12. Match the following electron configurations with the appropriate first ionization energy:
 - a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$ (i) 1356 kJ/mol
 - b. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ (ii) 595 kJ/mol
 - c. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$ (iii) 409 kJ/mol
- 5.13. One allotrope of carbon is graphite, which is an electrical conductor, is shown below. Predict whether silicon has an allotrope having a structure that is analogous to that for graphite. Explain your answer in detail.



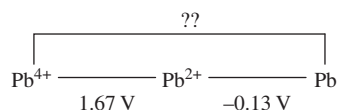
[E. Generalic, <http://www.periodni.com>, used with permission.]

- 5.14.** When lead is exposed to chlorine gas, the product of the reaction is PbCl_2 . Only under more extreme conditions will PbCl_4 form. However, when chlorine reacts with carbon, the product of the reaction is CCl_4 . Explain these differences.
- 5.15.** When PbO_2 reacts with water, it yields the hypothetical hydrated product: $\text{Pb}(\text{OH})_4$. On the other hand, CO_2 reacts with water to make carbonic acid, H_2CO_3 . Explain the differences in reactivity between these two molecules in as much detail as possible.
- 5.16.** Given the standard reduction potentials below, calculate the standard reduction potential for the $\text{Au}^{3+}/\text{Au}^+$ redox couple and sketch the Latimer diagram for gold.



Given the information above, sketch the Frost diagram for gold and predict the product when $\text{Au}(\text{s})$ is reacted with $\text{H}^+(\text{aq})$.

- 5.17.** Given the Latimer diagram shown below for lead, calculate the Gibbs free energy for the disproportionation reaction shown below. Also, fill in the missing skip potential.



Disproportionation reaction: $2 \text{Pb}^{2+}(\text{aq}) \rightarrow \text{Pb}(\text{s}) + \text{Pb}^{4+}(\text{aq})$

- 5.18.** Given the following bond dissociation energies, calculate the Pauling electronegativity of Br using Equations (5.41) and (5.42): $\text{Cl}-\text{Cl}$ (242 kJ/mol), $\text{Br}-\text{Br}$ (183 kJ/mol), and $\text{Br}-\text{Cl}$ (219 kJ/mol). The Pauling electronegativity of Cl is 3.16.
- 5.19.** Calculate χ_{spec} for O given that $\epsilon_{\text{p}} = 1529 \text{ kJ/mol}$ and $\epsilon_{\text{s}} = 3124 \text{ kJ/mol}$.

BIBLIOGRAPHY

- Atkins, P.; de Paula, J. *Physical Chemistry*, 7th ed., W. H. Freeman and Company, New York, 2002.
- Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. Covalent radii revisited, *Dalton Trans.*, 2008 [DOI: 10.1039/b801115j].

3. Douglas, B.; McDaniel, D.; Alexander, J. *Concepts and Models of Inorganic Chemistry*, 3rd ed., John Wiley & Sons, Inc., New York, 1994.
4. Gillespie, R. J.; Popelier, P. L. A. *Chemical Bonding and Molecular Geometry*, Oxford University Press, New York, 2001.
5. Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry*, 3rd ed., Pearson Education Limited, Essex, England, 2008.
6. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., Harper Collins College Publishers, New York, 1993.
7. Levine, I. N. *Quantum Chemistry*, 2nd ed., Allyn and Bacon, Inc., Boston, MA, 1974.
8. Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, 4th ed., Pearson Education Inc., Upper Saddle River, NJ, 2011.
9. Norrby, L. J. *J. Chem. Ed.*, 1991, 68, 110–113.
10. Rayner-Canham, G.; Overton, T. *Descriptive Inorganic Chemistry*, 5th ed., W. H. Freeman and Company, New York, 2010.
11. Rodgers, G. E. *Descriptive Inorganic, Coordination, and Solid-State Chemistry*, 3rd ed., Brooks/Cole, Cengage Learning, Belmont, CA, 2012.
12. Shannon, R. D. *Acta Crystallographica*, 1976, A32, 751–767.
13. Yam, V. W.-W.; Cheng, E. C.-C. *Chem. Soc. Rev.* 2008, 37, 1806–1813.