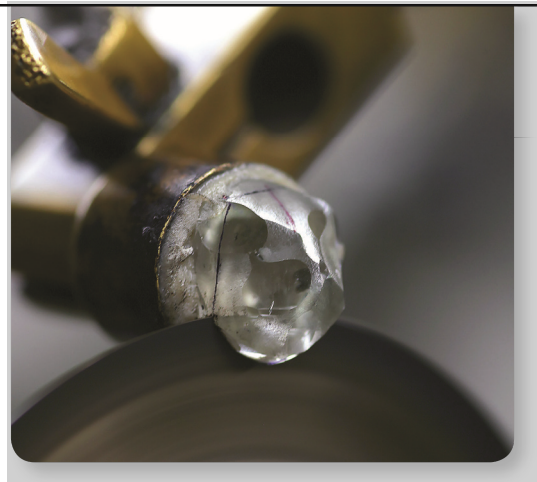


Models of Chemical Bonding

Key Principles

to focus on while studying this chapter

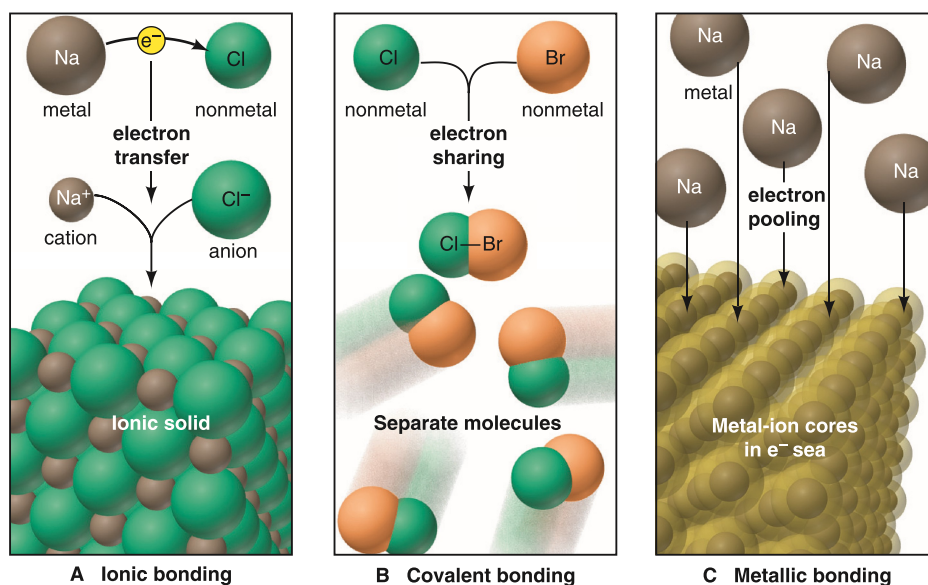
- Two classes of elements, metals and nonmetals, combine through three types of bonding: metal and nonmetal through *ionic bonding*, nonmetal and nonmetal through *covalent bonding*, and metal and metal through *metallic bonding*. (Section 9.1)
- Lewis symbols* predict bonding behavior and show how atoms obey the octet rule. (Section 9.1)
- Ionic bonding is the attraction among the ions that are created when metal atoms *transfer* electrons to nonmetal atoms. Ionic compounds form because of the large magnitude of the *lattice energy*. That is, even though energy is required to form the ions, much more energy is released when the ions attract each other to form a solid. (Section 9.2)
- The strong attractions among their ions make ionic compounds hard, high-melting solids that conduct a current only when melted or dissolved. (Section 9.2)
- A covalent bond is the attraction between the nuclei of two nonmetal atoms and the electron pair they share. Each covalent bond has a specific *energy* and *length* that depend on the bonded atoms and an *order* that depends on the number of electron pairs shared. Chemists study the types of covalent bonds in a compound spectroscopically. (Section 9.3)
- Most covalent compounds consist of separate molecules, so they have low melting and boiling points. These physical changes disrupt the weak attractions *between* the molecules while leaving the strong covalent bonds *within* the molecules intact. Some substances have covalent bonds throughout, and they are very hard and high melting. (Section 9.3)
- During a reaction, energy is *absorbed* to break certain bonds in the reactant molecules and is *released* to form the bonds in the product molecules; the enthalpy of reaction is the *difference* between the energy absorbed and the energy released. (Section 9.4)
- Each atom in a covalent bond attracts the shared electron pair according to its *electronegativity (EN)*. A covalent bond is *polar* if the two atoms have considerably different EN values; therefore, the *ionic character* of a bond—from highly ionic to nonpolar covalent—varies with the difference in EN values of the bonded atoms. (Section 9.5)



The Hard Cutting the Strong Only after some diamond dust forms a paste on the oil-coated saw blade can a diamond be cut in a reasonable time. Diamonds are so hard because of the number and strength of their covalent bonds.

Outline

- 9.1 Atomic Properties and Chemical Bonds**
 - Three Types of Bonding
 - Lewis Symbols and the Octet Rule
- 9.2 The Ionic Bonding Model**
 - Importance of Lattice Energy
 - Periodic Trends in Lattice Energy
 - How the Model Explains the Properties of Ionic Compounds
- 9.3 The Covalent Bonding Model**
 - Formation of a Covalent Bond
 - Bonding Pairs and Lone Pairs
 - Bond Order, Energy, and Length
 - How the Model Explains the Properties of Covalent Substances
 - IR Spectroscopy
- 9.4 Bond Energy and Chemical Change**
 - Where Does $\Delta H_{\text{rxn}}^{\circ}$ Come From?
 - Using Bond Energies to Calculate $\Delta H_{\text{rxn}}^{\circ}$
- 9.5 Between the Extremes: Electronegativity and Bond Polarity**
 - Electronegativity
 - Bond Polarity and Partial Ionic Character
 - Gradation in Bonding Across a Period

Figure 9.2 Three models of chemical bonding.

2. *Nonmetal with nonmetal: electron sharing and covalent bonding* (Figure 9.2B). When two atoms differ little, or not at all, in their tendencies to lose or gain electrons, we observe *electron sharing* and **covalent bonding**, which occurs most commonly between nonmetal atoms. Each atom holds onto its own electrons tightly (high IE) and attracts other electrons (highly negative EA). The nucleus of each atom attracts the valence electrons of the other, which draws the atoms together. The shared electron pair is typically *localized* between the two atoms, linking them in a covalent bond of a particular length and strength. In most cases, separate molecules result when atoms bond covalently. Note that the chemical formula of a covalent compound is the *molecular formula* because it gives the actual numbers of atoms in each molecule.

3. *Metal with metal: electron pooling and metallic bonding* (Figure 9.2C). Metal atoms are relatively large, and their few outer electrons are well shielded by filled inner levels (core electrons). Thus, they lose outer electrons easily (low IE) and do not gain them readily (slightly negative or positive EA). These properties lead metal atoms to share their valence electrons, but not by covalent bonding. In the simplest model of **metallic bonding**, the enormous number of atoms in a sample of a metal *pool* their valence electrons into a “sea” of electrons that “flows” between and around each metal-ion core (nucleus plus inner electrons), thereby attracting them and holding them together. Unlike the localized electrons in covalent bonding, electrons in metallic bonding are *delocalized*, moving freely throughout the entire piece of metal. (For the remainder of this chapter, we’ll focus on ionic and covalent bonding. We discuss electron delocalization in Chapter 11 and the structures of metallic and other solids in Chapter 12, so we’ll postpone the coverage of metallic bonding until then.)

In the world of real substances, there are exceptions to these idealized models, so you can’t always predict bond type from positions of the elements in the periodic table. As just one example, when the metal beryllium [Group 2A(2)] combines with the nonmetal chlorine [Group 7A(17)], the bonding fits the covalent model better than the ionic model. Thus, just as we see gradations in atomic behavior within a group or period, we see a gradation in bonding from one type to another (Figure 9.3).

Lewis Symbols and the Octet Rule

Before examining each model, let’s discuss a method for depicting the valence electrons of interacting atoms that predicts how they bond. In a **Lewis electron-dot symbol** (named for the American chemist G. N. Lewis), the element symbol represents the nucleus *and* inner electrons, and dots around the symbol represent the valence electrons (Figure 9.4). Note that the pattern of dots is the same for elements within a group.

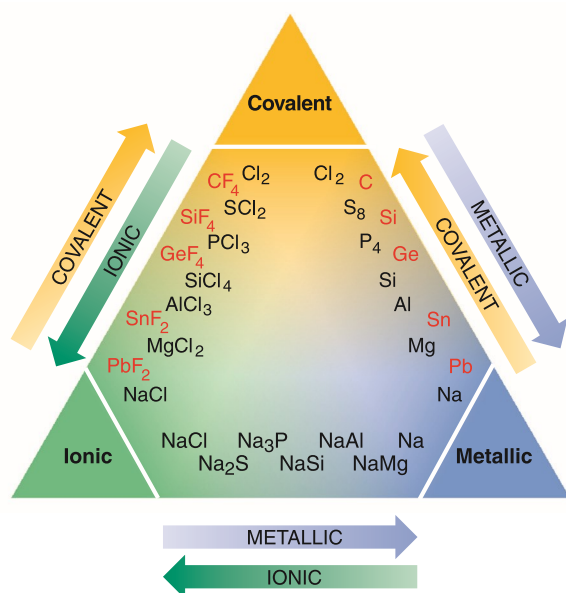
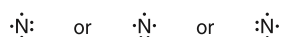


Figure 9.3 Gradations in bond type among Period 3 (black type) and Group 4A (red type) elements.

We use these steps to write the Lewis symbol for any main-group element:

1. Note its A-group number (1A to 8A), which tells the number of valence electrons.
2. Place one dot at a time on each of the four sides (top, right, bottom, left) of the element symbol.
3. Keep adding dots, pairing them, until all are used up.

The specific placement of dots is not important; that is, in addition to the one shown in Figure 9.4, the Lewis symbol for nitrogen can *also* be written as



The Lewis symbol provides information about an element's bonding behavior:

- For a *metal*, the *total* number of dots is the number of electrons an atom loses to form a cation.
- For a *nonmetal*, the number of *unpaired* dots equals either the number of electrons an atom *gains* to form an anion or the number it *shares* to form covalent bonds.

The Lewis symbol for carbon illustrates the last point. Rather than one pair of dots and two unpaired dots, as its electron configuration seems to call for ([He] 2s²2p²), carbon has four unpaired dots because it forms four bonds. Larger nonmetals can form as many bonds as the number of dots in their Lewis symbol (Chapter 10).

In his pioneering studies, Lewis generalized much of bonding behavior into the **octet rule**: *when atoms bond, they lose, gain, or share electrons to attain a filled outer level of eight electrons (or two, for H and Li).* The octet rule holds for nearly all of the compounds of Period 2 elements and a large number of others as well.

	1A(1)	2A(2)	3A(13)	4A(14)	5A(15)	6A(16)	7A(17)	8A(18)
	ns ¹	ns ²	ns ² np ¹	ns ² np ²	ns ² np ³	ns ² np ⁴	ns ² np ⁵	ns ² np ⁶
Period 2	• Li	• Be •	• B •	• C •	• N •	• O •	• F •	• Ne •
Period 3	• Na	• Mg •	• Al •	• Si •	• P •	• S •	• Cl •	• Ar •

Figure 9.4 Lewis electron-dot symbols for elements in Periods 2 and 3.

Summary of Section 9.1

- Nearly all naturally occurring substances consist of atoms or ions bonded to others. Chemical bonding allows atoms to lower their energy.
- Ionic bonding occurs when metal atoms transfer electrons to nonmetal atoms, and the resulting ions attract each other and form an ionic solid.
- Covalent bonding is most common between nonmetal atoms and usually results in individual molecules. Bonded atoms share one or more pairs of electrons that are localized between them.
- Metallic bonding occurs when many metal atoms pool their valence electrons into a delocalized electron “sea” that holds all the atoms in the sample together.
- The Lewis electron-dot symbol of a main-group atom shows valence electrons as dots surrounding the element symbol.
- The octet rule says that atoms bond by losing, gaining, or sharing electrons to attain a filled outer level of eight (or two) electrons.

9.2 • THE IONIC BONDING MODEL

The central idea of the ionic bonding model is the *transfer of electrons from metal atoms to nonmetal atoms to form ions that attract each other into a solid compound*. In most cases, for the main groups, the ion that forms has a filled outer level of either two or eight electrons, the number in the nearest noble gas (octet rule).

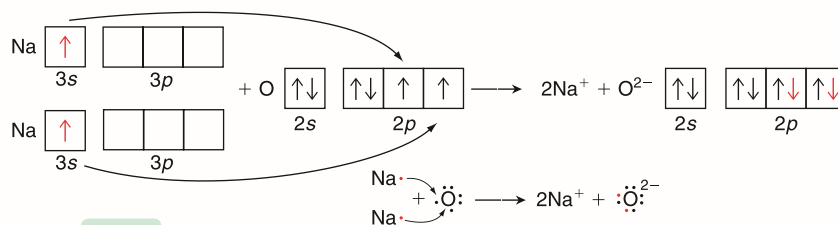
The transfer of an electron from a lithium atom to a fluorine atom is depicted in three ways in Figure 9.5. In each, Li loses its single outer electron and is left with a filled $n = 1$ level (two e^-), while F gains a single electron to fill its $n = 2$ level (eight e^-). In this case, each atom is one electron away from the configuration of its nearest noble gas, so the number of electrons lost by each Li equals the number gained by each F. Therefore, equal numbers of Li^+ and F^- ions form, as the formula LiF indicates. That is, in ionic bonding, *the total number of electrons lost by the metal atom(s) equals the total number of electrons gained by the nonmetal atom(s)*.

Sample Problem 9.1 Depicting Ion Formation

Problem Use partial orbital diagrams and Lewis symbols to depict the formation of Na^+ and O^{2-} ions from the atoms, and give the formula of the compound formed.

Plan First we draw the orbital diagrams and Lewis symbols for Na and O atoms. To attain filled outer levels, Na loses one electron and O gains two. To make the number of electrons lost equal the number gained, two Na atoms are needed for each O atom.

Solution



The formula is Na_2O .

FOLLOW-UP PROBLEM 9.1 Use condensed electron configurations and Lewis symbols to depict the formation of Mg^{2+} and Cl^- ions from the atoms, and give the formula of the compound formed.

Why Ionic Compounds Form: The Importance of Lattice Energy

You may be surprised to learn that energy is *absorbed* during electron transfer. So why does it occur? And, in view of this absorption of energy, why do ionic substances exist at all? As you'll see, the answer involves the enormous quantity of energy *released* as the ions that form coalesce into a solid.

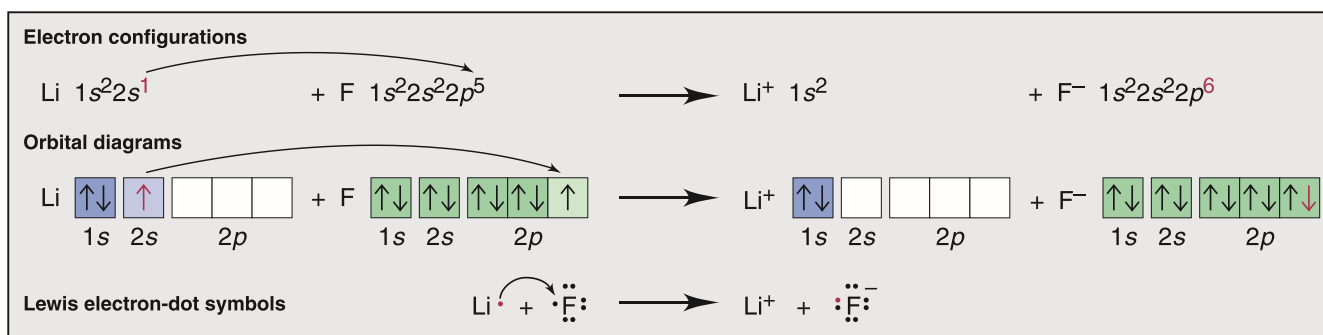
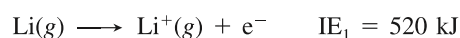


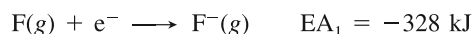
Figure 9.5 Three ways to depict electron transfer in the formation of Li^+ and F^- . The electron being transferred is shown in red.

1. *The electron-transfer process.* Consider the electron-transfer process for the formation of lithium fluoride, which involves a gaseous Li atom losing an electron, and a gaseous F atom gaining it:

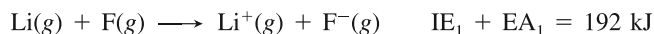
- The first ionization energy (IE_1) of Li is the energy absorbed when 1 mol of gaseous Li atoms loses 1 mol of valence electrons:



- The first electron affinity (EA_1) of F is the energy released when 1 mol of gaseous F atoms gains 1 mol of electrons:



- Taking the sum shows that electron transfer *by itself* requires energy:



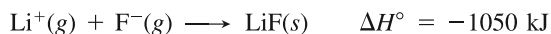
2. *Other steps that absorb energy.* The total energy needed prior to ion formation adds to the sum of IE_1 and EA_1 : metallic lithium must be made into gaseous atoms (161 kJ/mol), and fluorine molecules must be broken into separate atoms (79.5 kJ/mol).

3. *Steps that release energy.* Despite these endothermic steps, the standard enthalpy of formation (ΔH_f°) of solid LiF is -617 kJ/mol ; that is, 617 kJ is *released* when 1 mol of LiF(s) forms from its elements. Formation of LiF is typical of reactions between active metals and nonmetals: ionic solids form readily (Figure 9.6).

If the overall reaction releases energy, there must be some step that is exothermic enough to outweigh the endothermic steps. This step involves the *strong attraction between pairs of oppositely charged ions*. When 1 mol of $\text{Li}^+(\text{g})$ and 1 mol of $\text{F}^-(\text{g})$ form 1 mol of gaseous LiF molecules, a large quantity of heat is released:



But, as you know, under ordinary conditions, LiF does not exist as gaseous molecules: *even more energy is released when the separate gaseous ions coalesce into a crystalline solid* because each ion attracts *several* oppositely charged ions:



The negative of this enthalpy change is 1050 kJ, the lattice energy of LiF. The **lattice energy** ($\Delta H_{\text{lattice}}^\circ$) is the enthalpy change that occurs when 1 mol of ionic solid separates into gaseous ions. It indicates the strength of ionic interactions, which influence melting point, hardness, solubility, and other properties.

A key point to keep in mind is that *ionic solids exist only because the lattice energy exceeds the energy required for the electron transfer*. In other words, the energy *required* for elements to lose or gain electrons is *supplied* by the attraction between the ions they form: energy is expended to form the ions, but it is more than regained when they attract each other and form a solid.

Periodic Trends in Lattice Energy

The lattice energy results from electrostatic interactions among ions, so its magnitude depends on ionic size, ionic charge, and ionic arrangement in the solid. Therefore, we expect to see periodic trends in lattice energy.



A



B

Figure 9.6 The exothermic formation of sodium bromide. **A**, Sodium (in beaker under mineral oil) and bromine. **B**, The reaction is rapid and vigorous.

Explaining the Trends in $\Delta H^\circ_{\text{lattice}}$ with Coulomb's Law Recall from Chapter 2 that **Coulomb's law** states that the electrostatic energy between particles A and B is directly proportional to the product of their charges and inversely proportional to the distance between them:

$$\text{Electrostatic energy} \propto \frac{\text{charge A} \times \text{charge B}}{\text{distance}}$$

Lattice energy is directly proportional to electrostatic energy. In an ionic solid, cations and anions lie as close to each other as possible, so the distance between them is the sum of the ionic radii (see Figure 8.20):

$$\text{Electrostatic energy} \propto \frac{\text{cation charge} \times \text{anion charge}}{\text{cation radius} + \text{anion radius}} \propto \Delta H^\circ_{\text{lattice}} \quad (9.1)$$

This relationship helps us explain the effects of ionic size and charge on trends in lattice energy:

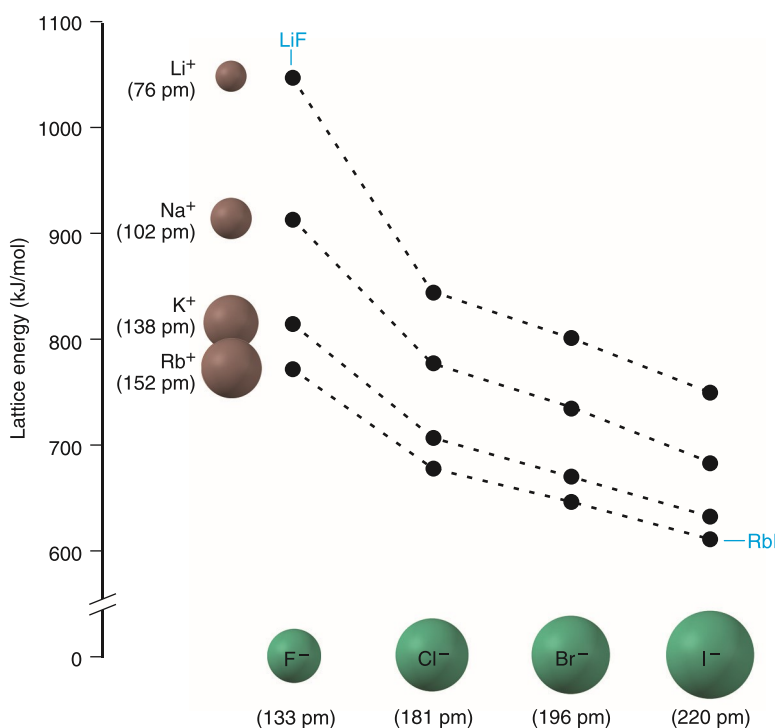
1. *Effect of ionic size.* As we move down a group, ionic radii increase, so the electrostatic energy between cations and anions decreases; thus, lattice energies should decrease as well. Figure 9.7 shows that, for the alkali-metal halides, lattice energy decreases down the group whether we hold the cation constant (LiF to LiI) or the anion constant (LiF to RbF).

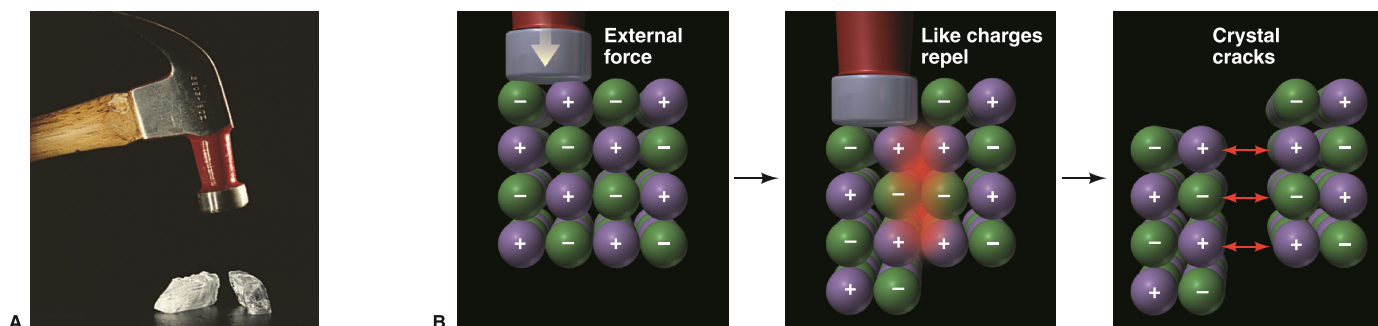
2. *Effect of ionic charge.* Across a period, ionic charge changes. For example, lithium fluoride and magnesium oxide have cations and anions of about equal radii ($\text{Li}^+ = 76 \text{ pm}$ and $\text{Mg}^{2+} = 72 \text{ pm}$; $\text{F}^- = 133 \text{ pm}$ and $\text{O}^{2-} = 140 \text{ pm}$). The major difference is between singly charged Li^+ and F^- ions and doubly charged Mg^{2+} and O^{2-} ions. The difference in the lattice energies of the two compounds is striking:

$$\Delta H^\circ_{\text{lattice}} \text{ of LiF} = 1050 \text{ kJ/mol} \quad \text{and} \quad \Delta H^\circ_{\text{lattice}} \text{ of MgO} = 3923 \text{ kJ/mol}$$

This nearly fourfold increase in $\Delta H^\circ_{\text{lattice}}$ reflects the fourfold increase in the product of the charges (1×1 vs. 2×2) in the numerator in Equation 9.1. The very large lattice energy of MgO more than compensates for the energy required to form the Mg^{2+} and O^{2-} ions. In fact, the lattice energy is the reason that compounds with $2+$ cations and $2-$ anions even exist.

Figure 9.7 Trends in lattice energy. The lattice energies are shown for compounds formed from a given Group 1A(1) cation (*left side*) and one of the Group 7A(17) anions (*bottom*). LiF (smallest ions) has the highest lattice energy, and RbI (largest ions) has the lowest.





How the Model Explains the Properties of Ionic Compounds

The central role of any model is to explain the facts. With atomic-level views, we can see how the ionic bonding model accounts for the properties of ionic solids:

1. *Physical behavior.* As a typical ionic compound, a piece of rock salt (NaCl) is *hard* (does not dent), *rigid* (does not bend), and *brittle* (cracks without deforming). These properties arise from the strong attractive forces that hold the ions *in specific positions*. Moving them out of position requires overcoming these forces, so rock salt does not dent or bend. If enough force *is* applied, ions of like charge are brought next to each other, and repulsions between them crack the sample suddenly (Figure 9.8).

2. *Electrical conductivity.* Ionic compounds typically *do not* conduct electricity in the solid state but *do* conduct when melted or dissolved. According to the model, the solid consists of fixed ions, but when it melts or dissolves, the ions can move and carry a current (Figure 9.9).

3. *Thermal conductivity.* Large amounts of energy are needed to free the ions from their fixed positions and separate them. Thus, we expect ionic compounds to have high melting points and much higher boiling points (Table 9.1). In fact, the interionic attraction is so strong that the vapor consists of **ion pairs**, gaseous ionic molecules, rather than individual ions. In their normal state, as you know, ionic compounds are solid arrays of ions, and *no separate molecules exist*.

Figure 9.8 Why ionic compounds crack.

A, Ionic compounds crack when struck with enough force. **B**, When a force moves like charges near each other, repulsions cause a crack.

Table 9.1 Melting and Boiling Points of Some Ionic Compounds

Compound	mp ($^{\circ}\text{C}$)	bp ($^{\circ}\text{C}$)
CsBr	636	1300
NaI	661	1304
MgCl_2	714	1412
KBr	734	1435
CaCl_2	782	>1600
NaCl	801	1413
LiF	845	1676
KF	858	1505
MgO	2852	3600

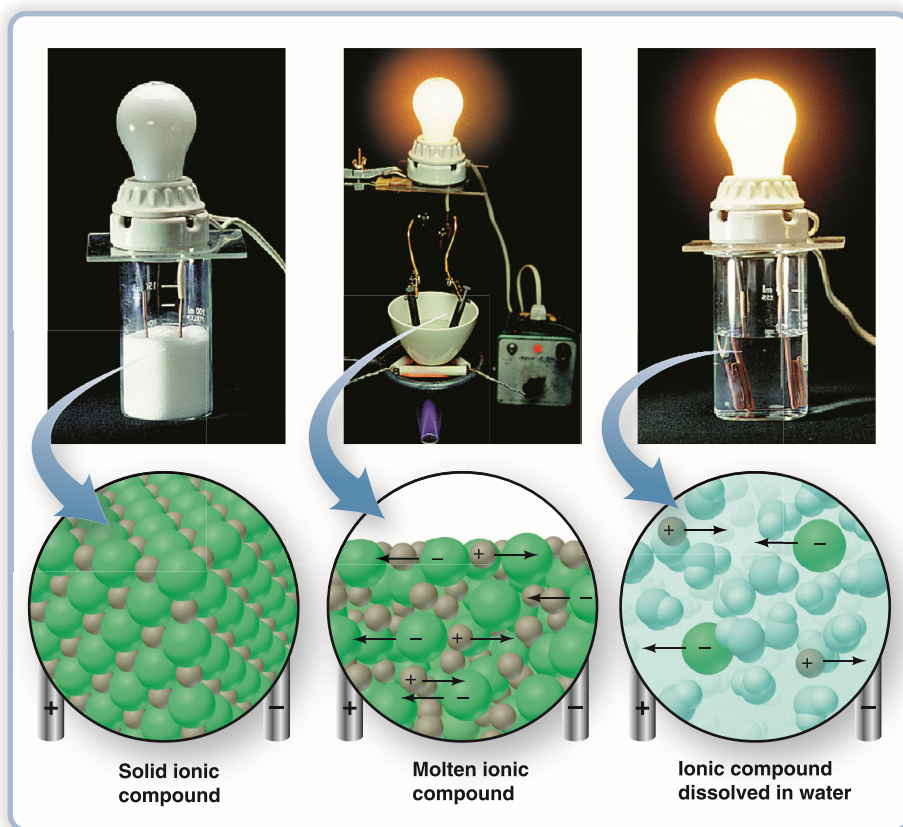


Figure 9.9 Electrical conductance and ion mobility.

Summary of Section 9.2

- In ionic bonding, a metal transfers electrons to a nonmetal, and the resulting ions attract each other to form a solid.
- Main-group elements often attain a filled outer level (either eight electrons or two) by forming ions with the electron configuration of the nearest noble gas.
- Ion formation by itself *absorbs* energy, but more than enough energy is *released* when the ions form a solid. The lattice energy, the energy required to separate the solid into gaseous ions, is the reason ionic solids exist.
- Lattice energies increase with higher ionic charge and decrease with larger ionic radius.
- According to the ionic bonding model, the strong electrostatic attractions that keep ions in position explain why ionic solids are hard, conduct a current only when melted or dissolved, and have high melting and boiling points.
- Ion pairs form when an ionic compound vaporizes.

9.3 • THE COVALENT BONDING MODEL

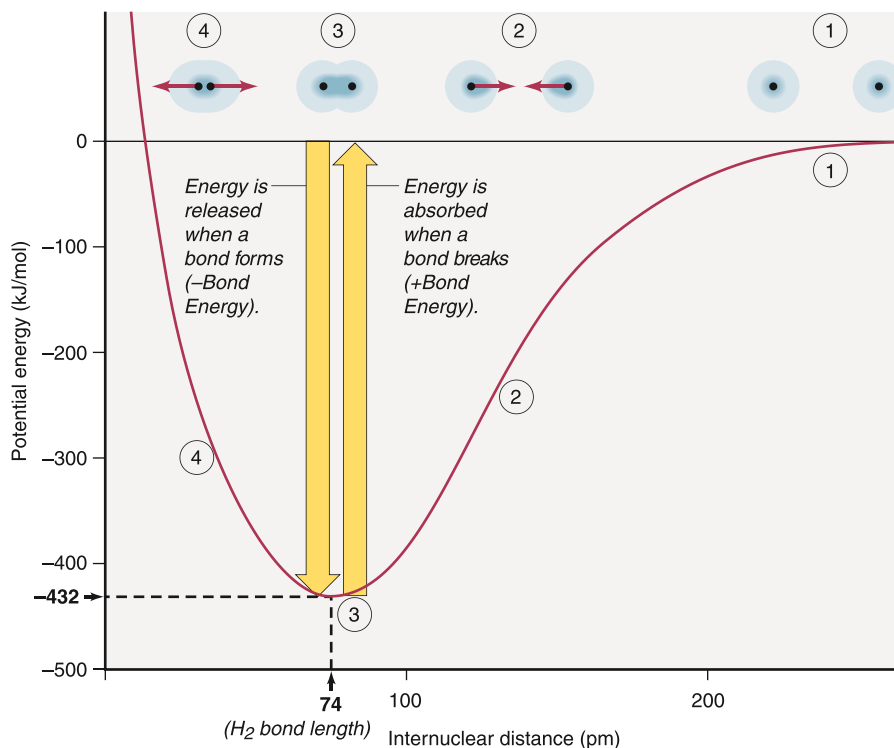
Look through the *Handbook of Chemistry and Physics*, and you'll find that the number of covalent compounds dwarfs the number of ionic compounds. Molecules held together by covalent bonds range from tiny, diatomic hydrogen to biological and synthetic macromolecules with thousands of atoms. And covalent bonds occur in all polyatomic ions, too. Without doubt, *sharing electrons is the main way that atoms interact*.

The Formation of a Covalent Bond

Why does hydrogen gas consist of H_2 molecules and not separate H atoms? Figure 9.10 plots the potential energy of a system of two isolated H atoms versus the distance between their nuclei (see also Figure 2.12). Let's start at the right end of the curve and move along it as the atoms get closer:

- At point 1, the atoms are far apart, and each acts as though the other were not present.

Figure 9.10 Covalent bond formation in H_2 . The energy difference between points 1 and 3 is the H_2 bond energy (432 kJ/mol); it is released when the bond forms and absorbed to break the bond. The internuclear distance at point 3 is the H_2 bond length (74 pm).



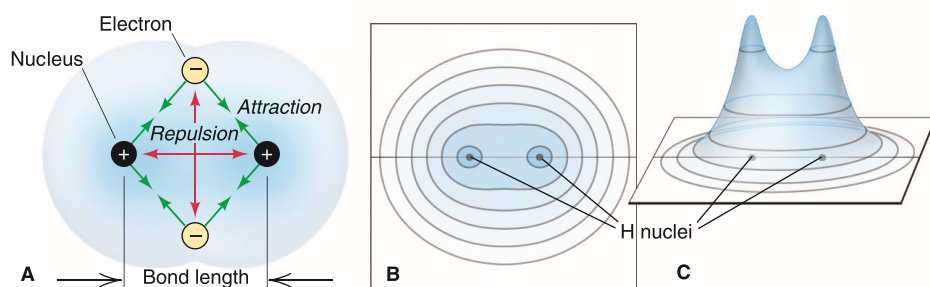


Figure 9.11 Distribution of electron density in H_2 . **A**, At some distance (bond length), attractions balance repulsions. Electron density (blue shading) is high around and between the nuclei. **B**, Electron density doubles with each concentric curve. **C**, The highest regions of electron density are shown as peaks.

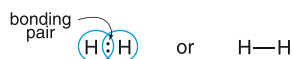
- At point 2, the distance between the atoms has decreased enough for each nucleus to start attracting the other atom's electron, which lowers the potential energy. As the atoms get closer, these attractions increase, but so do repulsions between the nuclei and between the electrons.
- At point 3 (bottom of the energy "well"), the maximum attraction is achieved in the face of the increasing repulsion, and the system has its minimum energy.
- At point 4, if it were reached, the atoms would be too close, and the rise in potential energy from increasing repulsions would push them apart toward point 3 again.

Thus, a **covalent bond** arises from the balance between the nuclei attracting the electrons and electrons and nuclei repelling each other. (We'll return to Figure 9.10 shortly.)

Formation of a covalent bond always results in greater electron density *between* the nuclei. Figure 9.11 depicts this fact with a cross section of a space-filling model (A), an *electron density contour map* (B), and an *electron density relief map* (C).

Bonding Pairs and Lone Pairs

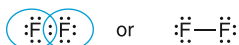
To achieve a full outer (valence) level of electrons, *each atom in a covalent bond "counts" the shared electrons as belonging entirely to itself*. Thus, the two shared electrons in H_2 simultaneously fill the outer level of *both* H atoms, as clarified by the blue circles added below (which are *not* part of the Lewis structures). The **shared pair**, or **bonding pair**, is represented by a pair of dots or a line:



An outer-level electron pair that is *not* involved in bonding is called a **lone pair**, or **unshared pair**. The bonding pair in HF fills the outer level of the H atom *and*, together with three lone pairs, fills the outer level of the F atom as well:



In F_2 the bonding pair and three lone pairs fill the outer level of *each* F atom:



(This text generally shows bonding pairs as lines and lone pairs as dots.)

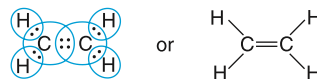
Properties of a Covalent Bond: Order, Energy, and Length

A covalent bond has three important properties that are closely related to one another and to the compound's reactivity—bond order, bond energy, and bond length.

1. **Bond order.** The **bond order** is the number of electron pairs being shared by a given pair of atoms:

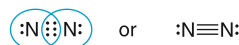
- A **single bond**, as shown above in H_2 , HF, or F_2 , is the most common bond and consists of one bonding pair of electrons. Thus, a *single bond has a bond order of 1*.
- Many molecules (and ions) contain *multiple bonds*, in which more than one pair is shared between two atoms. Multiple bonds usually involve C, O, and/or N atoms. A **double bond** consists of two bonding electron pairs, four electrons shared between

two atoms, so *the bond order is 2*. Ethylene (C_2H_4) contains a carbon-carbon double bond and four carbon-hydrogen single bonds:



Each carbon “counts” the four electrons in the double bond and the four in its two single bonds to hydrogens to attain an octet.

- A **triple bond** consists of three shared pairs: two atoms share six electrons, so *the bond order is 3*. The N_2 molecule has a triple bond, and each N atom also has a lone pair. Six shared and two unshared electrons give *each* N atom an octet:



2. **Bond energy.** The strength of a covalent bond depends on the magnitude of the attraction between the nuclei and shared electrons. The **bond energy (BE)** (also called *bond enthalpy* or *bond strength*) is the energy needed to overcome this attraction and is defined as the standard enthalpy change for breaking the bond in 1 mol of gaseous molecules. Bond breakage is an *endothermic* process, so *bond energy is always positive*:



The bond energy is the difference in energy between separated and bonded atoms (the potential energy difference between points 1 and 3, the energy “well” in Figure 9.10). *The same quantity of energy absorbed to break the bond is released when the bond forms.* Bond formation is an *exothermic* process, so *the sign of its enthalpy change is always negative*:



Table 9.2 lists the energies of some common bonds. By definition,

- *Stronger bonds are lower in energy (have a deeper energy well).*
- *Weaker bonds are higher in energy (have a shallower energy well).*

The energy of a given bond varies slightly from molecule to molecule and even within the same molecule, so each value is an *average* bond energy.

3. **Bond length.** A covalent bond has a **bond length**, the distance between the nuclei of two bonded atoms. In Figure 9.10, bond length is the distance between the nuclei at the point of minimum energy (bottom of the well), and Table 9.2 shows the lengths of some covalent bonds. Like bond energies, these values are *average* bond lengths for a bond in different substances. Bond length is related to the sum of the radii of the bonded atoms. In fact, most atomic radii are calculated from measured bond lengths (see Figure 8.9C). Bond lengths for a series of similar bonds, as in the halogens, increase with atomic size (Figure 9.12).

The order, energy, and length of a covalent bond are interrelated. Two nuclei are more strongly attracted to two shared pairs than to one, so double-bonded atoms are drawn closer together *and* are more difficult to pull apart than single-bonded atoms: *for a given pair of atoms, a higher bond order results in a shorter bond length and a higher bond energy.* Thus, as Table 9.3 shows, for a given pair of atoms, *a shorter bond is a stronger bond.*

In some cases, we can see a relation among atomic size, bond length, and bond energy by varying one of the atoms in a single bond while holding the other constant:

- *Variation within a group.* The trend in carbon-halogen single bond lengths, $\text{C}-\text{I} > \text{C}-\text{Br} > \text{C}-\text{Cl}$, parallels the trend in atomic size, $\text{I} > \text{Br} > \text{Cl}$, and is opposite to the trend in bond energy, $\text{C}-\text{Cl} > \text{C}-\text{Br} > \text{C}-\text{I}$.
- *Variation within a period.* Looking again at single bonds involving carbon, the trend in bond lengths, $\text{C}-\text{N} > \text{C}-\text{O} > \text{C}-\text{F}$, is opposite to the trend in bond energy, $\text{C}-\text{F} > \text{C}-\text{O} > \text{C}-\text{N}$.

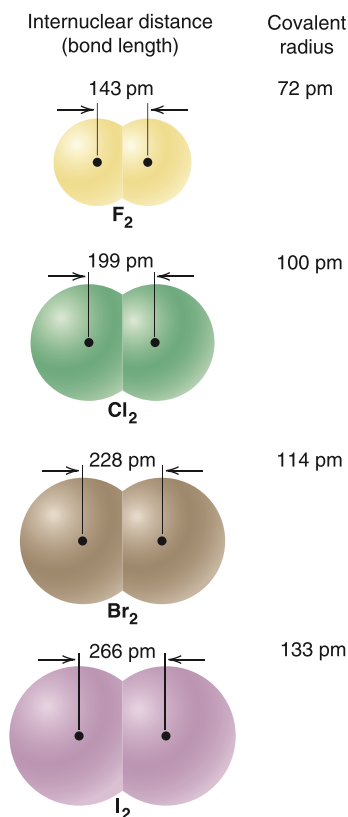


Figure 9.12 Bond length and covalent radius.

Table 9.2 Average Bond Energies (kJ/mol) and Bond Lengths (pm)

Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length
Single Bonds											
H—H	432	74	N—H	391	101	Si—H	323	148	S—H	347	134
H—F	565	92	N—N	160	146	Si—Si	226	234	S—S	266	204
H—Cl	427	127	N—P	209	177	Si—O	368	161	S—F	327	158
H—Br	363	141	N—O	201	144	Si—S	226	210	S—Cl	271	201
H—I	295	161	N—F	272	139	Si—F	565	156	S—Br	218	225
			N—Cl	200	191	Si—Cl	381	204	S—I	~170	234
C—H	413	109	N—Br	243	214	Si—Br	310	216	F—F	159	143
C—C	347	154	N—I	159	222	Si—I	234	240	F—Cl	193	166
C—Si	301	186							F—Br	212	178
C—N	305	147	O—H	467	96	P—H	320	142	F—I	263	187
C—O	358	143	O—P	351	160	P—Si	213	227	Cl—Cl	243	199
C—P	264	187	O—O	204	148	P—P	200	221	Cl—Br	215	214
C—S	259	181	O—S	265	151	P—F	490	156	Cl—I	208	243
C—F	453	133	O—F	190	142	P—Cl	331	204	Br—Br	193	228
C—Cl	339	177	O—Cl	203	164	P—Br	272	222	Br—I	175	248
C—Br	276	194	O—Br	234	172	P—I	184	246	I—I	151	266
C—I	216	213	O—I	234	194						
Multiple Bonds											
C=C	614	134	N=N	418	122	C≡C	839	121	N≡N	945	110
C=N	615	127	N=O	607	120	C≡N	891	115	N≡O	631	106
C=O	745	123	O ₂	498	121	C≡O	1070	113			
(799 in CO ₂)											

Table 9.3 The Relation of Bond Order, Bond Length, and Bond Energy

Bond	Bond Order	Average Bond Length (pm)	Average Bond Energy (kJ/mol)
C—O	1	143	358
C=O	2	123	745
C≡O	3	113	1070
C—C	1	154	347
C=C	2	134	614
C≡C	3	121	839
N—N	1	146	160
N=N	2	122	418
N≡N	3	110	945

Sample Problem 9.2 Comparing Bond Length and Bond Strength

Problem Without referring to Table 9.2, rank the bonds in each set in order of *decreasing* bond length and *decreasing* bond strength:

(a) S—F, S—Br, S—Cl (b) C=O, C—O, C≡O

Plan (a) S is singly bonded to three different halogen atoms, so the bond order is the same. Bond length increases and bond strength decreases as the halogen's atomic radius increases. (b) The same two atoms are bonded, but the bond orders differ. In this case, bond strength increases and bond length decreases as bond order increases.

Solution (a) Atomic size increases down a group, so $F < Cl < Br$.

Bond length: S—Br > S—Cl > S—F

Bond strength: S—F > S—Cl > S—Br

(b) By ranking the bond orders, $C\equiv O > C=O > C-O$, we obtain

Bond length: C—O > C=O > C≡O

Bond strength: C≡O > C=O > C—O

Check From Table 9.2, we see that the rankings are correct.

Comment Remember that for bonds involving pairs of different atoms, as in part (a), the *relationship between length and strength holds only for single bonds* and not in every case, so apply it carefully.

FOLLOW-UP PROBLEM 9.2 Rank the bonds in each set in order of *increasing* bond length and *increasing* bond strength: (a) Si—F, Si—C, Si—O; (b) N=N, N—N, N≡N.

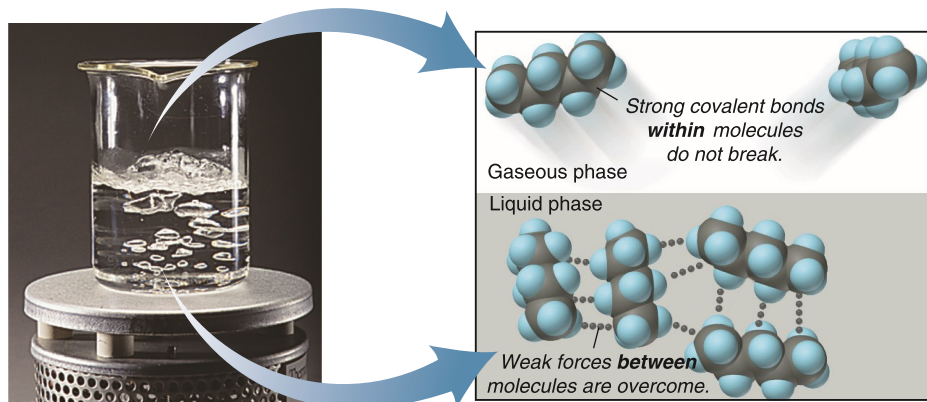
How the Model Explains the Properties of Covalent Substances

The covalent bonding model proposes that electron sharing between pairs of atoms leads to *strong, localized bonds*. Most, but not all, covalent substances consist of individual molecules. These *molecular* covalent substances have very different *physical* properties than *network* covalent solids because different types of forces give rise to them.

1. *Physical properties of molecular covalent substances.* At first glance, the model seems inconsistent with physical properties of covalent substances. Most are gases (such as methane and ammonia), liquids (such as benzene and water), or low-melting solids (such as sulfur and paraffin wax). If covalent bonds are so strong (~200 to 500 kJ/mol), why do covalent substances melt and boil at such low temperatures?

To answer this, we'll focus on two different forces: (1) *strong bonding forces* hold the atoms together within the molecule, and (2) *weak intermolecular forces* act between separate molecules in the sample. It is the weak forces *between* molecules that account for the physical properties of *molecular* covalent substances. For example, look what happens when pentane (C_5H_{12}) boils (Figure 9.13): weak forces *between* pentane molecules are overcome, not the strong C—C and C—H bonds *within* each pentane molecule.

Figure 9.13 Strong forces within molecules and weak forces between them.



2. *Physical properties of network covalent solids.* Some covalent substances do not consist of separate molecules. Rather, these *network covalent solids* are held together by covalent bonds *between atoms throughout the sample*, and their properties *do* reflect the strength of covalent bonds. Two examples are quartz and diamond (Figure 9.14). Quartz (SiO_2 ; *top*) has silicon-oxygen covalent bonds in three dimensions; no separate SiO_2 molecules exist. It is very hard and melts at 1550°C . Diamond (*bottom*; see also the chapter-opening photo) has covalent bonds connecting each carbon atom to four others. It is the hardest natural substance known and melts at around 3550°C . Thus, covalent bonds *are* strong, but most covalent substances consist of separate molecules with weak forces between them. (We discuss intermolecular forces in detail in Chapter 12.)

3. *Electrical conductivity.* An electric current is carried by either mobile electrons or mobile ions. Most covalent substances are poor electrical conductors, whether melted or dissolved, because their electrons are localized as either shared or unshared pairs, so they are not free to move, and no ions are present.

Using IR Spectroscopy to Study Covalent Compounds

Chemists often study the types of covalent bonds in a molecule using a technique called **infrared (IR) spectroscopy**. The bonds in all molecules, whether in a gas, a liquid, or a solid, undergo continual vibrations. We can think of any covalent bond between two atoms, say, the C—C bond in ethane ($\text{H}_3\text{C—CH}_3$), as a spring that is continually stretching, twisting, and bending. Each motion occurs at a particular frequency, which depends on the “stiffness” of the spring (the bond energy), the type of motion, and the masses of the atoms. The frequencies of these vibrational motions correspond to the wavelengths of photons that lie within the IR region of the electromagnetic spectrum. Thus, the energies of these motions are quantized. And, just as an atom can absorb a photon of a particular energy and attain a different electron energy level (Chapter 7), a molecule can absorb an IR photon of a particular energy and attain a different vibrational energy level.

Each kind of bond (C—C, C=C, C—O, etc.) absorbs a characteristic range of IR wavelengths and quantity of radiation, which depends on the molecule's overall structure. The absorptions by all the bonds in a given molecule create a unique pattern that appears as downward pointing peaks of varying depth and sharpness. Thus, *each compound has a characteristic IR spectrum* that can be used to identify it, much like a fingerprint is used to identify a person. As an example, consider the compounds 2-butanol and diethyl ether. These compounds have the same molecular formula ($\text{C}_4\text{H}_{10}\text{O}$) but different structural formulas and, therefore, are constitutional (structural) isomers. Figure 9.15 shows that they have very different IR spectra.

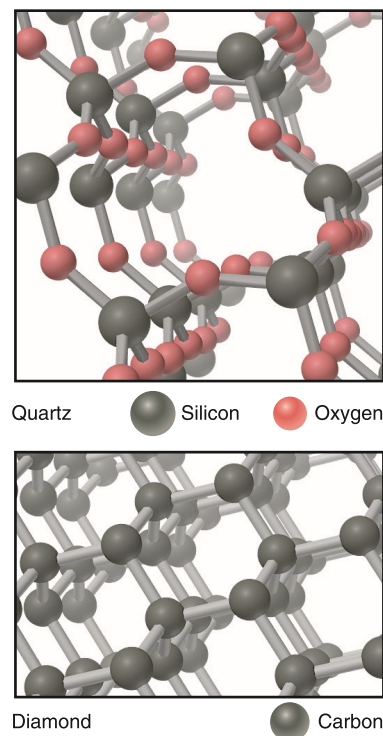
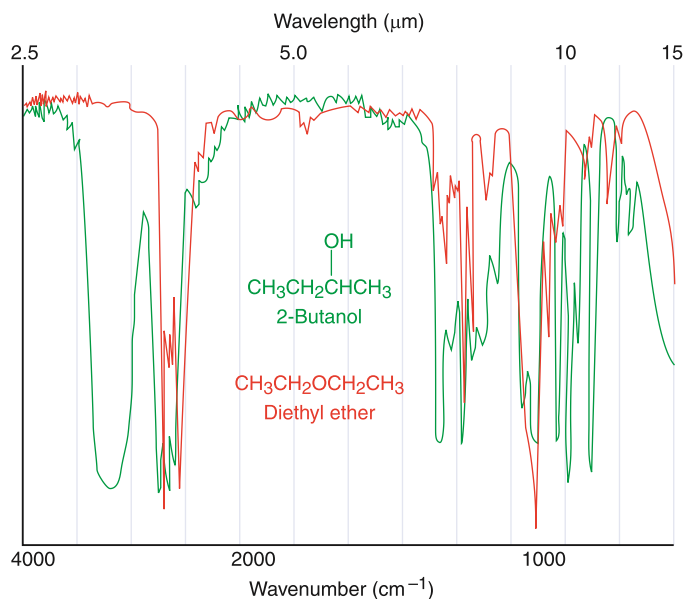


Figure 9.14 Covalent bonds of network covalent solids: quartz and diamond.

Figure 9.15 The infrared spectra of 2-butanol (green) and diethyl ether (red).

Summary of Section 9.3

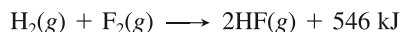
- A shared, localized pair of valence electrons holds the nuclei of two atoms together in a covalent bond, filling each atom's outer level.
- Bond order is the number of shared pairs between two atoms. Bond energy is the energy absorbed to separate the atoms; the same quantity of energy is released when the bond forms. Bond length is the distance between their nuclei.
- For a given pair of atoms, bond order is directly related to bond energy and inversely related to bond length.
- Molecular covalent substances are soft and low melting because of the weak forces *between* the molecules. Network covalent solids are hard and high melting because covalent bonds join all the atoms in the sample.
- Most covalent substances have low electrical conductivity because their electrons are localized and ions are absent.
- Atoms in a covalent bond vibrate, and the energies of these vibrations are studied with IR spectroscopy.

9.4 • BOND ENERGY AND CHEMICAL CHANGE

The relative strengths of the bonds in reactants and products determine whether heat is released or absorbed in a chemical reaction. In Chapter 20, you'll see that the change in bond energy is one of two factors determining whether the reaction occurs at all. In this section, we discuss the origin of the enthalpy of reaction ($\Delta H_{\text{rxn}}^{\circ}$), use bond energies to calculate it, and look at the energy available from fuels and foods.

Changes in Bond Energy: Where Does $\Delta H_{\text{rxn}}^{\circ}$ Come From?

In Chapter 6, we discussed the heat involved in a chemical change but never asked a central question: where does the enthalpy of reaction ($\Delta H_{\text{rxn}}^{\circ}$) come from? For example, when 1 mol of H_2 and 1 mol of F_2 react to form 2 mol of HF at 1 atm and 298 K,



where does the 546 kJ come from? We find the answer by looking closely at the energies of the molecules involved. A system's total internal energy is composed of its kinetic energy and potential energy. Let's see how these change during the formation of HF:

- *Kinetic energy.* The most important contributions to the kinetic energy are the molecules' movements in space, rotations, and vibrations. However, since kinetic energy is proportional to temperature, which is constant at 298 K, it doesn't change during the reaction.
- *Potential energy.* The most important contributions to the potential energy are phase changes and changes in the attraction between vibrating atoms, between nucleus and electrons (and between electrons) in each atom, between protons and neutrons in each nucleus, and between nuclei and the shared electron pair in each bond. Of these, there are no phase changes, vibrational forces vary only slightly as the bonded atoms change, and forces within the atoms and nuclei don't change at all. The only significant change in potential energy comes from changes in the attraction between the nuclei and the shared electron pair—the bond energy.

Thus, our answer to “where does $\Delta H_{\text{rxn}}^{\circ}$ come from?” is that it doesn't really “come from” anywhere: *the heat released or absorbed during a chemical change is due to differences between reactant bond energies and product bond energies.*

Using Bond Energies to Calculate $\Delta H_{\text{rxn}}^{\circ}$

Hess's law (see Section 6.5) allows us to think of any reaction as a two-step process, whether or not it actually occurs that way:

1. A quantity of heat is absorbed ($\Delta H^{\circ} > 0$) to break the reactant bonds and form separate atoms.

2. A different quantity of heat is then released ($\Delta H^\circ < 0$) when the atoms form product bonds.

The sum (symbolized by Σ) of these enthalpy changes is the enthalpy of reaction, $\Delta H^\circ_{\text{rxn}}$:

$$\Delta H^\circ_{\text{rxn}} = \Sigma \Delta H^\circ_{\text{reactant bonds broken}} + \Sigma \Delta H^\circ_{\text{product bonds formed}} \quad (9.2)$$

- In an exothermic reaction, the magnitude of $\Delta H^\circ_{\text{product bonds formed}}$ is *greater* than that of $\Delta H^\circ_{\text{reactant bonds broken}}$, so the sum, $\Delta H^\circ_{\text{rxn}}$, is *negative* (heat is released).
- In an endothermic reaction, the opposite situation is true, the magnitude of $\Delta H^\circ_{\text{product bonds formed}}$ is *smaller* than that of $\Delta H^\circ_{\text{reactant bonds broken}}$, so $\Delta H^\circ_{\text{rxn}}$ is *positive* (heat is absorbed).

An equivalent form of Equation 9.2 uses bond energies:

$$\Delta H^\circ_{\text{rxn}} = \Sigma \text{BE}_{\text{reactant bonds broken}} - \Sigma \text{BE}_{\text{product bonds formed}}$$

(We need the minus sign because all bond energies are positive.)

Typically, only certain bonds break and form during a reaction, but with Hess's law, the following is a simpler method of calculating $\Delta H^\circ_{\text{rxn}}$:

1. Break **all** the reactant bonds to obtain individual atoms.
2. Use the atoms to form **all** the product bonds.
3. Add the bond energies, with appropriate signs, to obtain the enthalpy of reaction.

(This method assumes reactants and products do not change physical state; additional heat is involved when phase changes occur. We address this topic in Chapter 12.)

Let's use the method to calculate $\Delta H^\circ_{\text{rxn}}$ for two reactions:

1. *Formation of HF.* When 1 mol of H—H bonds and 1 mol of F—F bonds absorb energy and break, the 2 mol of H atoms and 2 mol of F atoms form 2 mol of H—F bonds, which releases energy (Figure 9.16). We find the bond energy values in Table 9.2 and use a positive sign for bonds broken and a negative sign for bonds formed:

Bonds broken:

$$\begin{aligned} 1 \times \text{H—H} &= (1 \text{ mol})(432 \text{ kJ/mol}) = 432 \text{ kJ} \\ 1 \times \text{F—F} &= (1 \text{ mol})(159 \text{ kJ/mol}) = 159 \text{ kJ} \\ \hline \Sigma \Delta H^\circ_{\text{reactant bonds broken}} &= 591 \text{ kJ} \end{aligned}$$

Bonds formed:

$$2 \times \text{H—F} = (2 \text{ mol})(-565 \text{ kJ/mol}) = \Sigma \Delta H^\circ_{\text{product bonds formed}} = -1130 \text{ kJ}$$

Applying Equation 9.2 gives

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= \Sigma \Delta H^\circ_{\text{reactant bonds broken}} + \Sigma \Delta H^\circ_{\text{product bonds formed}} \\ &= 591 \text{ kJ} + (-1130 \text{ kJ}) = -539 \text{ kJ} \end{aligned}$$

The small discrepancy between this bond energy value (-539 kJ) and the value from tabulated ΔH° values (-546 kJ) is due to variations in experimental method.

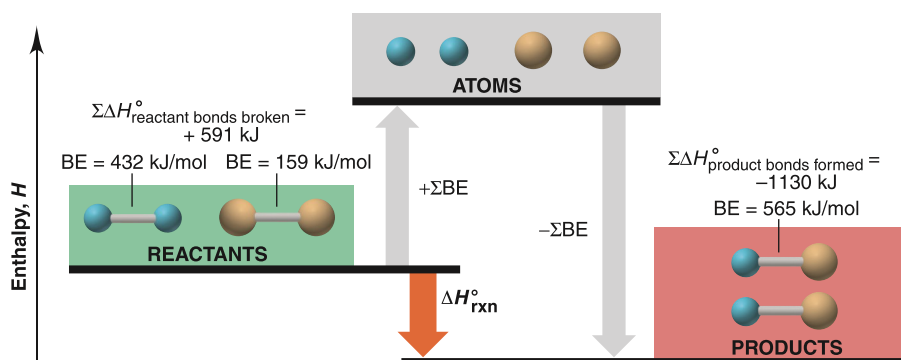


Figure 9.16 Using bond energies to calculate $\Delta H^\circ_{\text{rxn}}$ for HF formation.

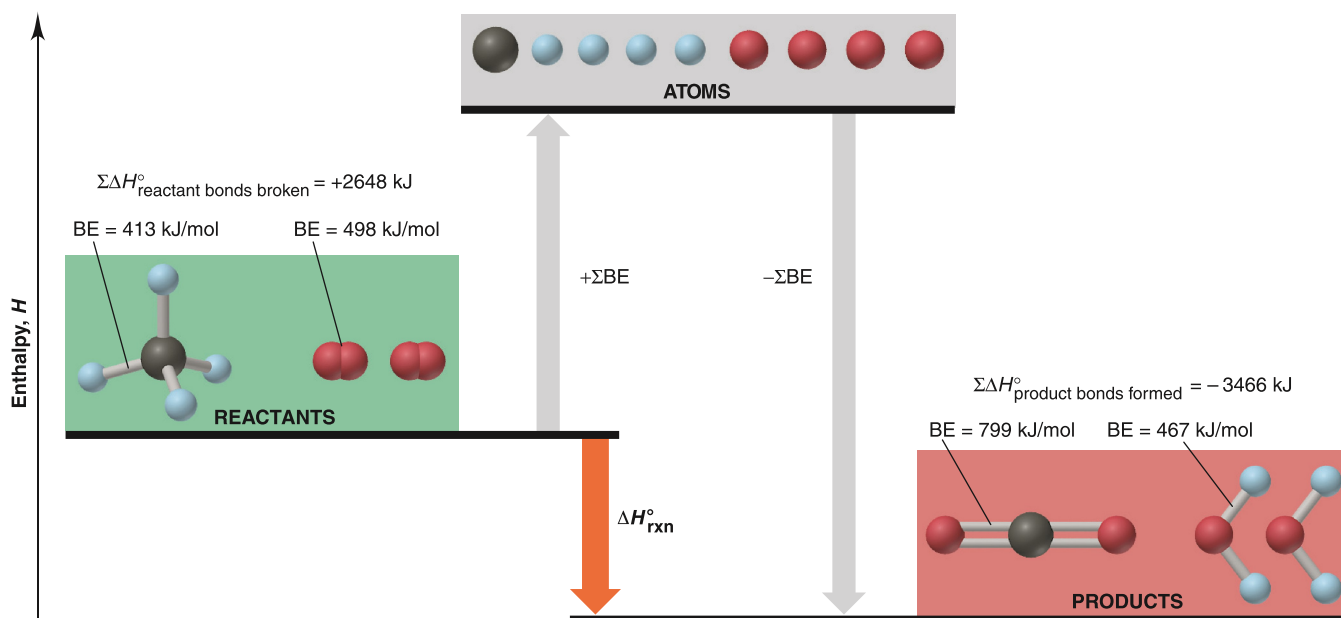


Figure 9.17 Using bond energies to calculate $\Delta H^\circ_{\text{rxn}}$ for the combustion of methane.

2. *Combustion of CH_4 .* In this more complicated reaction, all the bonds in CH_4 and O_2 break, and the atoms form all the bonds in CO_2 and H_2O (Figure 9.17). Once again, we use Table 9.2 and appropriate signs for bonds broken and bonds formed:

Bonds broken:

$$\begin{array}{rcl} 4 \times \text{C—H} & = & (4 \text{ mol})(413 \text{ kJ/mol}) = 1652 \text{ kJ} \\ 2 \times \text{O}_2 & = & (2 \text{ mol})(498 \text{ kJ/mol}) = 996 \text{ kJ} \\ \hline \Sigma\Delta H^\circ_{\text{reactant bonds broken}} & = & 2648 \text{ kJ} \end{array}$$

Bonds formed:

$$\begin{array}{rcl} 2 \times \text{C=O} & = & (2 \text{ mol})(-799 \text{ kJ/mol}) = -1598 \text{ kJ} \\ 4 \times \text{O—H} & = & (4 \text{ mol})(-467 \text{ kJ/mol}) = -1868 \text{ kJ} \\ \hline \Sigma\Delta H^\circ_{\text{product bonds formed}} & = & -3466 \text{ kJ} \end{array}$$

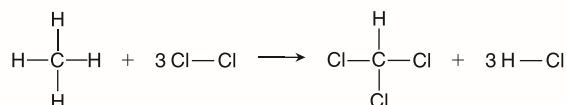
Applying Equation 9.2 gives

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= \Sigma\Delta H^\circ_{\text{reactant bonds broken}} + \Sigma\Delta H^\circ_{\text{product bonds formed}} \\ &= 2648 \text{ kJ} + (-3466 \text{ kJ}) = -818 \text{ kJ} \end{aligned}$$

In addition to variations in experimental method, there is a more basic reason for the discrepancy between the $\Delta H^\circ_{\text{rxn}}$ obtained from bond energies (-818 kJ) and the value obtained by calorimetry (-802 kJ ; Section 6.3). A bond energy is an *average* value for a given bond over many compounds. The value *in a particular substance* is usually close, but not equal, to the average. For example, the C—H bond energy of 413 kJ/mol is the average for C—H bonds in many molecules. In fact, 415 kJ is actually required to break 1 mol of C—H bonds in methane, or 1660 kJ for 4 mol of these bonds, which gives a $\Delta H^\circ_{\text{rxn}}$ closer to the calorimetric value. Thus, it isn't surprising to find small discrepancies between $\Delta H^\circ_{\text{rxn}}$ values obtained in different ways.

Sample Problem 9.3 Using Bond Energies to Calculate $\Delta H^\circ_{\text{rxn}}$

Problem Calculate $\Delta H^\circ_{\text{rxn}}$ for the chlorination of methane to form chloroform:



Plan All the reactant bonds break, and *all* the product bonds form. We find the bond energies in Table 9.2 and substitute the two sums, with correct signs, into Equation 9.2.

Solution Finding the standard enthalpy changes for bonds broken and for bonds formed: For bonds broken, the bond energy values are

$$\begin{array}{rcl} 4 \times \text{C—H} &= (4 \text{ mol})(413 \text{ kJ/mol}) &= 1652 \text{ kJ} \\ 3 \times \text{Cl—Cl} &= (3 \text{ mol})(243 \text{ kJ/mol}) &= 729 \text{ kJ} \\ \hline \Sigma \Delta H^\circ_{\text{bonds broken}} &= &2381 \text{ kJ} \end{array}$$

For bonds formed, the values are

$$\begin{array}{rcl} 3 \times \text{C—Cl} &= (3 \text{ mol})(-339 \text{ kJ/mol}) &= -1017 \text{ kJ} \\ 1 \times \text{C—H} &= (1 \text{ mol})(-413 \text{ kJ/mol}) &= -413 \text{ kJ} \\ 3 \times \text{H—Cl} &= (3 \text{ mol})(-427 \text{ kJ/mol}) &= -1281 \text{ kJ} \\ \hline \Sigma \Delta H^\circ_{\text{bonds formed}} &= &-2711 \text{ kJ} \end{array}$$

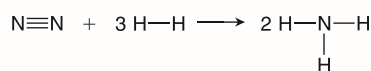
Calculating $\Delta H^\circ_{\text{rxn}}$:

$$\Delta H^\circ_{\text{rxn}} = \Sigma \Delta H^\circ_{\text{bonds broken}} + \Sigma \Delta H^\circ_{\text{bonds formed}} = 2381 \text{ kJ} + (-2711 \text{ kJ}) = -330 \text{ kJ}$$

Check The signs of the enthalpy changes are correct: $\Sigma \Delta H^\circ_{\text{bonds broken}} > 0$, and $\Sigma \Delta H^\circ_{\text{bonds formed}} < 0$. More energy is released than absorbed, so $\Delta H^\circ_{\text{rxn}}$ is negative:

$$\sim 2400 \text{ kJ} + [\sim (-2700 \text{ kJ})] = -300 \text{ kJ}$$

FOLLOW-UP PROBLEM 9.3 One of the most important industrial reactions is the formation of ammonia from its elements:



Use bond energies to calculate $\Delta H^\circ_{\text{rxn}}$.

Summary of Section 9.4

- The only component of internal energy that changes significantly during a reaction is the bond energies of reactants and products, and this change appears as the enthalpy of reaction, $\Delta H^\circ_{\text{rxn}}$.
- A reaction involves breaking reactant bonds and forming product bonds. Applying Hess's law, we use tabulated bond energies to calculate $\Delta H^\circ_{\text{rxn}}$.

9.5 • BETWEEN THE EXTREMES: ELECTRONEGATIVITY AND BOND POLARITY

Scientific models are idealized descriptions of reality. The ionic and covalent bonding models portray compounds as formed by *either* complete electron transfer *or* complete electron sharing. But, in real substances, most atoms are joined by *polar covalent bonds*—partly ionic and partly covalent (Figure 9.18). In this section, we explore the “in-between” nature of these bonds and its importance in the properties of substances.

Electronegativity

Electronegativity (EN) is the relative ability of a bonded atom to attract shared electrons.* We might expect the H—F bond energy to be the average of an H—H bond (432 kJ/mol) and an F—F bond (159 kJ/mol), or 296 kJ/mol. But, the actual HF bond energy is 565 kJ/mol, or 269 kJ/mol *higher!* To explain this difference, the American chemist Linus Pauling reasoned that it is due to an *electrostatic (charge) contribution* to the H—F bond energy. If F attracts the shared electron pair more strongly than H, that is, if F is more *electronegative* than H, the electrons will spend more time

*Electronegativity refers to a *bonded* atom attracting a shared pair; electron affinity refers to a gaseous atom gaining an electron to form an anion. Elements with a high EN also have a highly negative EA.

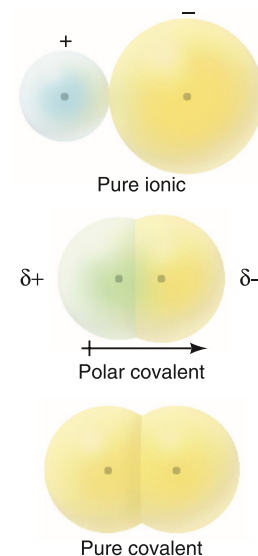


Figure 9.18 Bonding between the models. Pure ionic bonding (*top*) and pure covalent bonding (*bottom*) are far less common than polar covalent bonding (*middle*).

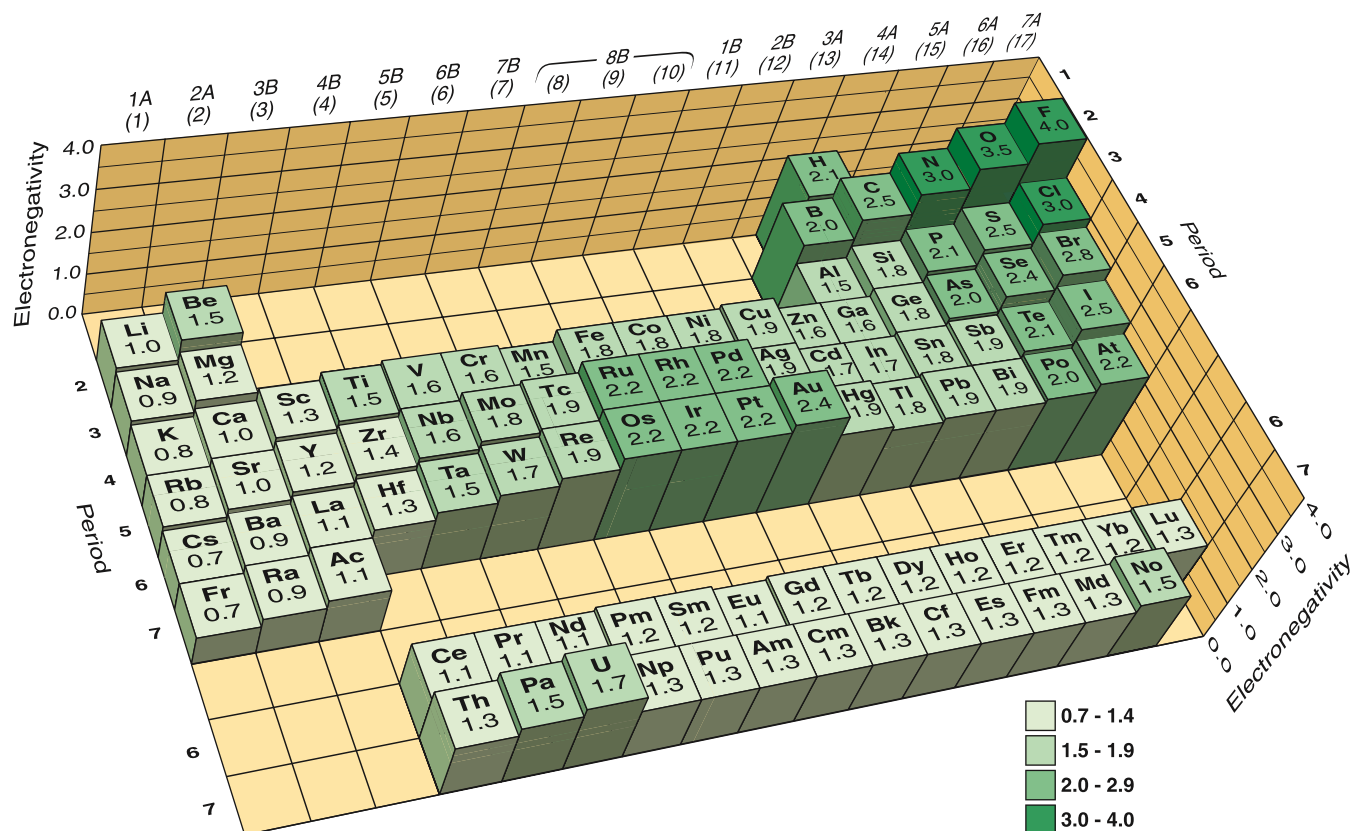


Figure 9.19 The Pauling electronegativity (EN) scale. The height of each post is proportional to the EN, which is shown on top. The key has several EN cutoffs. In the main groups, EN *increases* across and *decreases* down. The transition and inner transition elements show little change in EN. Here hydrogen is placed near elements with similar EN values.

closer to F. This unequal sharing makes the F end of the bond partially negative and the H end partially positive. The electrostatic attraction between these partial charges *increases* the energy required to break the bond. From studies with many other compounds, Pauling derived a scale of *relative EN values* based on fluorine having the highest EN value, 4.0 (Figure 9.19).

Trends in Electronegativity Because the nucleus of a smaller atom is closer to the shared pair than that of a larger atom, it attracts the bonding electrons more strongly. So, in general, electronegativity is inversely related to atomic size. Thus, for the main-group elements, *electronegativity generally increases up a group and across a period*.

Electronegativity and Oxidation Number An important use of electronegativity is in determining an atom's oxidation number (O.N.; see Section 4.5):

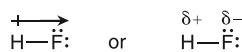
1. The more electronegative atom in a bond is assigned *all* the *shared* electrons; the less electronegative atom is assigned *none*.
2. Each atom in a bond is assigned *all* of its *unshared* electrons.
3. The oxidation number is given by

$$\text{O.N.} = \text{no. of valence } e^- - (\text{no. of shared } e^- + \text{no. of unshared } e^-)$$

In HCl, for example, Cl is more electronegative than H. Cl has 7 valence electrons and is assigned 8 (2 shared + 6 unshared), so its O.N. is $7 - 8 = -1$. The H atom has 1 valence electron and is assigned none, so its O.N. is $1 - 0 = +1$.

Bond Polarity and Partial Ionic Character

Whenever atoms of different electronegativities form a bond, such as H (2.1) and F (4.0) in HF, the bonding pair is shared *unequally*. This unequal distribution of electron density results in a **polar covalent bond**. It is depicted by a polar arrow ($\rightarrow$) pointing toward the partially negative pole or by $\delta+$ and $\delta-$ symbols (see Figure 4.1):



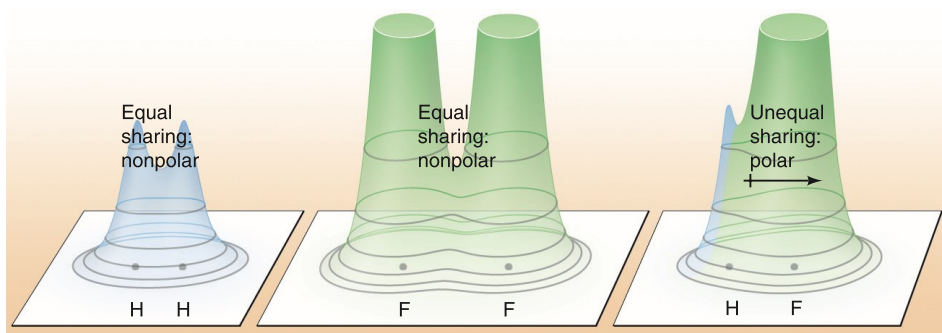


Figure 9.20 Electron density distributions in H_2 , F_2 , and HF . In HF , the electron density shifts from H to F . (The electron density peaks for F have been cut off in the relief maps to limit the figure height.)

In the $\text{H}-\text{H}$ and $\text{F}-\text{F}$ bonds, where the atoms are identical, the bonding pair is shared *equally*, and a **nonpolar covalent bond** results. In Figure 9.20, relief maps show the distribution of electron density in H_2 , F_2 , and HF .

The Importance of Electronegativity Difference (ΔEN) The **electronegativity difference (ΔEN)**, the difference between the EN values of the bonded atoms, is directly related to a bond's polarity. It ranges from 0.0 in a diatomic element, such as H_2 , O_2 , or Cl_2 , all the way up to 3.3, the difference between the most electronegative atom, F (4.0), and the most electropositive, Cs (0.7), in the ionic compound CsF .

Another parameter closely related to ΔEN is the **partial ionic character** of a bond: *a greater ΔEN results in larger partial charges and higher partial ionic character*. Consider three Cl -containing gaseous molecules: ΔEN for $\text{LiCl}(\text{g})$ is $3.0 - 1.0 = 2.0$; for $\text{HCl}(\text{g})$, it is $3.0 - 2.1 = 0.9$; and for $\text{Cl}_2(\text{g})$, it is $3.0 - 3.0 = 0.0$. Thus, the bond in LiCl has more ionic character than the one in HCl , which has more than the one in Cl_2 .

Here are two approaches that quantify ionic character. Both use arbitrary cutoffs, which is not really consistent with the actual gradation in bonding:

1. **ΔEN range.** This approach divides bonds into mostly ionic, polar covalent, mostly covalent, and nonpolar covalent based on a range of ΔEN values (Figure 9.21).

2. **Percent ionic character.** This approach is based on the behavior of a diatomic molecule in an electric field. A plot of *percent ionic character* vs. ΔEN for several gaseous molecules shows that, as expected, *percent ionic character generally increases with ΔEN* (Figure 9.22A). A value of 50% divides ionic from covalent bonds. Note that a substance like $\text{Cl}_2(\text{g})$ has 0% ionic character, but none has 100% ionic character: *electron sharing occurs to some extent in every bond*, even the bond in an alkali halide (Figure 9.22B).

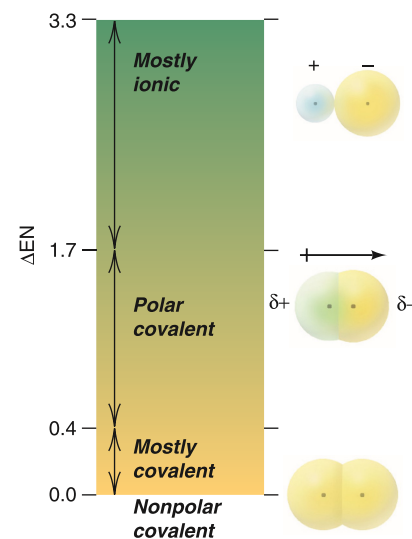


Figure 9.21 ΔEN ranges for classifying the partial ionic character of bonds.

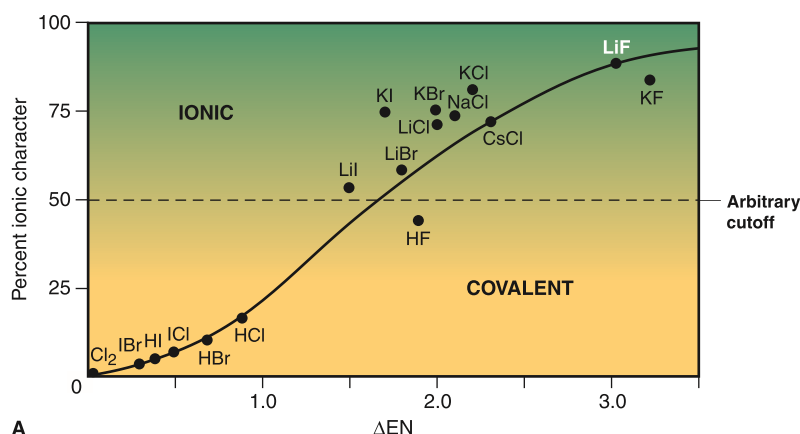


Figure 9.22 Percent ionic character as a function of ΔEN . **A**, ΔEN correlates with ionic character. **B**, Even for highly ionic LiF ($\Delta\text{EN} = 3.0$), the relief map shows some electron sharing between the ions.

Sample Problem 9.4 Determining Bond Polarity from EN Values

Problem (a) Use a polar arrow to indicate the polarity of each bond: N—H, F—N, I—Cl. (b) Rank the following bonds in order of *increasing* polarity and *decreasing* percent ionic character: H—N, H—O, H—C.

Plan (a) We use Figure 9.19 to find the EN values for the atoms and point the polar arrow toward the negative end. (b) To rank the bond polarity, we determine ΔEN : the higher the value, the greater the polarity. Percent ionic character is also directly related to ΔEN (and bond polarity); it decreases in the opposite order that polarity increases.

Solution (a) The EN of N = 3.0 and the EN of H = 2.1, so $\text{N} \leftarrow \text{H}$.
The EN of F = 4.0 and the EN of N = 3.0, so $\text{F} \leftarrow \text{N}$.

The EN of I = 2.5 and the EN of Cl = 3.0, so $\text{I} \rightarrow \text{Cl}$.

(b) The ΔEN values are 0.9 for H—N, 1.4 for H—O, and 0.4 for H—C.

The order of *increasing* bond polarity is $\text{H—C} < \text{H—N} < \text{H—O}$.

The order of *decreasing* percent ionic character is $\text{H—O} > \text{H—N} > \text{H—C}$.

Check In (b), we can check the order of bond polarity using periodic trends. Each bond involves H and a Period 2 atom. Since size decreases and EN increases across a period, the polarity is greatest for the bond to O (farthest to the right in Period 2).

Comment In Chapter 10, you'll see that the bond polarity contributes to the overall polarity of the molecule, which is a major factor determining behavior.

FOLLOW-UP PROBLEM 9.4 Arrange each set of bonds in order of increasing polarity, and indicate bond polarity with $\delta+$ and $\delta-$ symbols:

(a) Cl—F, Br—Cl, Cl—Cl (b) Si—Cl, P—Cl, S—Cl, Si—Si

The Gradation in Bonding Across a Period

A metal and a nonmetal—elements from the left and right sides of the periodic table—have a relatively large ΔEN and typically form an ionic compound. Two nonmetals—both from the right side of the table—have a small ΔEN and form a covalent compound. When we combine chlorine with each of the other Period 3 elements, starting with sodium, we observe a steady decrease in ΔEN and a gradation in bond type from ionic through polar covalent to nonpolar covalent.

Figure 9.23 shows samples of common Period 3 chlorides—NaCl, MgCl_2 , AlCl_3 , SiCl_4 , PCl_3 , and SCl_2 , as well as Cl_2 —along with the change in ΔEN and two physical properties:

- NaCl. Sodium chloride is a white (colorless) crystalline solid with a ΔEN of 2.1, a high melting point, and high electrical conductivity when molten—ionic by any criterion. Nevertheless, just as for LiF (Figure 9.22B), a small but significant amount of electron sharing appears in the NaCl electron density relief map.
- MgCl_2 . With a ΔEN of 1.8, magnesium chloride is still ionic, but it has a lower melting point and lower conductivity, as well as slightly more electron sharing.
- AlCl_3 . Rather than being a three-dimensional lattice of Al^{3+} and Cl^- ions, aluminum chloride, with a ΔEN value of 1.5, consists of layers of highly polar Al—Cl bonds. Weak forces between layers result in a much lower melting point, and the low conductivity implies few free ions. Electron density between the nuclei is even higher than in MgCl_2 .
- SiCl_4 , PCl_3 , SCl_2 , and Cl_2 . The trend toward more covalent bonding continues through the remaining substances. Each occurs as separate molecules, which have no conductivity and such weak forces *between* them that melting points are below 0°C . In Cl_2 , the bond is nonpolar ($\Delta\text{EN} = 0.0$). Electron density in the bonding region increases steadily.

Thus, as ΔEN decreases, the bond becomes more covalent, and the character of the substance changes from ionic solid to covalent gas.

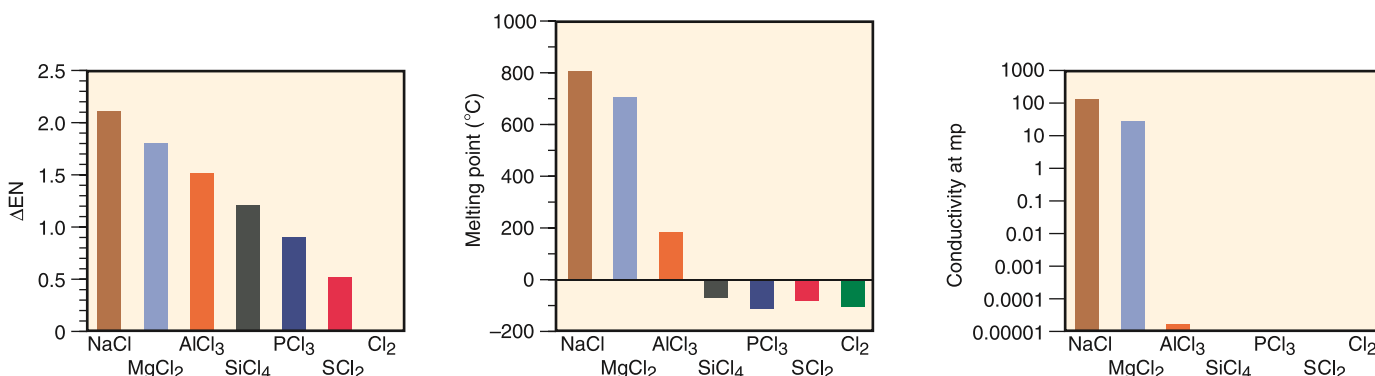
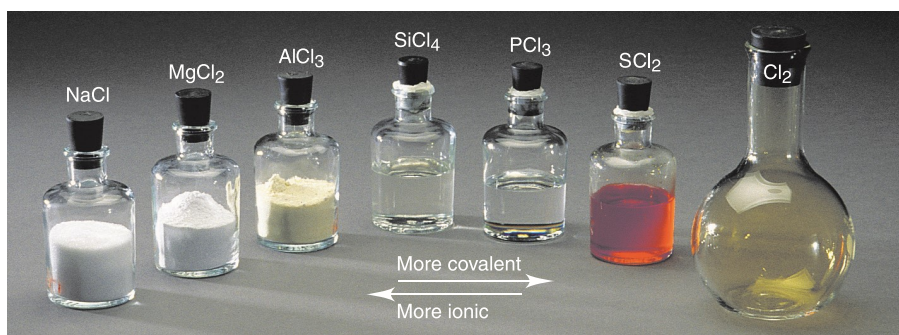


Figure 9.23 Properties of the Period 3 chlorides. As ΔEN decreases, melting point and electrical conductivity decrease because the bond type changes from ionic to polar covalent to nonpolar covalent.

Summary of Section 9.5

- Electronegativity is the ability of a bonded atom to attract shared electrons, which generates opposite partial charges at the ends of the bond and contributes to the bond energy.
- Electronegativity increases across a period and decreases down a group, the reverse of the trends in atomic size.
- The larger the ΔEN for two bonded atoms, the more polar the bond is and the greater its ionic character.
- For Period 3 chlorides, there is a gradation in bond type from ionic to polar covalent to nonpolar covalent.

CHAPTER REVIEW GUIDE

The following sections provide many aids to help you study this chapter. (Numbers in parentheses refer to pages, unless noted otherwise.)

Learning Objectives

These are concepts and skills to review after studying this chapter.

Related section (§), sample problem (SP), and upcoming end-of-chapter problem (EP) numbers are listed in parentheses.

1. Explain how differences in atomic properties lead to the three types of chemical bonding (§9.1) (EPs 9.1–9.7)
2. Depict main-group atoms with Lewis electron-dot symbols (§9.1) (EPs 9.8–9.11)
3. Understand the key features of ionic bonding, the significance of the lattice energy, and how the model explains the properties of ionic compounds (§9.2) (EPs 9.12–9.15, 9.20–9.22)
4. Depict the formation of binary ionic compounds with electron configurations, partial orbital diagrams, and Lewis electron-dot symbols (§9.2) (SP 9.1) (EPs 9.16–9.19)
5. Describe the formation of a covalent bond, the interrelationship among bond length, strength, and order, and how the model explains the properties of covalent compounds (§9.3) (SP 9.2) (EPs 9.23–9.31)
6. Understand how changes in bond energy account for $\Delta H_{\text{rxn}}^\circ$ and be able to divide a reaction into bond-breaking and bond-forming steps (§9.4) (SP 9.3) (EPs 9.32–9.39)
7. Describe the trends in electronegativity, and understand how the polarity of a bond and the partial ionic character of a compound relate to ΔEN of the bonded atoms (§9.5) (SP 9.4) (EPs 9.40–9.55)

Key Terms

These important terms appear in boldface in the chapter and are defined again in the Glossary.

Section 9.1

ionic bonding (277)
covalent bonding (278)
metallic bonding (278)
Lewis electron-dot symbol (278)
octet rule (279)

Section 9.2

lattice energy ($\Delta H^\circ_{\text{lattice}}$) (281)
Coulomb's law (282)
ion pair (283)

Section 9.3

covalent bond (285)
bonding (shared) pair (285)
lone (unshared) pair (285)

bond order (285)
single bond (285)
double bond (285)
triple bond (286)
bond energy (BE) (286)
bond length (286)
infrared (IR) spectroscopy (289)

Section 9.5

electronegativity (EN) (293)
polar covalent bond (294)
nonpolar covalent bond (295)
electronegativity difference (ΔEN) (295)
partial ionic character (295)

Key Equations and Relationships

Numbered and screened concepts are listed for you to refer to or memorize.

9.1 Relating the energy of attraction to the lattice energy (282):

$$\text{Electrostatic energy} \propto \frac{\text{cation charge} \times \text{anion charge}}{\text{cation radius} + \text{anion radius}} \propto \Delta H^\circ_{\text{lattice}}$$

9.2 Calculating enthalpy of reaction from bond enthalpies or bond energies (291):

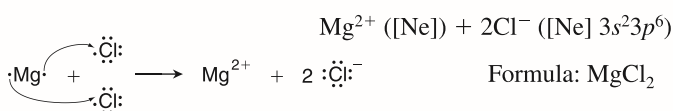
$$\Delta H^\circ_{\text{rxn}} = \Sigma \Delta H^\circ_{\text{reactant bonds broken}} + \Sigma \Delta H^\circ_{\text{product bonds formed}}$$

or

$$\Delta H^\circ_{\text{rxn}} = \Sigma \text{BE}_{\text{reactant bonds broken}} - \Sigma \text{BE}_{\text{product bonds formed}}$$

BRIEF SOLUTIONS TO FOLLOW-UP PROBLEMS

Compare your own solutions to these calculation steps and answers.

9.1 $\text{Mg} ([\text{Ne}] 3s^2) + 2\text{Cl} ([\text{Ne}] 3s^2 3p^5) \longrightarrow$ 9.2 (a) Bond length: $\text{Si}-\text{F} < \text{Si}-\text{O} < \text{Si}-\text{C}$ Bond strength: $\text{Si}-\text{C} < \text{Si}-\text{O} < \text{Si}-\text{F}$ (b) Bond length: $\text{N} \equiv \text{N} < \text{N}=\text{N} < \text{N}-\text{N}$ Bond strength: $\text{N}-\text{N} < \text{N}=\text{N} < \text{N} \equiv \text{N}$ 9.3 $\text{N} \equiv \text{N} + 3 \text{H}-\text{H} \longrightarrow 2 \text{H}-\text{N}-\text{H}$

$$\Sigma \Delta H^\circ_{\text{bonds broken}} = 1 \text{ N} \equiv \text{N} + 3 \text{ H}-\text{H}$$

$$= 945 \text{ kJ} + 1296 \text{ kJ} = 2241 \text{ kJ}$$

$$\Sigma \Delta H^\circ_{\text{bonds formed}} = 6 \text{ N}-\text{H} = -2346 \text{ kJ}$$

$$\Delta H^\circ_{\text{rxn}} = -105 \text{ kJ}$$

9.4 (a) $\text{Cl}-\text{Cl} < \overset{\delta+}{\text{Br}}-\overset{\delta-}{\text{Cl}} < \overset{\delta+}{\text{Cl}}-\overset{\delta-}{\text{F}}$ (b) $\text{Si}-\text{Si} < \overset{\delta+}{\text{S}}-\overset{\delta-}{\text{Cl}} < \overset{\delta+}{\text{P}}-\overset{\delta-}{\text{Cl}} < \overset{\delta+}{\text{Si}}-\overset{\delta-}{\text{Cl}}$

PROBLEMS

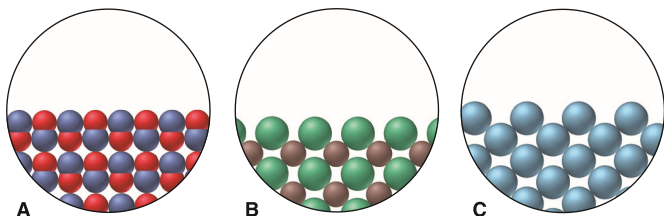
Problems with **colored** numbers are answered in Appendix E. Sections match the text and provide the numbers of relevant sample problems. Bracketed problems are grouped in pairs (indicated by a short rule) that cover the same concept. Comprehensive Problems are based on material from any section or previous chapter.

Atomic Properties and Chemical Bonds

9.1 In general terms, how does each of the following atomic properties influence the metallic character of the main-group elements in a period?

- (a) Ionization energy
- (b) Atomic radius
- (c) Number of outer electrons
- (d) Effective nuclear charge

9.2 Three solids are represented below. What is the predominant type of intramolecular bonding in each?



9.3 What is the relationship between the tendency of a main-group element to form a monatomic ion and its position in the periodic table? In what part of the table are the main-group elements that typically form cations? Anions?

9.4 Which member of each pair is *more* metallic?

- (a) Na or Cs
- (b) Mg or Rb
- (c) As or N

9.5 Which member of each pair is *less* metallic?

- (a) I or O
- (b) Be or Ba
- (c) Se or Ge

9.6 State the type of bonding—ionic, covalent, or metallic—you would expect in each: (a) $\text{CsF}(s)$; (b) $\text{N}_2(g)$; (c) $\text{Na}(s)$.

9.7 State the type of bonding—ionic, covalent, or metallic—you would expect in each: (a) $\text{ICl}_3(g)$; (b) $\text{N}_2\text{O}(g)$; (c) $\text{LiCl}(s)$.

9.8 Draw a Lewis electron-dot symbol for (a) Rb; (b) Si; (c) I.

9.9 Draw a Lewis electron-dot symbol for (a) Ba; (b) Kr; (c) Br.

9.10 Give the group number and general electron configuration of an element with each electron-dot symbol: (a) $\cdot\ddot{\text{X}}\cdot$ (b) $\cdot\ddot{\text{X}}\cdot$

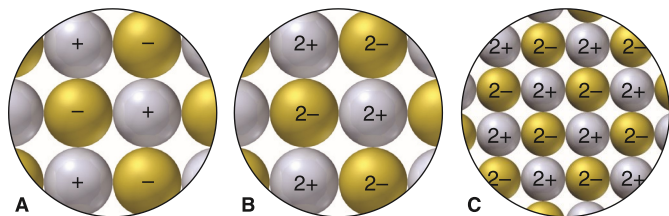
9.11 Give the group number and general electron configuration of an element with each electron-dot symbol: (a) $\cdot\ddot{\text{X}}\cdot$ (b) $\cdot\ddot{\text{X}}\cdot$

The Ionic Bonding Model

(Sample Problem 9.1)

9.12 If energy is required to form monatomic ions from metals and nonmetals, why do ionic compounds exist?

9.13 (a) In general, how does the lattice energy of an ionic compound depend on the charges and sizes of the ions? (b) Ion arrangements of three general salts are represented below. Rank them in order of increasing lattice energy.



9.14 When gaseous Na^+ and Cl^- ions form gaseous NaCl ion pairs, 548 kJ/mol of energy is released. Why, then, does NaCl occur as a solid under ordinary conditions?

9.15 To form S^{2-} ions from gaseous sulfur atoms requires 214 kJ/mol, but these ions exist in solids such as K_2S . Explain.

9.16 Use condensed electron configurations and Lewis electron-dot symbols to depict the ions formed from each of the following atoms, and predict the formula of their compound:

(a) Ba and Cl (b) Sr and O (c) Al and F (d) Rb and O

9.17 Use condensed electron configurations and Lewis electron-dot symbols to depict the ions formed from each of the following atoms, and predict the formula of their compound:

(a) Cs and S (b) O and Ga (c) N and Mg (d) Br and Li

9.18 For each ionic compound formula, identify the main group to which X belongs: (a) X_2O_3 ; (b) XCO_3 ; (c) Na_2X .

9.19 For each ionic compound formula, identify the main group to which X belongs: (a) CaX_2 ; (b) Al_2X_3 ; (c) XPO_4 .

9.20 For each pair, choose the compound with the lower lattice energy, and explain your choice: (a) CaS or BaS ; (b) NaF or MgO .

9.21 For each pair, choose the compound with the lower lattice energy, and explain your choice: (a) NaF or NaCl ; (b) K_2O or K_2S .

9.22 Aluminum oxide (Al_2O_3) is a widely used industrial abrasive (emery, corundum), for which the specific application depends on the hardness of the crystal. What does this hardness imply about the magnitude of the lattice energy? Would you have predicted from the chemical formula that Al_2O_3 is hard? Explain.

The Covalent Bonding Model

(Sample Problem 9.2)

9.23 Describe the interactions that occur between individual chlorine atoms as they approach each other and form Cl_2 . What combination of forces gives rise to the energy holding the atoms together and to the final internuclear distance?

9.24 Define bond energy using the $\text{H}-\text{Cl}$ bond as an example. When this bond breaks, is energy absorbed or released? Is the accompanying ΔH value positive or negative? How do the magnitude and sign of this ΔH value relate to the value that accompanies $\text{H}-\text{Cl}$ bond formation?

9.25 For single bonds between similar types of atoms, how does the strength of the bond relate to the sizes of the atoms? Explain.

9.26 How does the energy of the bond between a given pair of atoms relate to the bond order? Why?

9.27 When liquid benzene (C_6H_6) boils, does the gas consist of molecules, ions, or separate atoms? Explain.

9.28 Using the periodic table only, arrange the members of each of the following sets in order of increasing bond *strength*:

(a) $\text{Br}-\text{Br}$, $\text{Cl}-\text{Cl}$, $\text{I}-\text{I}$

(b) $\text{S}-\text{H}$, $\text{S}-\text{Br}$, $\text{S}-\text{Cl}$

(c) $\text{C}=\text{N}$, $\text{C}-\text{N}$, $\text{C}\equiv\text{N}$

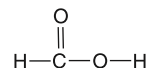
9.29 Using the periodic table only, arrange the members of each of the following sets in order of increasing bond *length*:

(a) $\text{H}-\text{F}$, $\text{H}-\text{I}$, $\text{H}-\text{Cl}$

(b) $\text{C}-\text{S}$, $\text{C}=\text{O}$, $\text{C}-\text{O}$

(c) $\text{N}-\text{H}$, $\text{N}-\text{S}$, $\text{N}-\text{O}$

9.30 Formic acid (HCOOH ; structural formula shown below) is secreted by certain species of ants when they bite.



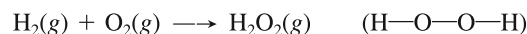
Rank the relative strengths of (a) the $\text{C}-\text{O}$ and $\text{C}=\text{O}$ bonds and (b) the $\text{H}-\text{C}$ and $\text{H}-\text{O}$ bonds. Explain these rankings.

9.31 In IR spectra, the stretching of a $\text{C}=\text{C}$ bond appears at a shorter wavelength than that of a $\text{C}-\text{C}$ bond. Would you expect the wavelength for the stretching of a $\text{C}\equiv\text{C}$ bond to be shorter or longer than that for a $\text{C}=\text{C}$ bond? Explain.

Bond Energy and Chemical Change

(Sample Problem 9.3)

9.32 Write a solution plan (without actual numbers, but including the bond energies you would use and how you would combine them algebraically) for calculating the total enthalpy change of the following reaction:

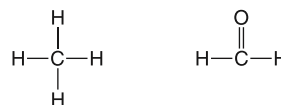


9.33 The text points out that, for similar types of substances, one with weaker bonds is usually more reactive than one with stronger bonds. Why is this generally true?

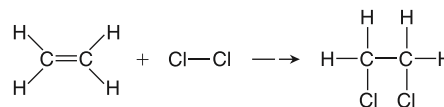
9.34 Why is there a discrepancy between an enthalpy of reaction obtained from calorimetry and one obtained from bond energies?

9.35 Which of the following gases would you expect to have the greater enthalpy of reaction per mole for combustion? Why?

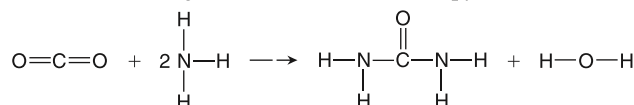
methane or formaldehyde



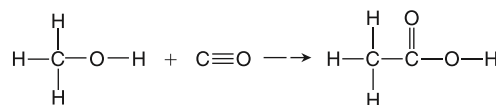
9.36 Use bond energies to calculate the enthalpy of reaction:



9.37 Use bond energies to calculate the enthalpy of reaction:

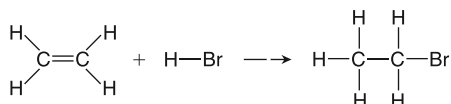


9.38 An important industrial route to extremely pure acetic acid is the reaction of methanol with carbon monoxide:



Use bond energies to calculate the enthalpy of reaction.

9.39 Sports trainers treat sprains and soreness with ethyl bromide. It is manufactured by reacting ethylene with hydrogen bromide:



Use bond energies to find the enthalpy of reaction.

Between the Extremes: Electronegativity and Bond Polarity

(Sample Problem 9.4)

9.40 Describe the vertical and horizontal trends in electronegativity (EN) among the main-group elements. According to Pauling's scale, what are the two most electronegative elements? The two least electronegative elements?

9.41 What is the general relationship between IE_1 and EN for the elements? Why?

9.42 Is the H—O bond in water nonpolar covalent, polar covalent, or ionic? Define each term, and explain your choice.

9.43 How does electronegativity differ from electron affinity?

9.44 How is the partial ionic character of a bond in a diatomic molecule related to ΔEN for the bonded atoms? Why?

9.45 Using the periodic table only, arrange the elements in each set in order of *increasing* EN: (a) S, O, Si; (b) Mg, P, As.

9.46 Using the periodic table only, arrange the elements in each set in order of *increasing* EN: (a) I, Br, N; (b) Ca, H, F.

9.47 Use Figure 9.19 (p. 294) to indicate the polarity of each bond with a *polar arrow*: (a) N—B; (b) N—O; (c) C—S; (d) S—O; (e) N—H; (f) Cl—O.

9.48 Use Figure 9.19 (p. 294) to indicate the polarity of each bond with *partial charges*: (a) Br—Cl; (b) F—Cl; (c) H—O; (d) Se—H; (e) As—H; (f) S—N.

9.49 Which is the more polar bond in each of the following pairs from Problem 9.47: (a) or (b); (c) or (d); (e) or (f)?

9.50 Which is the more polar bond in each of the following pairs from Problem 9.48: (a) or (b); (c) or (d); (e) or (f)?

9.51 Are the bonds in each of the following substances ionic, nonpolar covalent, or polar covalent? Arrange the substances with polar covalent bonds in order of increasing bond polarity: (a) S_8 (b) RbCl (c) PF_3 (d) SCl_2 (e) F_2 (f) SF_2

9.52 Are the bonds in each of the following substances ionic, nonpolar covalent, or polar covalent? Arrange the substances with polar covalent bonds in order of increasing bond polarity: (a) KCl (b) P_4 (c) BF_3 (d) SO_2 (e) Br_2 (f) NO_2

9.53 Rank the members of each set of compounds in order of *increasing* ionic character of their bonds. Use *polar arrows* to indicate the bond polarity of each:

(a) HBr, HCl, HI (b) H_2O , CH_4 , HF (c) SCl_2 , PCl_3 , SiCl_4

9.54 Rank the members of each set of compounds in order of *decreasing* ionic character of their bonds. Use *partial charges* to indicate the bond polarity of each:

(a) PCl_3 , PBr_3 , PF_3 (b) BF_3 , NF_3 , CF_4 (c) SeF_4 , TeF_4 , BrF_3

9.55 The energy of the C—C bond is 347 kJ/mol, and that of the Cl—Cl bond is 243 kJ/mol. Which of the following values might you expect for the C—Cl bond energy? Explain.

- (a) 590 kJ/mol (sum of the values given)
 (b) 104 kJ/mol (difference of the values given)
 (c) 295 kJ/mol (average of the values given)
 (d) 339 kJ/mol (greater than the average of the values given)

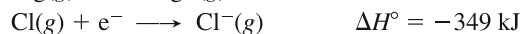
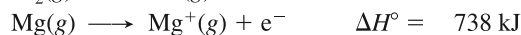
Comprehensive Problems

9.56 Geologists have a rule of thumb: when molten rock cools and solidifies, crystals of compounds with the smallest lattice energies appear at the bottom of the mass. Suggest a reason for this.

9.57 Acetylene gas (ethyne; $\text{HC}\equiv\text{CH}$) burns in an oxyacetylene torch to produce carbon dioxide and water vapor. The enthalpy of reaction for the combustion of acetylene is 1259 kJ/mol. (a) Calculate the $\text{C}\equiv\text{C}$ bond energy, and compare your value with that in Table 9.2 (p. 287). (b) When 500.0 g of acetylene burns, how many kilojoules of heat are given off? (c) How many grams of CO_2 form? (d) How many liters of O_2 at 298 K and 18.0 atm are consumed?

9.58 Even though so much energy is required to form a metal cation with a 2+ charge, the alkaline earth metals form halides with general formula MX_2 , rather than MX .

(a) Use the following data to calculate the ΔH_f° of MgCl :



$$\Delta H_{\text{lattice}}^\circ \text{ of MgCl} = 783.5 \text{ kJ/mol}$$

(b) Is MgCl favored energetically relative to Mg and Cl_2 ? Explain.

(c) Use Hess's law to calculate ΔH° for the conversion of MgCl to MgCl_2 and Mg (ΔH_f° of $\text{MgCl}_2 = -641.6 \text{ kJ/mol}$).

(d) Is MgCl favored energetically relative to MgCl_2 ? Explain.

9.59 By using photons of specific wavelengths, chemists can dissociate gaseous HI to produce H atoms with certain speeds. When HI dissociates, the H atoms move away rapidly, whereas the heavier I atoms move more slowly. (a) What is the longest wavelength (in nm) that can dissociate a molecule of HI? (b) If a photon of 254 nm is used, what is the excess energy (in J) over that needed for dissociation? (c) If this excess energy is carried away by the H atom as kinetic energy, what is its speed (in m/s)?

9.60 Carbon dioxide is a linear molecule. Its vibrational motions include symmetrical stretching, bending, and asymmetrical stretching, and the frequencies are $4.02 \times 10^{13} \text{ s}^{-1}$, $2.00 \times 10^{13} \text{ s}^{-1}$, and $7.05 \times 10^{13} \text{ s}^{-1}$, respectively. (a) In what region of the electromagnetic spectrum are these frequencies? (b) Calculate the energy (in J) of each vibration. Which occurs most readily (takes the least energy)?

9.61 In developing the concept of electronegativity, Pauling used the term *excess bond energy* for the difference between the actual bond energy of X—Y and the average bond energies of X—X and Y—Y (see text discussion for the case of HF). Based on the values in Figure 9.19 (p. 294), which of the following substances contains bonds with no excess bond energy?

(a) PH_3 (b) CS_2 (c) BrCl (d) BH_3 (e) Se_8

9.62 Without stratospheric ozone (O_3), harmful solar radiation would cause gene alterations. Ozone forms when the bond in O_2