Chapter 9

Atomic Properties and Chemical Bonds

Why do atoms bond at all?

In the most general of terms, they bond for one reason: bonding lowers the potential energy of the system (i.e., oppositely charged particles or atomic nuclei and the electrons surrounding them).

Types of Bonding: Three Ways Metals and Nonmetals Combine

The three types of bonding result from the three ways these types of atoms can combine:

1. **Metal with nonmetal** – electron transfer and ionic bonding.

Ionic bond between atoms with large differences in their tendencies differences in their tendencies to lose or gain electrons (i.e., low IE or high negative EA).

2. **Nonmetal with nonmetal** – electron-sharing and covalent bonding.

Each atom holds on to its own valence electrons tightly (high IE) but tend to attract the valence electrons of the other atom (very high negative EA).

3. **Metal with metal** – electron pooling and metallic bonding.

Metal atoms tend to lose their valence electrons easily (low IE) but do not regain them (slightly negative or positive EA). This tendency leads to large numbers of atoms sharing their valence electrons as a "sea" of electrons.

Three Models of Chemical Bonding
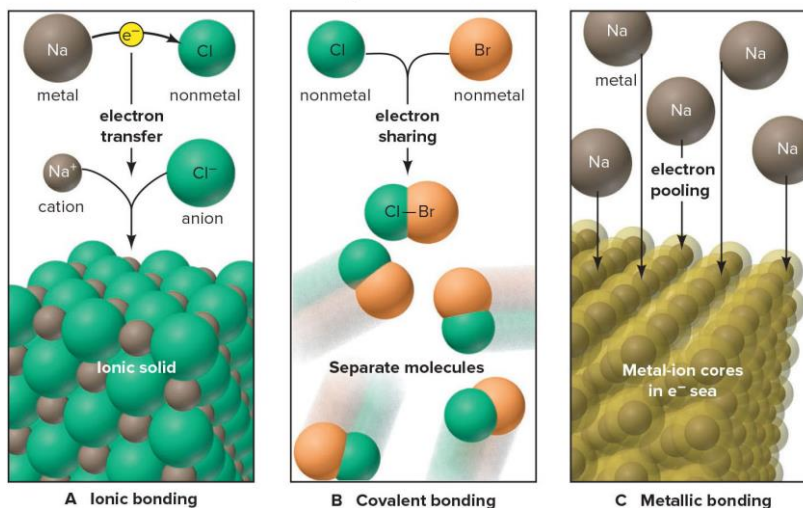
Figure 9.2

Gradations in Bond Type Among Period 3 and Group 4A Elements
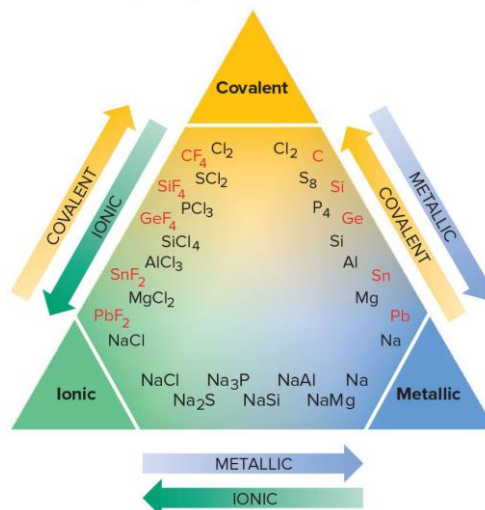
Figure 9.3

Lewis Symbols and the Octet Rule

Method for depicting valence electrons of atoms – *Lewis electron-dot symbol*

When writing the *Lewis electron-dot symbol*, the element's atomic symbol represents the nucleus and inner electrons and the surrounding dots represents the valence electrons.

1. Write the condensed electron configuration and determine the number of valence electrons.

2. Place one dot at a time (each dot representing a valence electron) on the four sides of an imaginary box surrounding the element's atomic symbol.

3. Keep adding dots, pairing the dots until the valence electrons are used up.

• For a metal, number of dots represents maximum number of electrons an atom loses to form a cation.

• For a nonmetal, number of <u>unpaired</u> dots is the number of electrons that the atom gains to form an anion or the number of covalent bonds the atom usually forms.

Example: Carbon (Z = 6) : [He]$2s^2 2p^2$ 4 valence electrons!

$\cdot\ \overset{\cdot}{\underset{\cdot}{C}}\ \cdot$

**Useful Short cut:
For Main Group Elements, number of valence electrons equals Group Number!**

Carbon is in Group 4A ⇒ 4 valence electrons!

In his studies of bonding in 1902, Gilbert N. Lewis generalized much of the bonding behavior in the *octet rule*: When atoms bond, they lose, gain or share electrons to attain a filled outer level of eight (or two for H or Li atoms) electrons.

Lewis Dot Symbols for Some Elements

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

Period (vertical label on left)

Figure 9.4

The Ionic Bonding Model

The central idea in the ionic bonding model is the transfer of electrons from metal atoms to nonmetal atoms to form ions that come together in an ionic solid.

Li (Z = 3)   F (Z = 9)

Group 1A   Group 7A

Orbital Diagrams: Li: $\underline{\uparrow}$ + F: $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ → Li⁺   + F⁻: $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$

                2s   2s   2p   ___   2s   2p

OR

Lewis electron-dot symbols: Li ·   + : F : → Li⁺   + [: F :]⁻
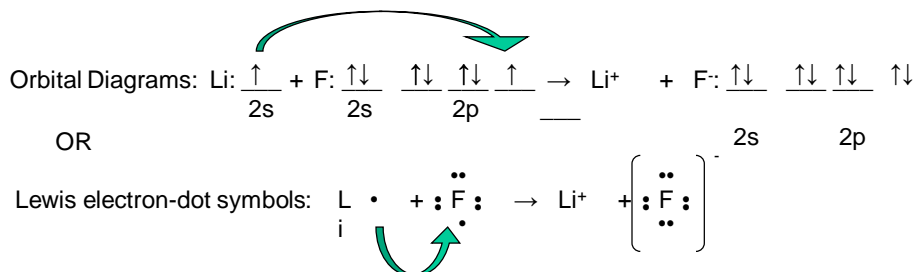
Why Ionic Compounds Form: The Importance of Lattice Energy

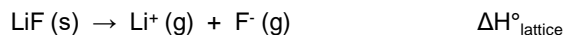Why do ionic compounds form? Because of the enormous release of energy that occurs when ions come together and form the solid.

The *lattice energy* ($\Delta H°_{lattice}$) - the enthalpy change that accompanies the separation of 1 mol ionic solid into gaseous ions

LiF (s) → Li$^+$ (g) + F$^-$ (g) $\Delta H°_{lattice}$

Periodic Trends in Lattice Energy

The magnitude of lattice energy is directly proportional to the electrostatic energy (as measured by coulomb's law) between charged particles in the ionic solid.

Electrostatic energy ∝ |cation charge x anion charge| ∝ $\Delta H°_{lattice}$
                    cation radius + anion radius

$$\frac{|cation\ charge\ x\ anion\ charge|}{cation\ radius\ +\ anion\ radius} \propto \Delta H°_{lattice}$$

The relationship predicts trends in lattice energy with respect to ion size and charge:

1. *Effect of ion size* – as ion size increases lattice energies decrease (**Figure 9.7**).

2. *Effect of ionic charge* - for ions of comparable size, lattice energies increase as the charge on the ions increase.

Let's compare LiF and MgO…
Li$^+$ radius = 76 pm   F$^-$ = 133 pm
Mg^{2+} radius = 72 pm   O^{2-}=140 pm

We observe a nearly four-fold increase in lattice energies:
$\Delta H°_{lattice}$ of LiF = 1050 kJ/mol $\Delta H°_{lattice}$ of MgO = 3923 kJ/mol
Reflecting the difference in ion charges (i.e., 1X1 versus 2X2)
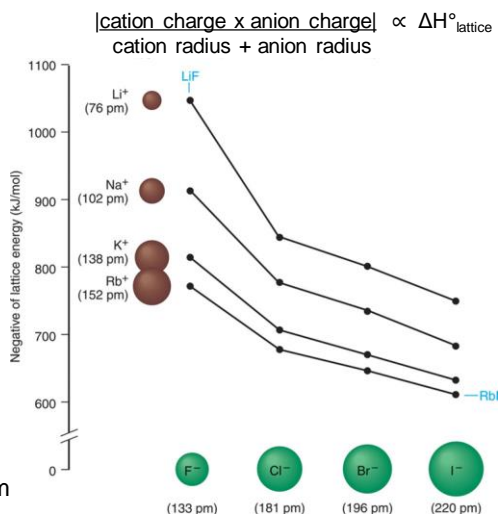
Predicting Relative Lattice Energies from Ionic Properties

PROBLEM: Use ionic properties to explain which compound in each pair has the larger lattice energy: **(a)** RbI or NaBr; **(b)** KCl or CaS.

Properties of Ionic Compounds

- Ionic compounds tend to be hard, rigid, and brittle, with high melting points.

- Ionic compounds do not conduct electricity in the solid state.

  – In the solid state, the ions are fixed in place in the lattice and do not move.

- Ionic compounds conduct electricity when melted or dissolved.

  – In the liquid state or in solution, the ions are free to move and carry a current.

Why Ionic Compounds Crack
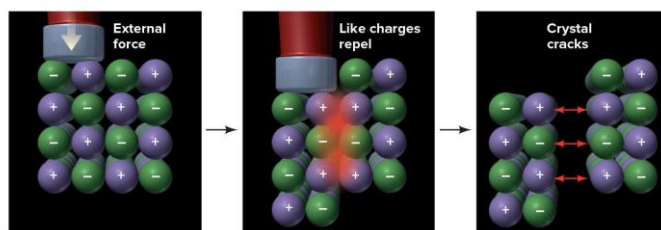
Figure 9.9

The Covalent Bonding Model

The Formation of a Covalent Bond

Why do the hydrogen atoms exist in bonded pairs?

Figure 9.10 illustrates what happens in terms of the potential energy of the system as two hydrogen atoms approach each other.

A ***covalent bond*** arises that balances the attractive forces between the nuclei and two electrons and the repulsive forces between the two nuclei and the two electrons.
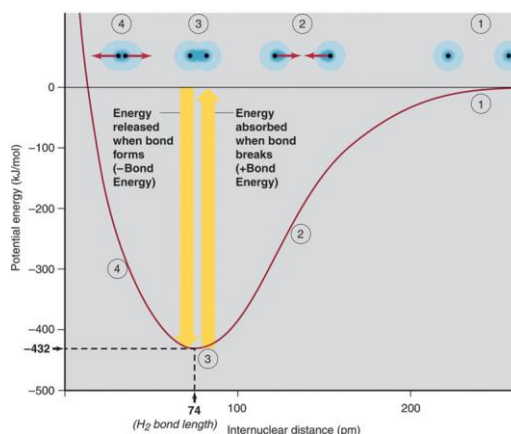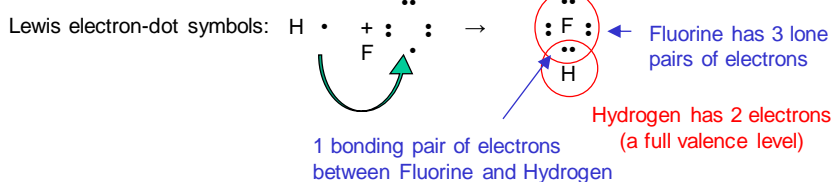
Bonding Pairs and Lone Pairs

Each atom participating in a covalent bond achieves a full valence level of electrons:

• Each atom in a covalent bond "counts" both electrons in the covalent bond (i.e., the **bonding pair**) as belonging entirely to itself.

• Valence electrons not involved in bonding are called **lone pairs**

Example: Let's look at the bonding in hydrogen fluoride, HF. . .

H (Z = 1)   F (Z = 9)

Group 1A   Group 7A

Lewis electron-dot symbols:

Fluorine has 8 electrons (a full valence level)

Fluorine has 3 lone pairs of electrons

Hydrogen has 2 electrons (a full valence level)

1 bonding pair of electrons between Fluorine and Hydrogen

Properties of a Covalent Bond: Order, Energy and Length

Bond **order** - number of electron pairs being shared by a pair of bonded atoms

• A **single bond** (one bonding electron pair) - bond order of 1

$$H - H \text{ and } H - \ddot{F}{\textstyle :}$$
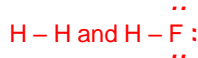
Some atoms share more than one electron pair (i.e. C, O, N and S)

• A **double bond** (two shared electron pairs) - bond order of 2

Example: Ethylene, C_2H_4

$$H_2C = CH_2$$
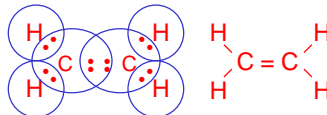
• A **triple bond** (three shared electron pairs) - bond order of 3

**Example:** Nitrogen gas, N_2

$$:N \equiv N:$$

Properties of a Covalent Bond: Bond Energy and Bond Length

*Bond energy* - the energy required to overcome the attractive forces between the nuclei and electrons

Bond energy - the standard enthalpy change for breaking the bond in 1 mol of gaseous molecules

• Stronger bonds - lower in energy (i.e., deep potential energy well).

• Weak bonds - higher in energy (i.e., shallow potential energy well).
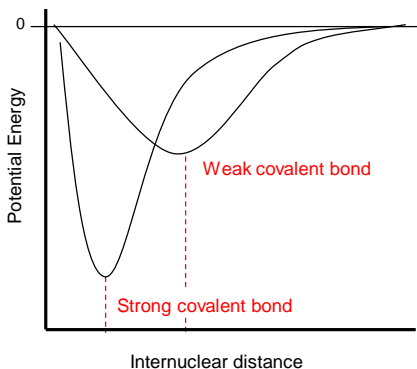
Strong covalent bonds are shorter than weak covalent bonds

Table 9.2 lists some average bond energies and bond lengths – that is, the average distance between nuclei of the two bonded atoms.
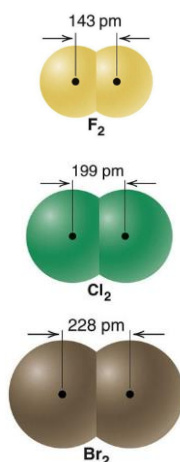
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Table 9.2 Average Bond Energies (kJ/mol) and Bond Lengths (pm)

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			
C—C	347	154	N—I	159	222	Si—I	234	240	F—F	159	143
C—Si	301	186							F—Cl	193	166
C—N	305	147	O—H	467	96	P—H	320	142	F—Br	212	178
C—O	358	143	O—P	351	160	P—Si	213	227	F—I	263	187
C—P	264	187	O—O	204	148	P—P	200	221	Cl—Cl	243	199
C—S	259	181	O—S	265	151	P—F	490	156	Cl—Br	215	214
C—F	453	133	O—F	190	142	P—Cl	331	204	Cl—I	208	243
C—Cl	339	177	O—Cl	203	164	P—Br	272	222	Br—Br	193	228
C—Br	276	194	O—Br	234	172	P—I	184	243	Br—I	175	248
C—I	216	213	O—I	234	194				I—I	151	266
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	O₂	498	121	C≡O	1070	113			
(799 in CO₂)											

143 pm F₂

199 pm Cl₂

228 pm Br₂

The higher the bond order, the stronger (and shorter) the bond length (**Table 9.3** in Silberberg Principles of General Chemistry 3rd Edition).

Table 9.4 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

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

Use bond energies to calculate ΔH°_{rxn} for the combustion of methane. . .
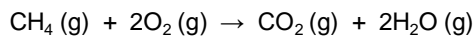
CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (g)

Using Bond Energies to Calculate ΔH°_{rxn} For HF Formation
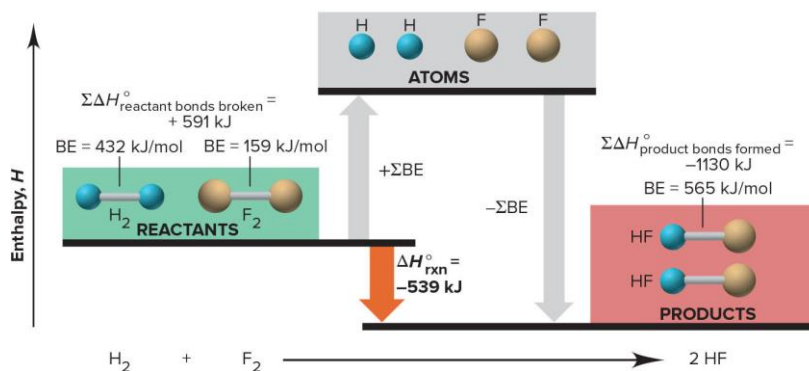
Figure 9.17

Changes in Bond Energy: Where does ΔH°$_{rxn}$ Come From?

Let's consider the reaction

H_2 (g) + F_2 (g) → 2HF (g)   ΔH°$_{rxn}$ = 546 kJ

Think of a reaction as a two-step process in which heat is absorbed (positive ΔH°) to break reactant bonds to form separate atoms <u>and</u> heat is released (negative ΔH°) when the atoms rearrange to form product bonds.

The sum of these enthalpy changes is the heat of reaction, ΔH°$_{rxn}$:

ΔH°$_{rxn}$ = Σ ΔH°$_{reactant\ bonds\ broken}$ + ΣΔH°$_{product\ bonds\ formed}$

• ΔH°$_{rxn}$ is negative (exothermic) when ΣΔH°$_{product\ bonds\ formed}$ is greater than ΣΔH°$_{reactant\ bonds\ broken}$

• ΔH°$_{rxn}$ is positive (endothermic) when ΣΔH°$_{product\ bonds\ formed}$ is smaller than ΣΔH°$_{reactant\ bonds\ broken}$

Using Bond Energies to Calculate ΔH°$_{rxn}$

PROBLEM: Calculate ΔH°$_{rxn}$ for the chlorination of methane to form chloroform.
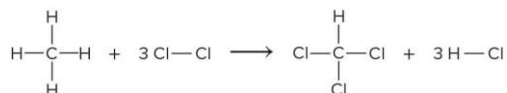
For bonds broken: 4 x C-H = (4 mol)(413 kJ/mol) = 1652 kJ

$\underline{3 \times Cl\text{-}Cl = (3 \text{ mol})(243 \text{ kJ/mol}) = \ \ 729 \text{ kJ}}$

$\Sigma \Delta H^o_{\text{bonds broken}} = \ 2381 \text{ kJ}$

For bonds formed: 3 x C-Cl = (3 mol)(–339 kJ/mol) = –1017 kJ

1 x C-H   = (1 mol)(–413 kJ/mol) =   –413 kJ

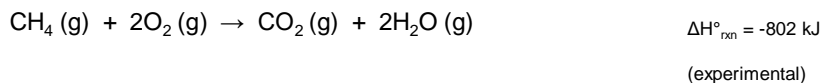$\underline{3 \times H\text{-}Cl = (3 \text{ mol})(-427 \text{ kJ/mol}) = -1281 \text{ kJ}}$

$\Sigma \Delta H^o_{\text{bonds formed}} = \ -2711 \text{ kJ}$

$\Delta H^o_{\textbf{reaction}} = \Sigma \Delta H^o_{\text{bonds \textbf{broken}}} + \Sigma \Delta H_{\textbf{bonds formed}}$

$= \textbf{2381 kJ} + (\textbf{--2711 kJ}) = \textbf{--330 kJ}$

We can use bond energies to calculate ΔH°_{rxn} by assuming all the reactant bonds break to give individual atoms, from which all the product bonds form.

Let's use bond energies to calculate ΔH°_{rxn} for the combustion of methane. . .

CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (g)

ΔH°_{rxn} = -802 kJ

(experimental)

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

Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length	Bond	Energy	Length
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	(799 in CO₂)										

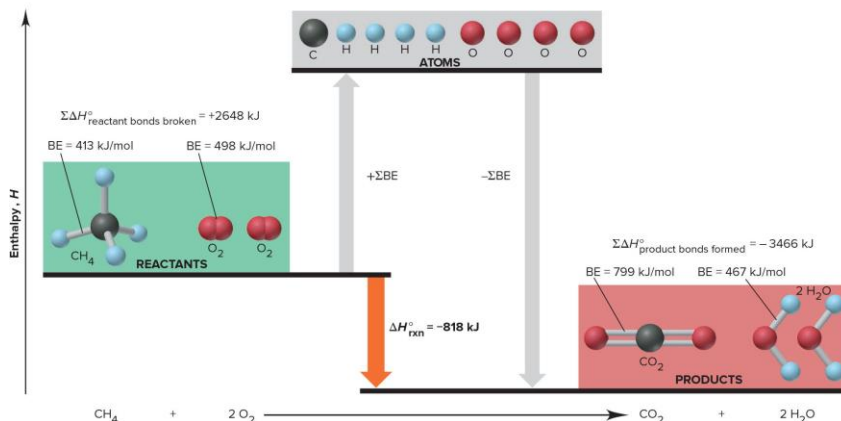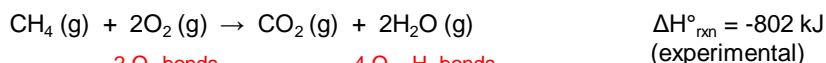# Using Bond Energies to Calculate $\Delta H°_{rxn}$ for the Combustion of Methane

Figure 9.18

We can use bond energies to calculate $\Delta H°_{rxn}$ by assuming all the reactant bonds break to give individual atoms, from which all the product bonds form.

Let's use bond energies to calculate $\Delta H°_{rxn}$ for the combustion of methane. . .

$$CH_4 \,(g) \;+\; 2O_2 \,(g) \;\rightarrow\; CO_2 \,(g) \;+\; 2H_2O \,(g)$$

$\Delta H°_{rxn}$ = -802 kJ (experimental)

4 C – H bonds   2 O$_2$ bonds   4 O – H bonds   2 C = O bonds

Reactant side: Use bond energies from Table 9.2

4 moles C – H bonds x $\dfrac{413 \text{ kJ}}{1 \text{ mole C – H bond}}$ = 1652 kJ

2 moles O$_2$ bonds x $\dfrac{498 \text{ kJ}}{1 \text{ mole O}_2 \text{ bond}}$ = $\dfrac{996 \text{ kJ}}{2648 \text{ kJ}}$

Product side:

2 moles C = O bonds x $\dfrac{(-799 \text{ kJ})}{1 \text{ mole C = O bond}}$ = -1598 kJ

4 moles O - H bonds x $\dfrac{(-467 \text{ kJ})}{1 \text{ mole O - H bond}}$ = $\dfrac{-1868 \text{ kJ}}{-3466 \text{ kJ}}$

$\Delta H°_{rxn}$ = 2648 kJ + (-3466 kJ) = -818 kJ

The difference between the calculated and experimental $\Delta H°_{rxn}$ arises because Table 9.2 lists *average* bond energies determined from several compounds.

Between the Extremes: Electronegativity and Bond Polarity

Electronegativity

One of the most important concepts in bonding is ***electronegativity*** – that is, the relative ability of a bonded atom to attract the shared electrons.

Trends in Electronegativity

Because the nucleus of a small atom is closer to the shared electron pair than a larger atom, the nucleus of a small atom attracts the bonding electrons more strongly.

In general, electronegativity is inversely related to atomic size.

16

Bonding Between the Models

Polar covalent bonds are much more common than either pure ionic or pure covalent bonds.

Figure 9.20

+   −

Pure ionic
No sharing of electrons

δ+   δ−

Polar covalent
Bonding electron pair shared unequally
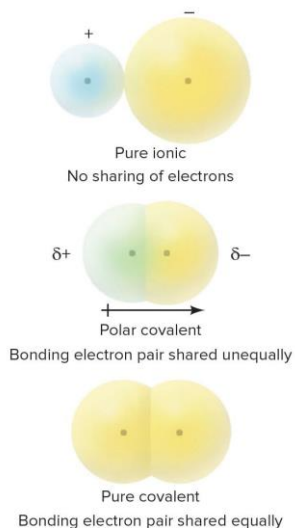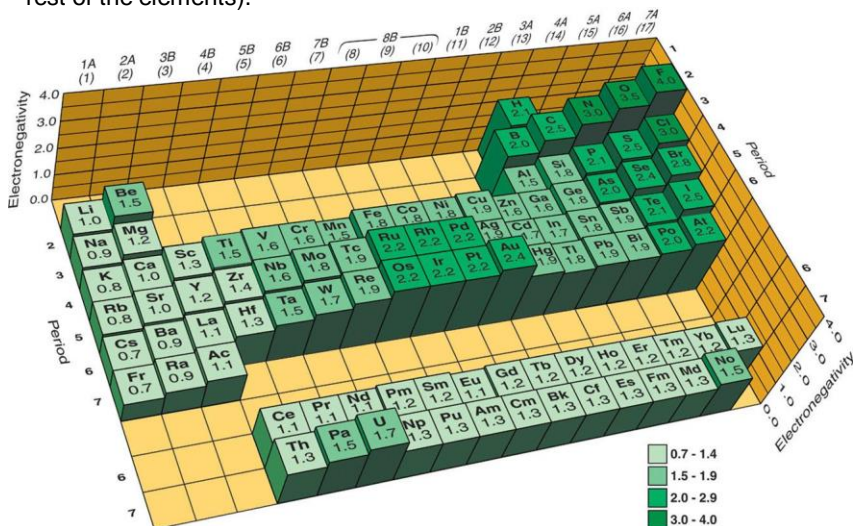
Pure covalent
Bonding electron pair shared equally

Linus Pauling assigned an electronegativity value of 4.0 to fluorine – the most electronegative atom (see **Figure 9.19** for electronegativities of the rest of the elements).

Electronegativity and Atomic Size
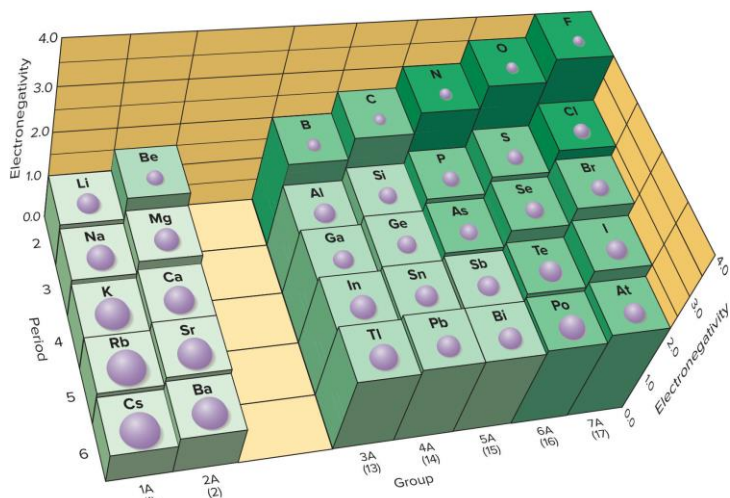
Figure 9.22

Select the element that has the highest electronegativity from the elements below.

A. Se   B. S   C. C   D. B   E. O

Bond Polarity and Partial Ionic Character

When atoms of different electronegativities form a bond, the bonding electron pair is shared unequally. This unequal distribution of electron density means the bond has partially negative and partially positive poles. Such a ***polar covalent bond*** is depicted by a polar arrow:

Example: Hydrogen fluoride, HF

$$\overset{\longmapsto}{\textbf{H - F}}$$

In H – H and F – F, the atoms are identical, so the bonding electron pair is equally shared and a ***nonpolar covalent bond*** results.

The Importance of Electronegativity Difference (ΔEN)

The existence of partial charges means that a polar covalent bond behaves as if it were partially ionic.

The ***partial ionic character*** of a bond is related to the electronegativity difference (ΔEN) between the bonded atoms. The larger the ΔEN value, the higher the partial ionic character of the bond.

Example: Calculate and compare the ionic character of the bonds in LiF (s) and HF (g).

LiF (s): ΔEN = 4.0 – 1.0 = 3.0

HF (g): ΔEN = 4.0 – 2.1 = 1.9

The Li – F bond is more ionic (larger ΔEN) in character than the H – F bond.