

Chapter 8

Bonding: General Concepts

Chapter 8

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Chapter 8

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Section 8.1

Types of Chemical Bonds

An Introduction to Chemical Bonds

- Bonds
 - Forces that hold groups of atoms together and make them function as a unit
- **Bond energy**: Energy required to break a bond
- **Ionic bonding**: Results from electrostatic attractions of closely packed, oppositely charged ions

Section 8.1

Types of Chemical Bonds

An Introduction to Chemical Bonds (continued)

- **ionic compound**: Results when a metal reacts with a nonmetal
 - Example - When Na and Cl react to form NaCl, electrons are transferred from the Na atoms to the Cl atoms to form Na^+ and Cl^- ions
 - Ions then aggregate to form solid sodium chloride

Section 8.1

Types of Chemical Bonds

Coulomb's Law

- Used to calculate the energy of interaction between a pair of ions

$$E = (2.31 \times 10^{-19} \text{ J} \cdot \text{nm}) \left(\frac{Q_1 Q_2}{r} \right)$$

- E has units of joules
- r - Distance between the ion centers in nanometers
- Q_1 and Q_2 - Numerical ion charges

Section 8.1

Types of Chemical Bonds

Coulomb's Law (continued)

- Used to calculate the repulsive energy when two like-charged ions are brought together
 - Calculated value of the energy will have a positive sign

Section 8.1

Types of Chemical Bonds

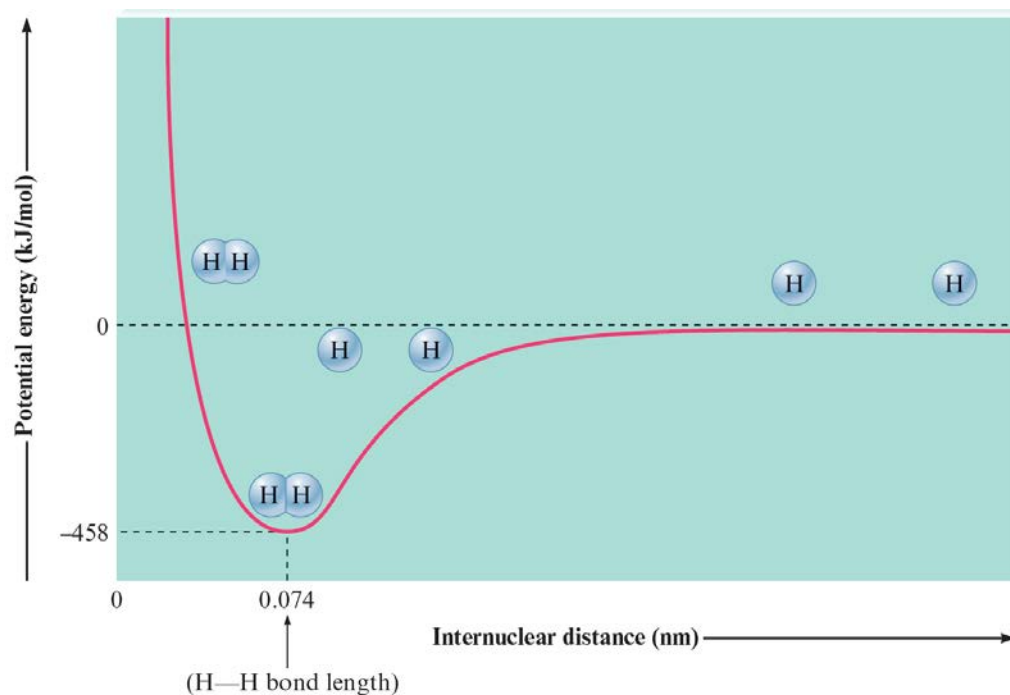
Development of Bonding Forces between Two Identical Atoms

- Bond will form if the system can lower its total energy in the process
 - System will act to minimize the sum of the positive (repulsive) energy terms and the negative (attractive) energy term
- **Bond length**: Distance between two atoms when potential energy is minimal

Section 8.1

Types of Chemical Bonds

Figure 8.1 - (b) Energy Profile as a Function of the Distance between the Nuclei of Hydrogen Atoms



As atoms approach each other (right side of graph), the energy decreases until the distance reaches 0.074 nm (74 pm) and then begins to increase again due to repulsions

Section 8.1

Types of Chemical Bonds

Interaction between Two Hydrogen Atoms: Important Features

- Energy terms involved are the:
 - Net potential energy that results from the attractions and repulsions among the charged particles
 - Kinetic energy due to the motions of the electrons
- Zero point of energy is defined with the atoms at infinite separation

Section 8.1

Types of Chemical Bonds

Interaction between Two Hydrogen Atoms: Important Features (continued)

- At very short distances the energy rises steeply because of the importance of the repulsive forces when the atoms are very close together
- Bond length is the distance at which the system has minimum energy

Section 8.1

Types of Chemical Bonds

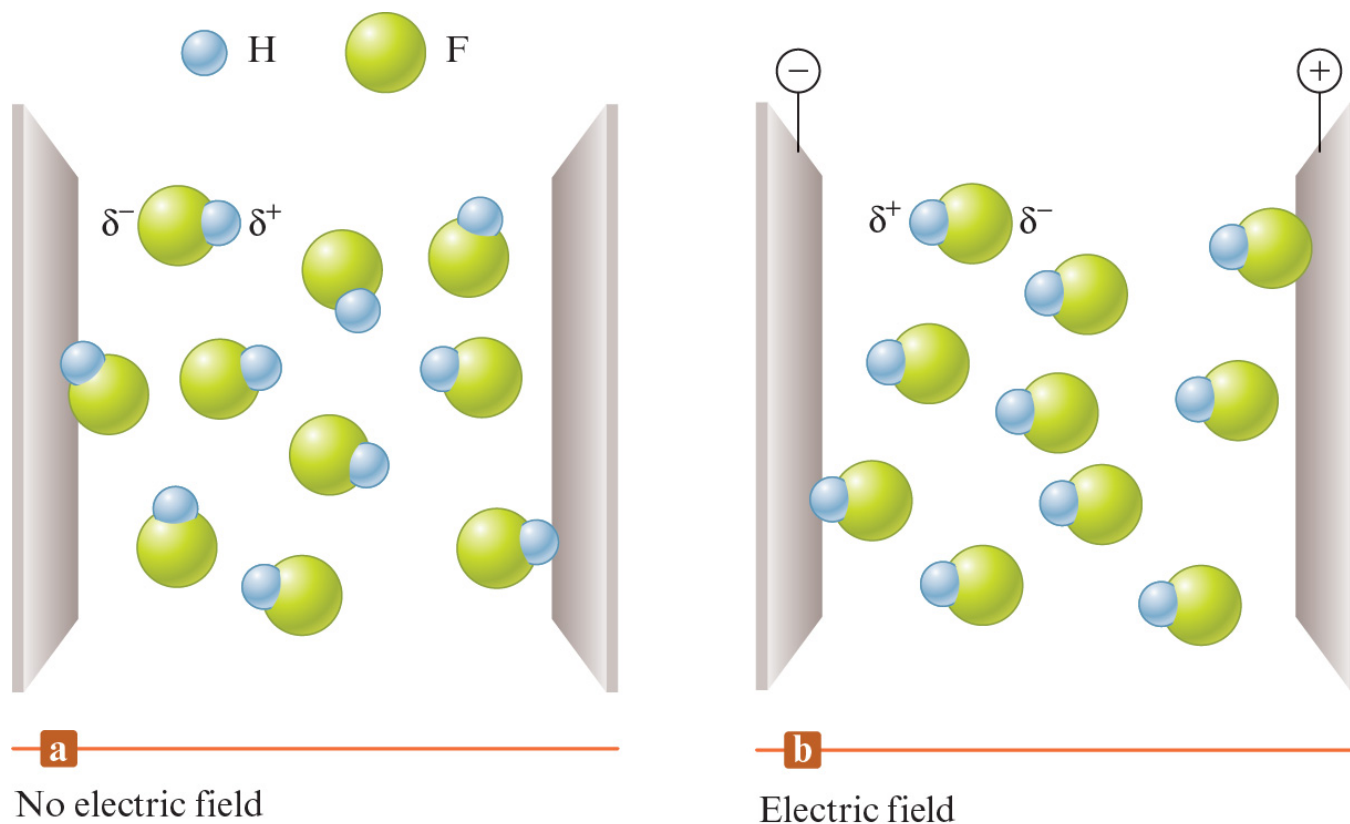
Covalent Bonding

- Two identical atoms share electrons equally
 - Bonding results from the mutual attraction of the nuclei for the shared electrons
- **Polar covalent bond**
 - Characterized by unequal sharing of electrons
 - Example
 - Bonding in the hydrogen fluoride (HF) molecule

Section 8.1

Types of Chemical Bonds

Figure 8.2 - The Effect of an Electric Field on Hydrogen Fluoride Molecules





Section 8.1

Types of Chemical Bonds

Join In (1)

- What type of bond is formed when electrons are unequally shared by nuclei?
 - a. Ionic
 - b. Covalent
 - c. Polar ionic
 - d. Polar covalent
 - e. None of the above

Section 8.2

Electronegativity

Electronegativity

- Ability of an atom in a molecule to attract shared electrons to itself
- Can be determined by using Pauling's model
 - Consider a hypothetical molecule HX
 - Relative electronegativities of the H and X atoms are determined by comparing the measured H—X bond energy with the expected H—X bond energy

$$\text{Expected H—X bond energy} = \frac{\text{H—H bond energy} + \text{X—X bond energy}}{2}$$

Section 8.2

Electronegativity

Electronegativity (continued 1)

- Difference (Δ) between actual and expected bond energies is given by the following equation:

$$\Delta = (\text{H—X})_{\text{act}} - (\text{H—X})_{\text{exp}}$$

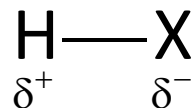
- If H and X have identical electronegativities:
 - Δ is 0
 - $(\text{H—X})_{\text{act}}$ and $(\text{H—X})_{\text{exp}}$ are the same

Section 8.2

Electronegativity

Electronegativity (continued 2)

- If X has a greater electronegativity than H:
 - Shared electron(s) will tend to be closer to the X atom
 - Molecule will be polar, with the following charge distribution:



Section 8.2

Electronegativity

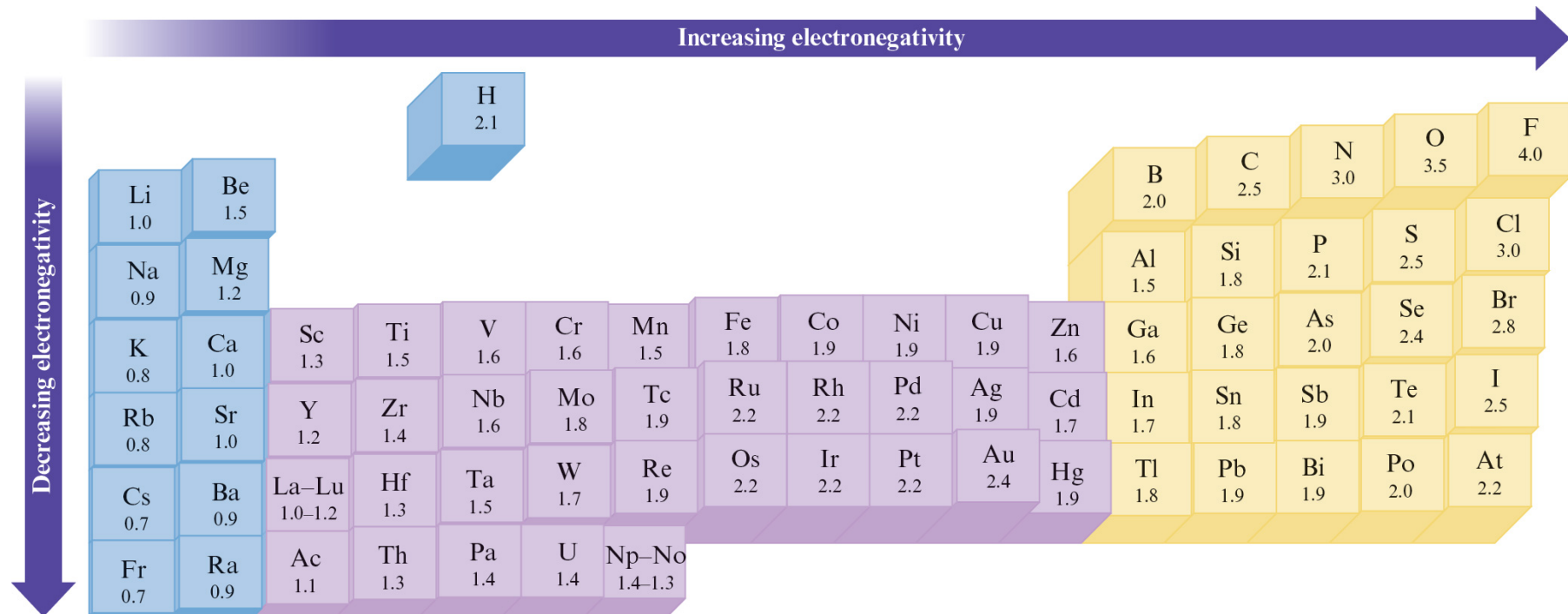
Electronegativity Trends

- Attraction between the partially (and oppositely) charged H and X atoms will lead to a greater bond strength
 - $(\text{H—X})_{\text{act}}$ will be larger than $(\text{H—X})_{\text{exp}}$
- Greater the difference in the electronegativities of the atoms, the greater is the ionic component of the bond and the greater is the value of Δ

Section 8.2

Electronegativity

Figure 8.3 - The Pauling Electronegativity Values



Section 8.2

Electronegativity

Table 8.1 - The Relationship between Electronegativity and Bond Type

| Electronegativity Difference in the Bonding Atoms | Bond Type | |
|--|----------------|--------------------|
| Zero | Covalent | Covalent character |
| ↓ | ↓ | ↑ |
| Intermediate | Polar covalent | ↓ |
| ↓ | ↓ | ↓ |
| Large | Ionic | Ionic character |

Section 8.2

Electronegativity

Interactive Example 8.1 - Relative Bond Polarities

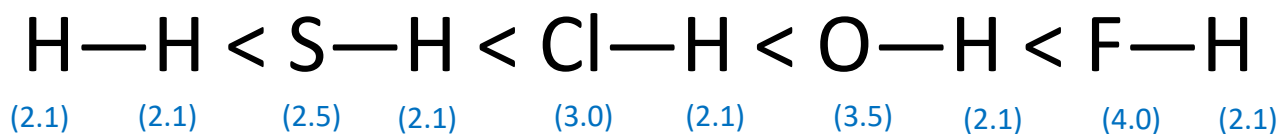
- Order the following bonds according to polarity:
 - H—H
 - O—H
 - Cl—H
 - S—H
 - F—H

Section 8.2

Electronegativity

Interactive Example 8.1 - Solution

- Polarity of bonds increases as difference in electronegativity increases
 - From Pauling's electronegativity values, the following variation in bond polarity is expected:

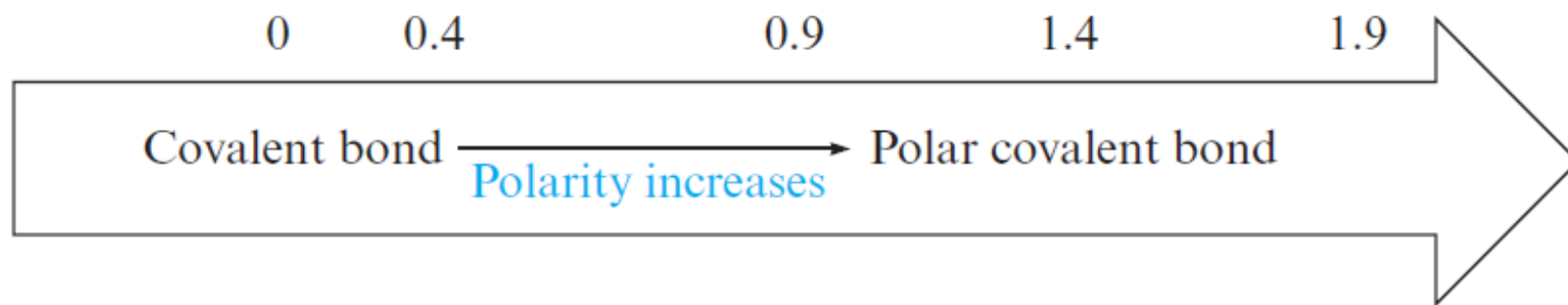


Section 8.2

Electronegativity

Interactive Example 8.1 - Solution (continued)

- Electronegativity difference



Section 8.2

Electronegativity

Exercise

- Without using Fig. 8.3, predict the order of increasing electronegativity in each of the following groups of elements

a. C, N, O

C < N < O

b. S, Se, Cl

Se < S < Cl

c. Si, Ge, Sn

Sn < Ge < Si

d. Tl, S, Ge

Tl < Ge < S

Section 8.2

Electronegativity

Critical Thinking

- We use differences in electronegativity to account for certain properties of bonds
 - What if all atoms had the same electronegativity values?
 - How would bonding between atoms be affected?
 - What are some differences we would notice?

Section 8.2

Electronegativity

Join In (2)

- Which of the following elements forms the most ionic bond with chlorine?
 - a. K
 - b. Al
 - c. P
 - d. Kr
 - e. Br



Section 8.2

Electronegativity

Join In (3)

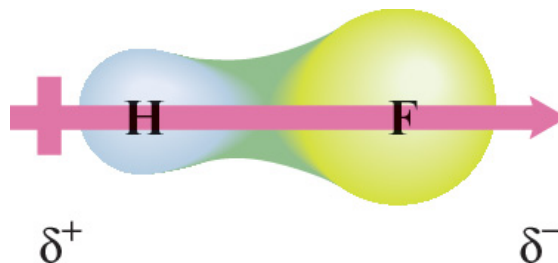
- As a general pattern, electronegativity is inversely related to:
 - a. ionization energy
 - b. atomic size
 - c. the polarity of the atom
 - d. the number of neutrons in the nucleus

Section 8.3

Bond Polarity and Dipole Moments

Dipole Moment

- Molecules that have a center of positive charge and a center of negative charge are called **dipolar**
- Representation of dipolar character
 - An arrow points to the negative charge center with the tail of the arrow indicating the positive center of charge



Section 8.3

Bond Polarity and Dipole Moments

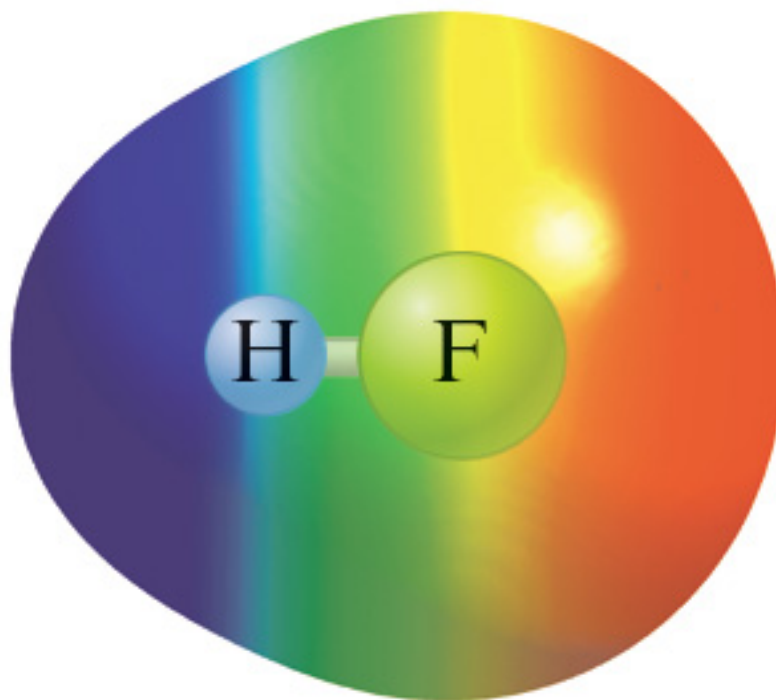
Electrostatic Potential Diagram

- Alternative method for representing charge distribution in a molecule
- Colors of visible light are used to show the variation in charge distribution
 - Red indicates the most electron-rich region
 - Blue indicates the most electron-poor region

Section 8.3

Bond Polarity and Dipole Moments

Figure 8.4 - An Electrostatic Potential Map of HF



Red indicates the most electron-rich area (the fluorine atom), and blue indicates the most electron-poor region (the hydrogen atom)

Section 8.3

Bond Polarity and Dipole Moments

Dipole Moments of Hydrogen Halides (HX)

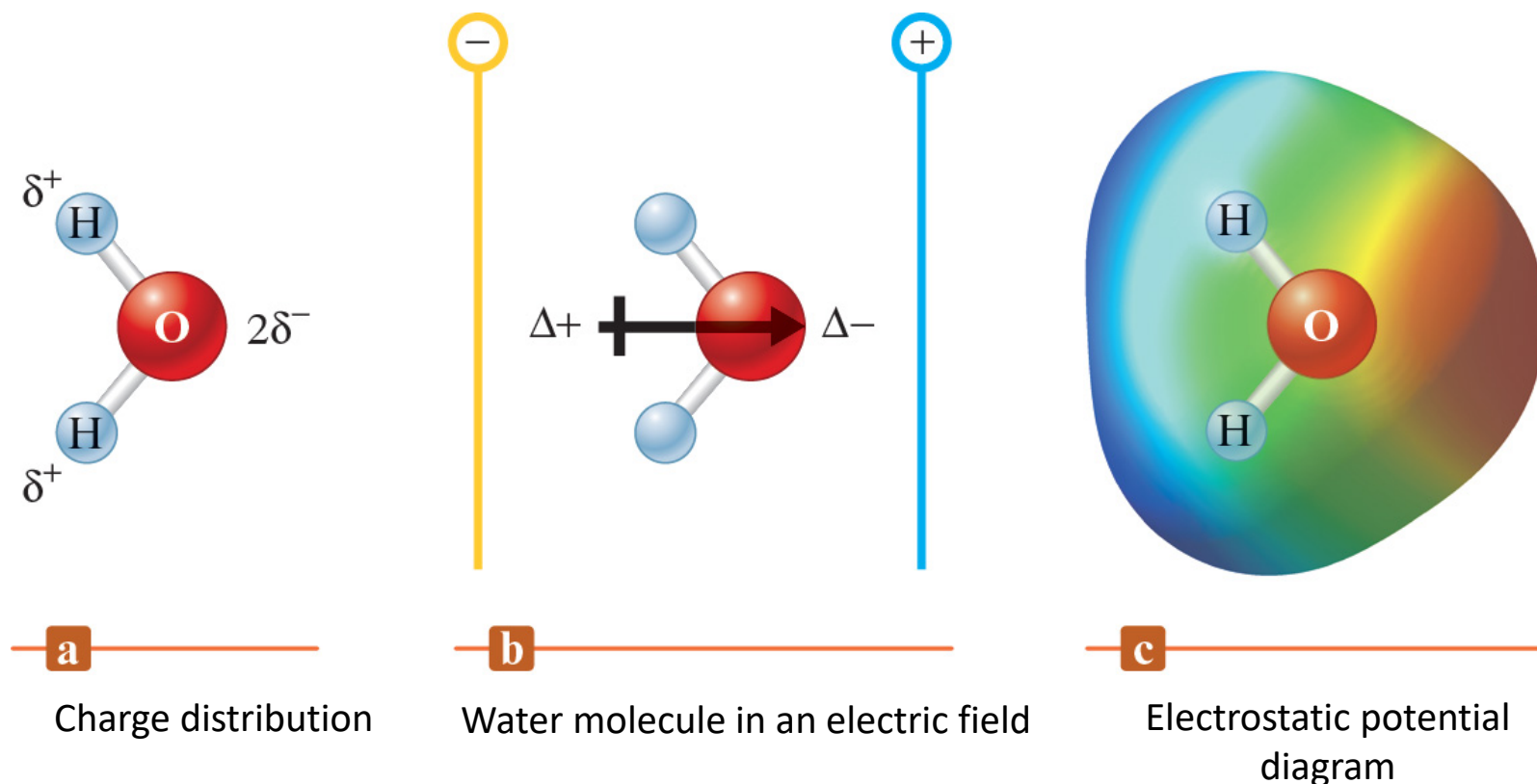
- Depends on the electronegativity of X

| Molecule | Electronegativity of Halogen | Dipole Moment (Debyes) |
|----------|------------------------------|------------------------|
| HF | 4.0 | 1.86 |
| HCl | 3.0 | 1.05 |
| HBr | 2.8 | 0.82 |
| HI | 2.5 | 0.38 |

Section 8.3

Bond Polarity and Dipole Moments

Figure 8.5 - Molecular Charge Distribution in a Water (H_2O) Molecule



Section 8.3

Bond Polarity and Dipole Moments

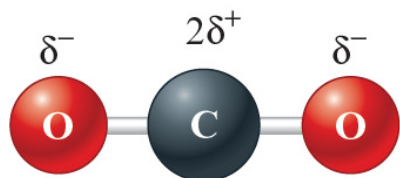
Dipole Moment in Other Molecules

- Some molecules have polar bonds but do not have a dipole moment
 - Occurs when individual bond polarities are arranged in such a way that they cancel each other out
 - Example - CO₂

Section 8.3

Bond Polarity and Dipole Moments

Figure 8.7 - Dipole Moment in a CO₂ Molecule



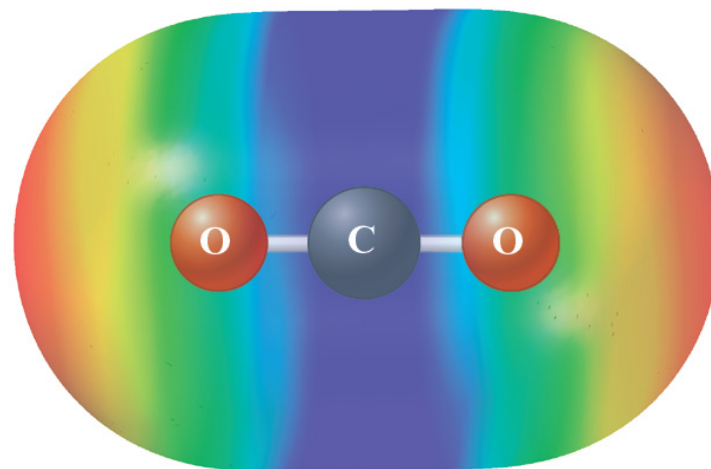
a

The carbon dioxide molecule



b

The molecule has no dipole moment because the opposed polarities cancel out



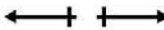

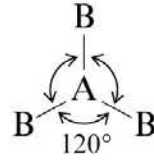
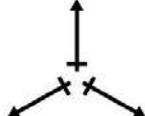

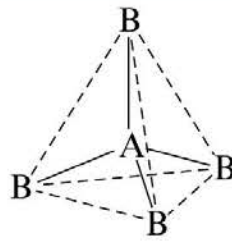
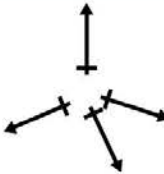

c

Electrostatic potential diagram for carbon dioxide

Section 8.3

Bond Polarity and Dipole Moments

Table 8.3 - Types of Molecules with Polar Bonds but No Resulting Dipole Moment

| Type | General Example | Cancellation of Polar Bonds | Specific Example | Ball-and-Stick Model |
|---|--|---|------------------|--|
| Linear molecules with two identical bonds | $B-A-B$ |  | CO_2 |  |
| Planar molecules with three identical bonds 120 degrees apart |  |  | SO_3 |  |
| Tetrahedral molecules with four identical bonds 109.5 degrees apart |  |  | CCl_4 |  |

Photos: Ken O'Donoghue © Cengage Learning

Section 8.3

Bond Polarity and Dipole Moments

Example 8.2 - Bond Polarity and Dipole Moment

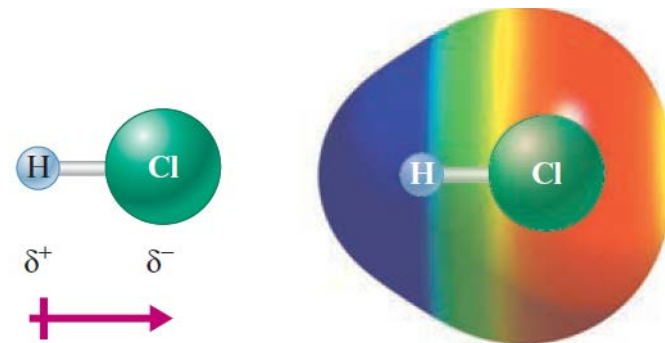
- For each of the following molecules, show the direction of the bond polarities and indicate which ones have a dipole moment:
 - HCl, Cl₂, and SO₃ (a planar molecule with the oxygen atoms spaced evenly around the central sulfur atom)
 - CH₄ (tetrahedral with the carbon atom at the center)
 - H₂S (V-shaped with the sulfur atom at the point)

Section 8.3

Bond Polarity and Dipole Moments

Example 8.2 - Solution

- The HCl molecule
 - Electronegativity of chlorine (3.0) is greater than that of hydrogen (2.1)
 - Thus the chlorine will be partially negative, and the hydrogen will be partially positive
 - The HCl molecule has a dipole moment



Section 8.3

Bond Polarity and Dipole Moments

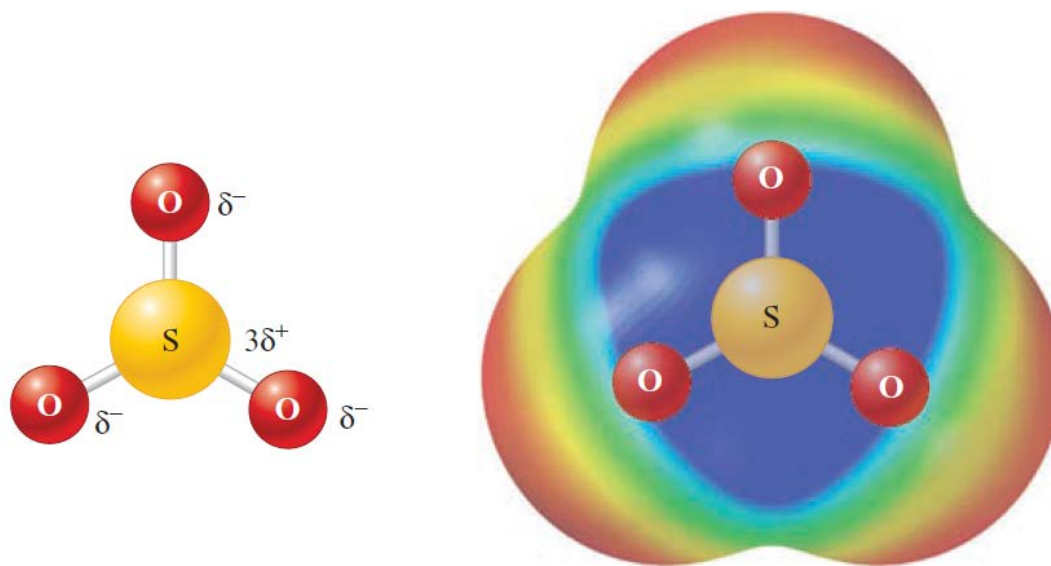
Example 8.2 - Solution (continued 1)

- The Cl_2 molecule
 - The two chlorine atoms share the electrons equally
 - No bond polarity occurs, and the Cl_2 molecule has no dipole moment
- The SO_3 molecule
 - The electronegativity of oxygen (3.5) is greater than that of sulfur (2.5)
 - This means that each oxygen will have a partial negative charge, and the sulfur will have a partial positive charge

Section 8.3

Bond Polarity and Dipole Moments

Example 8.2 - Solution (continued 2)



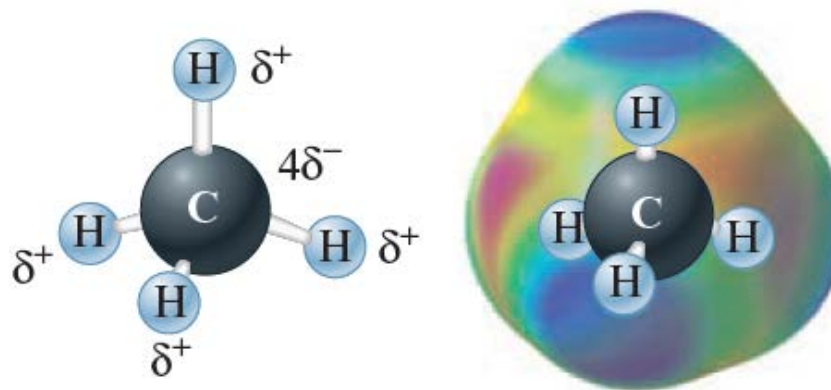
- The bond polarities arranged symmetrically as shown cancel, and the molecule has no dipole moment
- This molecule is the second type shown in Table 8.3

Section 8.3

Bond Polarity and Dipole Moments

Example 8.2 - Solution (continued 3)

- The CH₄ molecule
 - Carbon has a slightly higher electronegativity (2.5) than does hydrogen (2.1)
 - This leads to small partial positive charges on the hydrogen atoms and a small partial negative charge on the carbon



Section 8.3

Bond Polarity and Dipole Moments

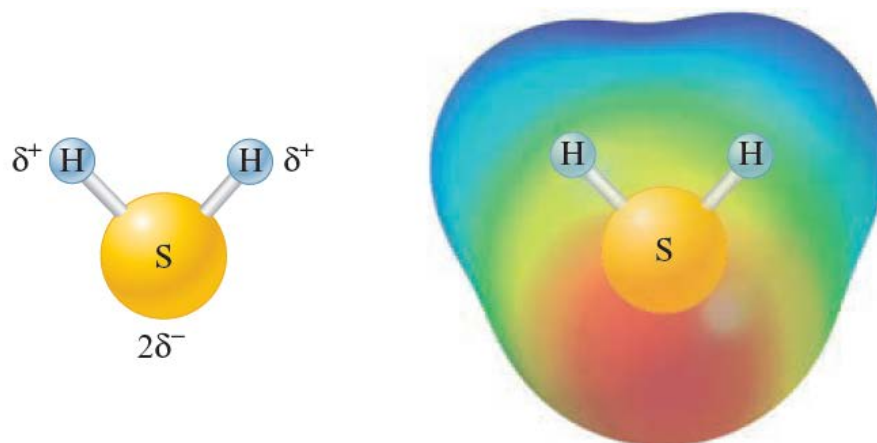
Example 8.2 - Solution (continued 4)

- This case is similar to the third type in Table 8.3, and the bond polarities cancel
- The molecule has no dipole moment
- The H_2S molecule
 - Since the electronegativity of sulfur (2.5) is slightly greater than that of hydrogen (2.1), the sulfur will have a partial negative charge, and the hydrogen atoms will have a partial positive charge

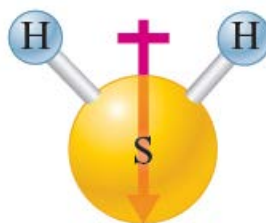
Section 8.3

Bond Polarity and Dipole Moments

Example 8.2 - Solution (continued 5)



- This case is analogous to the water molecule, and the polar bonds result in a dipole moment oriented as shown:





Section 8.3

Bond Polarity and Dipole Moments

Join In (4)

- Which of the following is the most polar bond without being considered ionic?
 - a. C—O
 - b. Mg—O
 - c. N—O
 - d. O—O
 - e. O—F



Section 8.3

Bond Polarity and Dipole Moments

Join In (5)

- Which of the following is the least polar bond, yet still considered polar covalent?
 - a. C—O
 - b. Mg—O
 - c. N—O
 - d. O—O
 - e. O—F

Section 8.4

Ions: Electron Configurations and Sizes

Generalizations That Apply to Electron Configurations in Stable Compounds

- When two nonmetals react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms
 - Both nonmetals attain noble gas electron configurations

Section 8.4

Ions: Electron Configurations and Sizes

Generalizations That Apply to Electron Configurations in Stable Compounds (continued)

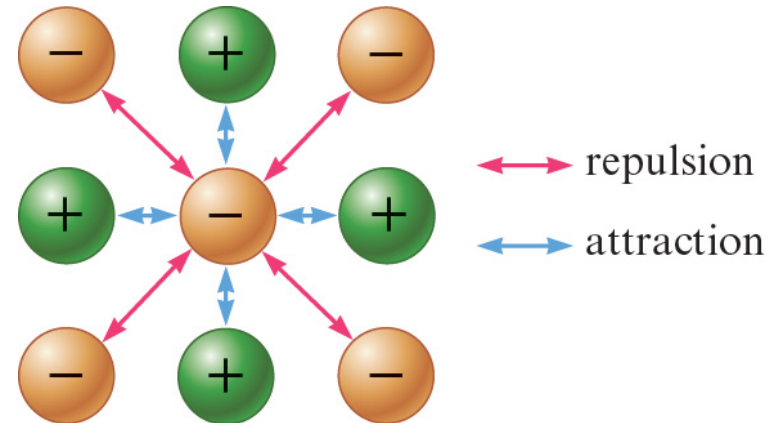
- When a nonmetal and a representative-group metal react to form a binary ionic compound, the ions form so that the:
 - Valence electron configuration of the nonmetal achieves the electron configuration of the next noble gas atom
 - Valence orbitals of the metal are emptied
 - Both ions achieve noble gas electron configurations

Section 8.4

Ions: Electron Configurations and Sizes

Solid State of Ionic Compounds

- Solid ionic compounds contain large collection of positive and negative ions packed together in a way that:
 - Minimizes the $- \dots -$ and $+ \dots +$ repulsions
 - Maximizes $+ \dots -$ attractions

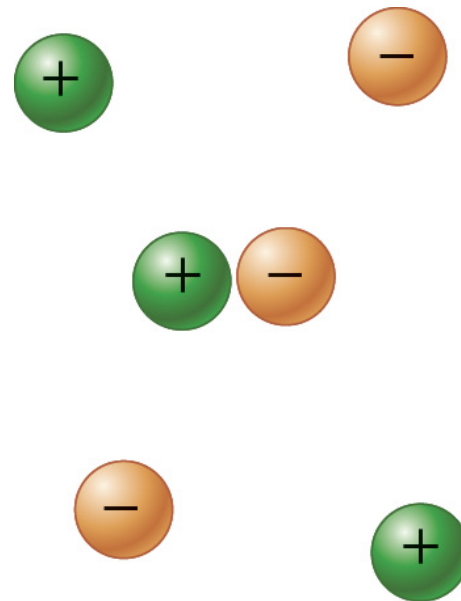


Section 8.4

Ions: Electron Configurations and Sizes

Gas Phase of an Ionic Substance

- Ions are relatively far apart and would not contain large groups of ions



Section 8.4

Ions: Electron Configurations and Sizes

Predicting Formulas of Ionic Compounds - Example

- Consider Ca and O
 - Valence electron configuration for Ca is $[\text{Ar}]s^2$ and for O is $[\text{He}]2s^22p^4$
 - Electronegativity of oxygen (3.5) is much greater than that of calcium (1.0)
 - Electrons will be transferred from calcium to oxygen to form oxygen anions and calcium cations in the compound

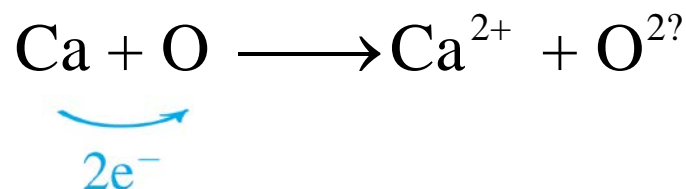
Section 8.4

Ions: Electron Configurations and Sizes

Predicting Formulas of Ionic Compounds - Example

(continued)

- Oxygen needs two electrons to fill its $2s$ and $2p$ valence orbitals and to achieve the configuration of neon ($1s^2 2s^2 2p^6$)
- By losing two electrons, calcium can achieve the configuration of argon



- Since there are equal numbers of Ca^{2+} and O^{2-} , the empirical formula of the compound is CaO

Section 8.4

Ions: Electron Configurations and Sizes

Table 8.4 - Common Ions with Noble Gas Configurations in Ionic Compounds

| Group 1A | Group 2A | Group 3A | Group 6A | Group 7A | Electron Configuration |
|------------------------------|------------------|------------------|------------------|---------------|------------------------|
| H^- , Li^+ | Be^{2+} | | | | [He] |
| Na^+ | Mg^{2+} | Al^{3+} | O^{2-} | F^- | [Ne] |
| K^+ | Ca^{2+} | | S^{2-} | Cl^- | [Ar] |
| Rb^+ | Sr^{2+} | | Se^{2-} | Br^- | [Kr] |
| Cs^+ | Ba^{2+} | | Te^{2-} | I^- | [Xe] |

Section 8.4

Ions: Electron Configurations and Sizes

Noble Gas Electron Configurations in Ionic Compounds - Trends

- In losing electrons to form cations:
 - Metals in Group 1A lose one electron
 - Metals in Group 2A lose two electrons
 - Metals in Group 3A lose three electrons
- In gaining electrons to form anions:
 - Nonmetals in Group 7A (the halogens) gain one electron
 - Nonmetals in Group 6A gain two electrons

Section 8.4

Ions: Electron Configurations and Sizes

Noble Gas Electron Configurations in Ionic Compounds - Exceptions

- Representative elements
 - Tin forms both Sn^{2+} and Sn^{4+} ions
 - Lead forms both Pb^{2+} and Pb^{4+} ions
 - Bismuth forms both Bi^{3+} and Bi^{5+} ions
 - Thallium forms both Tl^{+} and Tl^{3+} ions

Section 8.4

Ions: Electron Configurations and Sizes

Ion Size

- Plays an important role in determining:
 - Structure and stability of ionic solids
 - Properties of ions in aqueous solution
 - Biologic effects of ions
- Ionic radii are determined from the measured distance between ion centers in ionic compounds
 - Involves an assumption about how the distance should be divided up between the two ions

Section 8.4

Ions: Electron Configurations and Sizes

Factors That Influence Ionic Size

- Relative sizes of an ion and its parent atom
 - Positive ion is formed by removing one or more electrons from a neutral atom
 - Resulting cation is smaller than its parent atom
 - Negative ions are formed by adding electrons to a neutral atom
 - Resulting anion is larger than its parent atom

Section 8.4

Ions: Electron Configurations and Sizes

Factors That Influence Ionic Size (continued)

- Position of the parent element in the periodic table
 - Ion sizes increase down a group
 - A given period contains both elements that:
 - Give up electrons to form cations
 - Accept electrons to form anions

Section 8.4

Ions: Electron Configurations and Sizes

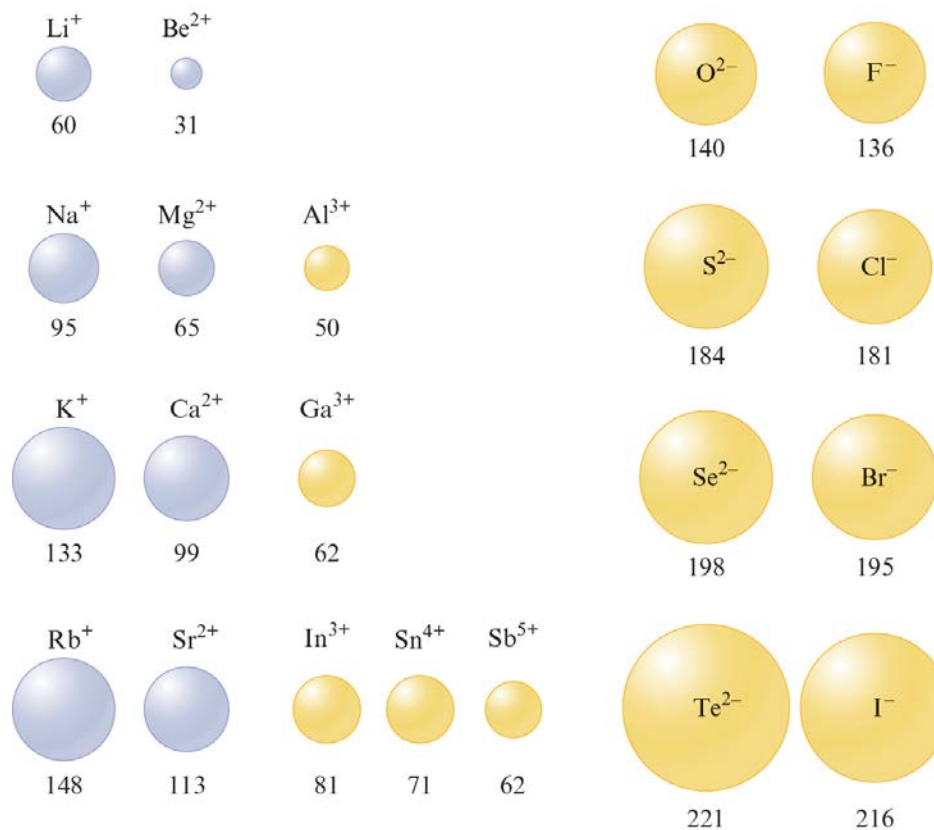
Isoelectronic Ions

- Series of ions containing the same number of electrons
- Examples
 - O^{2-} , F^{-} , Na^{+} , Mg^{2+} , and Al^{3+}
- Trend
 - Size decreases as Z (nuclear charge) increases

Section 8.4

Ions: Electron Configurations and Sizes

Figure 8.8 - Sizes of Ions Related to Positions of the Elements on the Periodic Table



Section 8.4

Ions: Electron Configurations and Sizes

Critical Thinking

- Ions have different radii than their parent atoms
 - What if ions stayed the same size as their parent atoms?
 - How would this affect ionic bonding in compounds?

Section 8.4

Ions: Electron Configurations and Sizes

Interactive Example 8.3 - Relative Ion Size I

- Arrange the following ions in order of decreasing size:
 - Se^{2-} , Br^- , Rb^+ , and Sr^{2+}

Section 8.4

Ions: Electron Configurations and Sizes

Interactive Example 8.3 - Solution

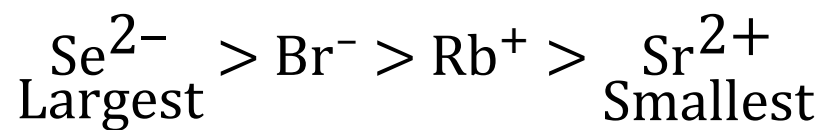
- This is an isoelectronic series of ions with the krypton electron configuration
 - Since these ions all have the same number of electrons, their sizes will depend on the nuclear charge
 - The Z values are 34 for Se^{2-} , 35 for Br^- , 37 for Rb^+ , and 38 for Sr^{2+}

Section 8.4

Ions: Electron Configurations and Sizes

Interactive Example 8.3 - Solution (continued)

- Since the nuclear charge is greatest for Sr^{2+} , it is the smallest of these ions
- The Se^{2-} ion is largest:





Section 8.4

Ions: Electron Configurations and Sizes

Join In (8)

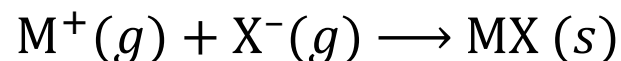
- Which of the following has the largest radius?
 - a. S^{2-}
 - b. Cl^-
 - c. Ar
 - d. K^+
 - e. Ca^{2+}

Section 8.5

Energy Effects in Binary Ionic Compounds

Lattice Energy

- Change in energy that takes place when separated gaseous ions are packed together to form an ionic solid

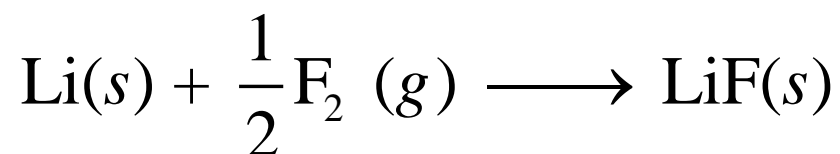


- Defined as the energy released when an ionic solid forms from its ions
 - Lattice energy has a negative sign

Section 8.5

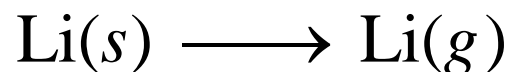
Energy Effects in Binary Ionic Compounds

Energy Changes in the Formation of Lithium Fluoride



1. Sublimation of solid lithium

- Sublimation involves taking a substance from the solid state to the gaseous state



- Enthalpy of sublimation for Li(s) is 161 kJ/mol

Section 8.5

Energy Effects in Binary Ionic Compounds

Energy Changes in the Formation of Lithium Fluoride

(continued 1)

2. Ionization of lithium atoms to form Li^+ ions in the gas phase



- Process corresponds to the first ionization energy for lithium, which is 520 kJ/mol

3. Dissociation of fluorine molecules

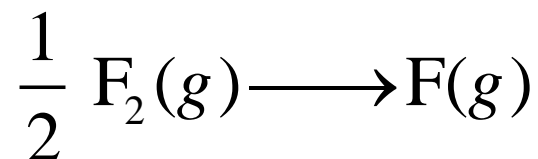
- Form a mole of fluorine atoms by breaking the F—F bonds in a half mole of F_2 molecules

Section 8.5

Energy Effects in Binary Ionic Compounds

Energy Changes in the Formation of Lithium Fluoride

(continued 2)



- Energy required to break this bond is 154 kJ/mol
- Since the bonds are broken in a half mole of fluorine, energy required is (154 kJ)/2 or 77 kJ

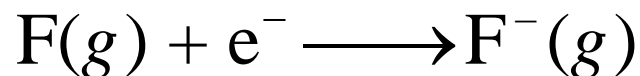
Section 8.5

Energy Effects in Binary Ionic Compounds

Energy Changes in the Formation of Lithium Fluoride

(continued 3)

4. Formation of F^- ions from fluorine atoms in the gas phase



- Energy change for this process corresponds to the electron affinity of fluorine, which is -328 kJ/mol

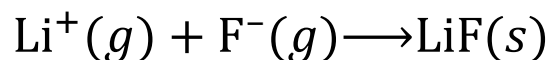
Section 8.5

Energy Effects in Binary Ionic Compounds

Energy Changes in the Formation of Lithium Fluoride

(continued 5)

5. Formation of solid lithium fluoride from the gaseous Li^+ and F^- ions



- This corresponds to the lattice energy for LiF, which is -1047 kJ/mol

Section 8.5

Energy Effects in Binary Ionic Compounds

Energy Changes in the Formation of Lithium Fluoride

(continued 6)

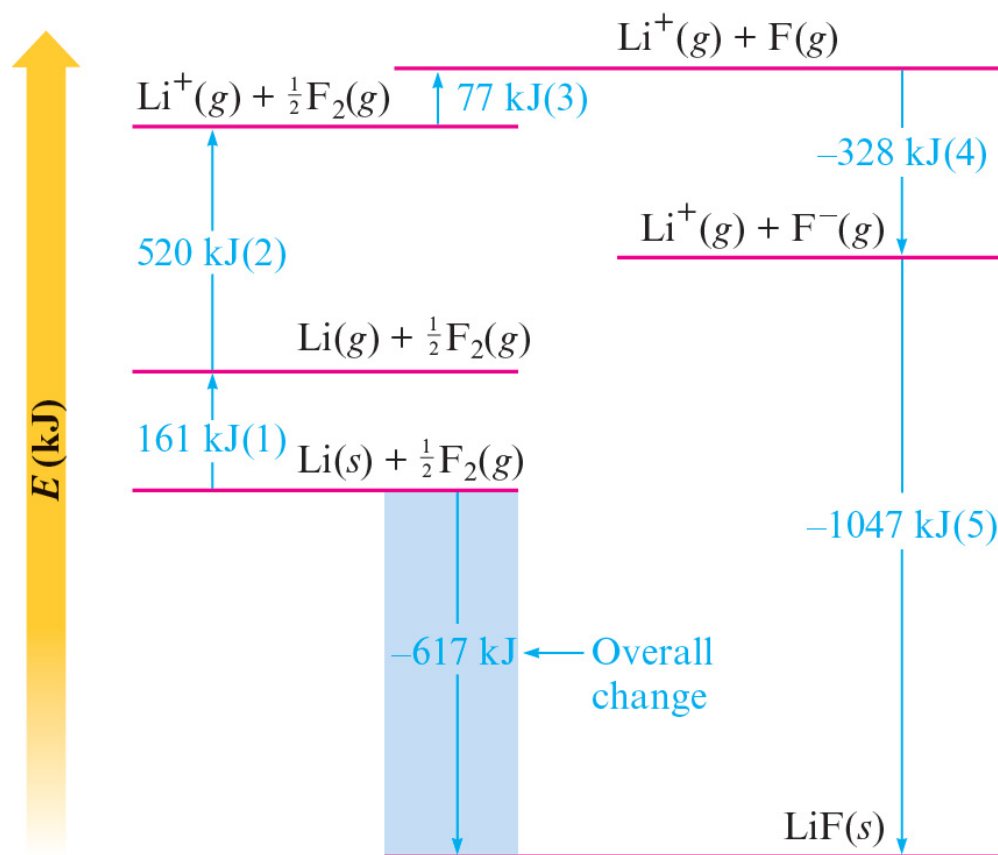
- Sum of the five processes yields the desired overall reaction, and the sum of the individual energy changes gives the overall energy change

| Process | Energy Change (kJ) |
|--|---------------------------|
| $\text{Li}(s) \rightarrow \text{Li}(g)$ | 161 |
| $\text{Li}(g) \rightarrow \text{Li}^+(g) + e^-$ | 520 |
| $\frac{1}{2}\text{F}_2(g) \rightarrow \text{F}(g)$ | 77 |
| $\text{F}(g) + e^- \rightarrow \text{F}^-(g)$ | -328 |
| $\text{Li}^+(g) + \text{F}^-(g) \rightarrow \text{LiF}(s)$ | -1047 |
| Overall: $\text{Li}(s) + \frac{1}{2}\text{F}_2(g) \rightarrow \text{LiF}(s)$ | -617 kJ (per mole of LiF) |

Section 8.5

Energy Effects in Binary Ionic Compounds

Figure 8.9 - The Energy Changes Involved in the Formation of Solid Lithium Fluoride from Its Elements



Numbers in parentheses refer to the reaction steps discussed in the text

Section 8.5

Energy Effects in Binary Ionic Compounds

Lattice Energy: Calculations

- Represented by a modified form of Coulomb's law

$$\text{Lattice energy} = k \left(\frac{Q_1 Q_2}{r} \right)$$

- k - Proportionality constant
 - Depends on the structure of the solid and the electronic configurations of the ions
- Q_1 and Q_2 - Charges on the ions
- r - Shortest distance between the centers of the anions and the cations

Section 8.5

Energy Effects in Binary Ionic Compounds

Lattice Energy: Calculations (continued)

- Lattice energy has a negative sign when Q_1 and Q_2 have opposite signs
 - Result is expected because bringing cations and anions together is an exothermic process
- Process becomes more exothermic as:
 - Ionic charges increase
 - Distances between ions in the solid decrease

Section 8.5

Energy Effects in Binary Ionic Compounds

Factor Influencing the Composition and Structure of Solid Ionic Compounds

- Most important factor involves the balancing of:
 - Energies required to form highly charged ions
 - Energy released when highly charged ions combine to form the solid



Section 8.5

Energy Effects in Binary Ionic Compounds

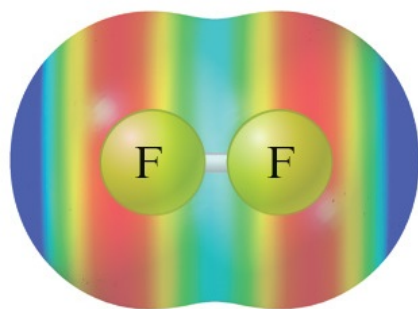
Join In (9)

- Which of the following ionic compounds has the largest lattice energy (i.e., the lattice energy most favorable to a stable lattice)?
 - a. CsI
 - b. NaCl
 - c. LiF
 - d. CsF
 - e. MgO

Section 8.6

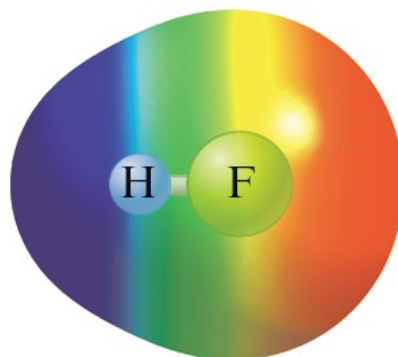
Partial Ionic Character of Covalent Bonds

Figure 8.12 - The Three Possible Types of Bonds



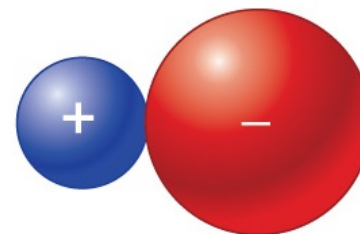
a

Covalent bond formed
between identical F atoms



b

Polar covalent bond of HF,
with both ionic and
covalent components



c

An ionic bond with no
electron sharing

Section 8.6

Partial Ionic Character of Covalent Bonds

Formula for Percent Ionic Character of a Bond

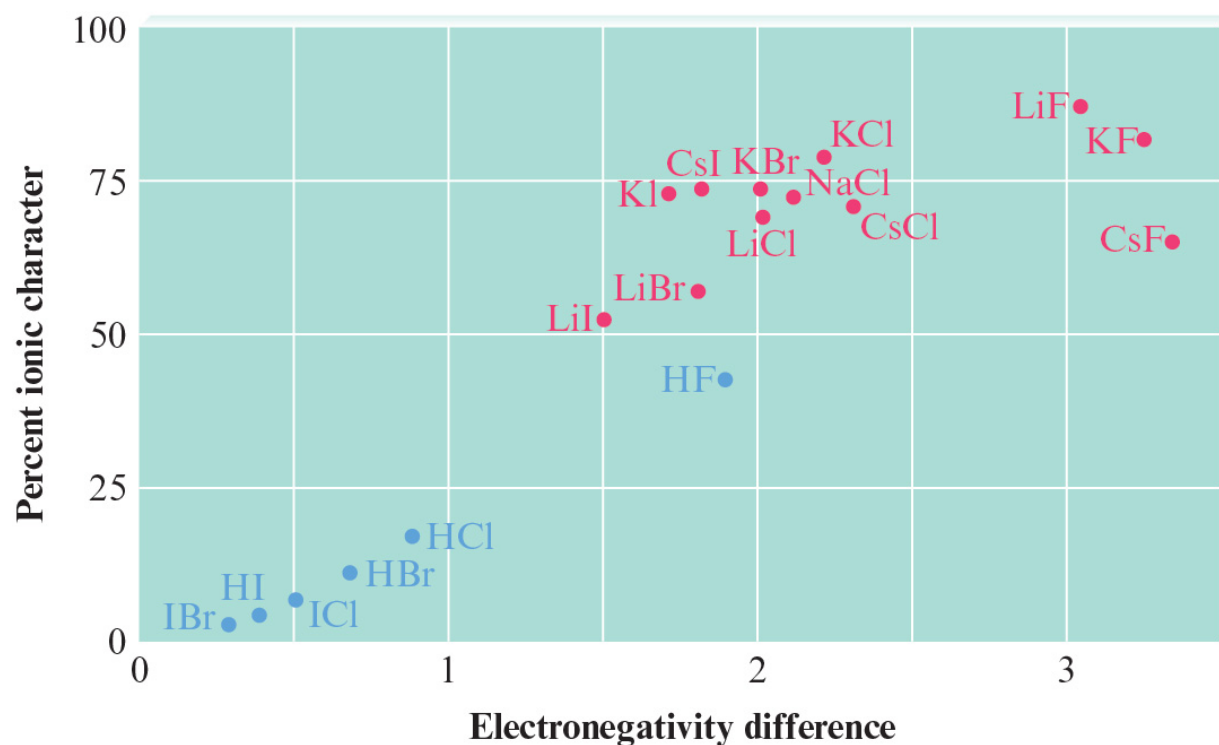
- Totally ionic bonds between discrete pairs of atoms do not exist
 - Evident from calculations of percent ionic character for bonds of various binary compounds in the gas phase

$$\text{Percent ionic character of a bond} = \left(\frac{\text{Measured dipole moment of X—Y}}{\text{Calculated dipole moment of X}^+\text{Y}^-} \right) \times 100\%$$

Section 8.6

Partial Ionic Character of Covalent Bonds

Figure 8.13 - Relationship between the Ionic Character of a Covalent Bond and the Electronegativity Difference of the Bonded Atoms



Note that the compounds with ionic character greater than 50% (red) are normally considered to be ionic compounds

Section 8.6

Partial Ionic Character of Covalent Bonds

Complications in Identifying Ionic Compounds

- Ionic character increases with electronegativity difference, but none of the bonds reaches 100% ionic character
 - Therefore, no individual bonds are completely ionic
- Many substances contain polyatomic ions
 - Bonds within the ions are covalent

Section 8.6

Partial Ionic Character of Covalent Bonds

Complications in Identifying Ionic Compounds (continued)

- Avoided by adopting the operational definition of ionic compound
 - Any compound that conducts an electric current when melted will be classified as ionic

Section 8.7

The Covalent Chemical Bond: A Model

Bonds

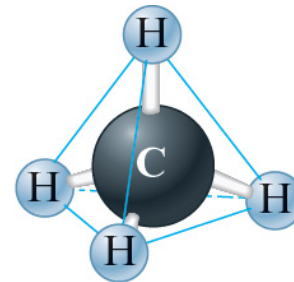
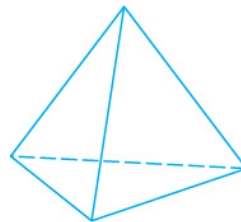
- Forces that cause a group of atoms to behave as a unit
- Result from the tendency of a system to seek its lowest possible energy
 - Bonds occur when collections of atoms are more stable (lower in energy) than the separate atoms

Section 8.7

The Covalent Chemical Bond: A Model

Chemical Bonds

- Models that depict molecular stability
 - Example - Methane has a tetrahedron structure (four equal triangular faces)



- Bond concept is a human invention
 - Provides a method for dividing up the energy evolved when a stable molecule is formed from its component atoms

Section 8.7

The Covalent Chemical Bond: A Model

Models

- Attempt to explain how nature operates on the microscopic level based on experiences in the macroscopic world
- Originate from observations of the properties of nature

Section 8.7

The Covalent Chemical Bond: A Model

Bonding Model

- Provides a framework to systematize chemical behavior
 - Molecules are perceived as collections of common fundamental components
- Physically sensible
 - Makes sense that atoms can form stable compounds by sharing electrons
 - Shared electrons give a lower energy state because they are simultaneously attracted by two nuclei

Section 8.8

Covalent Bond Energies and Chemical Reactions

Types of Bonds

- **Single bond**
 - One pair of electrons is shared
- **Double bond**
 - Two pairs of electrons are shared
- **Triple bond**
 - Three pairs of electrons are shared
- Bond length shortens with the increase in the number of shared electrons

Section 8.8

Covalent Bond Energies and Chemical Reactions

Table 8.5 - Average Bond Energies (kJ/mol)

| Single Bonds | | | | | | Multiple Bonds | |
|--------------|-----|-------|-----|-------|-----|----------------|------|
| H—H | 432 | N—H | 391 | I—I | 149 | C=C | 614 |
| H—F | 565 | N—N | 160 | I—Cl | 208 | C≡C | 839 |
| H—Cl | 427 | N—F | 272 | I—Br | 175 | O=O | 495 |
| H—Br | 363 | N—Cl | 200 | | | C=O* | 745 |
| H—I | 295 | N—Br | 243 | S—H | 347 | C≡O | 1072 |
| | | N—O | 201 | S—F | 327 | N=O | 607 |
| C—H | 413 | O—H | 467 | S—Cl | 253 | N=N | 418 |
| C—C | 347 | O—O | 146 | S—Br | 218 | N≡N | 941 |
| C—N | 305 | O—F | 190 | S—S | 266 | C≡N | 891 |
| C—O | 358 | O—Cl | 203 | | | C=N | 615 |
| C—F | 485 | O—I | 234 | Si—Si | 340 | | |
| C—Cl | 339 | | | Si—H | 393 | | |
| C—Br | 276 | F—F | 154 | Si—C | 360 | | |
| C—I | 240 | F—Cl | 253 | Si—O | 452 | | |
| C—S | 259 | F—Br | 237 | | | | |
| | | Cl—Cl | 239 | | | | |
| | | Cl—Br | 218 | | | | |
| | | Br—Br | 193 | | | | |

*C=O(CO₂) = 799

Section 8.8

Covalent Bond Energies and Chemical Reactions

Table 8.6 - Bond Lengths and Bond Energies for Selected Bonds

| Bond | Bond Type | Bond Length (pm) | Bond Energy (kJ/mol) |
|------|-----------|------------------|----------------------|
| C—C | Single | 154 | 347 |
| C=C | Double | 134 | 614 |
| C≡C | Triple | 120 | 839 |
| C—O | Single | 143 | 358 |
| C=O | Double | 123 | 745 |
| C—N | Single | 143 | 305 |
| C=N | Double | 138 | 615 |
| C≡N | Triple | 116 | 891 |

Section 8.8

Covalent Bond Energies and Chemical Reactions

Bond Energy

- Energy must be added to the system to break bonds (endothermic process)
 - Energy terms associated with bond breaking have positive signs
- Energy is released when bonds are formed (exothermic process)
 - Energy terms associated with bond making carry a negative sign

Section 8.8

Covalent Bond Energies and Chemical Reactions

Enthalpy Change for a Reaction

- Can be calculated as follows:

$$\Delta H = \underbrace{\sum D (\text{bonds broken})}_{\text{Energy required}} - \underbrace{\sum D (\text{bonds formed})}_{\text{Energy released}}$$

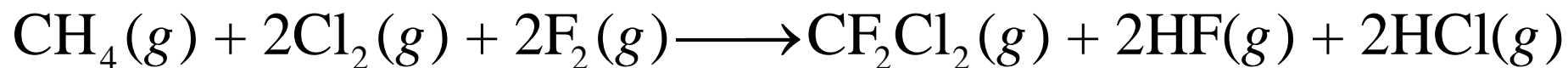
- Σ - Sum of terms
- D - Bond energy per mole of bonds
 - Always has a positive sign
- n - Moles of a particular type of bond

Section 8.8

Covalent Bond Energies and Chemical Reactions

Interactive Example 8.5 - ΔH from Bond Energies

- Use the bond energies listed in Table 8.5, and calculate ΔH for the reaction of methane with chlorine and fluorine to give Freon-12 (CF_2Cl_2)



Section 8.8

Covalent Bond Energies and Chemical Reactions

Interactive Example 8.5 - Solution

- Break the bonds in the gaseous reactants to give individual atoms and then assemble these atoms into the gaseous products by forming new bonds



- Then combine the energy changes to calculate ΔH :
 - $\Delta H = \text{Energy required to break bonds} - \text{energy released when bonds form}$
 - Minus sign gives the correct sign to the energy terms for the exothermic processes

Section 8.8

Covalent Bond Energies and Chemical Reactions

Interactive Example 8.5 - Solution (continued 1)

■ Reactant bonds broken:

$$\text{CH}_4: \quad 4 \text{ mol C—H} \qquad 4 \text{ mol} \times \frac{413 \text{ kJ}}{\text{mol}} = 1652 \text{ kJ}$$

$$2\text{Cl}_2: \quad 2 \text{ mol Cl—Cl} \qquad 2 \text{ mol} \times \frac{239 \text{ kJ}}{\text{mol}} = 478 \text{ kJ}$$

$$2\text{F}_2: \quad 2 \text{ mol F—F} \qquad 2 \text{ mol} \times \frac{154 \text{ kJ}}{\text{mol}} = 308 \text{ kJ}$$

$$\text{Total energy required} = 2438 \text{ kJ}$$

Section 8.8

Covalent Bond Energies and Chemical Reactions

Interactive Example 8.5 - Solution (continued 2)

■ Product bonds formed:

$$\text{CF}_2\text{Cl}_2: \quad 2 \text{ mol C—F} \qquad 2 \text{ mol} \times \frac{485 \text{ kJ}}{\text{mol}} = 970 \text{ kJ}$$

and

$$2 \text{ mol C—Cl} \qquad 2 \text{ mol} \times \frac{339 \text{ kJ}}{\text{mol}} = 3678 \text{ kJ}$$

$$\text{HF:} \quad 2 \text{ mol H—F} \qquad 2 \text{ mol} \times \frac{565 \text{ kJ}}{\text{mol}} = 1130 \text{ kJ}$$

$$\text{HCl:} \quad 2 \text{ mol H—Cl} \qquad 2 \text{ mol} \times \frac{427 \text{ kJ}}{\text{mol}} = 3854 \text{ kJ}$$

$$\text{Total energy released} = \underline{3632 \text{ kJ}}$$

Section 8.8

Covalent Bond Energies and Chemical Reactions

Interactive Example 8.5 - Solution (continued 3)

- We now can calculate ΔH :

$$\begin{aligned}\Delta H &= \text{energy required to break bonds} - \text{energy released when bonds form} \\ &= 2438 \text{ kJ} - 3632 \text{ kJ} \\ &= -1194 \text{ kJ}\end{aligned}$$

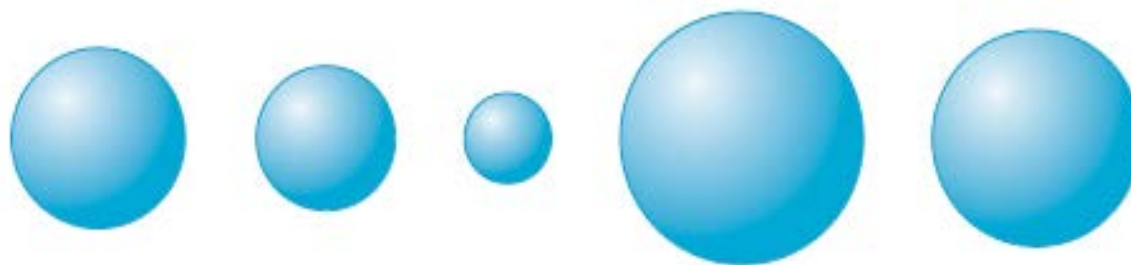
- Since the sign of the value for the enthalpy change is negative, this means that 1194 kJ of energy is released per mole of CF_2Cl_2 formed

Section 8.8

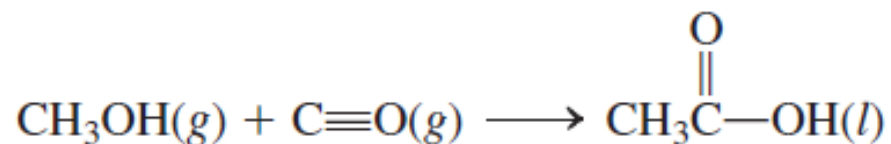
Covalent Bond Energies and Chemical Reactions

Homework

1. Consider the ions Sc^{3+} , Cl^- , K^+ , Ca^{2+} , and S^{2-} . Match these ions to the following pictures that represent the relative sizes of the ions.



2. Acetic acid is responsible for the sour taste of vinegar. It can be manufactured using the following reaction



Use tabulated values of bond energies (Table 8.4) to estimate ΔH for this reaction.