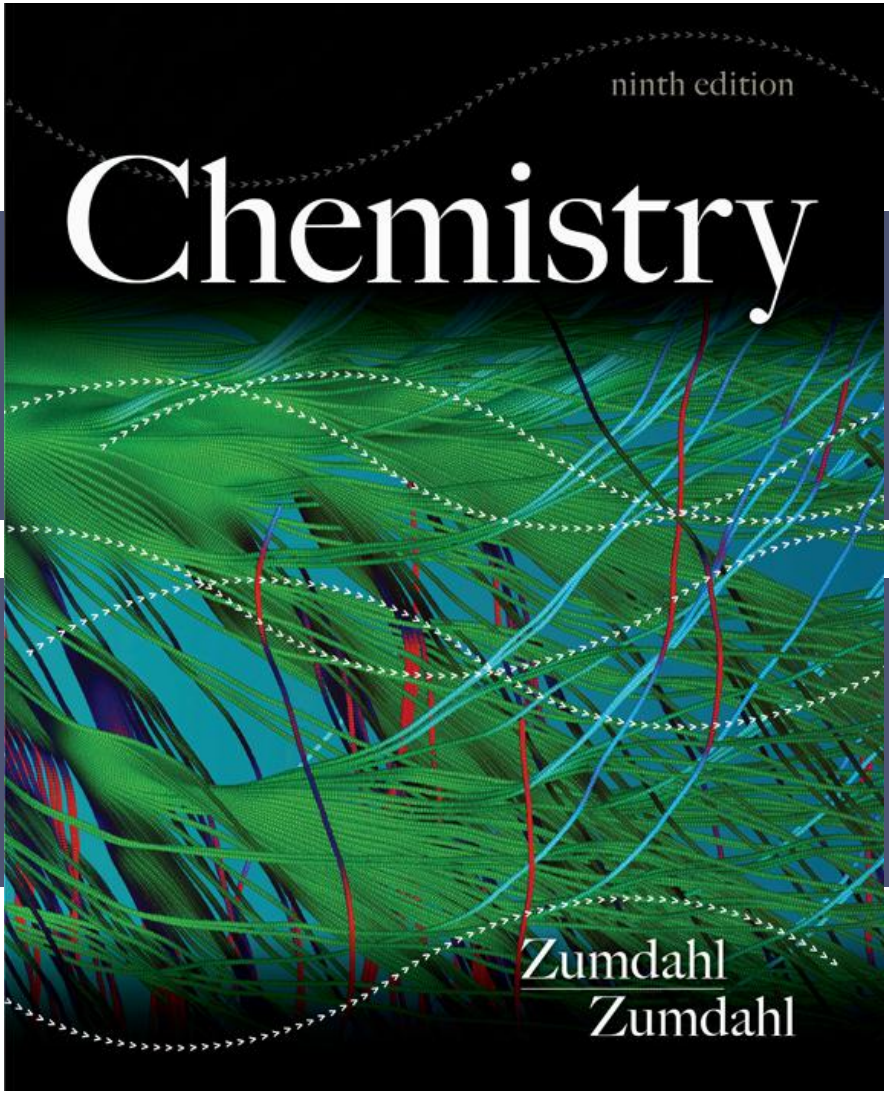


Chapter 8

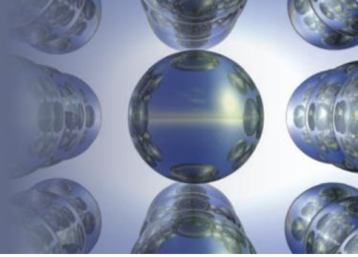
Bonding: General Concepts

Chapter 8

Table of Contents

Chapter 8

Table of Contents



Bond Energy and Ionic Bonding

- **Bond energy**: Energy required to break a chemical bond
  - Indicates the strength of a bonding interaction
- **Ionic bonding**: Occurs when an atom that loses electrons easily reacts with an atom that has high affinity for electrons
  - **Ionic compound**: Forms when a metal reacts with a nonmetal
    - Example - Sodium chloride

Coulomb's Law

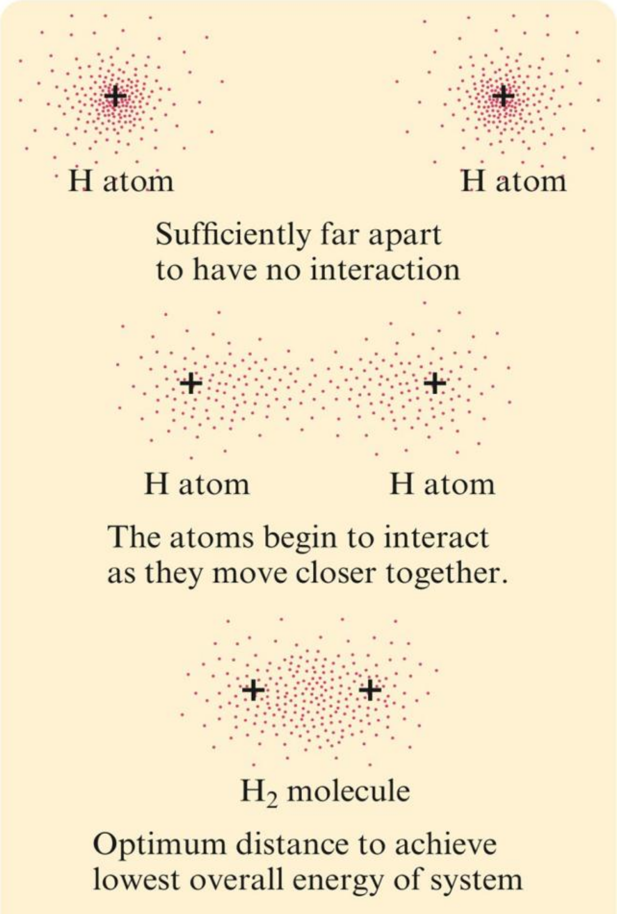
- Determines the energy of interaction between a pair of ions using the following formula:

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

  - E - Units of joules
  - r - Distance between ion centers in nanometers
  - Q_1 and Q_2 - Numerical ion charges
- Used to determine repulsive energy when two like-charged ions are brought together

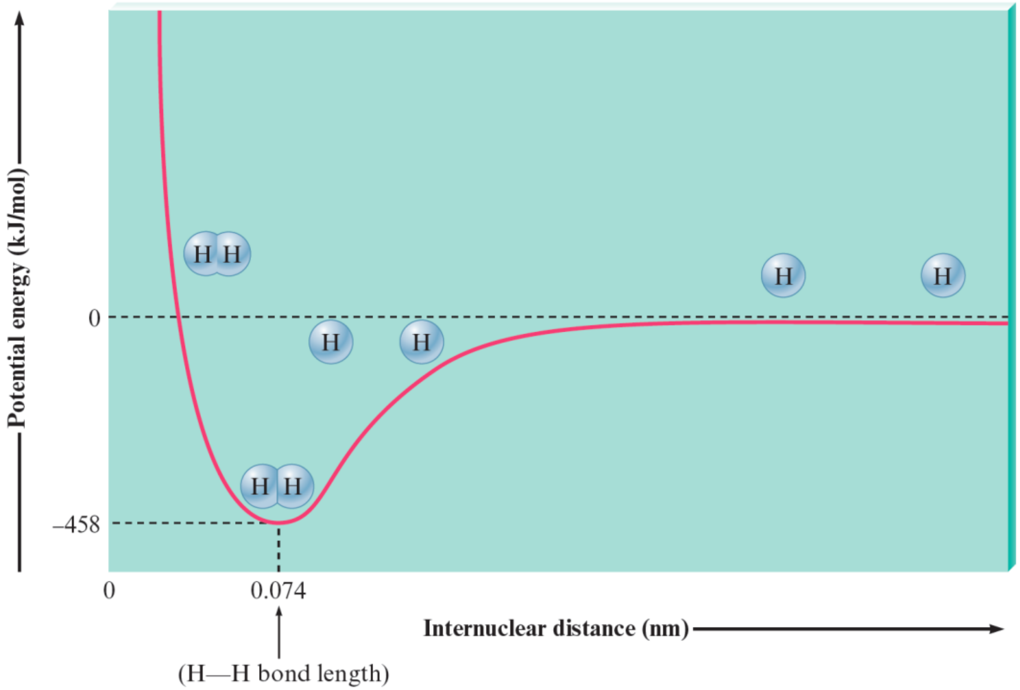
Figure 8.1 (a) - The Interaction of Two Hydrogen Atoms

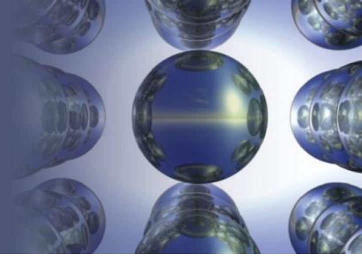
- A bond will form if the energy of the aggregate is lower than that of the separated atoms



Bond Length

- Distance between two atoms when potential energy is minimal

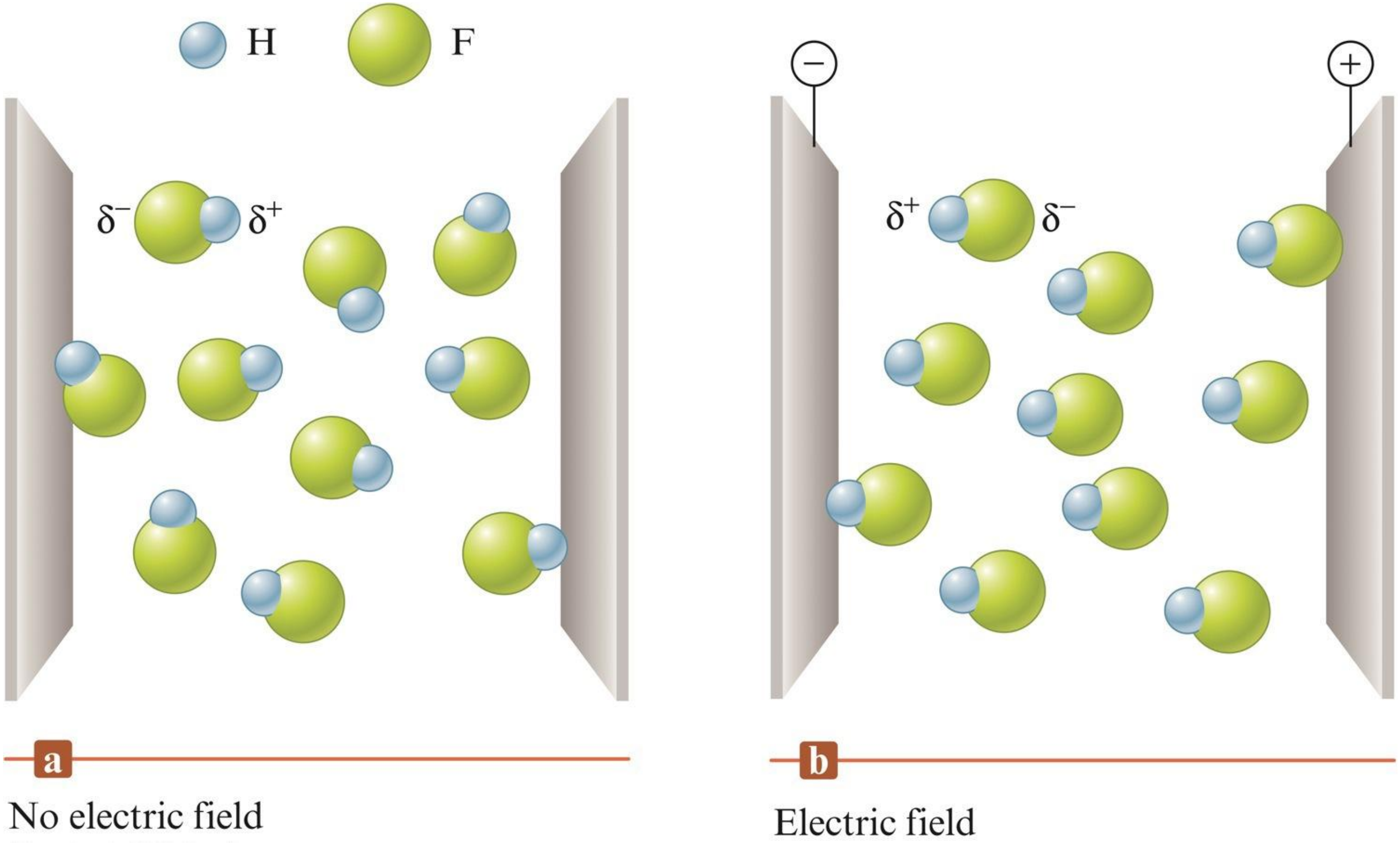




Covalent Bonding

- Equal sharing of electrons between two identical atoms
    - Caused by the mutual attraction of nuclei for shared electrons
- **Polar covalent bond**: Bond in which the electrons are not shared equally because one atom attracts them more strongly than the other
    - Example - Bonding in hydrogen fluoride

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



Electronegativity

- Ability of an atom in a molecule to attract shared electrons to itself
- Pauling’s method of determining electronegativity
  - 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

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

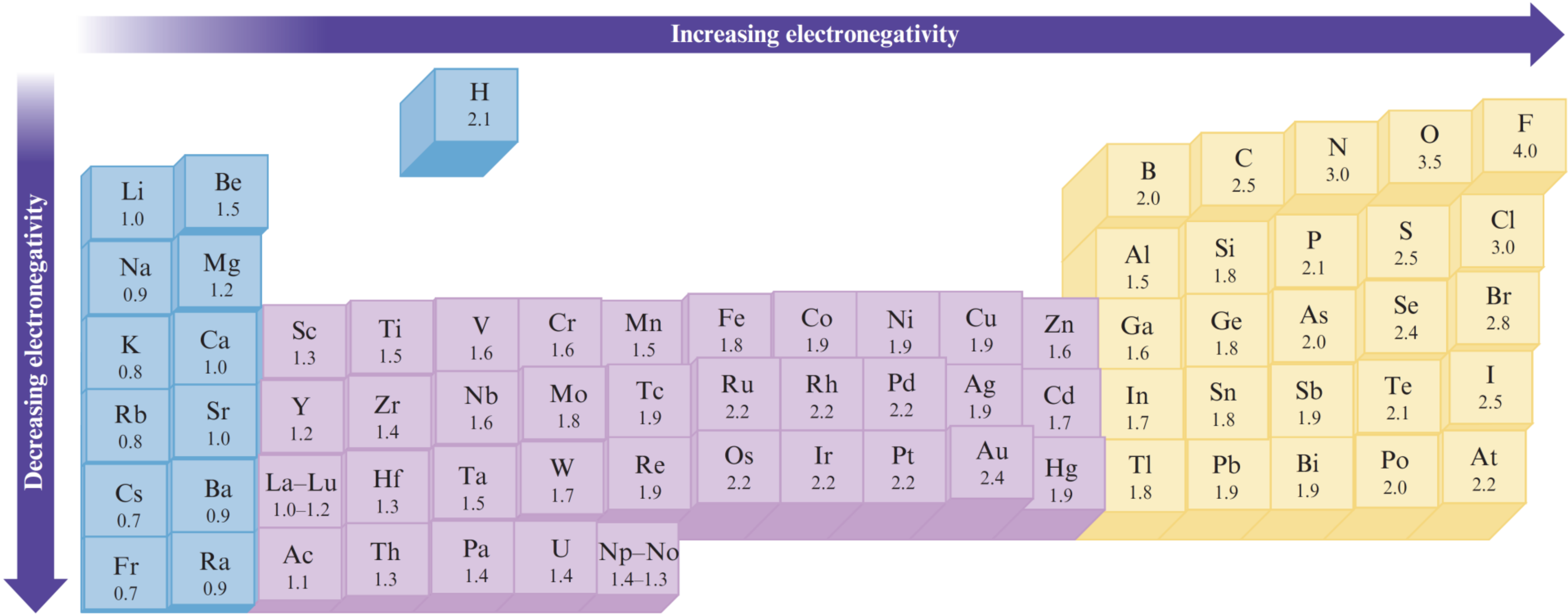
Electronegativity (Continued)

- Difference (Δ) between actual and expected bond energies

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

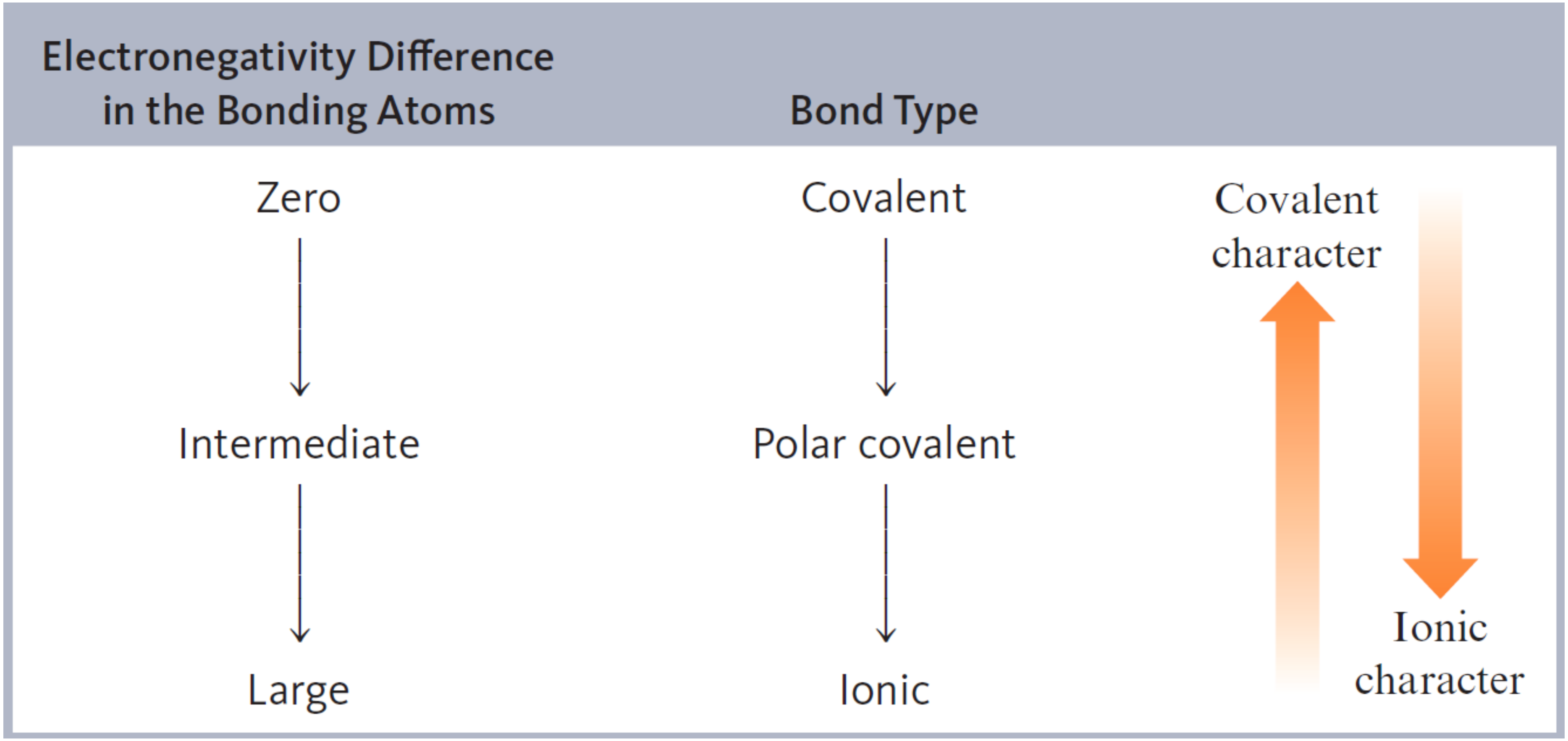
- If H and X have identical electronegativities:
  - Δ is 0
  - $(\mathrm{H{-}X})_{\mathrm{act}}$ and $(\mathrm{H{-}X})_{\mathrm{exp}}$ are the same
- If X has a greater electronegativity than H, the shared electron(s) will tend to be closer to the X atom
  - Charge distribution: $\underset{\delta^+}{\mathrm{H}}{-}\underset{\delta^-}{\mathrm{X}}$

Table 8.3 - The Pauling Electronegativity Values



				H 2.1												
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La–Lu 1.0–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np–No 1.4–1.3										

Table 8.1 - Relationship between Electronegativity and Bond Type



Electronegativity Difference in the Bonding Atoms	Bond Type
Zero	Covalent
Intermediate	Polar covalent
Large	Ionic

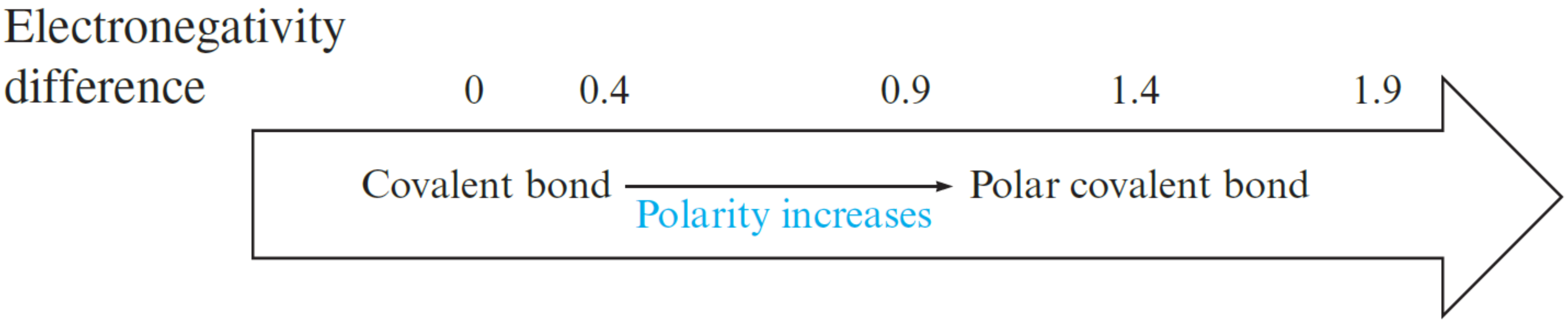
Interactive Example 8.1 - Relative Bond Polarities

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

Interactive Example 8.1 - Solution

- Polarity of bonds increases as difference in electronegativity increases

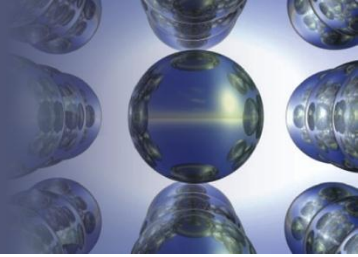
$$\underset{(2.1)}{\mathrm{H}} - \underset{(2.1)}{\mathrm{H}} < \underset{(2.5)}{\mathrm{S}} - \underset{(2.1)}{\mathrm{H}} < \underset{(3.0)}{\mathrm{Cl}} - \underset{(2.1)}{\mathrm{H}} < \underset{(3.5)}{\mathrm{O}} - \underset{(2.1)}{\mathrm{H}} < \underset{(4.0)}{\mathrm{F}} - \underset{(2.1)}{\mathrm{H}}$$



Exercise

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

C, N, O	**C < N < O**
S, Se, Cl	**Se < S < Cl**
Si, Ge, Sn	**Sn < Ge < Si**
Tl, S, Ge	**Tl < Ge < S**



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?

Dipole Moment

- Property of a molecule possessing a center of positive charge and a center of negative charge
- Methods of representing **dipolar** molecules

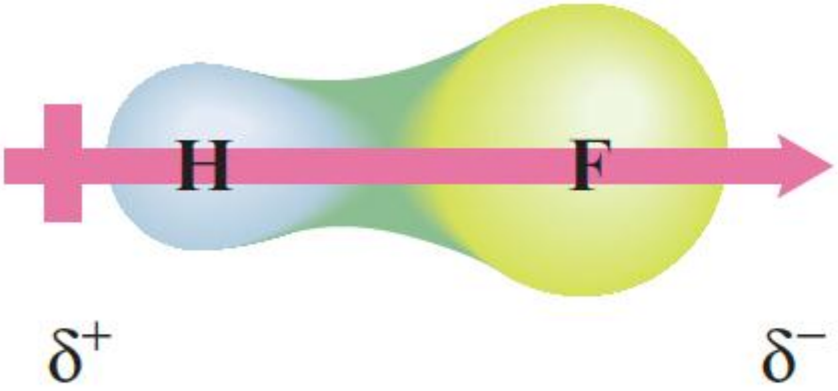
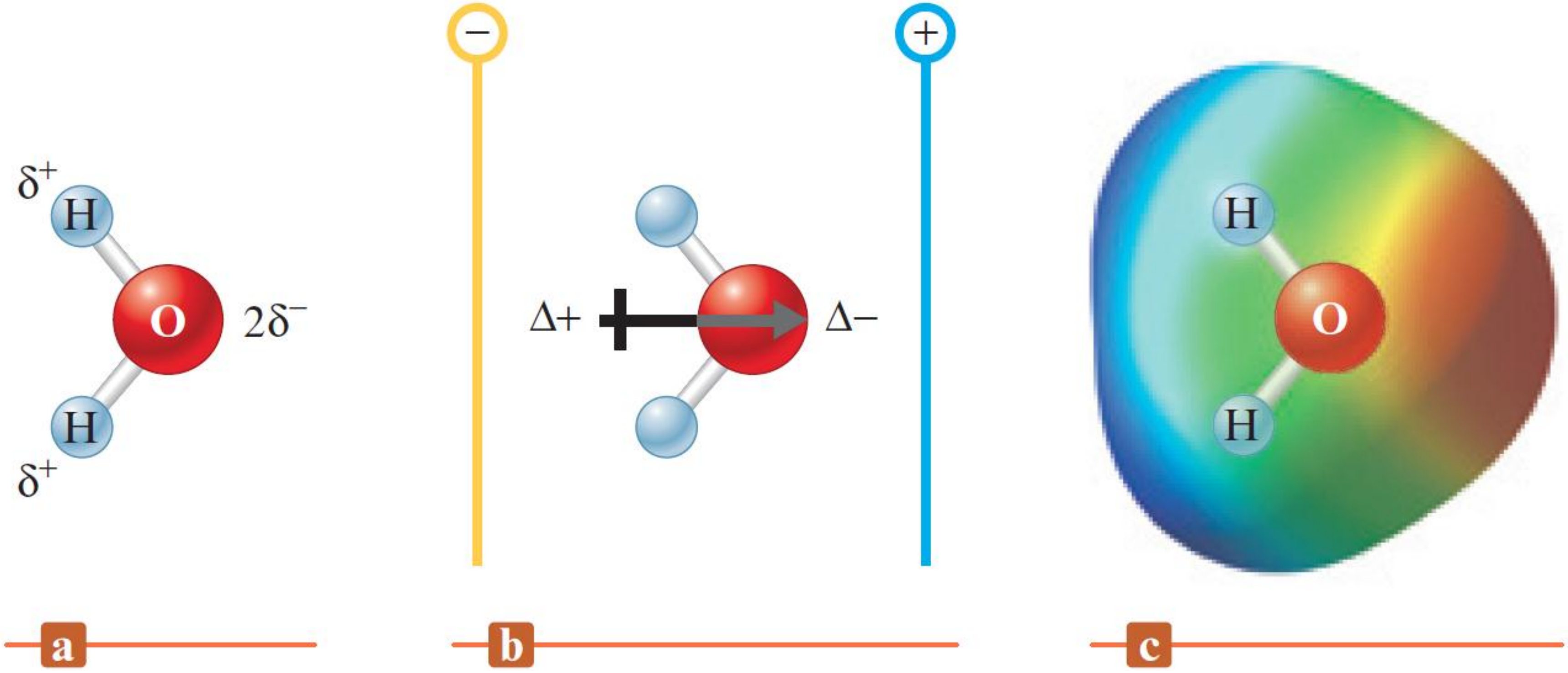


Figure 8.5 - H_2O Molecule

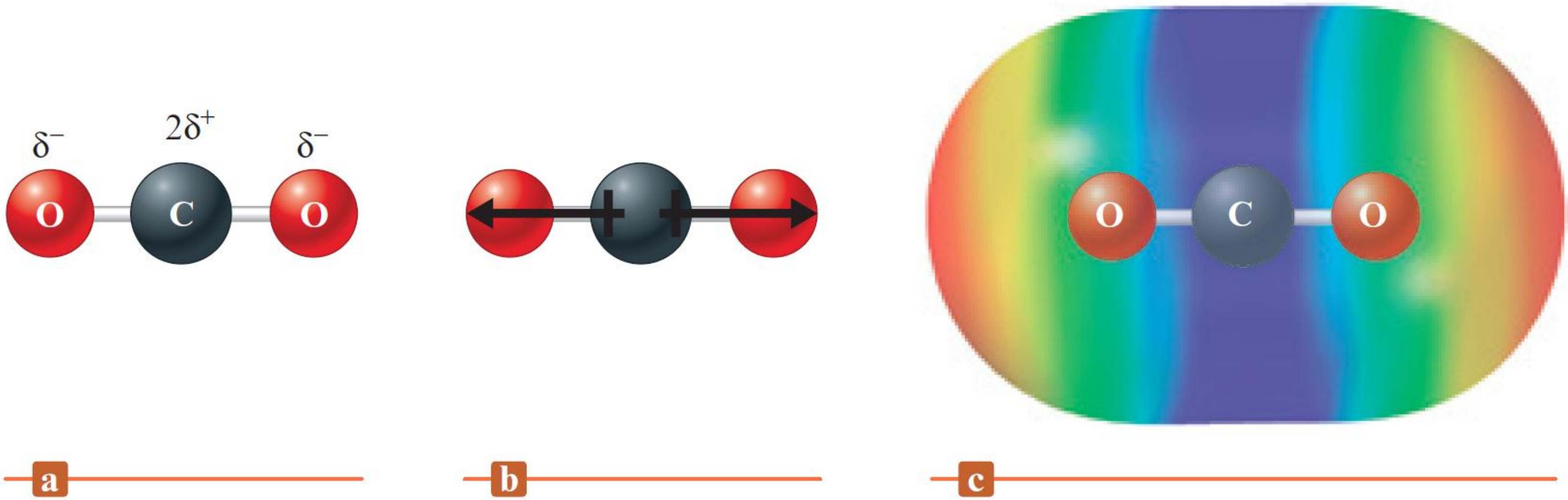


Charge distribution

Water molecule in an electric field

Electrostatic potential diagram

Figure 8.7 - CO_2 Molecule

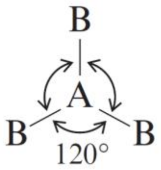
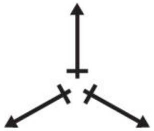
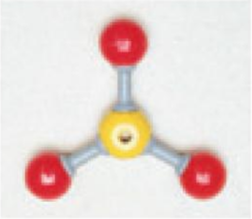
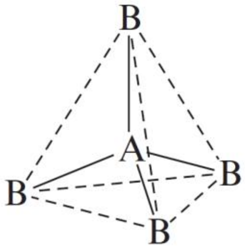
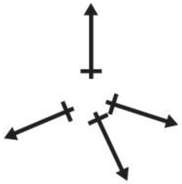


a: Charge distribution

b: The molecule has no dipole moment as the opposed polarities cancel out

c: Electrostatic potential diagram

Table 8.2 - 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

Example 8.2 - Bond Polarity and Dipole Moment

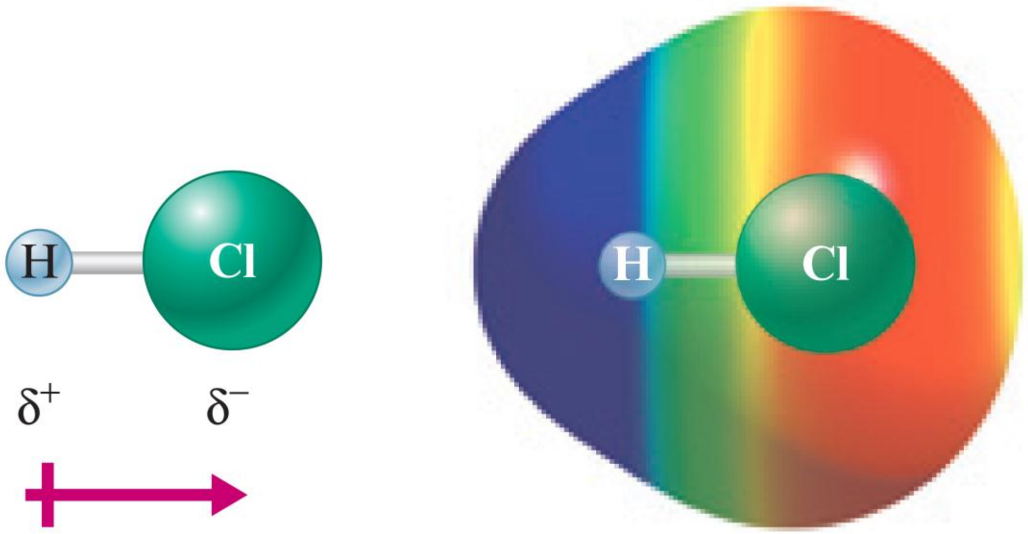
- For each of the following molecules, show the direction of the bond polarities and indicate which ones have a dipole moment
    - HCl
    - Cl_2
    - SO_3

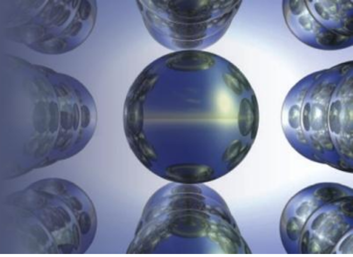
Example 8.2 - Solution

- HCl molecule
  - The electronegativity of chlorine (3.0) is greater than that of hydrogen (2.1)
    - Chlorine will be partially negative
    - Hydrogen will be partially positive

Example 8.2 - Solution (Continued 1)

- The HCl molecule has a dipole moment





Example 8.2 - Solution (Continued 2)

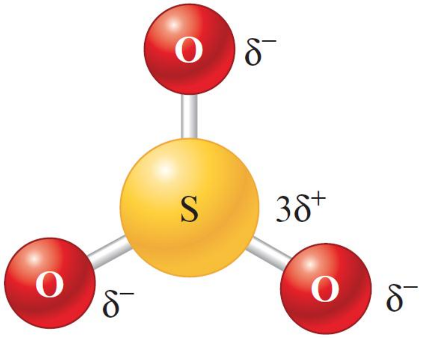
- Cl_2 molecule
    - The two chlorine atoms share the electrons equally
    - No bond polarity occurs
    - The Cl_2 molecule has no dipole moment

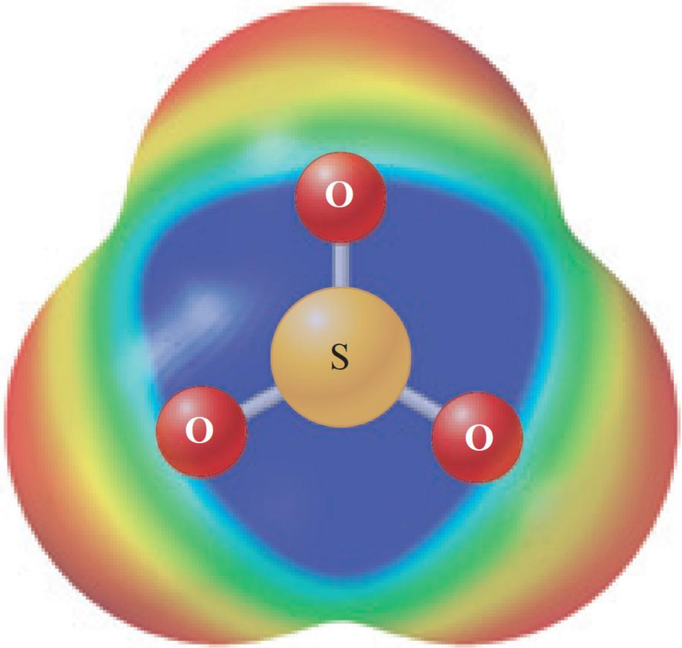
Example 8.2 - Solution (Continued 3)

- SO_3 molecule
    - The electronegativity of oxygen (3.5) is greater than that of sulfur (2.5)
        - Each oxygen will have a partial negative charge
        - Sulfur will have a partial positive charge

Example 8.2 - Solution (Continued 4)

- The molecule has no dipole moment
  - Symmetrically arranged bonds cancel





Electron Configurations in Stable Compounds

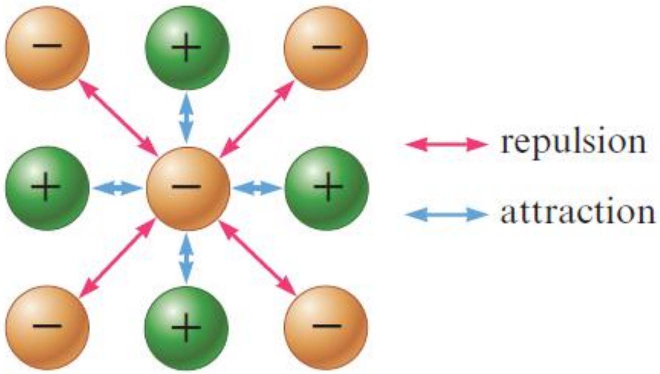
- When two nonmetals react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms
    - Both nonmetals attain noble gas electron configurations

Electron Configurations in Stable Compounds (Continued)

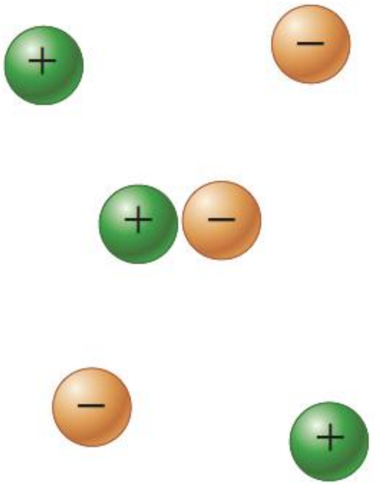
- When a nonmetal and a representative-group metal react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal achieves the electron configuration of the next noble gas atom
  - Valence orbitals of the metal are emptied
  - Both ions achieve noble gas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

Solid and Gaseous States of Ionic Compounds

- Solid state of ionic compounds
  - Ions are relatively close together
  - Many ions are simultaneously interacting



- Gas phase of an ionic substance
  - Ions are relatively far apart
  - Do not contain large groups of ions



Predicting Formulas of Ionic Compounds

- Information required - Valence electron configurations of the combining atoms
- Consider atoms of oxygen and calcium
    - Electronegativity of oxygen - 3.5
    - Electronegativity of calcium - 1.0
    - Electrons are transferred from calcium to oxygen
        - Oxygen anions and calcium cations are formed in the compound

Predicting Formulas of Ionic Compounds (Continued)

- Determining the number of electrons transferred
    - Oxygen requires two electrons to fill its 2*s* and 2*p* valence orbitals
        - Results in the configuration of neon
    - Calcium loses two electrons
        - Results in configuration of argon
- Chemical compounds are always neutral

$$\underbrace{\mathrm{Ca} + \mathrm{O}}_{2e^-} \longrightarrow \mathrm{Ca}^{2+} + \mathrm{O}^{2-}$$

- Empirical formula of the compound - CaO

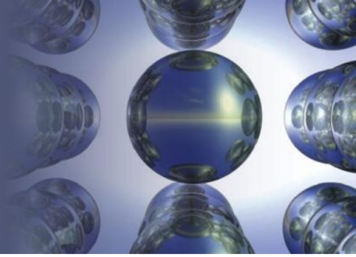


Table 8.3 - Common Ions with Noble Gas Configurations

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]

Exceptions to Rules of Noble Gas Configurations in Ionic Compounds

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

Sizes of Ions

- Ionic radii - Determined from the measured distances between ion centers in ionic compounds
- Factors that influence ionic size are based on the:
  - Size of the parent atom
    - Cation is smaller than its parent atom
    - Anion is larger than its parent atom
  - Position of the parent element in the periodic table
    - Ion sizes increase down a group

Isoelectronic Ions

- Series of ions that contain the same number of electrons
- Examples
  - O^{2-}, F^{-}, Na^{+}, Mg^{2+}, and Al^{3+}
- Size decreases with increasing atomic number

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?

Interactive Example - Relative Ion Size I

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

Interactive Example 8.3 - Solution

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

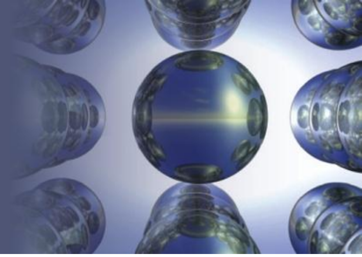
$$\underset{\text{Largest}}{Se^{2-}} > Br^{-} > Rb^{+} > \underset{\text{Smallest}}{Sr^{2+}}$$

Lattice Energy

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

$$\mathrm{M}^{+}(g) + \mathrm{X}^{-}(g) \longrightarrow \mathrm{MX}(s)$$

- Has a negative sign



Energy Changes in the Formation of Lithium Fluoride

$$\mathrm{Li}(s) + \frac{1}{2}\mathrm{F}_2\,(g) \longrightarrow \mathrm{LiF}(s)$$

- Sublimation of solid lithium
  - Enthalpy of sublimation for Li(*s*) - 161 kJ/mol

$$\mathrm{Li}(s) \longrightarrow \mathrm{Li}(g)$$

- Ionization of lithium atoms - Li^+ ions are formed
  - Energy involved - 520 kJ/mol

$$\mathrm{Li}(g) \longrightarrow \mathrm{Li}^{+}(g) + \mathrm{e}^{-}$$

Energy Changes in the Formation of Lithium Fluoride

(Continued 1)

- Dissociation of fluorine molecules
    - A mole of fluorine atoms formed by breaking the F—F bonds in a half mole of F_2 molecules
        - Energy required to break the bond

$$(154\text{kJ})/2 = 77\text{kJ}$$

$$\frac{1}{2}\,\mathrm{F_2}(g) \longrightarrow \mathrm{F}(g)$$

Energy Changes in the Formation of Lithium Fluoride

(Continued 2)

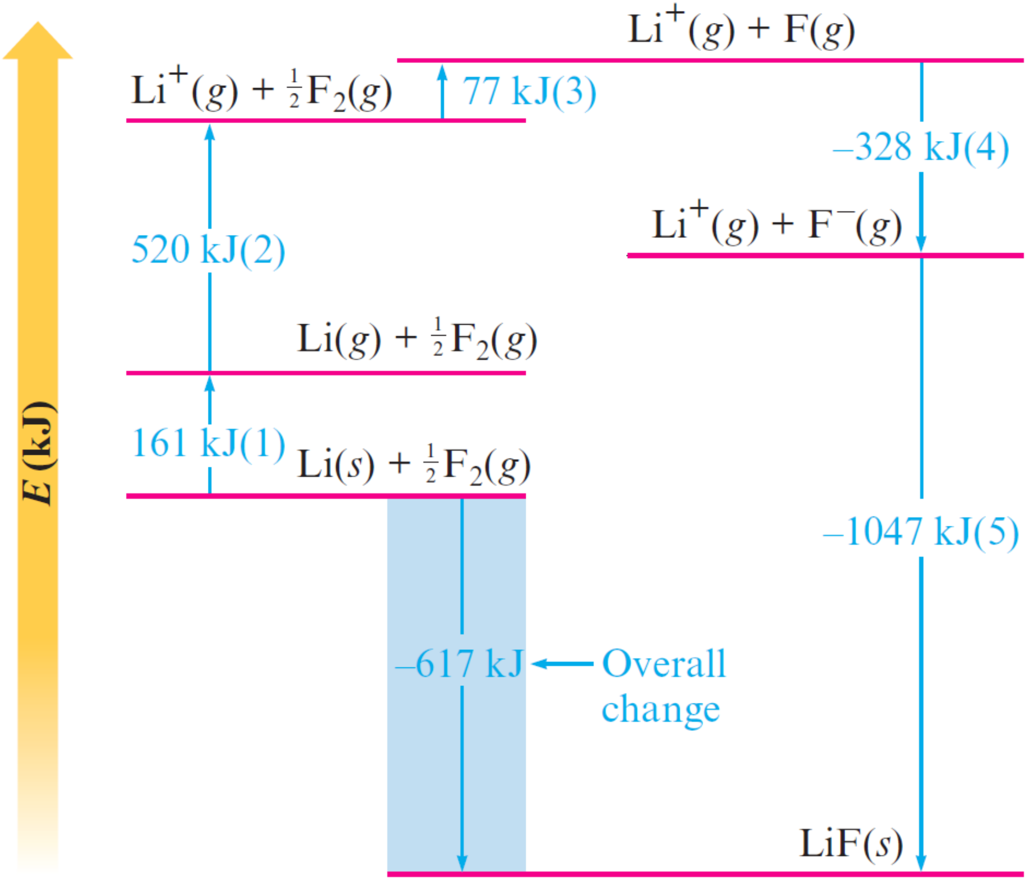
- Formation of F^- ions from fluorine atoms in the gas phase
  - Energy change: –328 kJ/mol

$$F(g) + e^- \longrightarrow F^-(g)$$

- Formation of solid lithium fluoride from gaseous Li^+ and F^- ions
  - Energy involved: –1047 kJ/mol

$$Li^+(g) + F^-(g) \longrightarrow LiF(s)$$

Figure 8.9 - Energy Changes Involved in the Formation of Lithium Fluoride

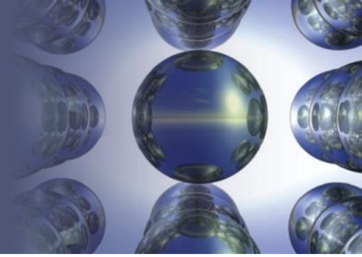


Energy Changes in the Formation of Lithium Fluoride

(Continued 3)

- Sum of individual energy changes gives the overall energy change

Process	Energy Change (kJ)
$\text{Li}(s) \rightarrow \text{Li}(g)$	161
$\text{Li}(g) \rightarrow \text{Li}^+(g) + \text{e}^-$	520
$\frac{1}{2}\text{F}_2(g) \rightarrow \text{F}(g)$	77
$\text{F}(g) + \text{e}^- \rightarrow \text{F}^-(g)$	−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)

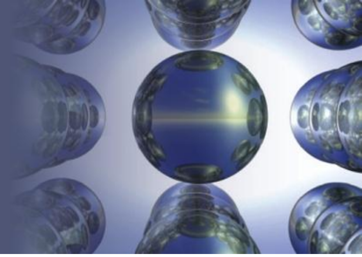


Lattice Energy Calculations

- Represented by a modified form of Coulomb's law

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

  - *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



Formula for Percent Ionic Character of a Bond

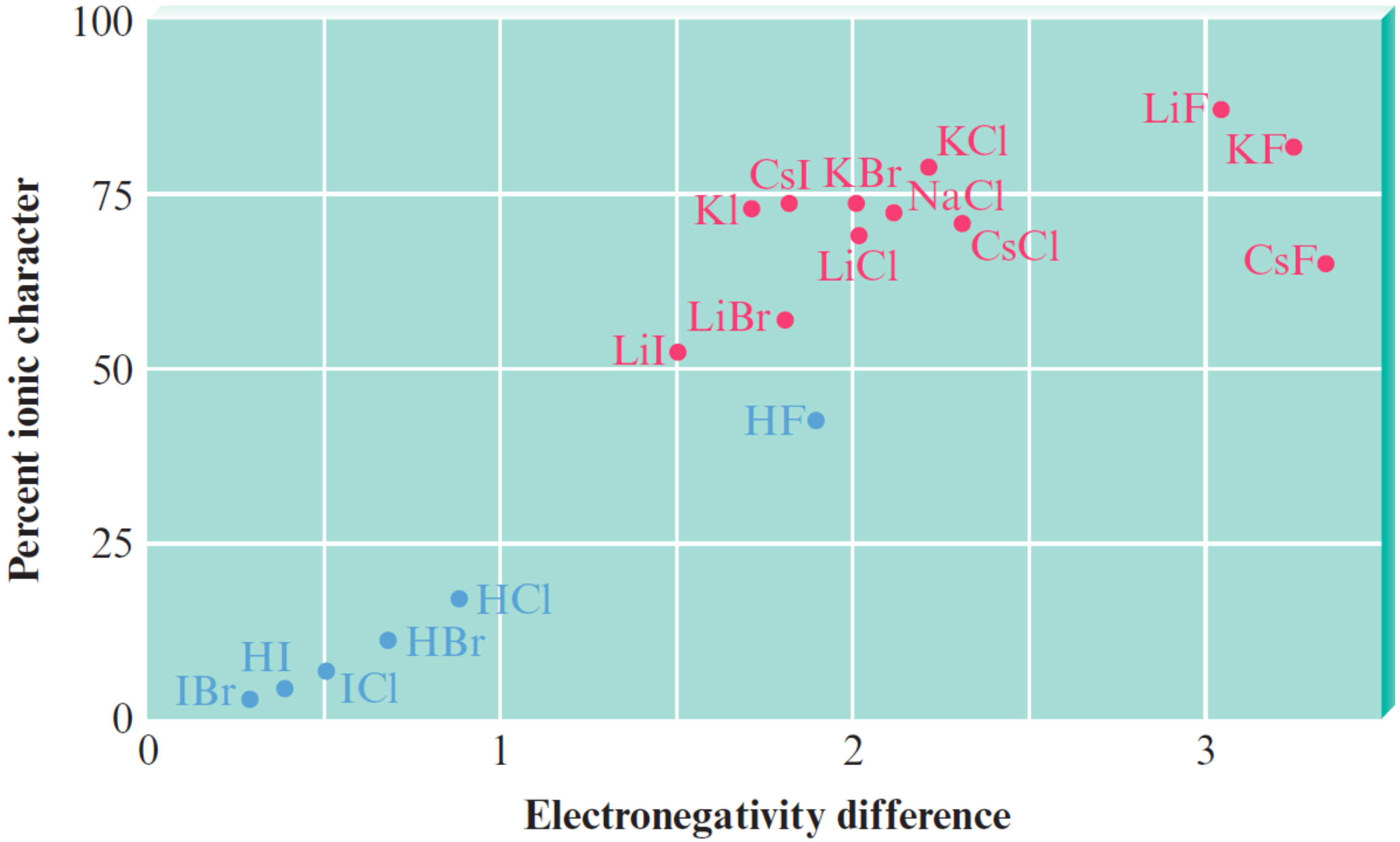
- Totally ionic bonds between discrete pairs of atoms do not exist
  - Evidence comes from calculations of the percent ionic character for bonds of various binary compounds in the gas phase
    - Formula used to determine the percent ionic character of bonds

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

Section 8.6

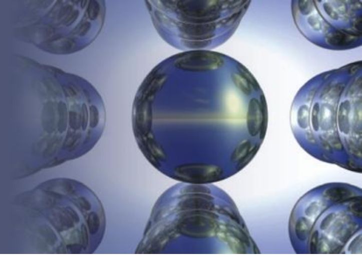
Partial Ionic Character of Covalent Bonds

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



Operational Definition of Ionic Compound

- Any compound that conducts an electric current when melted



Bonds

- Result from the tendency of a system to seek its lowest possible energy
- Occur when collections of atoms are more stable (lower in energy) than the separate atoms
- Molecular stability can be depicted in the form of models called chemical bonds
- Concept of bonds is a human invention

Models

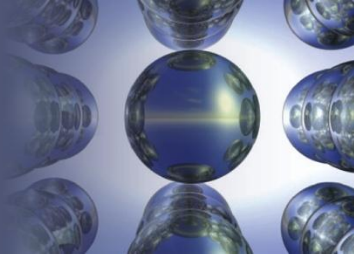
- Attemptx to explain how nature operates on microscopic level based on experiences in the macroscopic world
- Based on observations of the properties of nature
- Bonding model
  - Provides a framework to systematize chemical behavior
    - Molecules are perceived as collections of common fundamental components

Establishing the Sensitivity of Bonds to their Molecular Environment

- Consider the decomposition of methane

Process	Energy Required
$CH_4(g) \longrightarrow CH_3(g) + H(g)$	435
$CH_3(g) \longrightarrow CH_2(g) + H(g)$	453
$CH_2(g) \longrightarrow CH(g) + H(g)$	425
$CH(g) \longrightarrow C(g) + H(g)$	339
Total =	1652

$$\text{Average} = \frac{1652}{4} = 413$$



Establishing the Sensitivity of Bonds to their Molecular Environment (Continued)

- The energy required to break a C—H bond varies in a nonsystematic way
    - The bond is sensitive to its environment
- The average of the individual bond dissociation energies are used

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

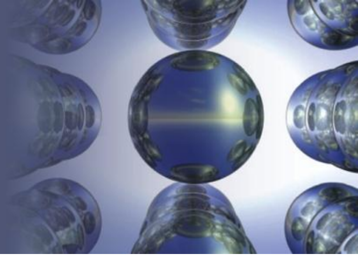
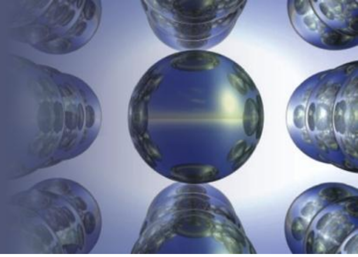


Table 8.4 - Average Bond Energies

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(CO_2) = 799



Bond Energy

- Energy must be added to the system in order to break bonds
    - Endothermic process
    - Associated energy terms carry positive signs
- Energy is released when bonds are formed
    - Exothermic process
    - Associated energy terms carry negative signs

Calculating Change in Enthalpy

- The following formula is used

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

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

Interactive Example 8.5 - Δ*H* from Bond Energies

- Use the bond energies listed in Table 8.4, and calculate Δ*H* for the reaction of methane with chlorine and fluorine to give Freon-12 (CF_2Cl_2)

$$CH_4(g) + 2Cl_2(g) + 2F_2(g) \longrightarrow CF_2Cl_2(g) + 2HF(g) + 2HCl(g)$$

Interactive Example 8.5 - Solution

- Break the bonds in the gaseous reactants to give individual atoms
  - Assemble the atoms into gaseous products by forming new bonds

$$\text{Reactants} \xrightarrow[\text{required}]{\text{Energy}} \text{atoms} \xrightarrow[\text{released}]{\text{Energy}} \text{products}$$

  - Combine energy changes to calculate Δ*H*

ΔH = energy required to break bonds – energy released when bonds form

    - The minus sign gives the correct sign to the energy terms for the exothermic processes

Interactive Example 8.5 - Solution (Continued 1)

- Reactant bonds broken

$$\mathrm{CH_4}\text{: 4 mol C—H} \qquad 4\ \cancel{\text{mol}} \times \frac{413\ \text{kJ}}{\cancel{\text{mol}}} = 1652\ \text{kJ}$$

$$2\mathrm{Cl_2}\text{: 2 mol Cl—Cl} \qquad 2\ \cancel{\text{mol}} \times \frac{239\ \text{kJ}}{\cancel{\text{mol}}} = 478\ \text{kJ}$$

$$2\mathrm{F_2}\text{: 2 mol F—F} \qquad 2\ \cancel{\text{mol}} \times \frac{154\ \text{kJ}}{\cancel{\text{mol}}} = \underline{308\ \text{kJ}}$$

Total energy requied = 2438 kJ

Interactive Example 8.5 - Solution (Continued 2)

- Product bonds formed

$$CF_2Cl_2\text{: 2 mol C—F} \qquad 2\ \cancel{\text{mol}} \times \frac{485\ \text{kJ}}{\cancel{\text{mol}}} = 970\ \text{kJ}$$

and

$$\text{2 mol C—Cl} \qquad 2\ \cancel{\text{mol}} \times \frac{339\ \text{kJ}}{\cancel{\text{mol}}} = 678\ \text{kJ}$$

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

$$\text{2HCl: 2 mol H—Cl} \qquad 2\ \cancel{\text{mol}} \times \frac{427\ \text{kJ}}{\cancel{\text{mol}}} = \underline{\quad 854\ \text{kJ}}$$

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

Interactive Example 8.5 - Solution (Continued 3)

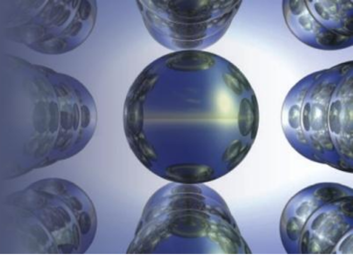
- Calculating ΔH

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

  - 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

Localized Electron (LE) Model

- A molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms
  - **Lone pairs**: Pairs of electrons localized on an atom
  - **Bonding pairs**: Pairs of electrons found in the space between atoms



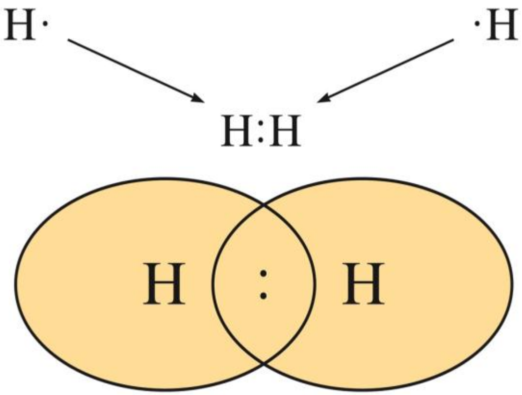
Parts of the LE Model

- Description of the valence electron arrangement in the molecule using Lewis structures
- Prediction of the geometry of the molecule using the valence shell electron-pair repulsion (VSEPR) model
- Description of the type of atomic orbitals used by the atoms to share electrons or hold lone pairs

Lewis Structure

- Named after G.N. Lewis
- Depicts the arrangement of valence electrons among atoms in a molecule
- Stable compounds are formed only when atoms achieve noble gas electron configurations
- Only valence electrons are included

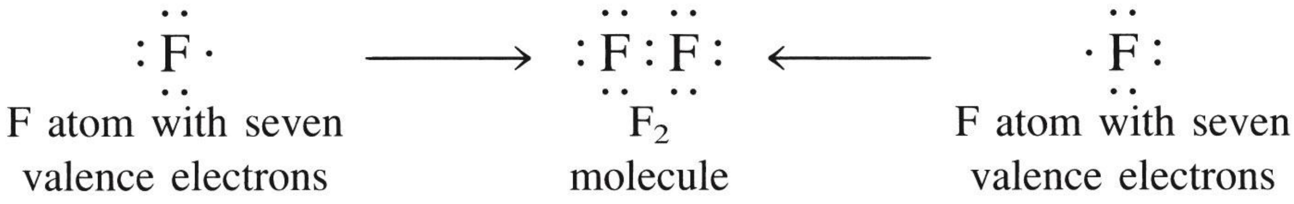
Principle of Achieving a Noble Gas Electron Configuration - Hydrogen and Helium



- Hydrogen forms stable molecules where it shares two electrons
  - Follows a **duet rule**
- Helium
  - Does not form bonds as its valence orbital is already filled
  - Electron configuration - $1s^2$

Principle of Achieving a Noble Gas Electron Configuration - Carbon, Nitrogen, Oxygen, and Fluorine

- Form stable molecules when surrounded by enough electrons to fill valence orbitals
- Obey the octet rule
  - **Octet rule**: Elements form stable molecules when surrounded by eight electrons



Principle of Achieving a Noble Gas Electron Configuration - Neon

- Neon does not form bonds because it already has an octet of valence electrons
- Only the valence electrons ($2s^2 2p^6$) are represented in the Lewis structure

Problem Solving Strategy - Steps for Writing Lewis Structures

1. Sum the valence electrons from all the atoms
2. Use a pair of electrons to form a bond between each pair of bound atoms
3. Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements

Drawing the Lewis Structure of Water

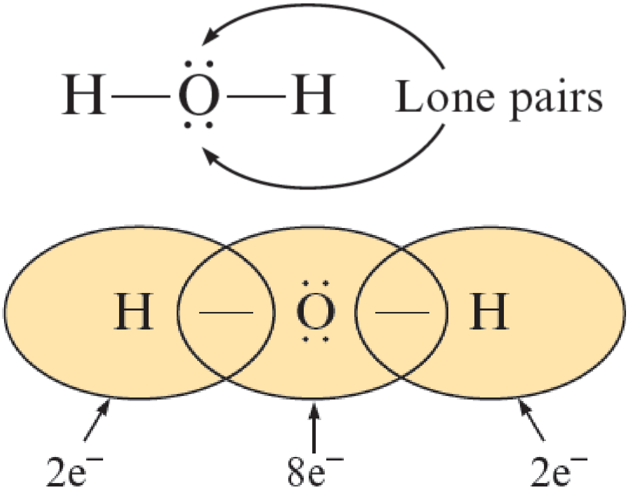
- Sum the valence electrons for H_2O
  - $\underset{\mathrm{H}}{\underset{\uparrow}{1}} + \underset{\mathrm{H}}{\underset{\uparrow}{1}} + \underset{\mathrm{O}}{\underset{\uparrow}{6}} = 8$ valence electrons
- Draw the O—H single bonds

$$\mathrm{H{-}O{-}H}$$

  - A line is used to indicate each pair of bonding electrons

Drawing the Lewis Structure of Water (Continued)

- Distribute the remaining electrons to achieve a noble gas electron configuration for each atom
  - Dots represent lone electron pairs



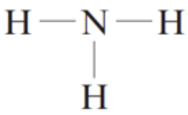
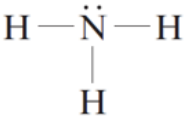
Interactive Example 8.6 - Writing Lewis Structures

- Give the Lewis structure for each of the following
  - HF
  - N_2
  - NH_3
  - NO^+

Interactive Example 8.6 - Solution

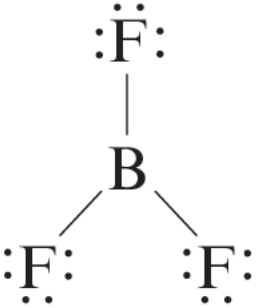
- Three steps are applied for writing Lewis structures
  - Lines are used to indicate shared electron pairs, and dots are used to indicate nonbonding pairs (lone pairs)

Interactive Example 8.6 - Solution (Continued)

	Total Valence Electrons	Draw Single Bonds	Calculate Number of Electrons Remaining	Use Remaining Electrons to Achieve Noble Gas Configurations	Check Number of Electrons
HF	$1 + 7 = 8$	$\text{H}-\text{F}$	6	$\text{H}-\ddot{\underset{..}{\text{F}}}:$	H, 2 F, 8
N_2	$5 + 5 = 10$	$\text{N}-\text{N}$	8	$:\text{N}\equiv\text{N}:$	N, 8
NH_3	$5 + 3(1) = 8$	 $\begin{array}{c}\text{H}-\text{N}-\text{H}\\ \vert\\ \text{H}\end{array}$	2	 $\begin{array}{c}\text{H}-\ddot{\text{N}}-\text{H}\\ \vert\\ \text{H}\end{array}$	H, 2 N, 8
NO^+	$5 + 6 - 1 = 10$	$\text{N}-\text{O}$	8	$[:\text{N}\equiv\text{O}:]^+$	N, 8 O, 8

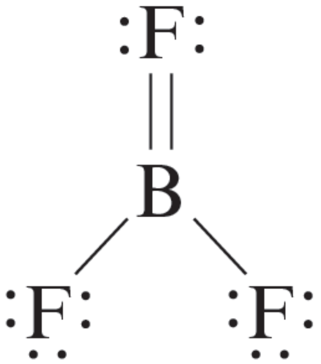
Boron

- Tends to form compounds in which the boron atom has fewer than eight electrons around it
- Boron trifluoride (BF_3) reacts energetically with molecules that have available electron pairs (lone pairs)
  - Boron atom is electron-deficient
  - Has 24 valence electrons



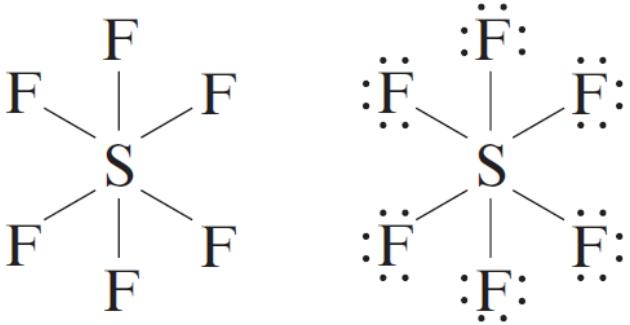
Boron (Continued)

- Drawing a structure with a double bond to the Lewis structure satisfies the octet rule for boron



Sulfur Hexafluoride (SF_6)

- Highly stable molecule
- Sum of valence electrons
  - 6 + 6(7) = 48 electrons



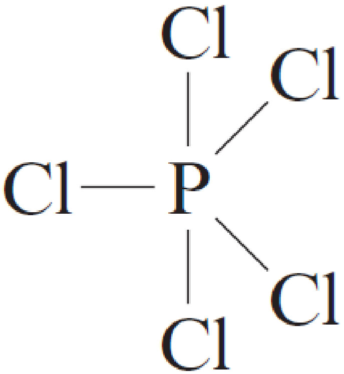
- Sulfur exceeds the octet rule
  - Localized electron model assumes that the empty 3*d* orbitals can be used to accommodate extra electrons

Interactive Example 8.7 - Lewis Structures for Molecules That Violate the Octet Rule I

- Write the Lewis structure for PCl_5

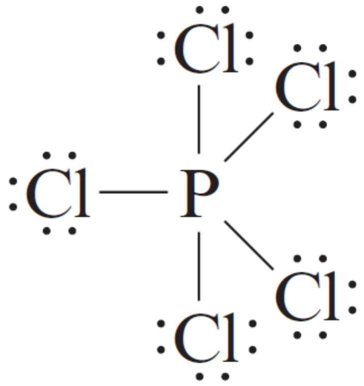
Interactive Example 8.7 - Solution

- Sum the valence electrons
  - $\underset{\underset{\text{P}}{\uparrow}}{5} + \underset{\underset{\text{Cl}}{\uparrow}}{5}(7) = 40$ electrons
- Indicate single bonds between bound atoms



Interactive Example 8.7 - Solution (Continued)

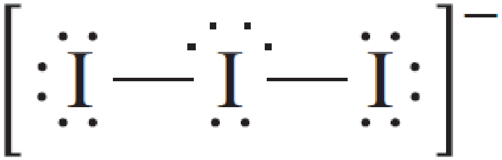
- Distribute the remaining electrons
  - 30 electrons remain
    - Used to satisfy the octet rule for each chlorine atom



  - Phosphorus, a third-row element, has exceeded the octet rule by two electrons

Exceeding the Octet Rule - Molecules with More Than One Atom

- When it is necessary to exceed the octet rule for one of several third-row (or higher) elements, assume that the extra electrons should be placed on the central atom
- Example - Lewis structure of I_3^-
    - Contains 22 valence electrons

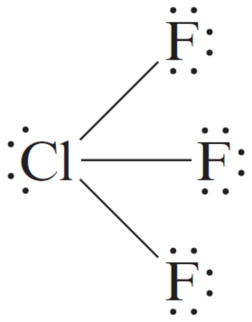


Interactive Example 8.8 - Lewis Structures for Molecules That Violate the Octet Rule II

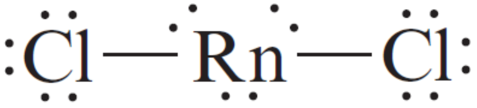
- Write the Lewis structure for the following:
  a. ClF_3
  b. $RnCl_2$
  c. ICl_4^-

Interactive Example 8.8 - Solution

a. The chlorine atom accepts the extra electrons

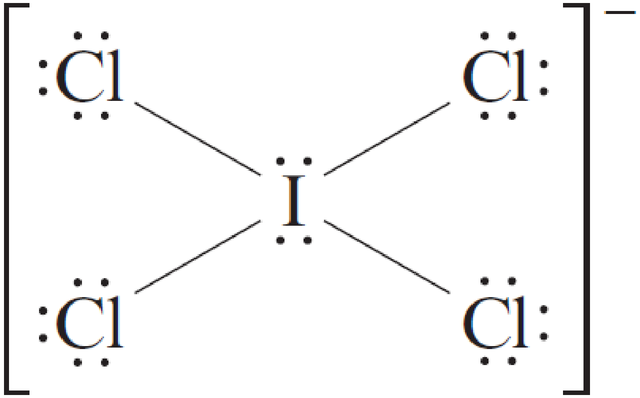


b. Radon, a noble gas in Period 6, accepts the extra electrons



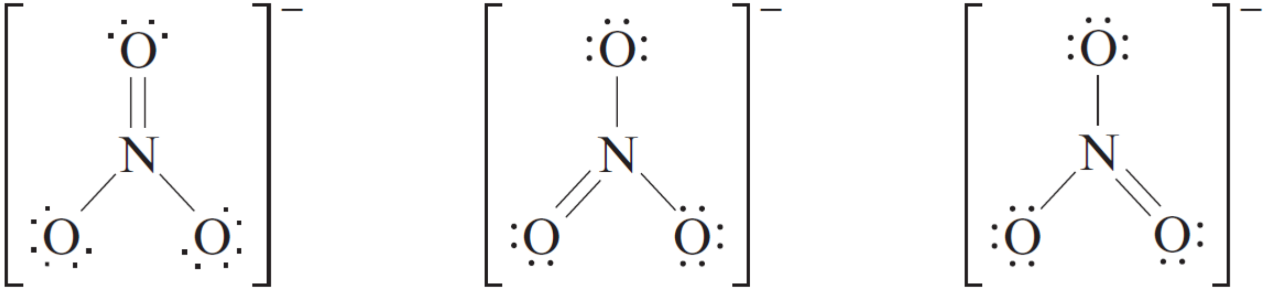
Interactive Example 8.8 - Solution (Continued)

c. Iodine exceeds the octet rule



Resonance

- Some molecules can be described by more than one Lewis structure
  - Example - Nitrate ion
    - Has three valid Lewis structures



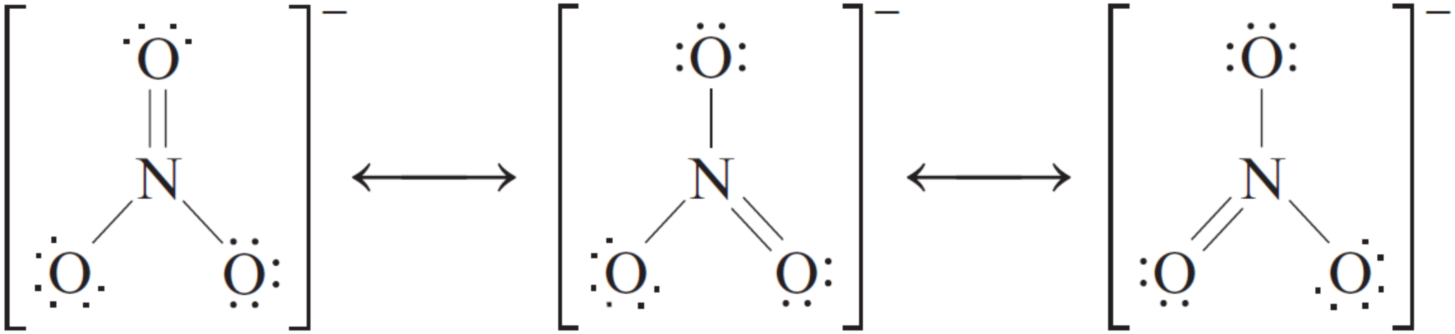
    - The most accurate structure is obtained when the three structures are superimposed

Resonance (Continued 1)

- Occurs when more than one Lewis structure can be written for a particular molecule
  - Resulting electron structure is an average of the **resonance structures**

Resonance (Continued 2)

- Represented by double-headed arrows



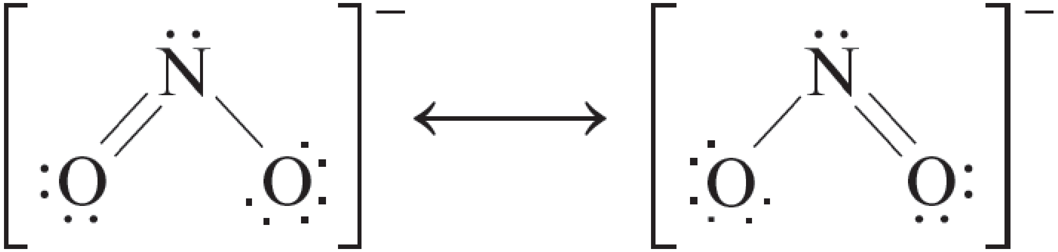
  - Arrangement of nuclei is the same across all structures
  - The arrows denote that the actual structure is an average of the three resonance structures

Example 8.9 - Resonance Structures

- Describe the electron arrangement in the nitrite anion (NO_2^-) using the localized electron model

Example 8.9 - Solution

- NO_2^- possesses 18 valence electrons
  - 5 + 2(6) + 1 = 18
- Indicating the single bonds gives the structure O—N—O
- The remaining 14 electrons (18 – 4) can be used to produce these structures



Example 8.9 - Solution (Continued)

- This is a resonance situation
  - Two equivalent Lewis structures can be drawn
    - The electronic structure of the molecule is correctly represented not by either resonance structure but by the average of the two
  - There are two equivalent N—O bonds, each one intermediate between a single and a double bond

Odd-Electron Molecules

- Few molecules formed from nonmetals possess electrons in odd numbers
  - Example - Nitric oxide (NO) emitted by automobiles
    - Reacts with oxygen in the air to form NO_2, which is another odd-electron molecule
  - A more sophisticated model than the localized electron model is required to treat odd-electron molecules

Formal Charge

- The difference between the number of valence electrons on the free atom and the number of valence electrons assigned to the atom in the molecule
- Used to evaluate nonequivalent Lewis structures

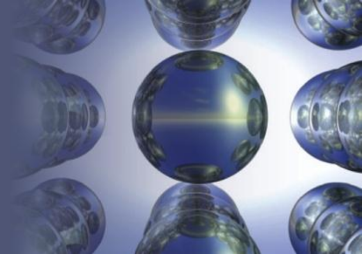
Formal Charge (Continued)

- Computed by assigning valence electrons in the molecule to the various atoms
  - Assumptions
    - Lone pair electrons belong entirely to the atom in question
    - Shared electrons are divided equally between the two sharing atoms
- Determining valence electrons in a given atom

$$(\text{Valence electrons})_{\text{assigned}} = (\text{number of lone pair electrons}) + \frac{1}{2}(\text{number of shared electrons})$$

Fundamental Assumptions about Formal Charges

- Atoms in molecules try to achieve formal charges as close to zero as possible
- Any negative formal charges are expected to reside on the most electronegative atoms



Rules Governing Formal Charge

- To calculate the formal charge on an atom:
    - Take the sum of the lone pair electrons and one-half the shared electrons
        - This is the number of valence electrons assigned to the atom in the molecule
    - Subtract the number of assigned electrons from the number of valence electrons on the free, neutral atom to obtain the formal charge

Rules Governing Formal Charge (Continued)

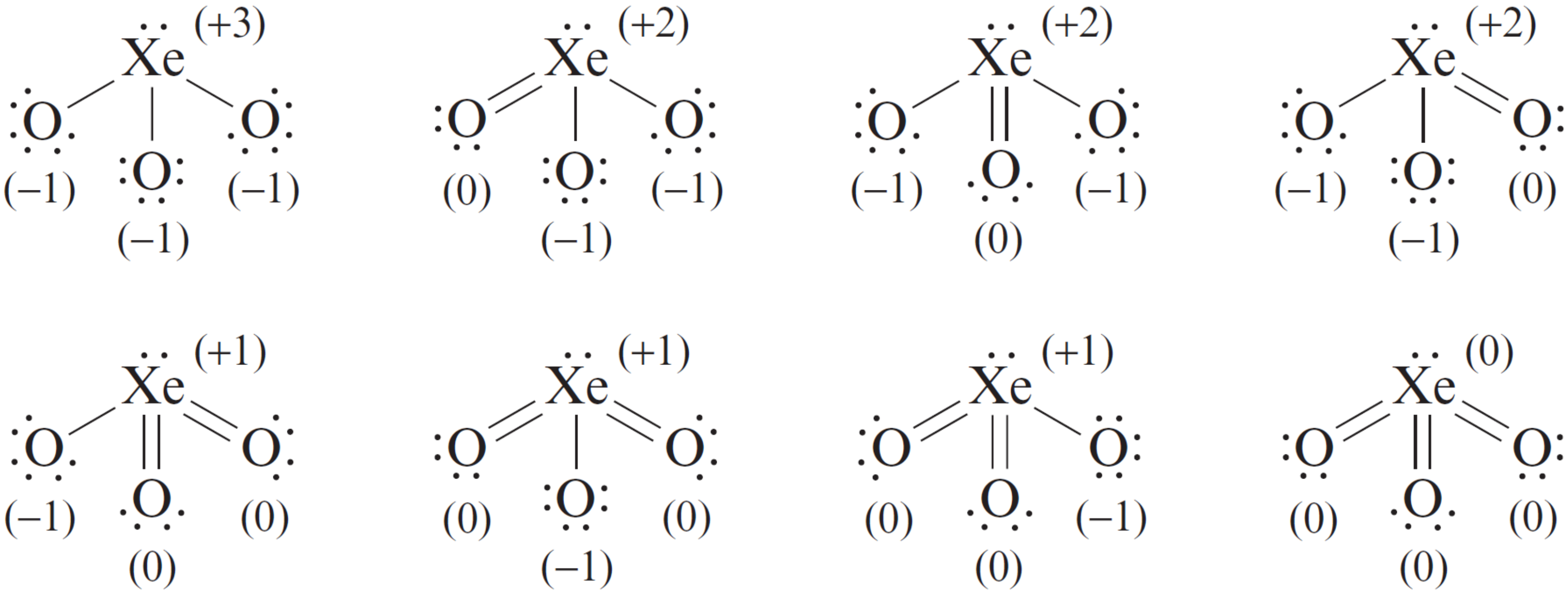
- The sum of the formal charges of all atoms in a given molecule or ion must be equal to the overall charge on that species
- If nonequivalent Lewis structures exist for a species, those with formal charges closest to zero and with any negative formal charges on the most electronegative atoms are considered to best describe the bonding in the molecule or ion

Example 8.10 - Formal Charges

- Give possible Lewis structures for XeO_3, an explosive compound of xenon
  - Which Lewis structure or structures are most appropriate according to the formal charges?

Example 8.10 - Solution

- XeO_3 has 26 valence electrons
- Possible Lewis structures



Example 8.10 - Solution (Continued)

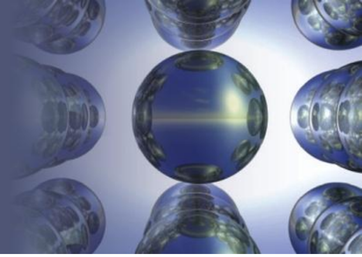
- Based on the ideas of formal charge, it can be predicted that the Lewis structures with the lower values of formal charge would be most appropriate for describing bonding in XeO_3

Cautions about Formal Charge

- Formal charges provide estimates of charge
  - Not to be considered as actual atomic charges
- Evaluation of Lewis structures using formal charge ideas can lead to erroneous predictions

Valence Shell Electron-Pair Repulsion (VSEPR) Model

- The structure around a given atom is determined principally by minimizing electron-pair repulsions
  - Binding and nonbonding pairs around a given atom will be placed as far apart as possible
- Used to predict approximate molecular structures



Molecular Structure

- Three dimensional arrangement of the atoms in a molecule
- Types
  - **Linear structure**: Molecule with a 180-degree bond angle
  - **Trigonal planar structure**: The electron pairs form 120-degree bond angles
  - **Tetrahedral structure**: Has angles of 109.5 degrees

Problem-Solving Strategy - Steps to Apply the VSEPR Model

- Draw the Lewis structure for the molecule
- Count the electron pairs and arrange them in the way that minimizes repulsion
- Determine the positions of the atoms from the way electron pairs are shared
- Determine the name of the molecular structure from the positions of the atoms

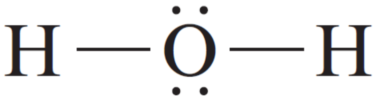
Example 8.11 - Prediction of Molecular Structure I

- Describe the molecular structure of the water molecule

$$\mathrm{H{-}\ddot{\underset{\cdot\cdot}{O}}{-}H}$$

Example 8.11 - Solution

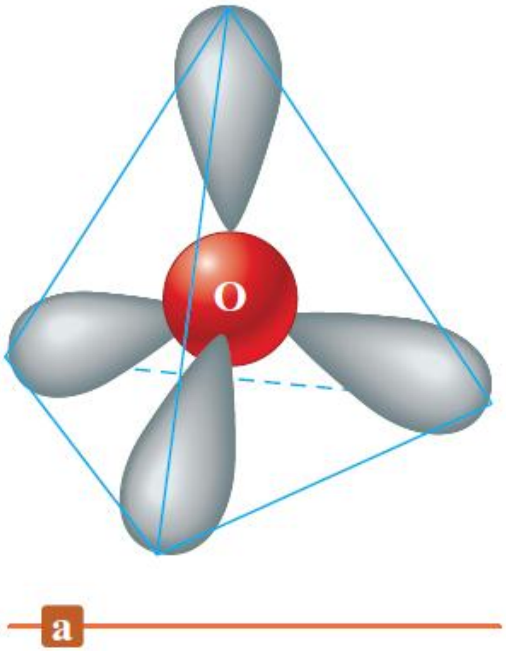
- The Lewis structure for water



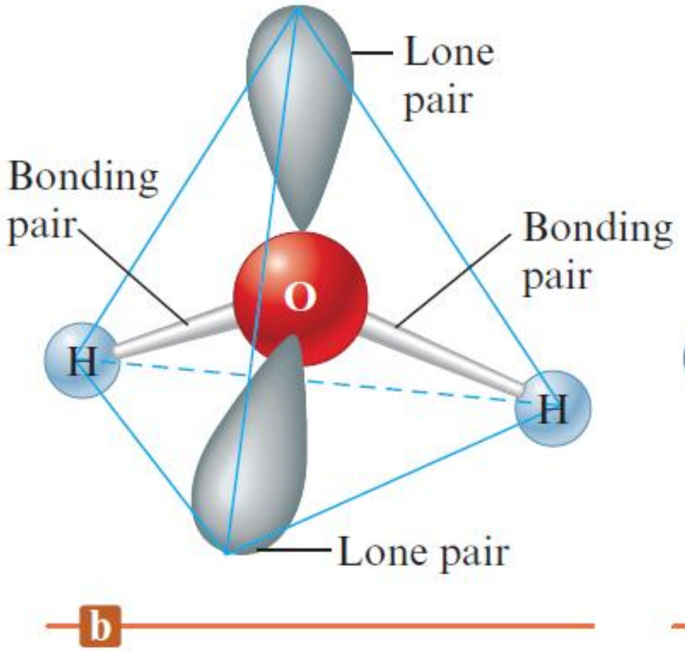
$H-\underset{\cdot\cdot}{\ddot{O}}-H$

- There are four pairs of electrons
  - Two bonding pairs and two nonbonding pairs
- To minimize repulsions, the pairs are best arranged in a tetrahedral array
  - The atoms in the H_2O molecule form a V shape

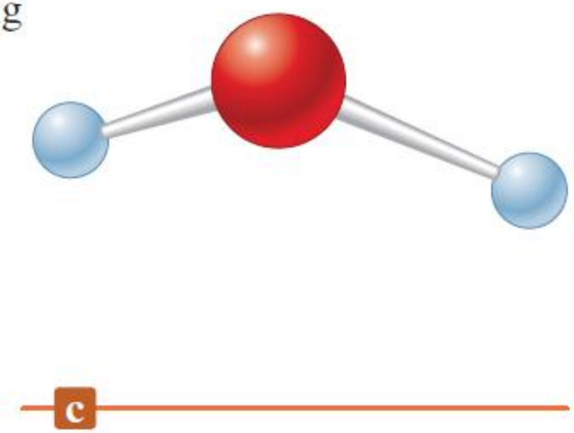
Example 8.11 - Solution (Continued)



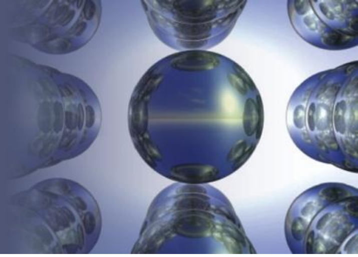
The tetrahedral arrangement of the electron pairs around oxygen in the water molecule



Two of the electron pairs are shared between oxygen and the hydrogen atoms and two are lone pairs

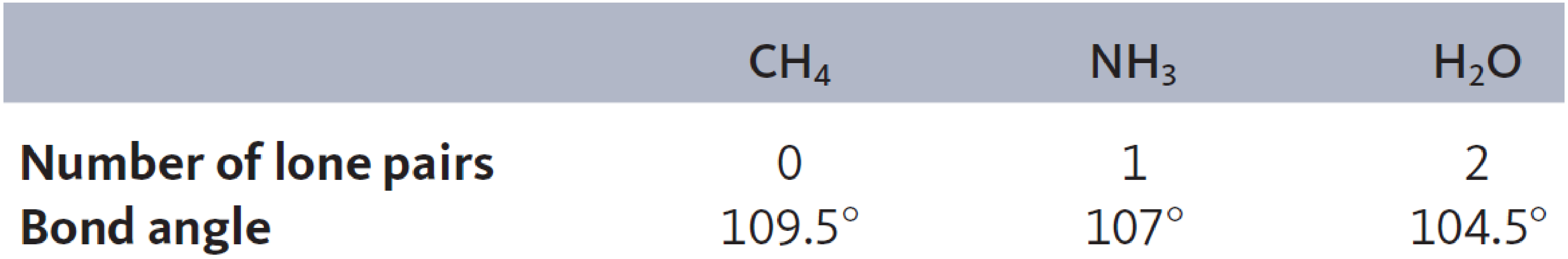


The V-shaped molecular structure of the water molecule



Modifications to the Postulate of the VSEPR Model

- Predictions suggest that the H—X—H bond angle in CH_4, NH_3, and H_2O should be a tetrahedral angle
  - Experimental studies show the following data



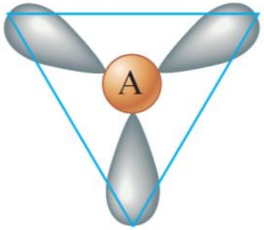
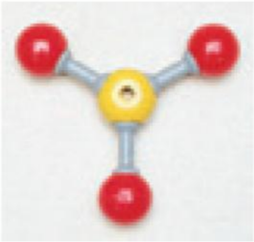
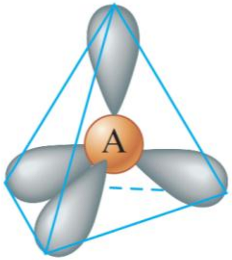
	CH_4	NH_3	H_2O
Number of lone pairs	0	1	2
Bond angle	109.5°	107°	104.5°

Modifications to the Postulate of the VSEPR Model

(Continued)

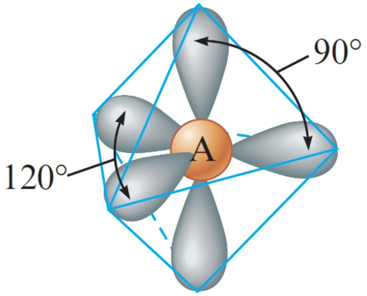
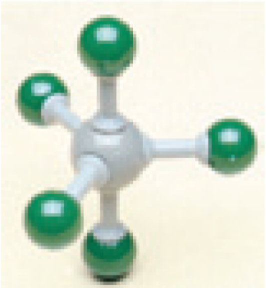
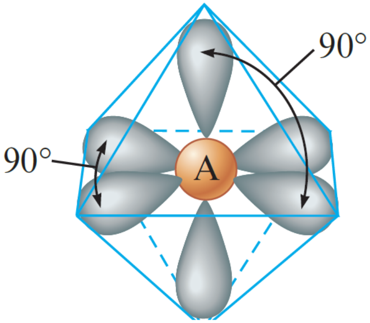
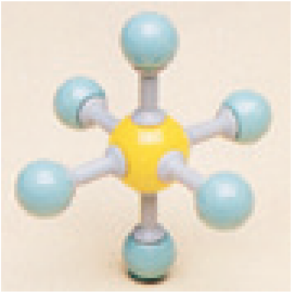
- Addition to original postulate
    - Lone pairs require more space than bonding pairs and tend to compress the angles between bonding pairs

Table 8.6 - Arrangements of Electron Pairs around an Atom Yielding Minimum Repulsion

Number of Electron Pairs	Arrangement of Electron Pairs		Example
2	Linear		
3	Trigonal planar		
4	Tetrahedral		

Photos: Ken O'Donoghue © Cengage Learning

Table 8.6 - Arrangements of Electron Pairs around an Atom Yielding Minimum Repulsion (Continued)

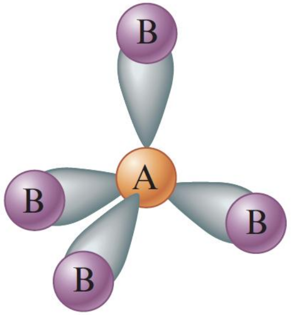
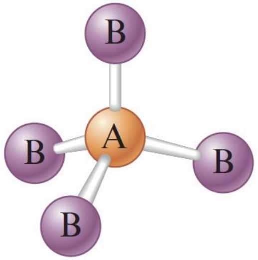
Number of Electron Pairs	Arrangement of Electron Pairs	Example
5	Trigonal bipyramidal  	
6	Octahedral  	

Photos: Ken O'Donoghue © Cengage Learning

Critical Thinking

- You and a friend are studying for a chemistry exam
    - What if your friend tells you that all molecules with polar bonds are polar molecules?
        - How would you explain to your friend that this is not correct?
        - Provide two examples to support your answer

Table 8.7 - Structures of Molecules with Four Electron Pairs around the Central Atom

Electron-Pair Arrangement	Molecular Structure
	 Tetrahedral

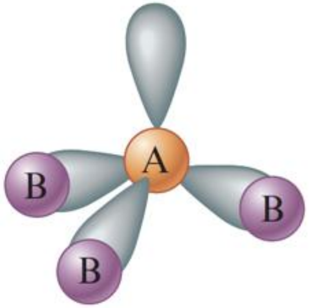
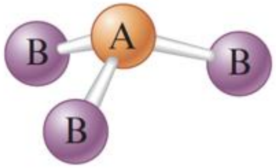
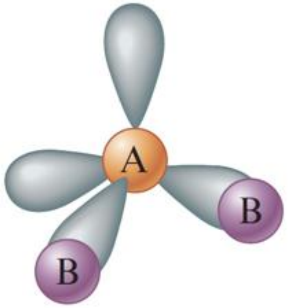
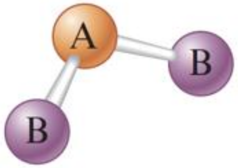
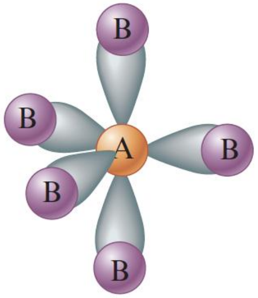
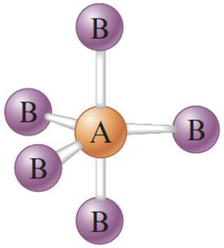
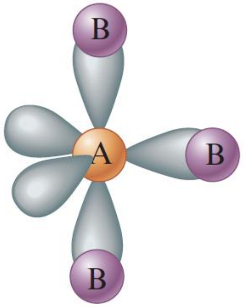
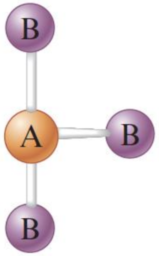
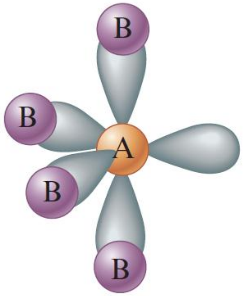
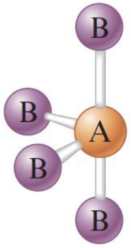
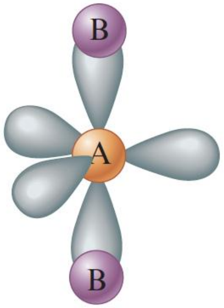
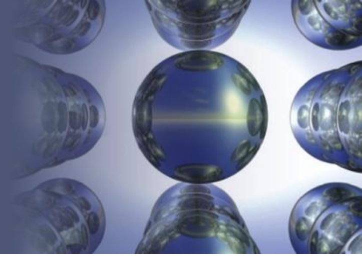
Electron-Pair Arrangement	Molecular Structure
	 Trigonal pyramid
	 V-shaped (bent)

Table 8.8 - Structures of Molecules with Five Electron Pairs around the Central Atom

Electron-Pair Arrangement	Molecular Structure	Electron-Pair Arrangement	Molecular Structure
	 Trigonal bipyramidal		 T-shaped
	 See-saw		 Linear

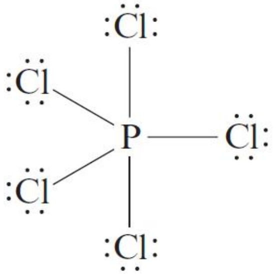


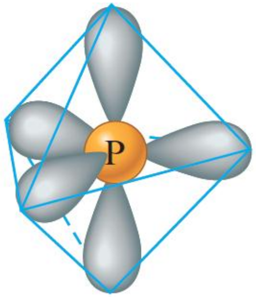
Interactive Example 8.12 - Prediction of Molecular Structure II

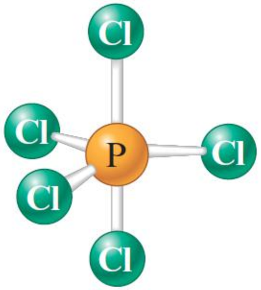
- When phosphorus reacts with excess chlorine gas, the compound phosphorus pentachloride (PCl_5) is formed
    - In the gaseous and liquid states, this substance consists of PCl_5 molecules, but in the solid state, it consists of a 1:1 mixture of PCl_4^+ and PCl_6^- ions
- Predict the geometric structures of PCl_5, PCl_4^+, and PCl_6^-

Interactive Example 8.12 - Solution

- The Lewis structure for PCl_5 is shown
  - Five pairs of electrons around the phosphorus atom require a trigonal bipyramidal arrangement
    - When chlorine atoms are included, a trigonal bipyramidal molecule results

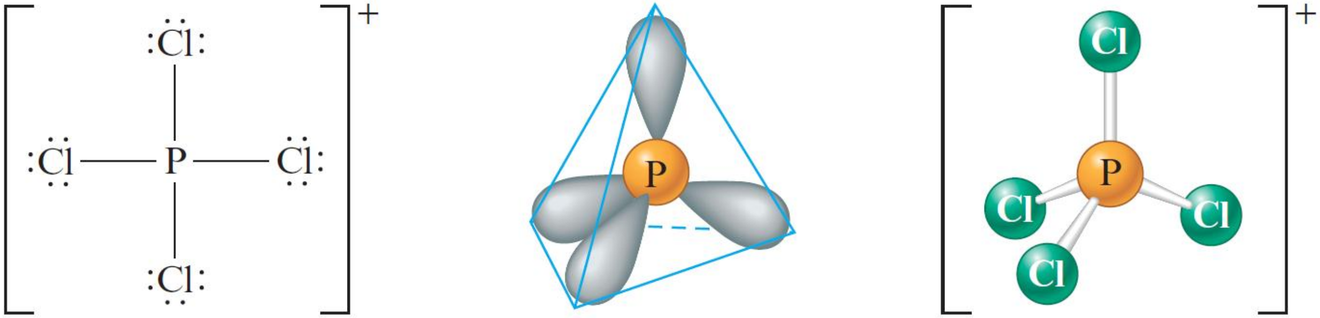






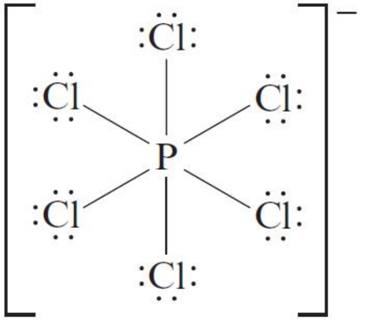
Interactive Example 8.12 - Solution (Continued 1)

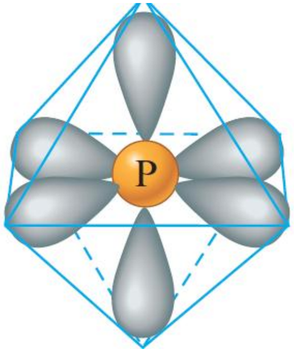
- PCl_4^+ has 32 valence electrons
    - Four pairs of electrons surround the phosphorus atom in the PCl_4^+ ion, which requires a tetrahedral arrangement of the pairs
        - Since each pair is shared with a chlorine atom, a tetrahedral PCl_4^+ cation results

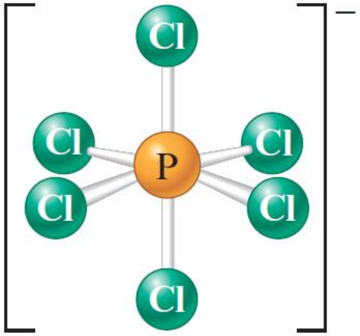


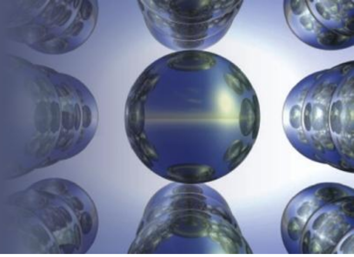
Interactive Example 8.12 - Solution (Continued 2)

- PCl_6^- has 48 valence electrons
  - Since phosphorus is surrounded by six pairs of electrons, an octahedral arrangement is required to minimize repulsions
    - Since each electron pair is shared with a chlorine atom, an octahedral PCl_6^- anion is predicted









Interactive Example 8.13 - Prediction of Molecular Structure III

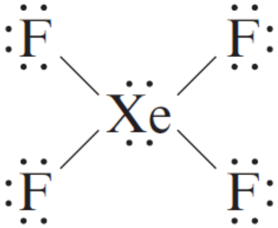
- Because the noble gases have filled *s* and *p* valence orbitals, they were not expected to be chemically reactive
  - For many years these elements were called inert gases because of this supposed inability to form any compounds
- In the early 1960s several compounds of krypton, xenon, and radon were synthesized

Interactive Example 8.13 - Prediction of Molecular Structure III (Continued)

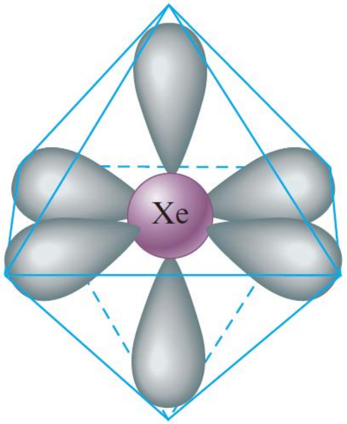
- For example, a team at the Argonne National Laboratory produced the stable colorless compound xenon tetrafluoride (XeF_4)
  - Predict its structure and whether it has a dipole moment

Interactive Example 8.13 - Solution

- The Lewis structure for XeF_4 is:

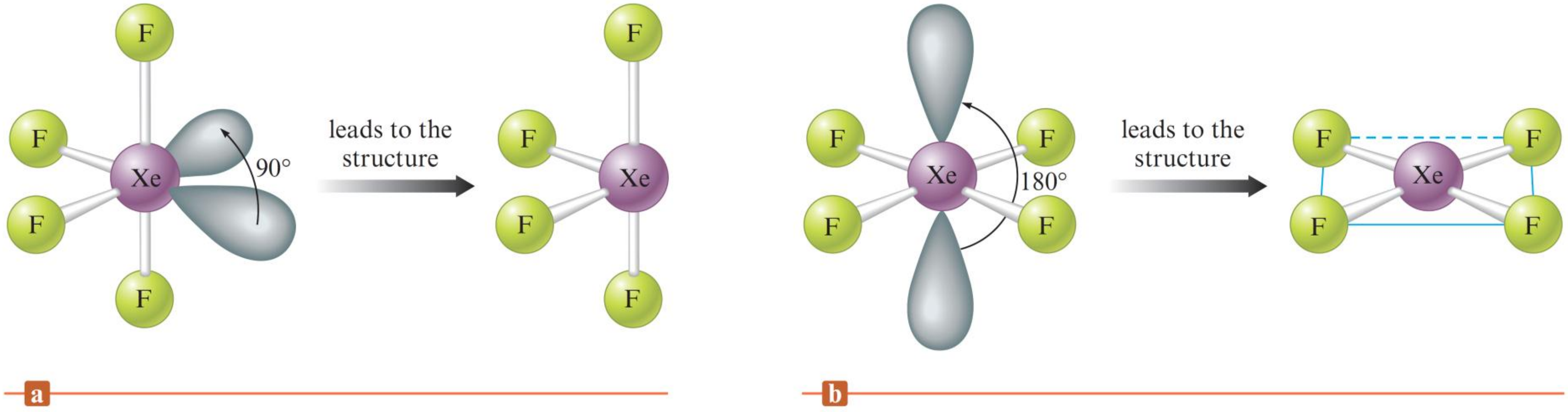


- The xenon atom in this molecule is surrounded by six pairs of electrons, which means an octahedral arrangement



Interactive Example 8.13 - Solution (Continued 1)

- The structure predicted will depend on the arrangement of lone pairs and bonding pairs
  - Consider the following possibilities



Interactive Example 8.13 - Solution (Continued 2)

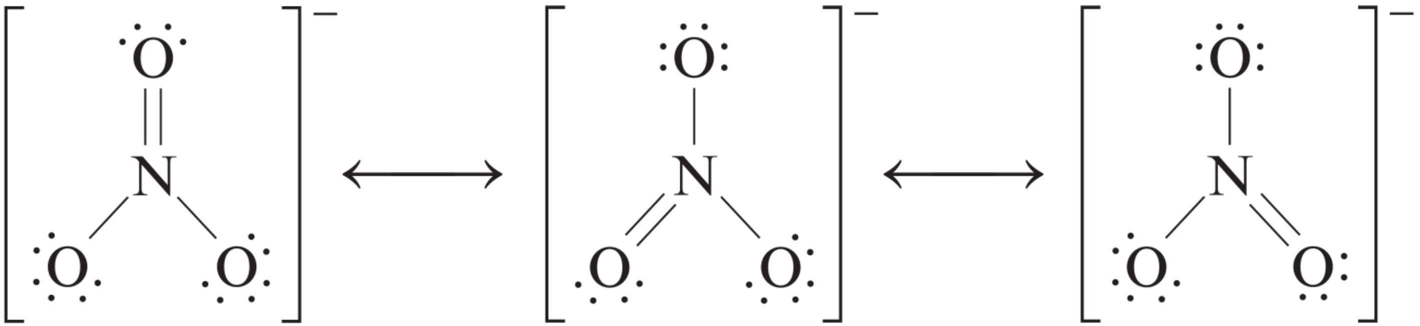
- In the structure in part (a), the lone pair–lone pair angle is 90 degrees
  - Since lone pairs require more room than bonding pairs, this structure is not favourable
- In the structure in part (b), the lone pairs are separated by 180 degrees
  - This structure is preferred
  - Though there is an octahedral arrangement of electron pairs, the atoms form a **square planar structure**

Interactive Example 8.13 - Solution (Continued 3)

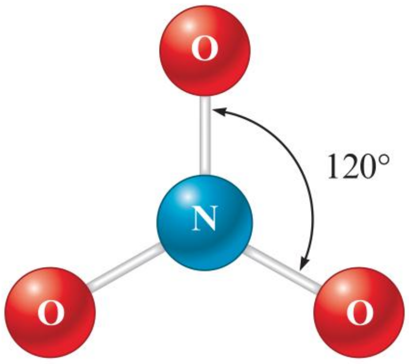
- Although each Xe—F bond is polar (fluorine has a greater electronegativity than xenon), the square planar arrangement of these bonds causes the polarities to cancel
    - XeF_4 has no dipole moment

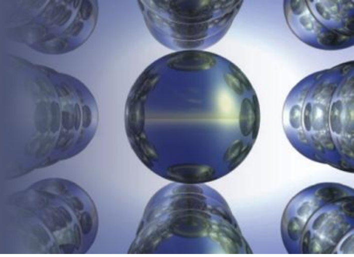
The VSEPR Model and Multiple Bonds

- Consider the NO_3^- ion



  - Planar with 120-degree bond angles





The VSEPR Model and Multiple Bonds (Continued)

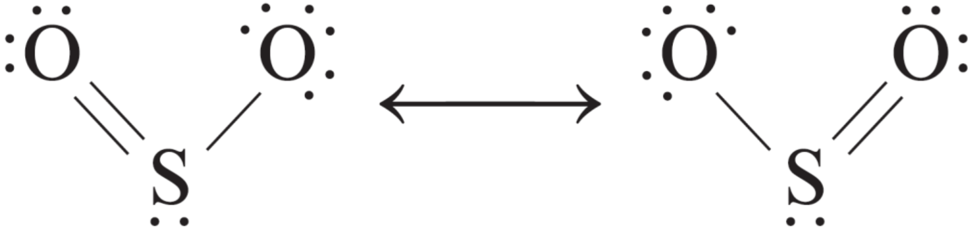
- Rules
  - Multiple bonds count as one effective electron pair
  - When a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular structure using the VSEPR model

Interactive Example 8.14 - Structures of Molecules with Multiple Bonds

- Predict the molecular structure of the sulfur dioxide molecule
    - Is this molecule expected to have a dipole moment?

Interactive Example 8.14 - Solution

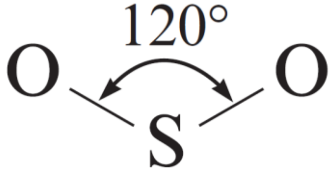
- First, we must determine the Lewis structure for the SO_2 molecule, which has 18 valence electrons
  - Expected resonance structures



- To determine the molecular structure, we must count the electron pairs around the sulfur atom

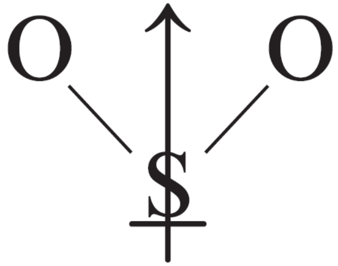
Interactive Example 8.14 - Solution (Continued 1)

- In each resonance structure the sulfur has one lone pair, one pair in a single bond, and one double bond
  - Counting the double bond as one pair yields three effective pairs around the sulfur
  - A trigonal planar arrangement is required, which yields a V-shaped molecule



Interactive Example 8.14 - Solution (Continued 2)

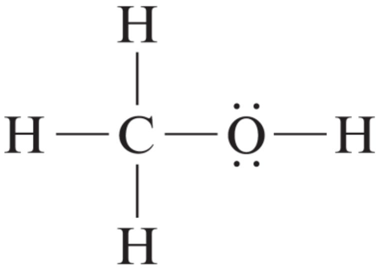
- The structure of the SO_2 molecule is expected to be V-shaped with a 120-degree bond angle
  - The dipole moment of the sulfur dioxide molecule is as depicted below:



    - Since the molecule is V-shaped, the polar bonds do not cancel

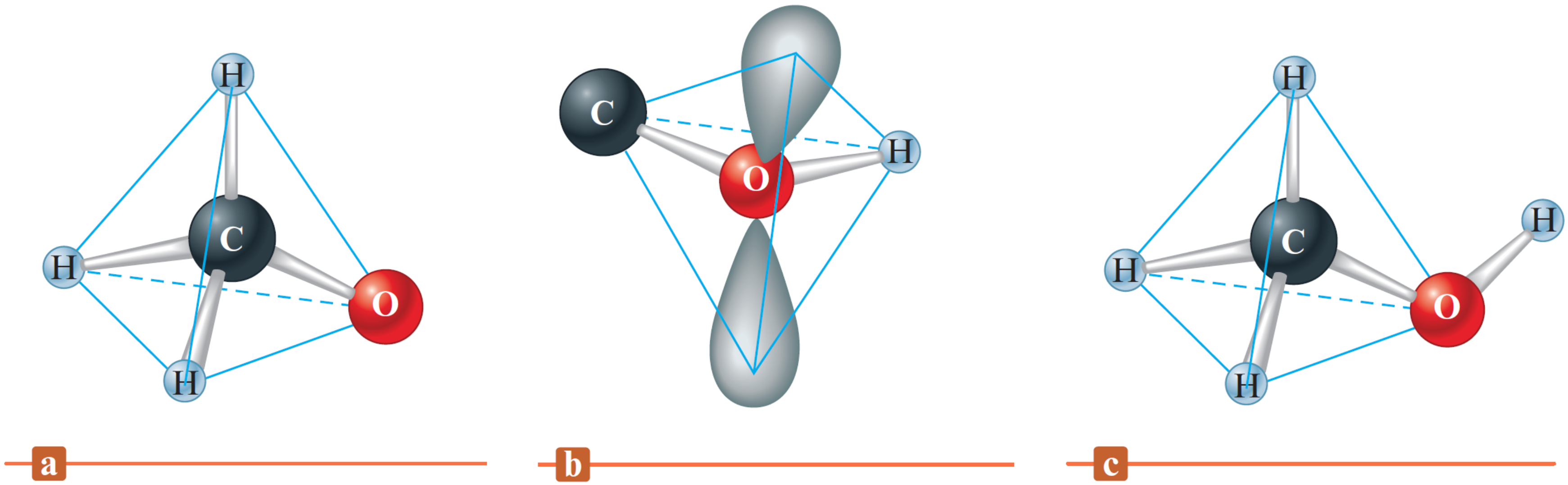
Molecules Containing No Single Atom

- Consider a methanol (CH_3OH) molecule



- The molecular structure can be predicted from the arrangement of pairs around the carbon and oxygen atoms

Figure 8.22 - The Molecular Structure of Methanol



The arrangement of electron pairs and atoms around the carbon atom

The arrangement of bonding and lone pairs around the oxygen atom

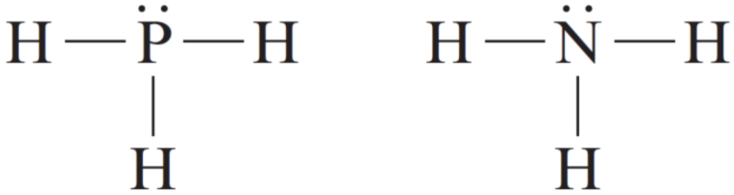
The molecular structure

Advantages of the VSEPR Model

- Correctly predicts the molecular structures of most molecules formed from nonmetallic elements
- Molecules of any size can be treated by applying the VSEPR model to each appropriate atom
    - Can be used to predict the structures molecules with hundreds of atoms

Limitations of the VSEPR Model

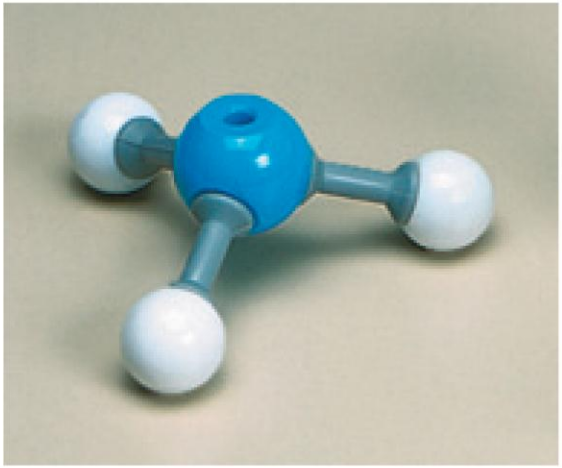
- Does not always predict accurately
    - Example - The structures of phosphine (PH_3) is analogous to that of ammonia (NH_3)



        - The molecular structure of PH_3 would be predicted to be similar to that of NH_3 with bond angles of approximately 107 degrees

Limitations of the VSEPR Model (Continued)

- The bond angles of phosphine are 94 degrees



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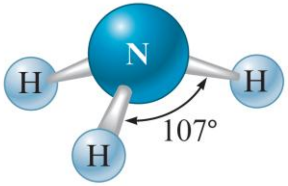
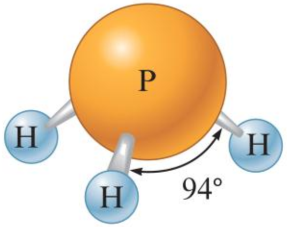


NH_3



PH_3