Chapter 10

The Shapes of Molecules

The Shapes of Molecules

On the Value of Lewis Structures

A Lewis structure is a two-dimensional (2D) representation of a molecule.

Lewis structures are used in conjunction with valence shell electron-pair repulsion (VSEPR) theory to predict the three-dimensional (3D) shapes of molecules.

We first consider Lewis structures for molecules with single bonds (bond order = 1).

Steps to convert a molecular formula into a Lewis structure

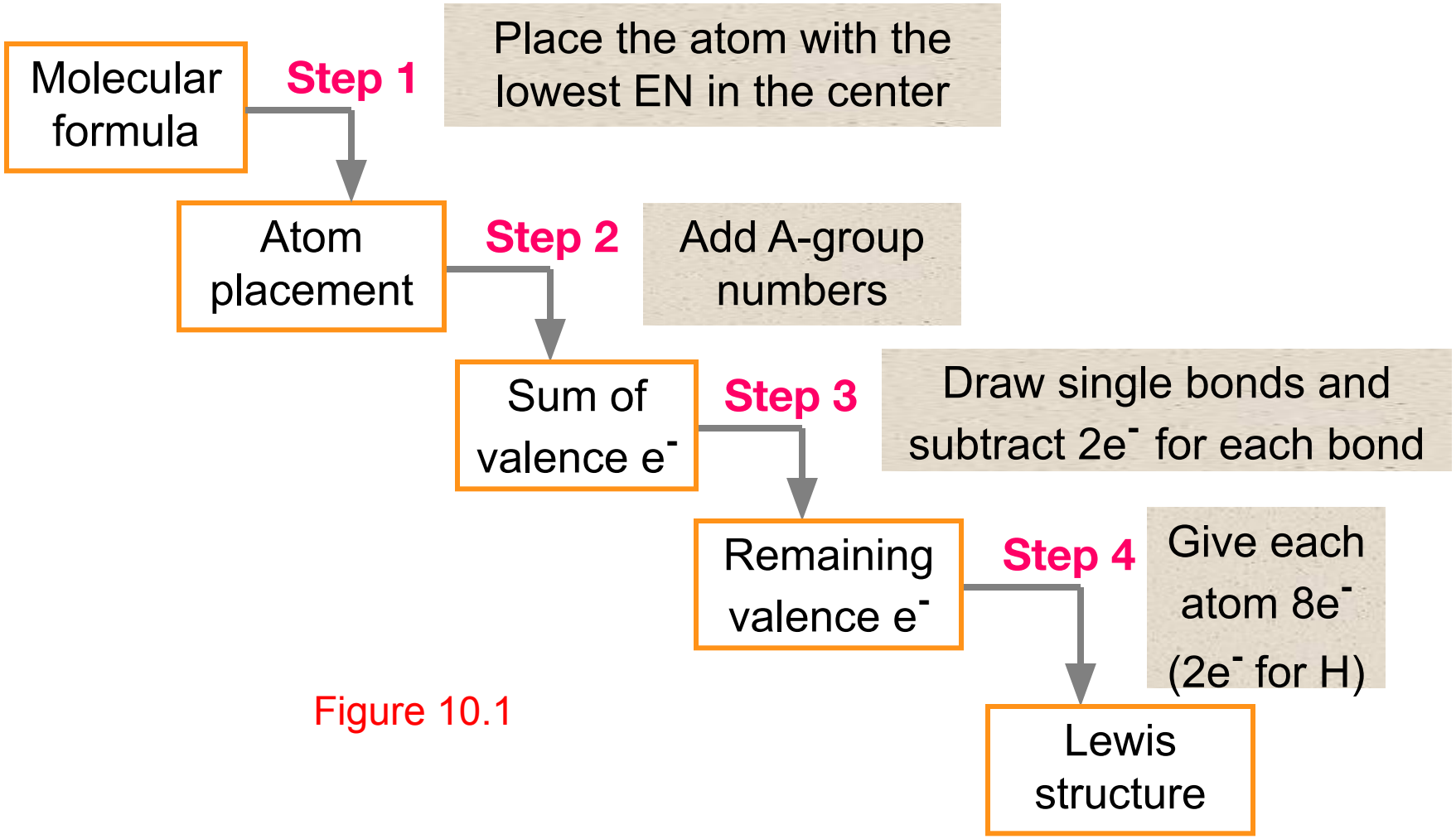


Figure 10.1

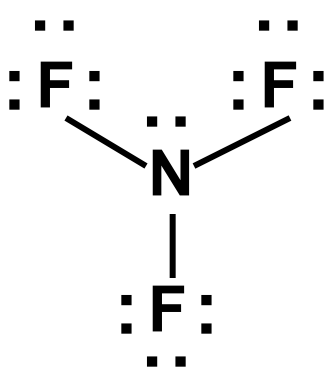
Molecular formula

Atom placement

Sum of valence e^-

Remaining valence e^-

Lewis structure



N is less electronegative than F; N is the central atom

For NF_3

N 5 valence e^-

F 7 e^- x 3 = 21 valence e^-

Total of 26 valence e^-

Three single bonds = 6 e^-

20 remaining valence e^-; 6 e^- on each F, 2 e^- on N (10 lone-pairs of electrons)

SAMPLE PROBLEM 10.1

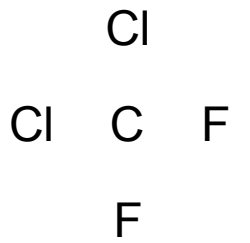
Writing Lewis Structures for Molecules with One Central Atom

PROBLEM: Write a Lewis structure for CCl_2F_2, a compound responsible for the depletion of stratospheric ozone.

PLAN: Follow the steps outlined in Slide 4.

SOLUTION:

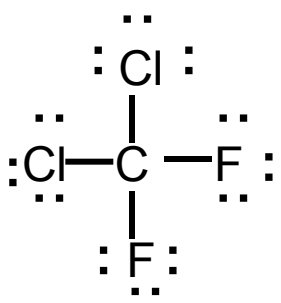
Step 1: Carbon has the lowest EN and is the central atom. The four remaining atoms are placed around it.



Steps 2-4:

C has 4 valence e^-, Cl and F each have 7. The sum is 4 + 4(7) = 32 valence e^-.

Make bonds and fill in the remaining valence electrons, placing $8e^-$ around each atom.



SAMPLE PROBLEM 10.2

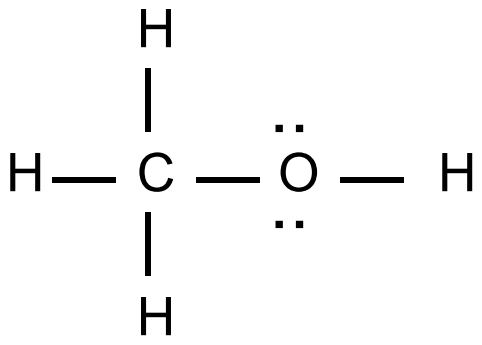
Writing Lewis Structures for Molecules with More than One Central Atom

PROBLEM: Write the Lewis structure for methanol (molecular formula, CH_4O), a compound used as a gasoline additive/alternative in auto engines.

SOLUTION: Hydrogen can have only one bond. Thus, C and O must be next to each other, with H filling in the bonds.

There are 4(1) + 1(4) + 1(6) = 14 valence electrons.

C has 4 bonds and O has 2. O has two pairs of unshared e^-.



Lewis Structures for Molecules with Multiple Bonds

After applying Steps 1-4, there may not be enough electrons for the central atom (or one of the central atoms) to attain an octet. This situation suggests that a multiple bond (bond order of 2 or 3) is present in the molecule.

STEP 5: If, after Step 4, a central atom still does not have an octet, make a multiple bond by changing a lone-pair from one of the surrounding atoms into a bonding pair to the central atom.

SAMPLE PROBLEM 10.3

Writing Lewis Structures for Molecules with Multiple Bonds

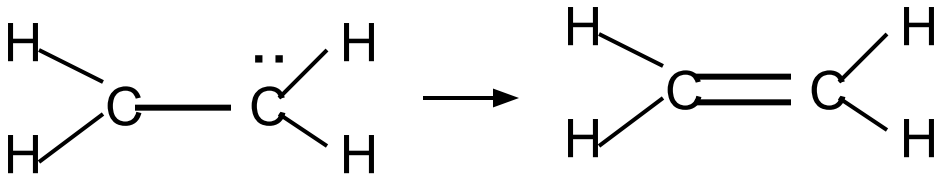
PROBLEM: Write Lewis structures for the following:

(a) Ethylene (C_2H_4), an important reactant in the manufacture of polymers

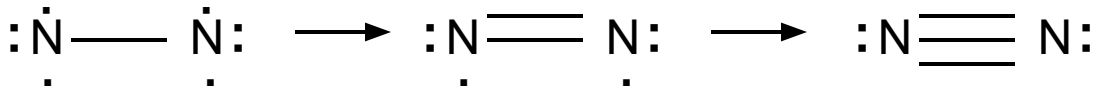
(b) Nitrogen (N_2), the most abundant atmospheric gas

PLAN: For molecules with multiple bonds, **Step 5** follows the other steps in Lewis structure construction. If a central atom does not have 8 e^- (an octet), then electrons can be moved to form a multiple bond.

SOLUTION: **(a)** There are 2(4) + 4(1) = 12 valence electrons. H can have only one bond per atom.

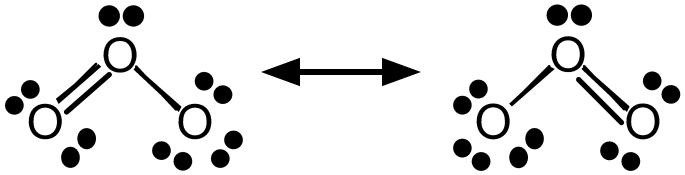


(b) N_2 has 2(5) = 10 valence electrons. Therefore, a triple bond is required to make the octet around each N.

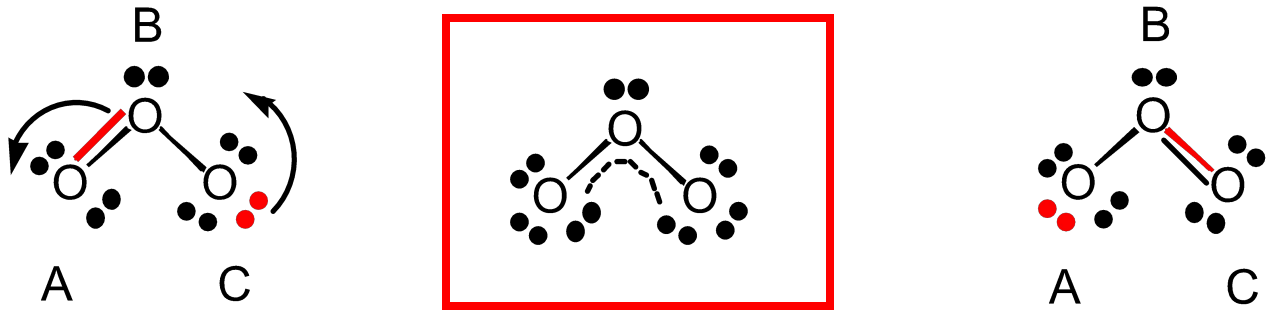


Resonance: Delocalized Electron-Pair Bonding

O_3 can be drawn in two ways:



Neither structure is actually correct but can be redrawn to represent a structure that is a hybrid of the two - a resonance structure.



Resonance structures have the same relative placement of atoms but different locations of bonding and non-bonding electron pairs.

Resonance structures are not real bonding depictions. The actual molecule is a resonance hybrid, an average of the resonance forms.

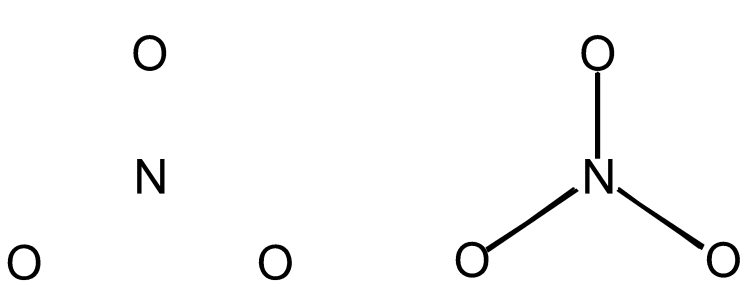
For O_3, two of the electron pairs (one bonding, one non-bonding) are delocalized (*i.e.*, their density is spread over the entire molecule). This effect yields two identical O-O bonds, each consisting of a single bond (localized electron pair) and a partial double bond (from one of the delocalized electron pairs). Resonance effects lead to fractional bond orders.

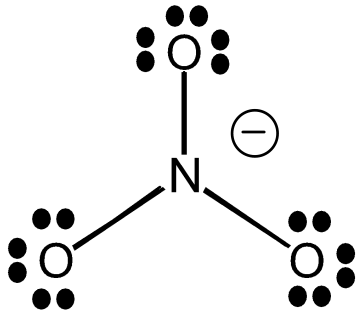
SAMPLE PROBLEM 10.4 **Writing Resonance Structures**

PROBLEM: Write resonance structures for the nitrate anion, NO_3^-.

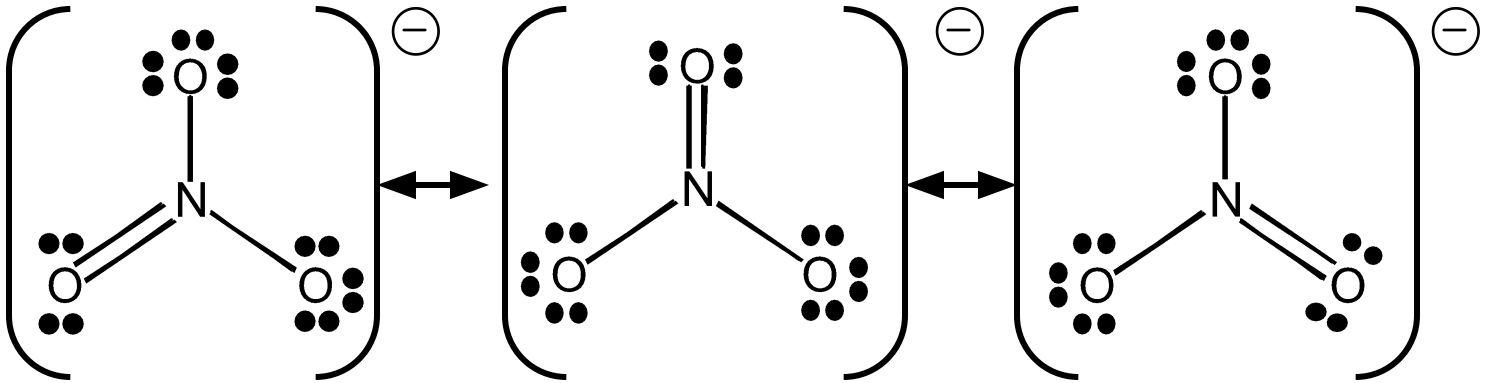
PLAN: After Steps 1-4, apply Step 5. Then determine if other structures can be drawn in which the electrons can be delocalized over more than two atoms.

SOLUTION: Nitrate has 1(5) + 3(6) + 1 = 24 valence electrons.





N does not have an octet; a pair of e^- is used to form a double bond.



When two or more unsymmetrical resonance forms exist: How do you determine which form exerts the most influence on the resonance hybrid?

Because the resonance hybrid is an average of the resonance forms, one form may contribute more than the others and "weight" the average in its favor.

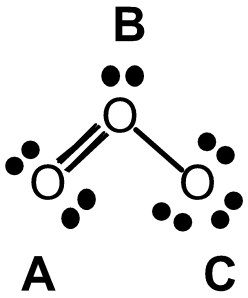
Calculating formal charge in resonance forms

Formal Charge: Selecting the Best Resonance Structure

An atom "owns" all of its non-bonding electrons and half of its bonding electrons.

Formal charge of atom =

 # valence e^- - (# unshared electrons + 1/2 # shared electrons)



For O_A

valence e^- = 6

non-bonding e^- = 4

bonding e^- = 4 x 1/2 = 2

Formal charge = 0

For O_B

valence e^- = 6

non-bonding e^- = 2

bonding e^- = 6 x 1/2 = 3

Formal charge = +1

For O_C

valence e^- = 6

non-bonding e^- = 6

bonding e^- = 2 x 1/2 = 1

Formal charge = -1

Resonance (continued)

Three criteria for choosing the more important resonance structure are:

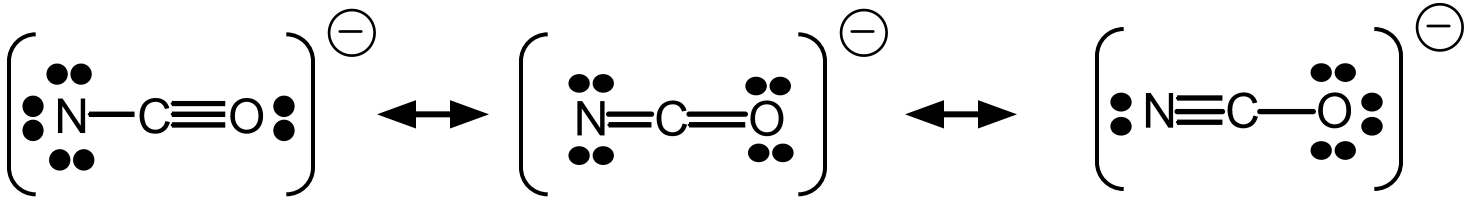
Smaller formal charges (either positive or negative) are preferable to larger formal charges.

Avoid like charges (+ + or - -) on adjacent atoms.

A more negative formal charge should reside on an atom with a larger EN value.

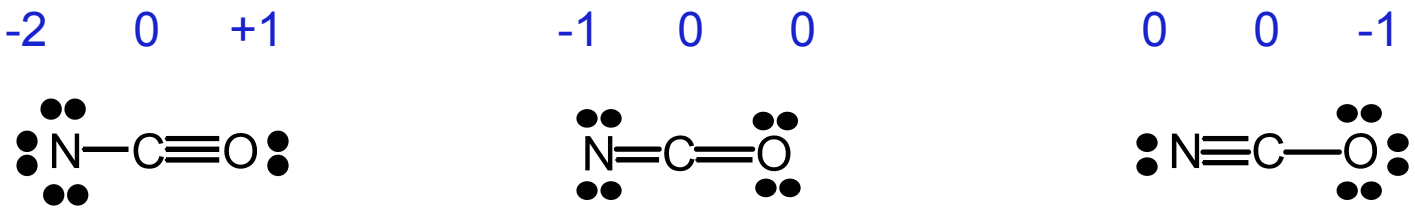
Resonance (continued)

EXAMPLE: NCO^- has three possible resonance forms.



A **B** **C**

Formal charges:



Forms B and C have negative formal charges on N and O. These forms are more important than Form A.

Form C has a negative charge on O which is more electronegative than N. Therefore, Form C contributes the most to the resonance hybrid.

Lewis Structures for Exceptions to the Octet Rule

(a) Electron-Deficient Molecules: gaseous molecules containing either Be or B as the central atom; have fewer than 8 electrons around the Be or B (4 e^- around Be and 6 e^- around B) (BF_3).

(b) Odd-Electron Molecules: have an odd number of valence electrons; examples include free radicals, which contain a lone (unpaired) electron and are paramagnetic (use formal charges to locate the lone electron) (NO_2).

(c) Expanded Valence Shells: for molecules that have more than 8 electrons around the central atom; use empty outer *d* orbitals; occurs only with a central atom from Period 3 or higher (SF_6, PCl_5).

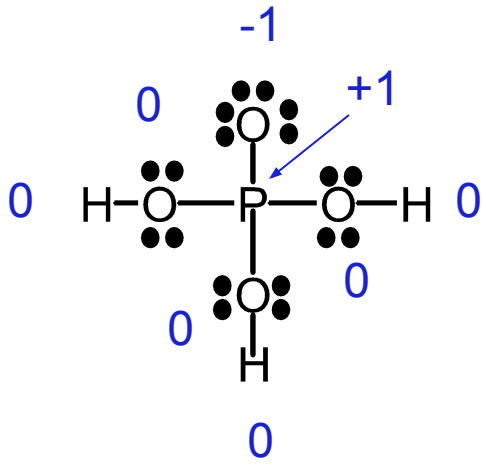
SAMPLE PROBLEM 10.5

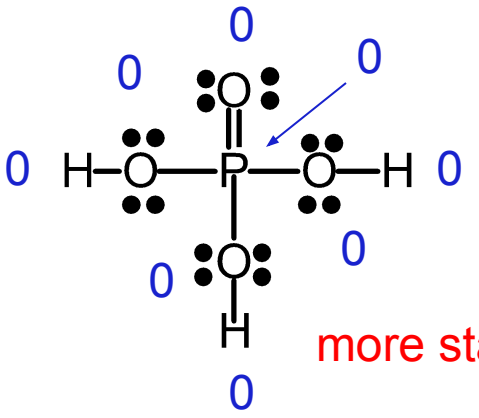
Writing Lewis Structures for Exceptions to the Octet Rule

PROBLEM: Write Lewis structures for (a) H_3PO_4 and (b) $BFCl_2$. In (a), decide on the most likely structure.

PLAN: Draw the Lewis structures for the molecule and determine if there is an element that is an exception to the "octet rule". Note that (a) contains P which is a Period-3 element and can have an expanded valence shell.

SOLUTION: **(a)** H_3PO_4 has two resonance forms, and formal charges indicate the more important form.

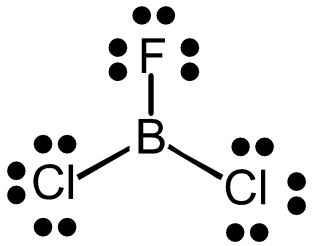




more stable

lower formal charges

(b) $BFCl_2$ has only one Lewis structure.



Heats of Reactions from Lewis Structures and Bond Energies

Procedure

(1) Break all bonds found in the reactants to give free atoms

(2) Reform new bonds to the free atoms to give the products

Using bond energies to calculate ΔH°_{rxn}

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

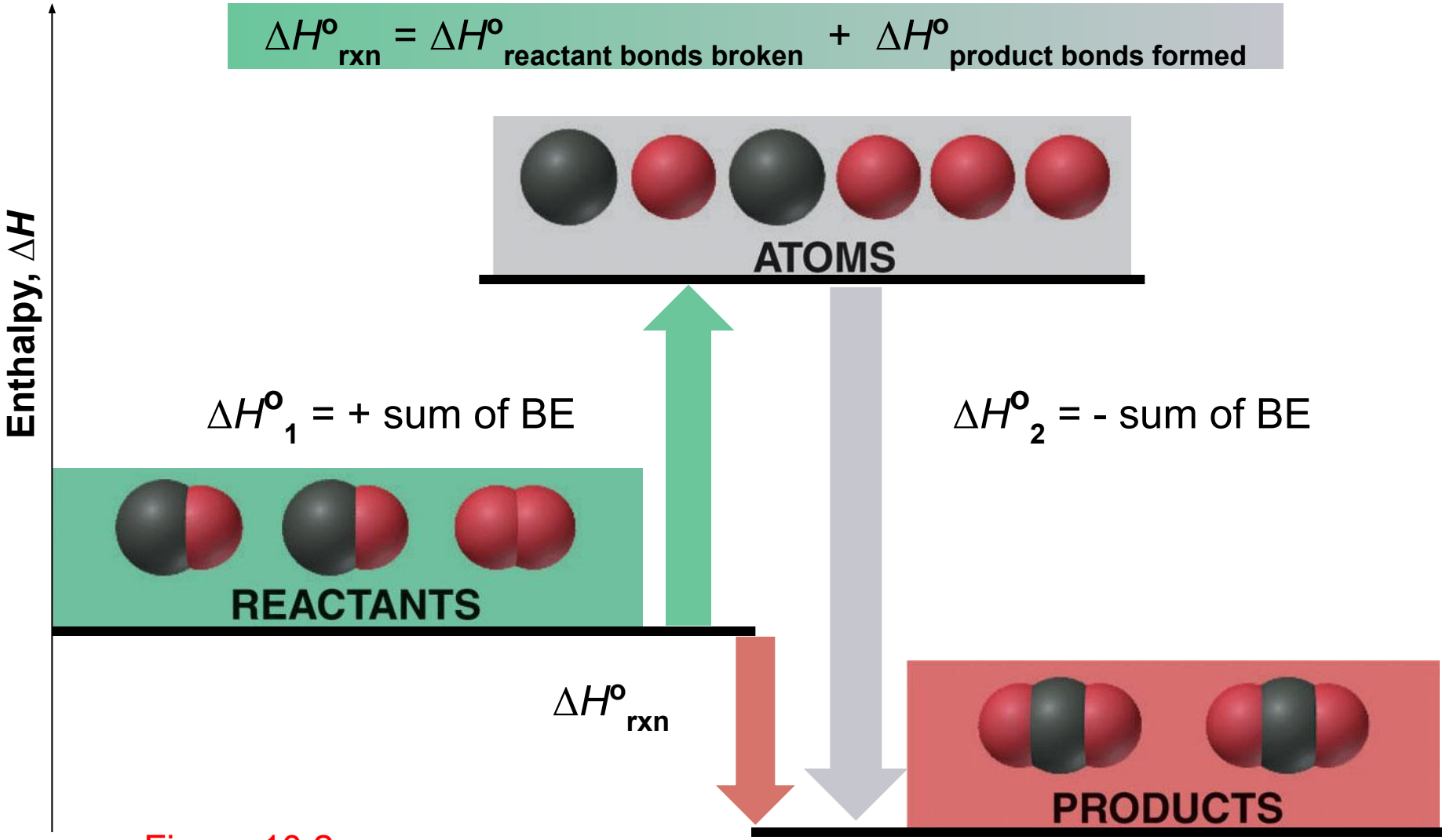


Figure 10.2

Using bond energies to calculate ΔH°_{rxn} of methane combustion

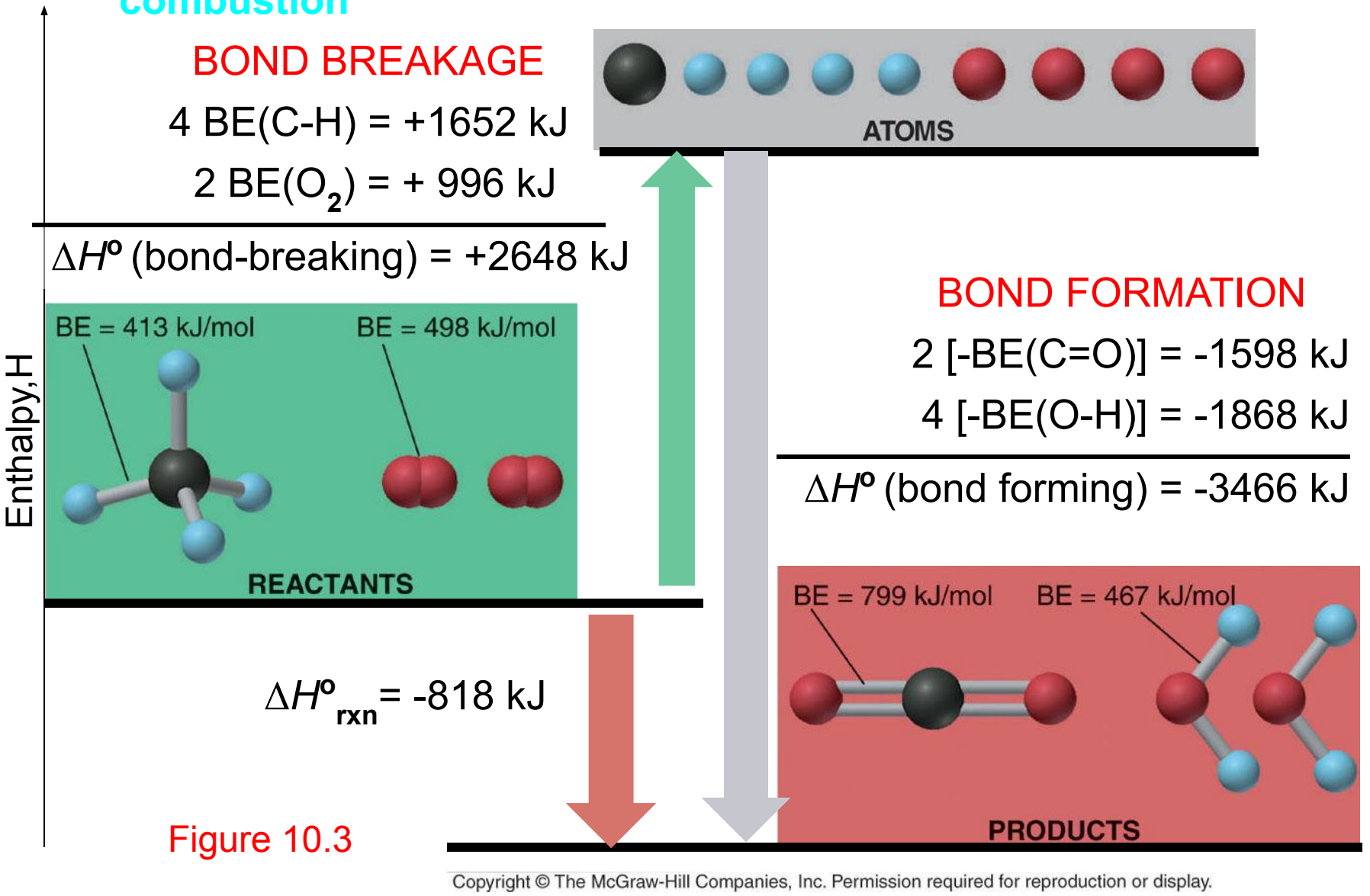


Figure 10.3

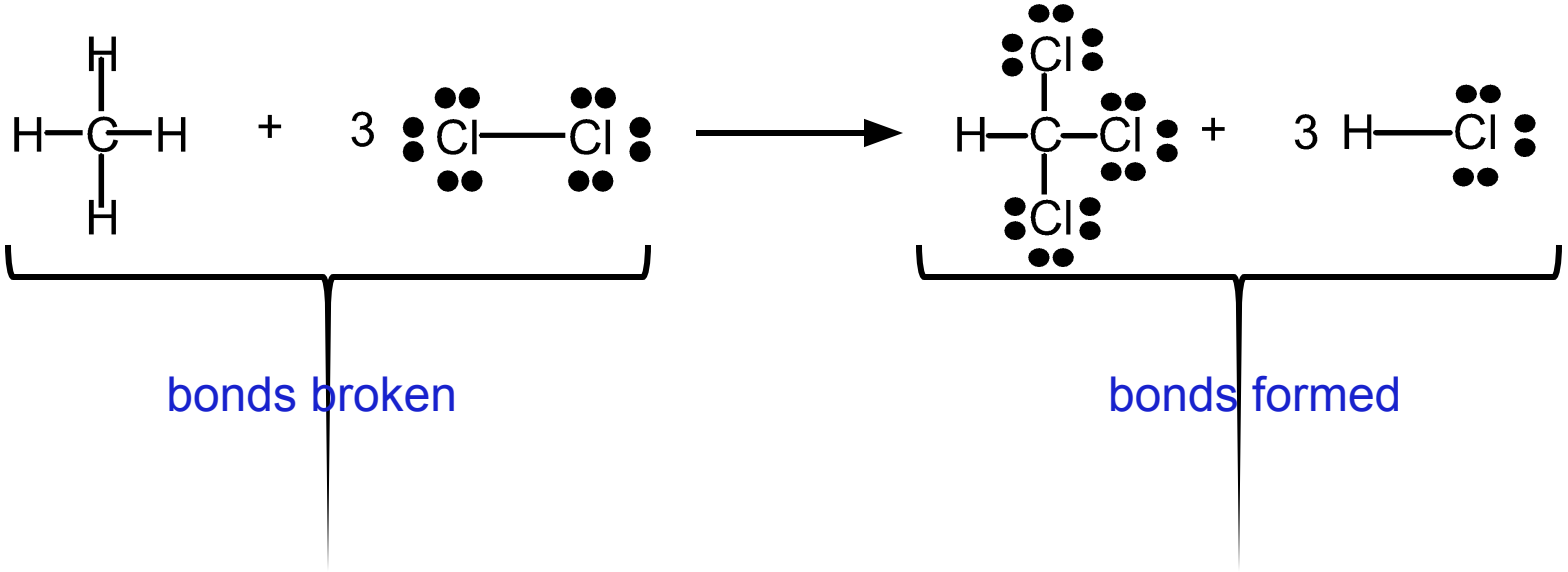
SAMPLE PROBLEM 10.6 **Calculating Enthalpy Changes from Bond Energies**

PROBLEM: Calculate ΔH^{o}_{rxn} for the following reaction:

$$CH_4(g) + 3Cl_2(g) \longrightarrow CHCl_3(g) + 3HCl(g)$$

PLAN: Write the Lewis structures of all reactants and products and calculate the number of bonds broken and formed.

SOLUTION:



SAMPLE PROBLEM 10.6 (continued)

bonds broken

4 C-H = 4 mol (413 kJ/mol) = 1652 kJ

3 Cl-Cl = 3 mol (243 kJ/mol) = 729 kJ

$\Delta H^{o}_{\text{bonds broken}}$ = 2381 kJ

bonds formed

3 C-Cl = 3 mol (-339 kJ/mol) = -1017 kJ

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

3 H-Cl = 3 mol (-427 kJ/mol) = -1281 kJ

$\Delta H^{o}_{\text{bonds formed}}$ = -2711 kJ

$\Delta H^{o}_{\text{reaction}} = \Delta H^{o}_{\text{bonds broken}} + \Delta H^{o}_{\text{bonds formed}}$ = 2381 kJ + (-2711 kJ) = - 330 kJ

Valence-shell Electron-Pair Repulsion (VSEPR) Theory

A method to predict the shapes of molecules from their electronic structures (*Lewis structures do not depict shape*)

Basic principle: each group of valence electrons around a central atom is located as far away as possible from the others in order to minimize repulsions

Both bonding and non-bonding valence electrons around the central atom are considered.

AX_mE_n symbolism: A = central atom, X = surrounding atoms, E = non-bonding electrons (usually a lone pair)

A balloon analogy for the mutual repulsion of electron groups

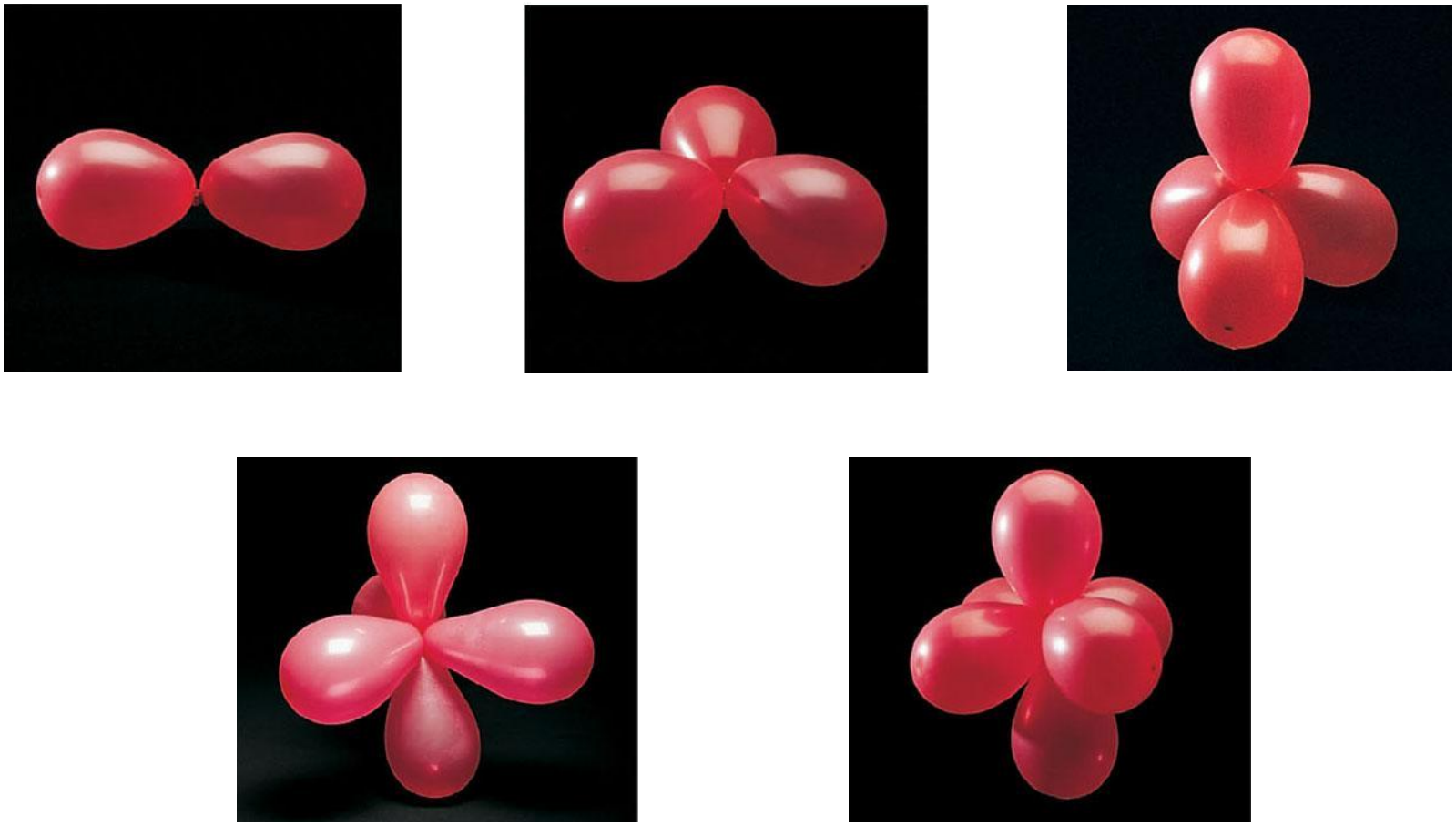


Figure 10.4

Electron-group repulsions and the five basic molecular shapes

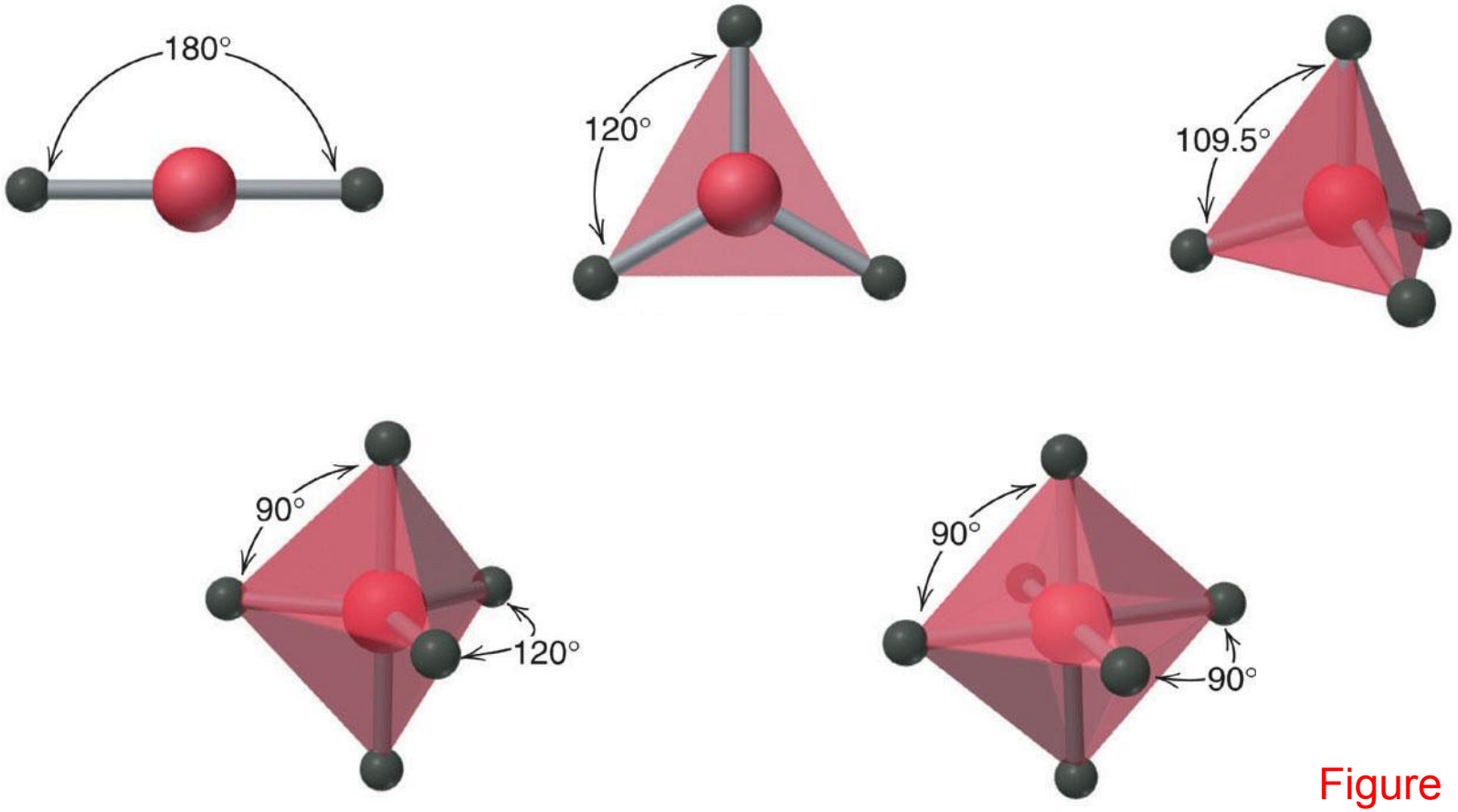
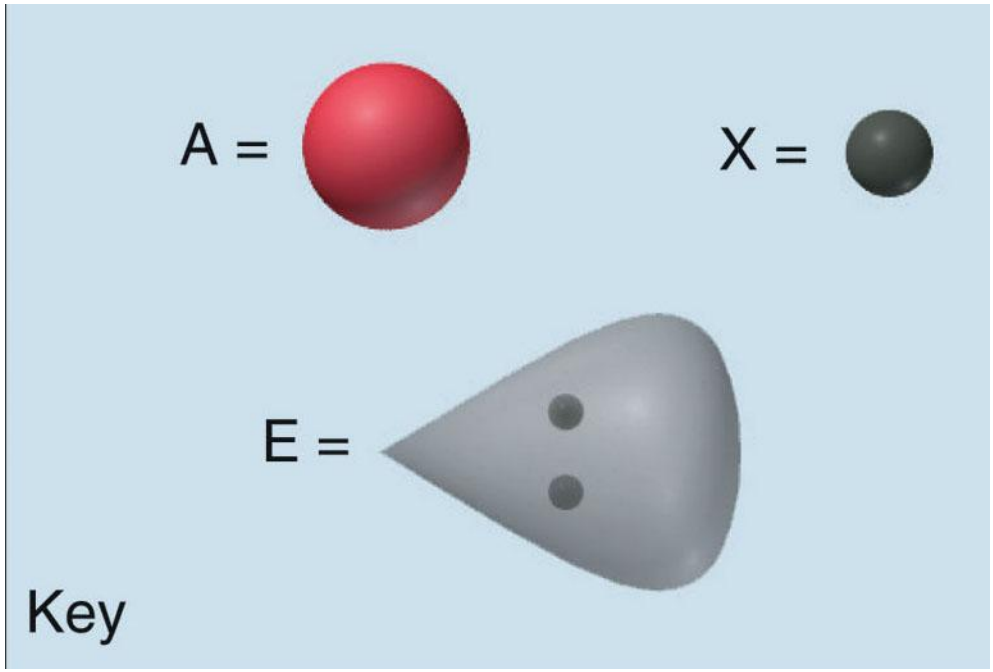
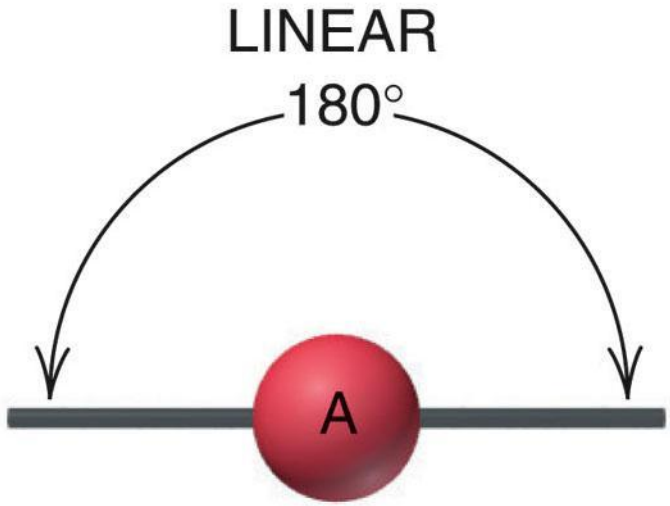


Figure 10.5

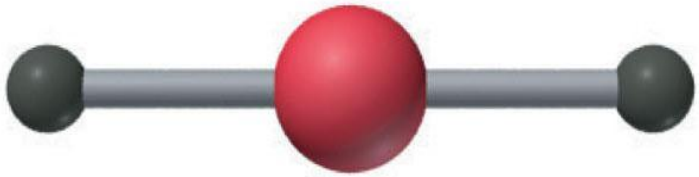
Ideal bond angles are shown for each shape.

The single molecular shape of the linear electron-group arrangement





AX_2



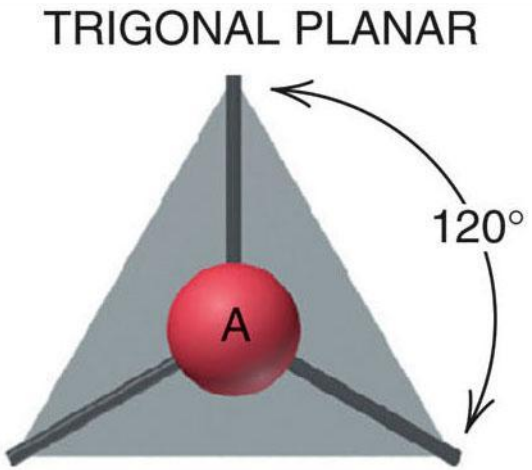
Linear

Examples:

CS_2, HCN, BeF_2

Figure 10.6

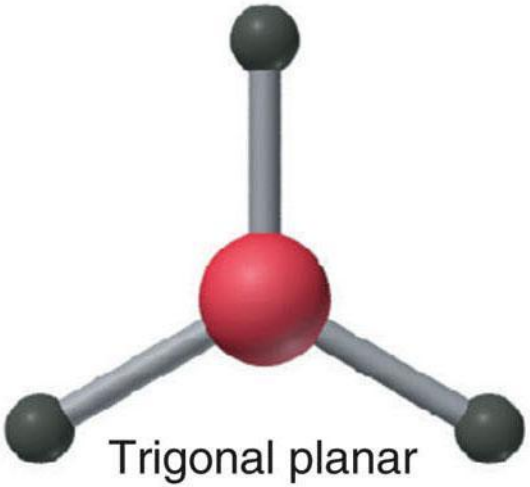
The two molecular shapes of the trigonal planar electron-group arrangement



Class

↓

AX_3

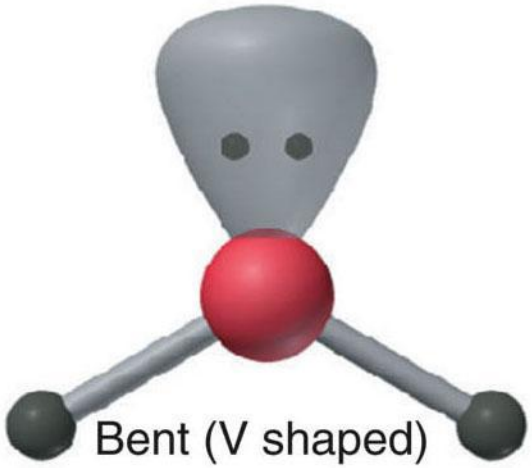


Shape

Examples:

SO_2, O_3, $PbCl_2$, $SnBr_2$

AX_2E



Examples:

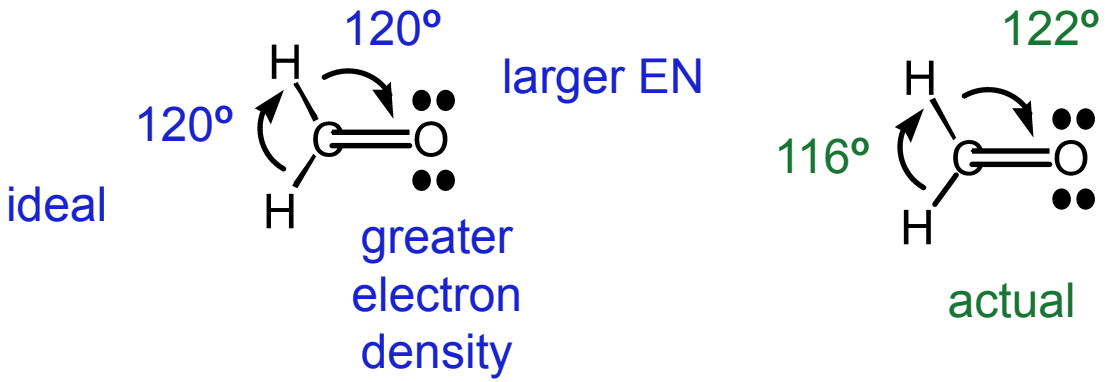
SO_3, BF_3, NO_3^-, CO_3^{2-}

Figure 10.7

Factors Affecting Actual Bond Angles

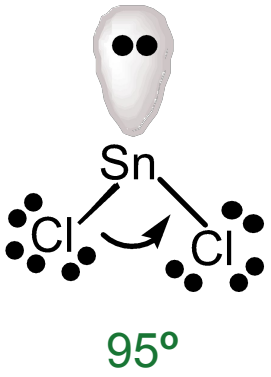
Observed bond angles are consistent with theoretical angles when (a) the atoms attached to the central atom are the same and (b) when all electrons are bonding electrons of the same order.

Effect of Double Bonds

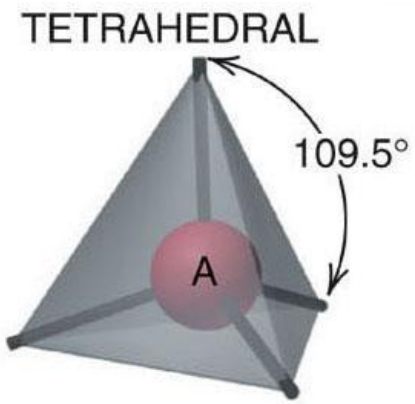


Effect of Non-bonding Pairs

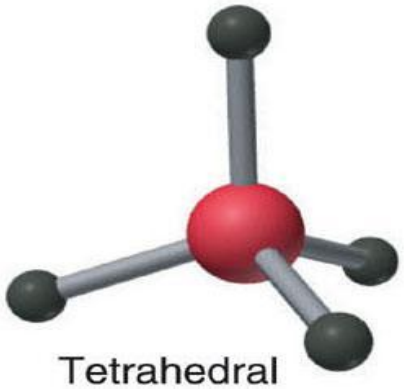
Lone pairs (unshared electron pairs) repel bonding pairs more strongly than bonding pairs repel each other.



The three molecular shapes of the tetrahedral electron-group arrangement



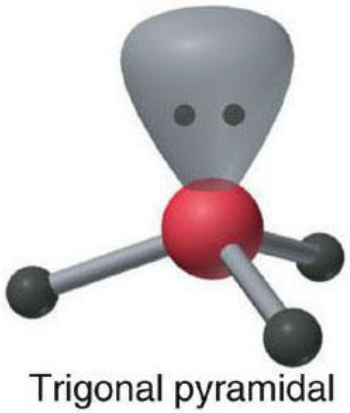
AX_4



Examples:

CH_4, $SiCl_4$, SO_4^{2-}, ClO_4^-

AX_3E



Examples:

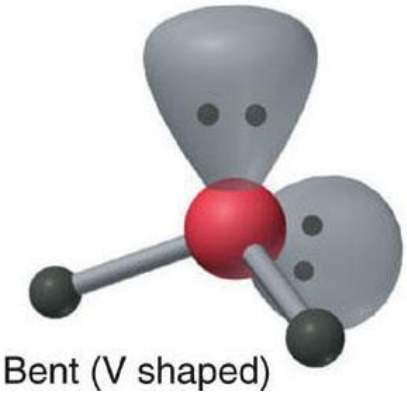
NH_3

PF_3

ClO_3

H_3O^+

AX_2E_2



Examples:

H_2O

OF_2

SCl_2

Figure 10.8

Lewis structures and molecular shapes

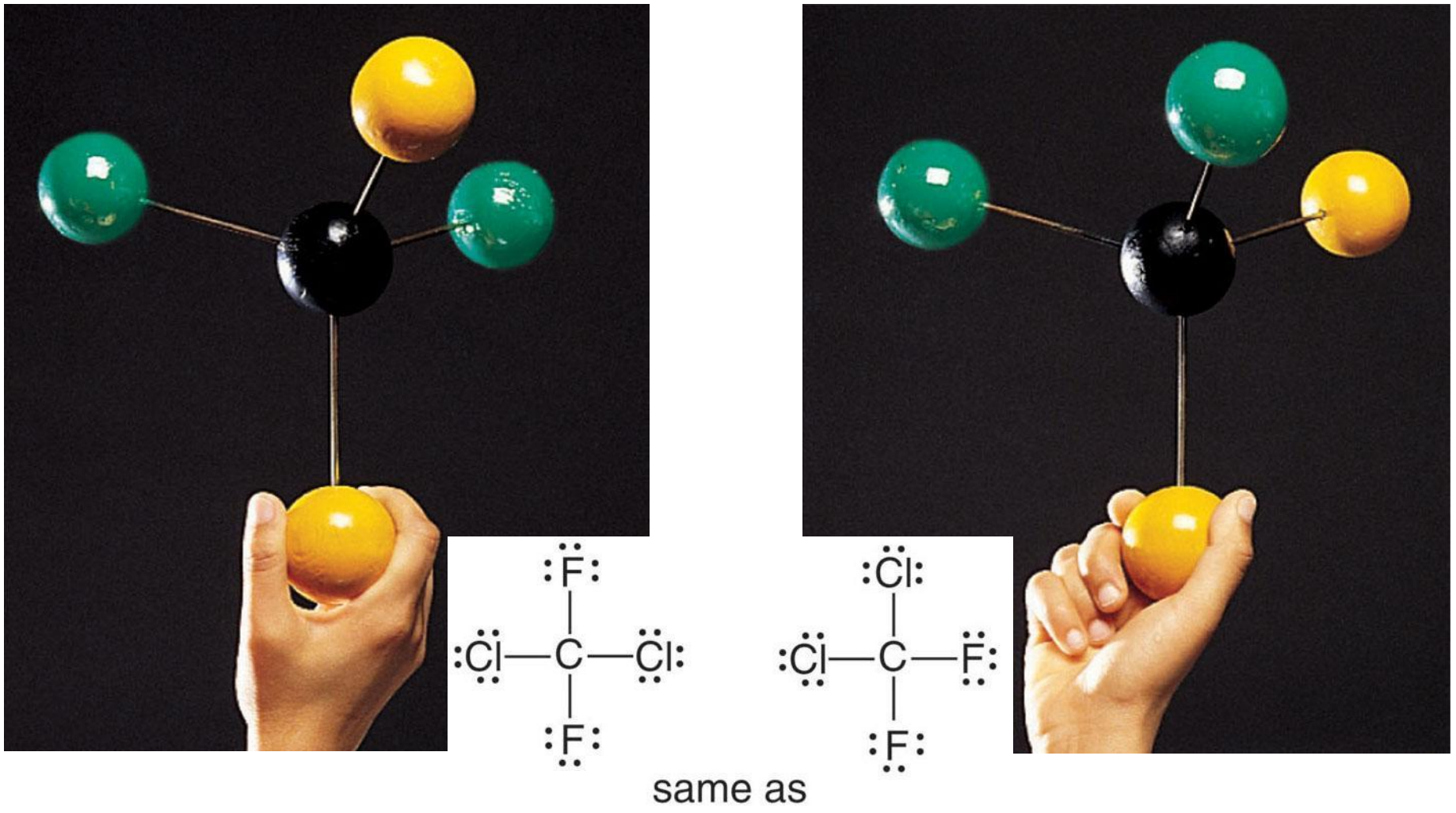
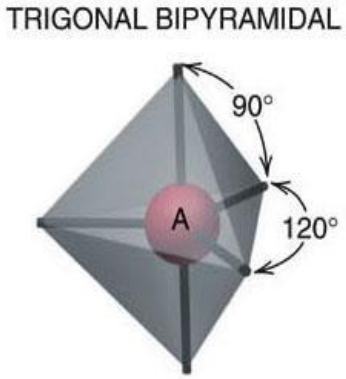
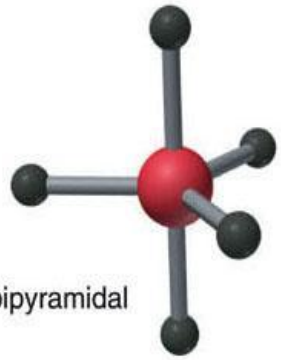


Figure 10.9

The four molecular shapes of the trigonal bipyramidal electron-group arrangement



AX_5



Trigonal bipyramidal

Examples:

PF_5

AsF_5

SOF_4

AX_4E

Seesaw

Examples:

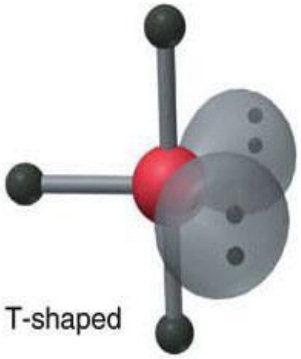
SF_4

XeO_2F_2

IF_4^+

$IO_2F_2^-$

AX_3E_2



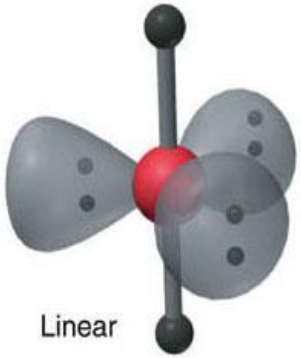
T-shaped

Examples:

ClF_3

BrF_3

AX_2E_3



Linear

Examples:

XeF_2

I_3^-

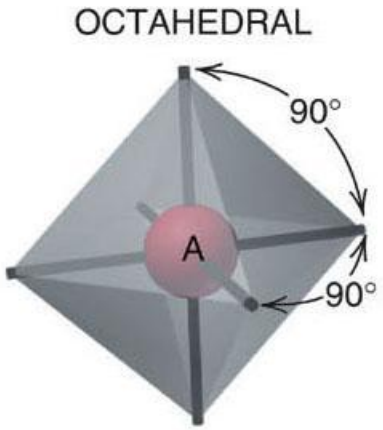
IF_2^-

Figure 10.10

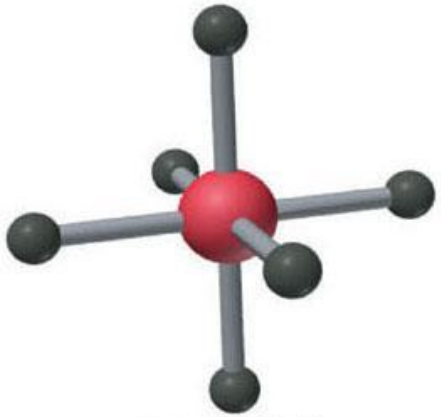
General trend for electron-pair repulsions for similar molecules with a given electron-group arrangement:

Lone pair - lone pair > lone pair - bonding pair > bonding pair - bonding pair

The three molecular shapes of the octahedral electron-group arrangement



AX_6



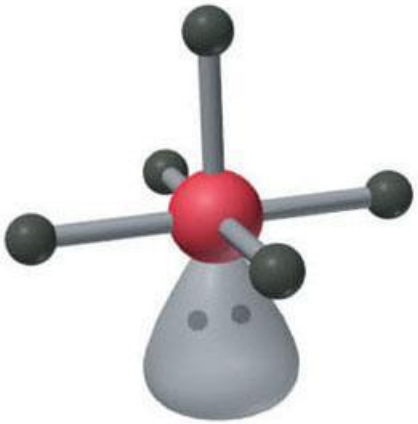
Octahedral

Examples:

SF_6

IOF_5

AX_5E



Square pyramidal

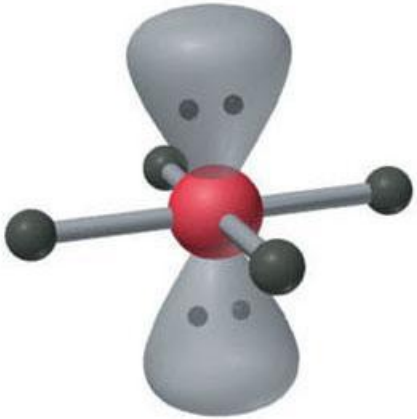
Examples:

BrF_5

TeF_5^-

$XeOF_4$

AX_4E_2



Square planar

Examples:

XeF_4

ICl_4^-

Figure 10.11

The steps in determining a molecular shape

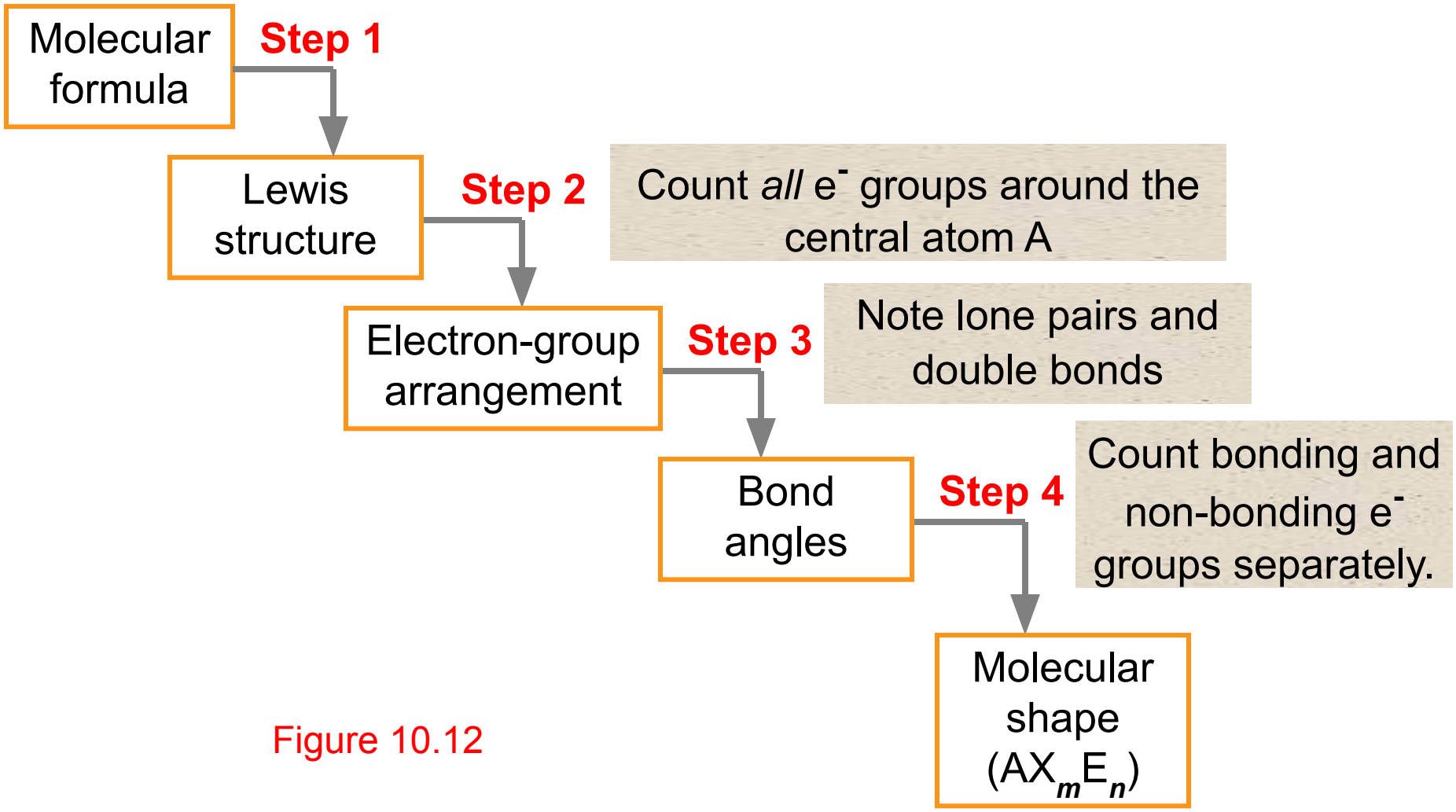


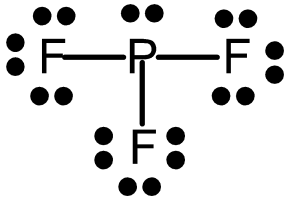
Figure 10.12

SAMPLE PROBLEM 10.7

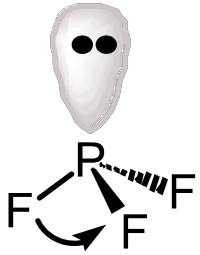
Predicting Molecular Shapes with Two, Three, or Four Electron Groups

PROBLEM: Draw the molecular shape and predict the bond angles (relative to the ideal bond angles) of (a) PF_3 and (b) $COCl_2$.

SOLUTION: **(a)** For PF_3, there are 26 valence electrons and 1 non-bonding pair.



The shape is based on the tetrahedral arrangement.



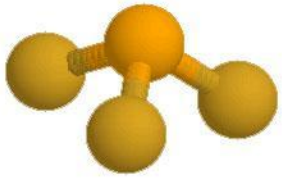
< 109.5°

The F-P-F bond angles should be < 109.5° due to the repulsion of the non-bonding electron pair.

The final shape is trigonal pyramidal.

The type of shape is:

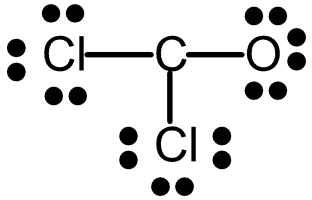
AX_3E



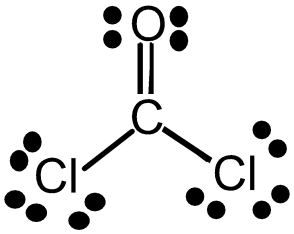
SAMPLE PROBLEM 10.7 (continued)

(b) For $COCl_2$, C has the lowest EN and will be the center atom.

There are 24 valence e^-, with 3 atoms attached to the center atom.



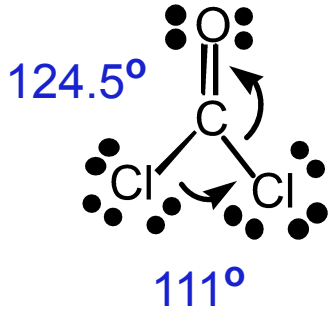
C does not have an octet; a pair of non-bonding electrons will move in from the O to produce a double bond.

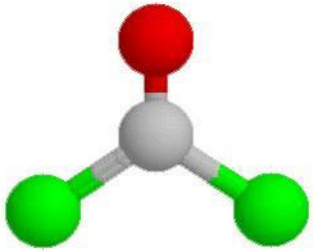


The shape for an atom with three atom attachments and no non-bonding pairs on the central atom is trigonal planar.

Type **AX_3**

The Cl-C-Cl bond angle will be less than 120° due to the electron density of the C=O.



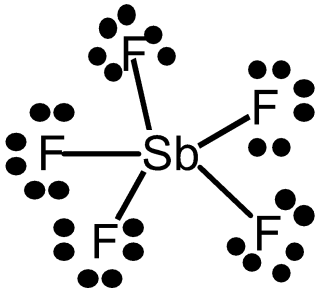


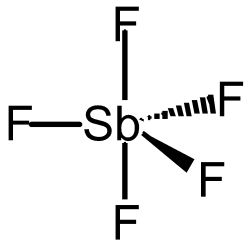
SAMPLE PROBLEM 10.8

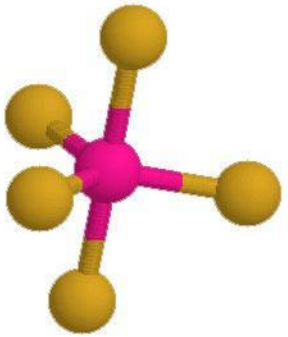
Predicting Molecular Shapes with Five or Six Electron Groups

PROBLEM: Determine the molecular shape and predict the bond angles (relative to the ideal bond angles) of (a) SbF_5 and (b) BrF_5.

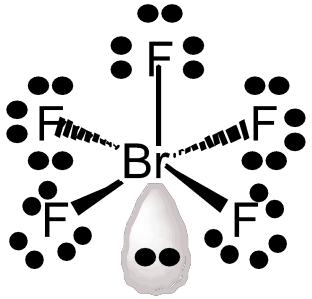
SOLUTION: **(a)** SbF_5 - 40 valence e^-; all electrons around the central atom will be in bonding pairs; shape is AX_5 - trigonal bipyramidal.







(b) BrF_5 - 42 valence e^-; 5 bonding pairs and 1 non-bonding pair on the central atom. Shape is AX_5E, square pyramidal.

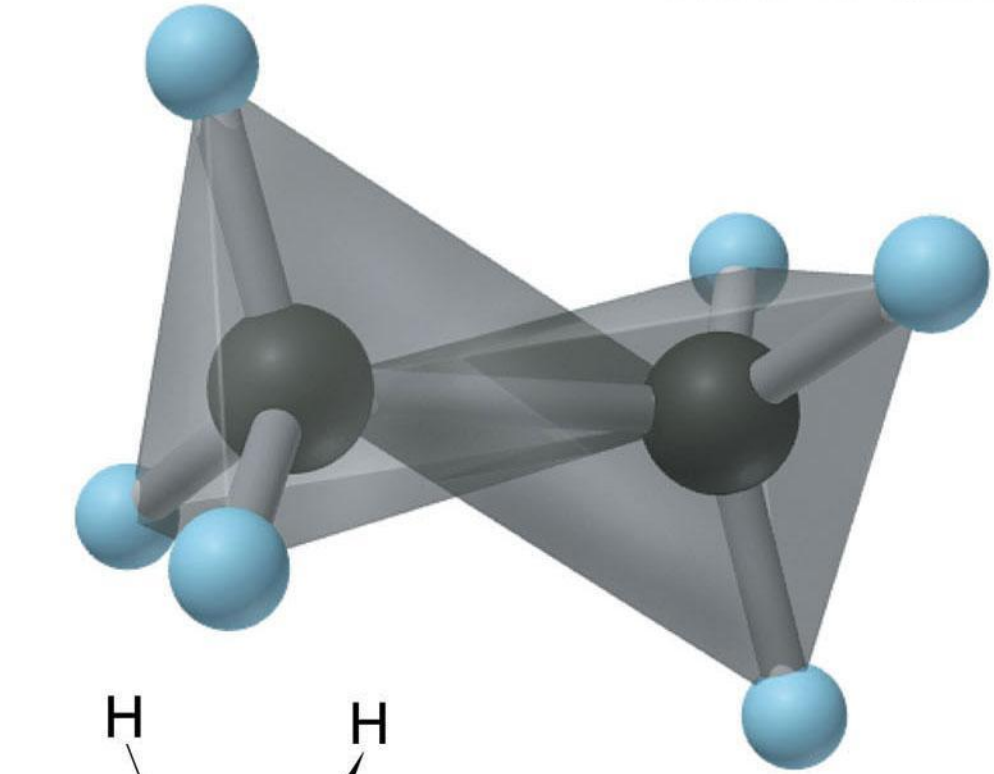


Molecular Shapes With More Than One Central Atom

Combinations of the molecular shapes observed when a single central atom is present

Examples: CH_3-CH_3 (ethane) and CH_3CH_2OH (ethanol)

The tetrahedral centers of ethane



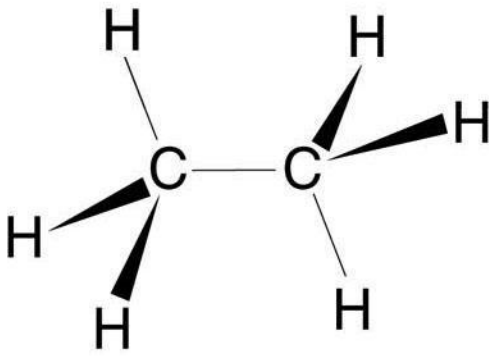


Figure 10.13

The tetrahedral centers of ethanol

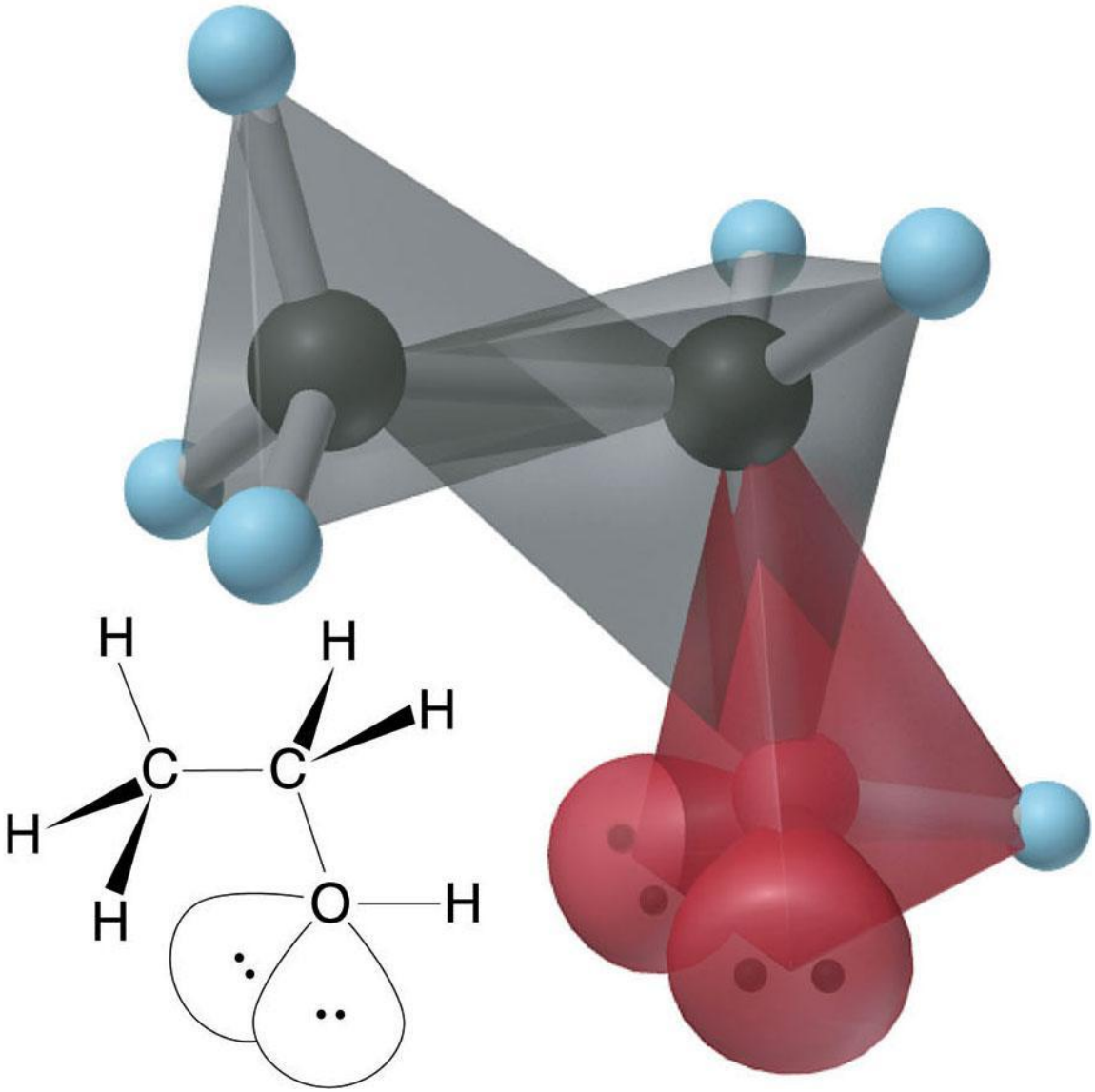


Figure 10.13

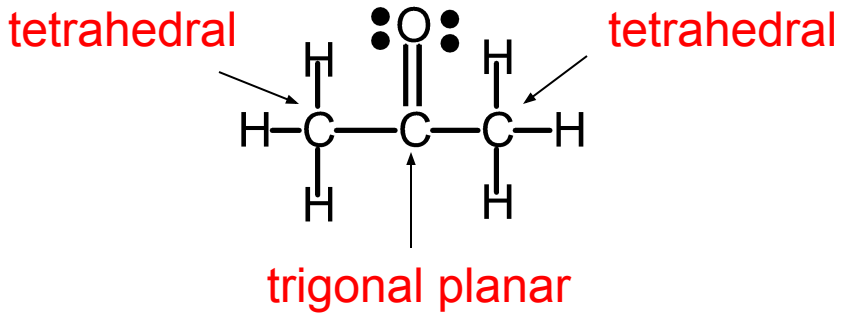
SAMPLE PROBLEM 10.9

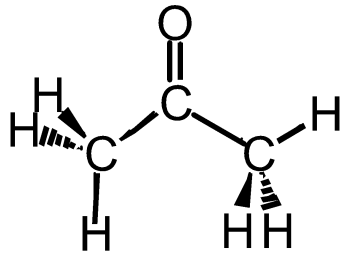
Predicting Molecular Shapes with More Than One Central Atom

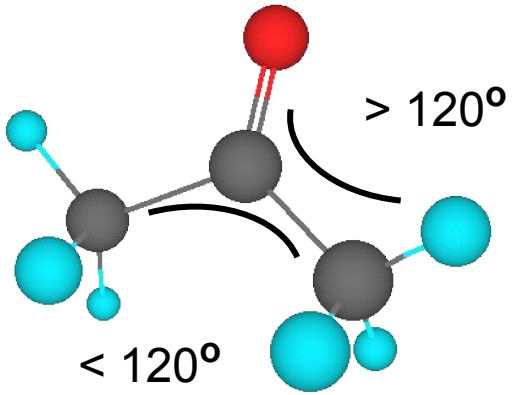
PROBLEM: Determine the shape around each of the central atoms in acetone, $(CH_3)_2C{=}O$.

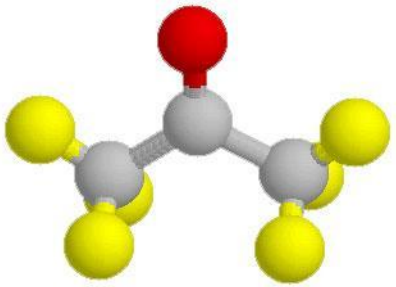
PLAN: Find the shape of one atom at a time after writing the Lewis structure.

SOLUTION:







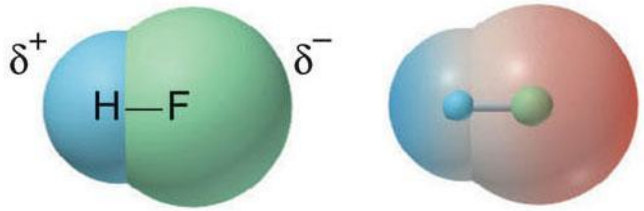


Molecular Polarity

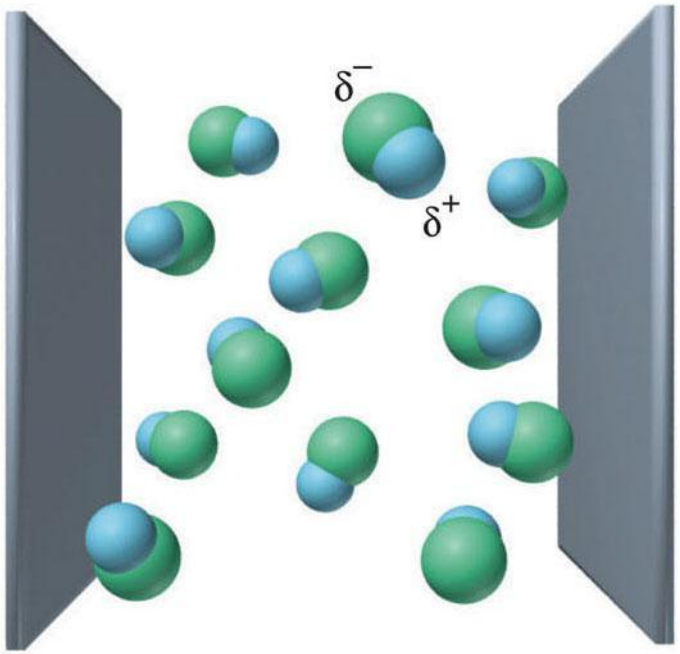
Both **shape** and **bond polarity** determine molecular polarity.

Dipole moment (μ) = the product of the partial charges caused by polar bonds and the distances between them; *debye* (D) units,

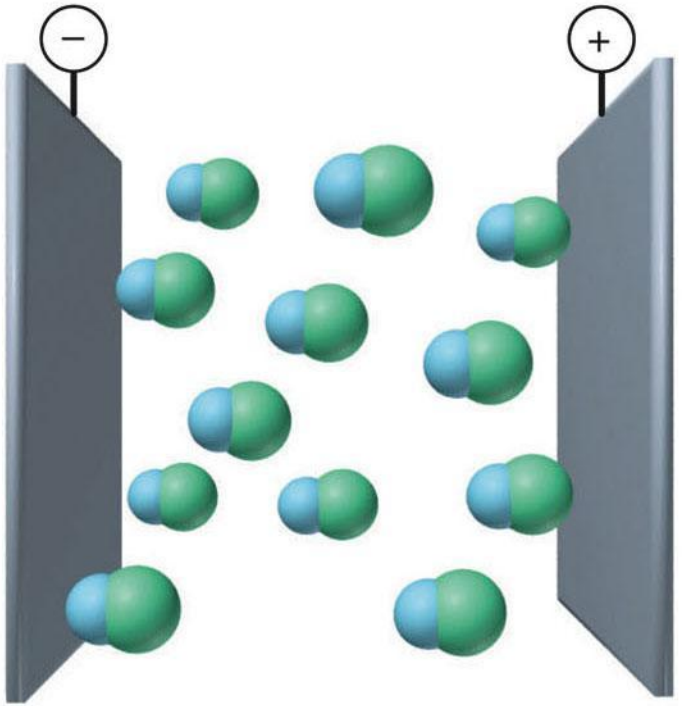
where 1 D = 3.34×10^{-30} coulomb $\cdot$ meter



The orientation of polar molecules in an electric field



Electric field OFF



Electric field ON

Figure 10.14

SAMPLE PROBLEM 10.10 **Predicting the Polarity of Molecules**

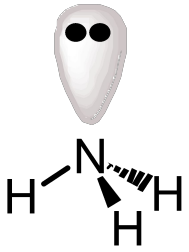
PROBLEM: From electronegativity (EN) values and their periodic trends, predict whether each of the following molecules is polar and show the direction of bond dipoles and the overall molecular dipole when applicable.

(a) ammonia, NH_3 (b) boron trifluoride, BF_3

(c) carbonyl sulfide (atom sequence, SCO)

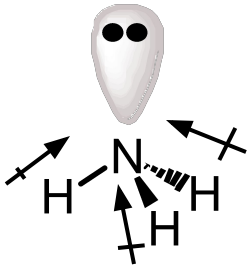
PLAN: Draw the shape, find the EN values and combine the concepts to determine the polarity.

SOLUTION: **(a)** NH_3

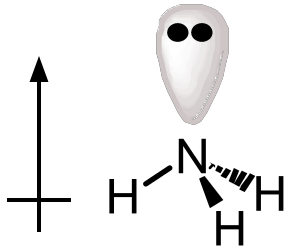


$EN_N = 3.0$

$EN_H = 2.1$

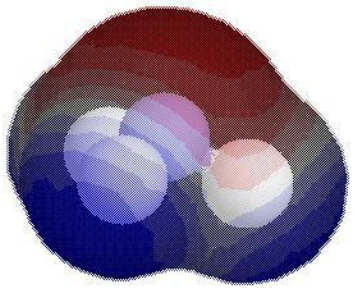


bond dipoles



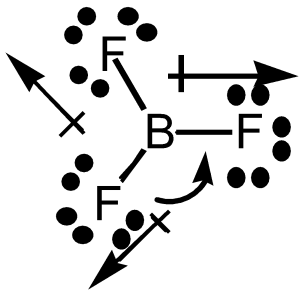
molecular dipole

The bond dipoles reinforce each other, so the overall molecule is polar.



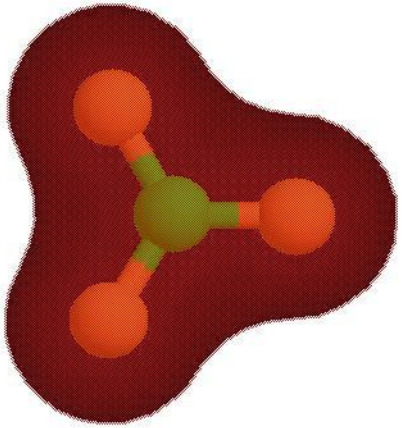
SAMPLE PROBLEM 10.10 (continued)

(b) BF_3 has 24 valence electrons and all electrons around the B will be involved in bonds. The shape is AX_3 (trigonal planar).

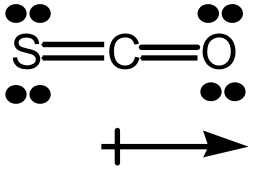


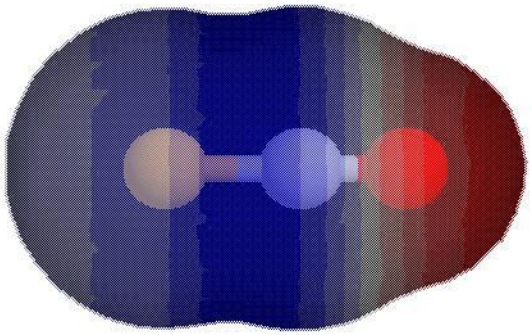
120°

F (EN 4.0) is more electronegative than B (EN 2.0) and all of the bond dipoles will be directed from B to F. Because all are at the same angle and of the same magnitude, the molecule is <u>non-polar</u>.

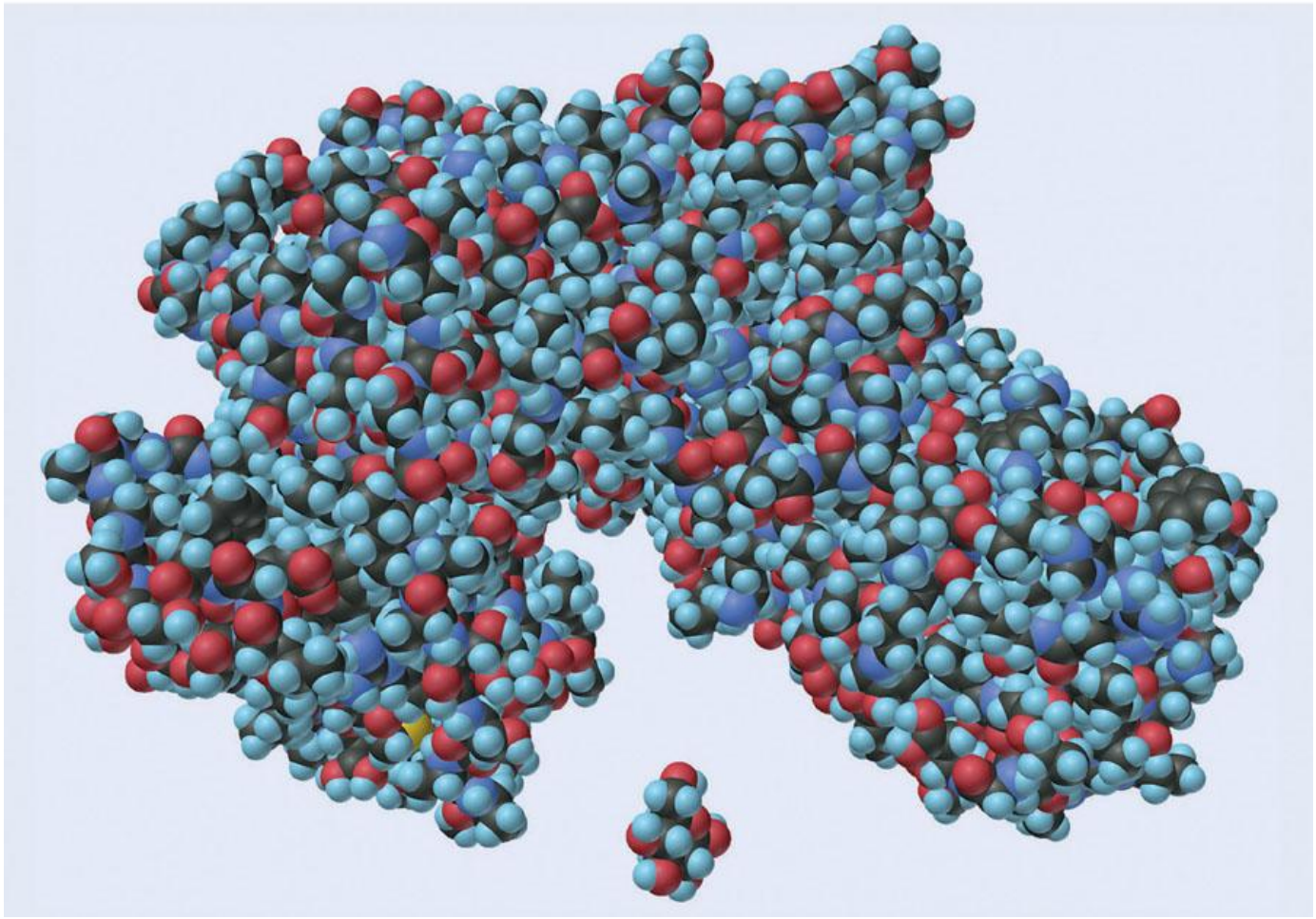


(c) SCO is linear. C and S have the same EN (2.0), but the C=O bond is polar(ΔEN = 1.0), so the molecule is <u>polar</u>.

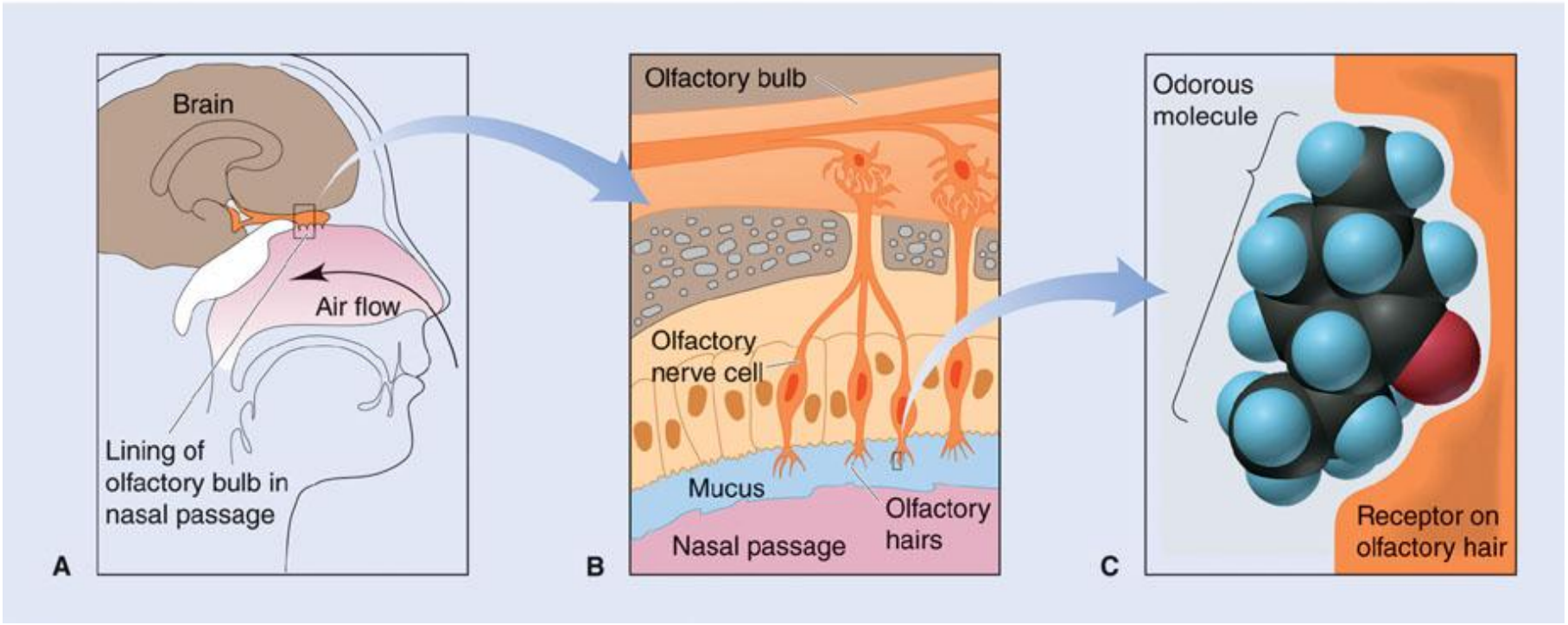




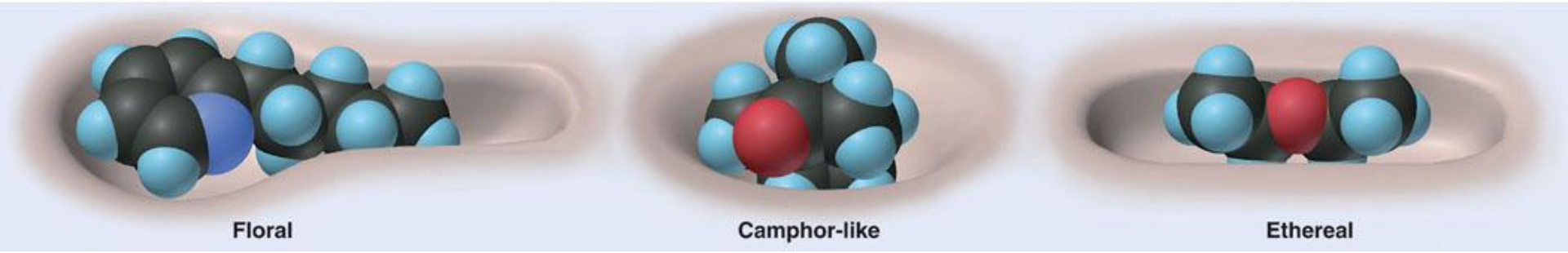
The Complementary Shapes of an Enzyme and Its Substrate



Biological Receptors: Olfactory Biochemistry

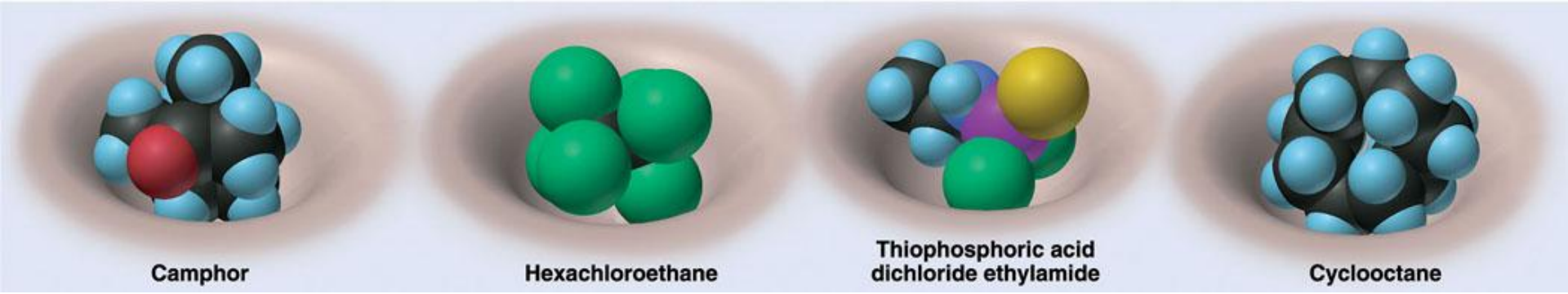


Shapes of Some Olfactory Receptor Sites



Three of the proposed seven olfactory receptors having different shapes

Different Molecules That Elicit the Same Odor



All bind to the same receptor based on their shapes.