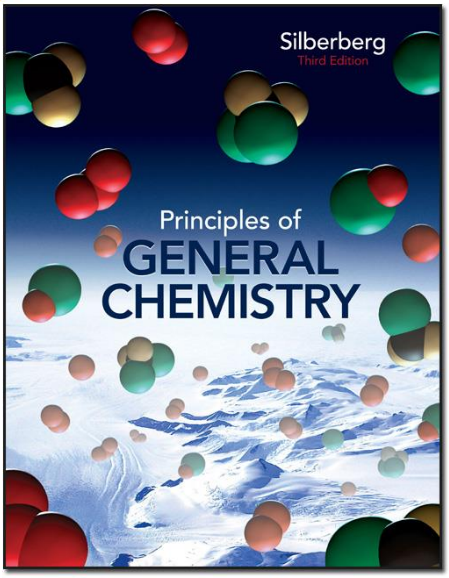


Chapter 10

Lecture Outline

See separate *Image PowerPoint* slides for all figures and tables pre-inserted into PowerPoint without notes.

Chapter 10

The Shapes of Molecules

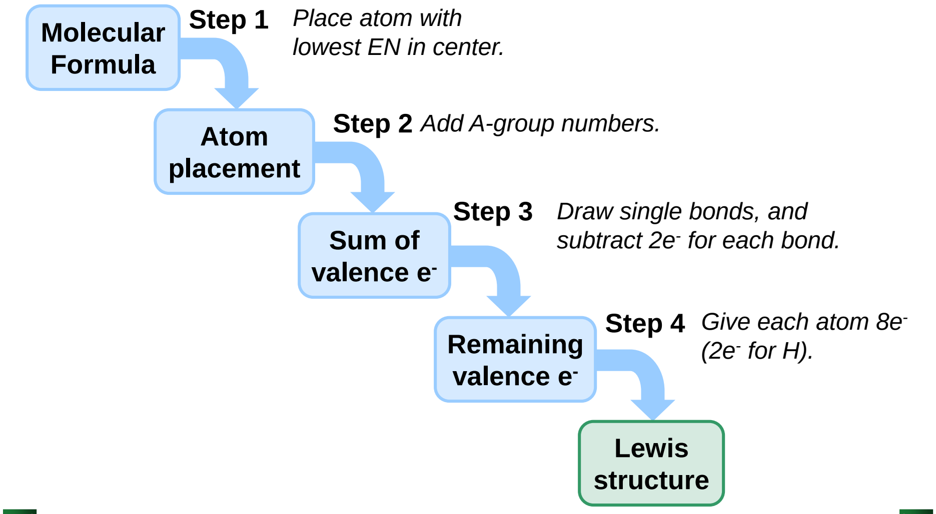
The Shapes of Molecules

10.1 Depicting Molecules and Ions with Lewis Structures

10.2 Valence-Shell Electron-Pair Repulsion (VSEPR) Theory and Molecular Shape

10.3 Molecular Shape and Molecular Polarity

Figure 10.1 **The steps in converting a molecular formula into a Lewis structure.**



Molecular Formula

Step 1 *Place atom with lowest EN in center.*

Atom placement

Step 2 *Add A-group numbers.*

Sum of valence e^-

Step 3 *Draw single bonds, and subtract $2e^-$ for each bond.*

Remaining valence e^-

Step 4 *Give each atom $8e^-$ ($2e^-$ for H).*

Lewis structure

Example: NF_3

Molecular Formula

Atom placement

Sum of valence e^-

Remaining valence e^-

Lewis structure

N has a lower EN than F, so N is placed in the center.

F

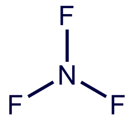
N

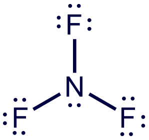
F F

$1 \times N = 1 \times 5 = 5e^-$

$3 \times F = 3 \times 7 = 21\ e^-$

Total = $28\ e^-$





Sample Problem 10.1 **Writing Lewis Structures for Molecules with One Central Atom**

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

SOLUTION:

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

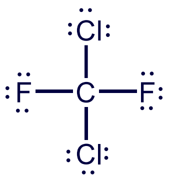
Cl

F C F

Cl

Step 2: [1 x C(4e⁻)] + [2 x F(7e⁻)] + [2 x Cl(7e⁻)] = 32 valence e⁻

Step 3-4: Add single bonds, then give each atom a full octet.



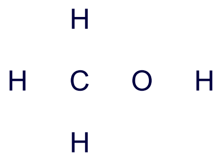
Sample Problem 10.2

Writing Lewis Structures for Molecules with More than One Central Atom

PROBLEM: Write the Lewis structure for methanol (molecular formula CH_4O), an important industrial alcohol that is being used as a gasoline alternative in car engines.

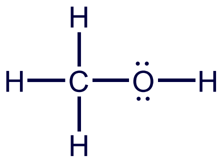
SOLUTION:

Step 1: Place the atoms relative to each other. H can only form one bond, so C and O must be central and adjacent to each other.



Step 2: [1 x C($4e^-$)] + [1 x O($6e^-$)] + [4 x H($1e^-$)] = 14 valence e^-

Step 3-4: Add single bonds, then give each atom (other than H) a full octet.



Multiple Bonds

If there are not enough electrons for the ***central*** atom to attain an octet, a multiple bond is present.

Step 5: If the central atom does not have a full octet, change a lone pair on a surrounding atom into another bonding pair to the central atom, thus forming a multiple bond.

Sample Problem 10.3

Writing Lewis Structures for Molecules with Multiple Bonds

PROBLEM: Write Lewis structures for the following:

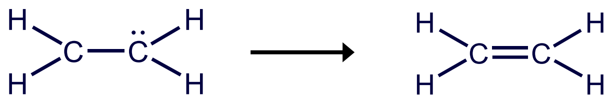
(a) Ethylene (C_2H_4), the most important reactant in the manufacture of polymers

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

PLAN: After following steps 1 to 4 we see that the central atom does not have a full octet. We must therefore add step 5, which involves changing a lone pair to a bonding pair.

SOLUTION:

(a) C_2H_4 has 2(4) + 4(1) = 12 valence e^-. H can have only one bond per atom.

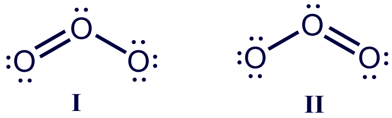


Sample Problem 10.3

(b) N_2 has 2(5) = 10 valence e^-.

Resonance Structures

O_3 can be drawn in 2 ways:



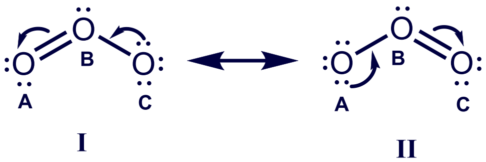
These are two different reasonable Lewis structures for the ***same*** molecule.

Neither structure depicts O_3 accurately, because in reality the O-O bonds are identical in length and energy.

Resonance Structures

The structure of O_3 is shown more correctly using both Lewis structures, called ***resonance structures***.

A two-headed resonance arrow is placed between them.



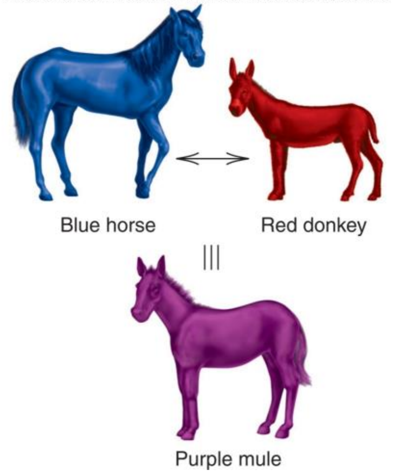
Resonance structures have the *same relative placement of atoms but different locations of bonding and lone electron pairs.*

The Resonance Hybrid

A species like O_3, which can be depicted by more than one valid Lewis structure, is called a ***resonance hybrid***.

Resonance forms ***are not real bonding depictions***. O_3 does ***not*** change back and forth between its two resonance forms.

The ***real structure*** of a resonance hybrid is an ***average*** of its contributing resonance forms.

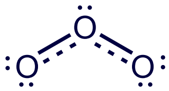


A mule is a genetic mix, a hybrid, of a horse and a donkey. It is not a horse one instant and a donkey the next. Likewise, a resonance hybrid has a **single** structure although it retains characteristics of its resonance forms.

Electron Delocalization

Lewis structures depict electrons as ***localized*** either on an individual atom (lone pairs) or in a bond between two atoms (shared pair).

In a resonance hybrid, electrons are ***delocalized***: their density is “spread” over a few adjacent atoms.

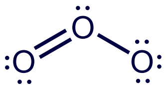


Dotted lines are used to show delocalized electrons.

Fractional Bond Orders

Resonance hybrids often have ***fractional bond orders*** due to partial bonding.

For O_3, bond order = $\dfrac{\text{3 electron pairs}}{\text{2 bonded-atom pairs}}$ = 1½



Sample Problem 10.4 Writing Resonance Structures

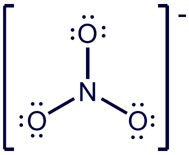
PROBLEM: Write resonance structures for the nitrate ion, NO_3^- and find the bond order.

PLAN: Write the Lewis structure, remembering to add $1e^-$ to the total number of valence e^- for the -1 charge. We apply Step 5 to form multiple bonds. Since multiple bonds can be formed in more than one location, there are resonance forms.

SOLUTION:

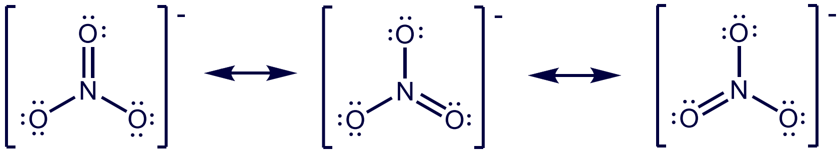
Nitrate has $[1 \times N(5e^-)] + [3 \times O(6e^-)] + 1e^-] = 24$ valence e^-

After Steps 1-4:



Sample Problem 10.4

Step 5. Since N does not have a full octet, we change a lone pair from O to a bonding pair to form a double bond.

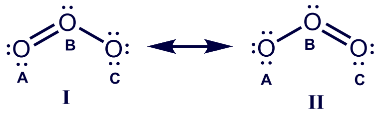


$$\textbf{Bond order} = \frac{\textbf{4 shared electron pairs}}{\textbf{3 bonded-atom pairs}} = 1\tfrac{1}{3}$$

Formal Charge

Formal charge is the charge an atom would have if all electrons were shared ***equally***.

Formal charge of atom =
# of valence e$^-$ - (# of unshared valence e$^-$ + ½ # of shared valence e$^-$)

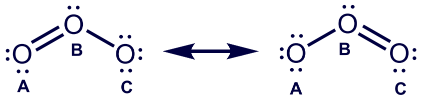


For O_A in resonance form I, the formal charge is given by

6 valence e$^-$ - (4 unshared e$^-$ + ½(4 shared e$^-$) = 6 – 4 – 2 = 0

Formal Charge

Formal charges must sum to the actual charge on the species for ***all*** resonance forms.



O_A [6 – 4 – ½(4)] = 0	O_A [6 – 6 – ½(2)] = -1
O_B [6 – 2 – ½(6)] = +1	O_B [6 – 2 – ½(6)] = +1
O_C [6 – 6 – ½(2)] = -1	O_C [6 – 4 – ½(4)] = 0

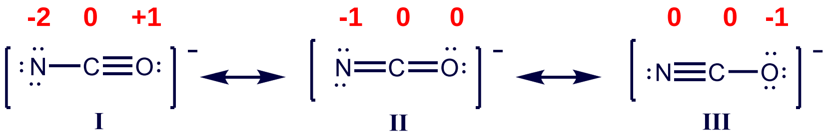
For both these resonance forms the formal charges sum to zero, since O_3 is a neutral molecule.

Choosing the More Important Resonance Form

- Smaller formal charges (positive or negative) are preferable to larger ones.
- The ***same*** nonzero formal charges on adjacent atoms are not preferred.

  Avoid like charges on adjacent atoms.
- A more negative formal charge should reside on a more electronegative atom.

Example: NCO⁻ has 3 possible resonance forms:



Resonance forms with smaller formal charges are preferred. Resonance form I is therefore ***not*** an important contributor.

A negative formal charge should be placed on a more electronegative atom, so resonance form III is preferred to resonance form II.

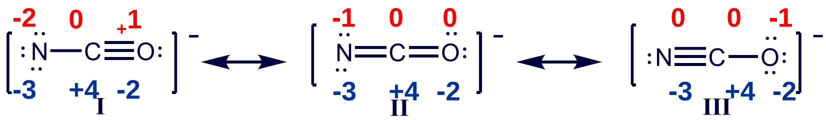
The overall structure of the NCO⁻ ion is still an ***average*** of all three forms, but **resonance form III** contributes ***most*** to the average.

Formal Charge Versus Oxidation Number

For a ***formal charge***, bonding electrons are ***shared equally*** by the atoms.

The formal charge of an atom may change between resonance forms.

Formal charges



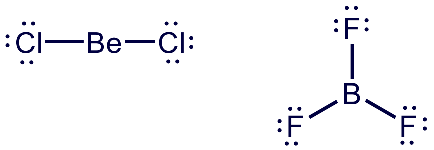
Oxidation numbers

For an ***oxidation number***, bonding electrons are ***transferred*** to the ***more*** electronegative atom.

The oxidation number of an atom is the ***same*** in all resonance forms.

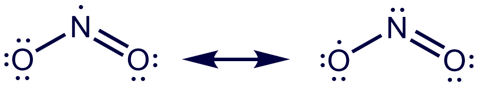
Exceptions to the Octet Rule

Molecules with Electron-Deficient Atoms



B and Be are commonly electron-deficient.

Odd-Electron Species

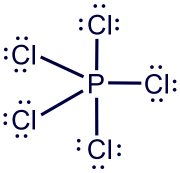


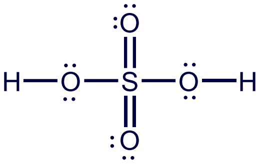
A molecule with an odd number of electrons is called a ***free radical***.

enigma - something that baffles understanding and cannot be explained; "how it got out is a mystery"; "it remains one of nature's secrets"

Exceptions to the Octet Rule

Expanded Valence Shells





An expanded valence shell is only possible for ***nonmetals from Period 3 or higher*** because these elements have available ***d orbitals***.

Sample Problem 10.5

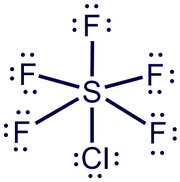
Drawing Lewis Structures for Octet-Rule Exceptions

PROBLEM: Write a Lewis structure and identify the octet-rule exception for **(a)** $SClF_5$; **(b)** H_3PO_4 (draw two resonance forms and select the more important); **(c)** $BFCl_2$.

PLAN: Draw each Lewis structure and examine it for exceptions to the octet rule. Period 3 elements can have an expanded octet, while B commonly forms electron-deficient species.

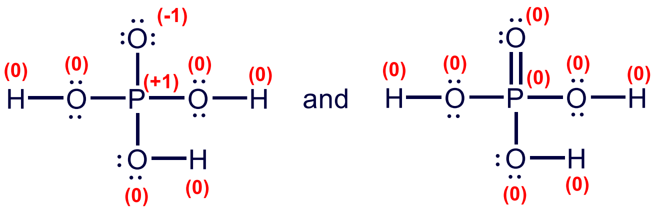
SOLUTION:

(a) The central atom is S, which is in Period 3 and can have an expanded valence shell.

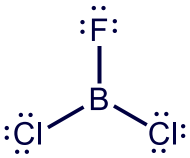


Sample Problem 10.5

(b) H_3PO_4 has two resonance forms and formal charges indicate the more important form.



(c) $BFCl_2$ is an electron-deficient molecule. B has only six electrons surrounding it.



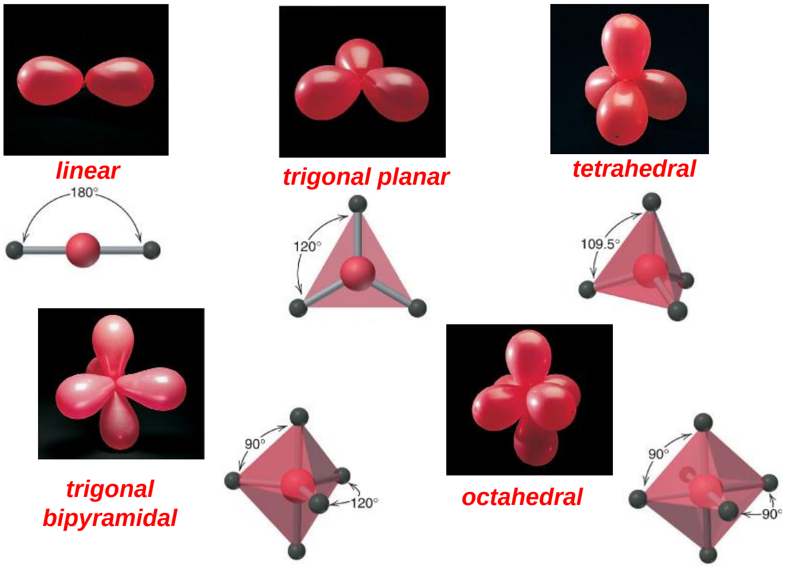
Valence-Shell Electron-Pair Repulsion Theory (VSEPR) and Molecular Shape

Each group of valence electrons around a central atom is located as far as possible from the others, to minimize repulsions.

A “group” of electrons is any number of electrons that occupies a localized region around an atom.

A single bond, double bond, triple bond, lone pair, or single electron all count as a single group.

Figure 10.2 Electron-group repulsions and molecular shapes.



Electron-group Arrangement and Molecular Shape

The ***electron-group arrangement*** is defined by both bonding and nonbonding electron groups.

The ***molecular shape*** is the three-dimensional arrangement of nuclei joined by the bonding groups. This is defined only by the relative positions of the nuclei.

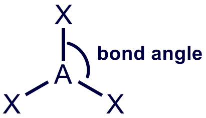
Molecular shape is classified using the designation

$\mathbf{AX}_m\mathbf{E}_n$

A = central atom
X = surrounding atom
E = nonbonding valence-electron group
m and *n* are integers

Bond Angle

The ***bond angle*** is the angle formed by the nuclei of two surrounding atoms with the nucleus of the central atom.



The angles shown in Figure 10.2 are ***ideal*** bond angles, determined by basic geometry alone. Real bond angles deviate from the ideal value in many cases.

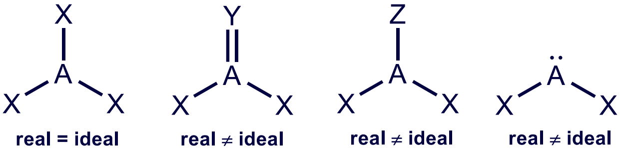
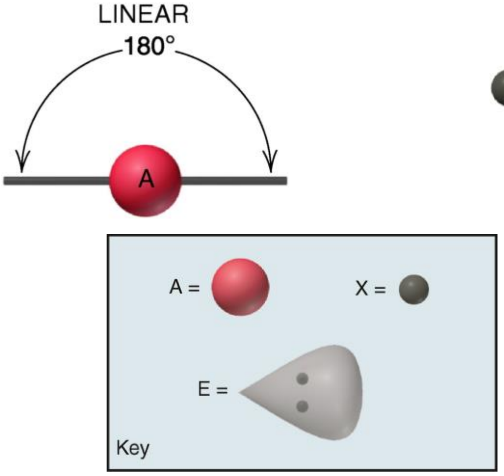
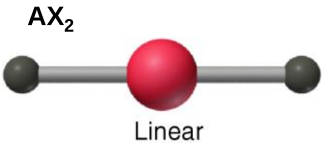


Figure 10.3 **The single molecular shape of the linear electron-group arrangement.**

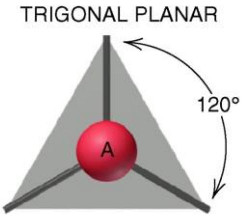




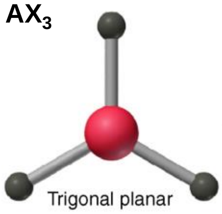
Examples:
CS_2, HCN, BeF_2

This key refers to Figures 10.3 through 10.8.

Figure 10.4 **The two molecular shapes of the trigonal planar electron-group arrangement.**

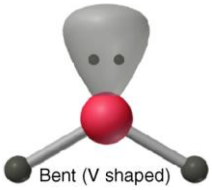


AX_3



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

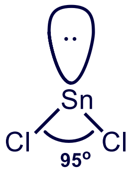
AX_2E



Examples:
SO_2, O_3, $PbCl_2$, $SnBr_2$

Factors Affecting Bond Angles

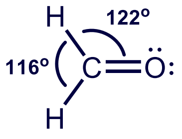
Nonbonding (Lone) Pairs



A lone pair repels bonding pairs more strongly than bonding pairs repel each other. This decreases the angle between the bonding pairs.

Repulsion of: Lp/Lp > Lp/Bp > Bp/Bp

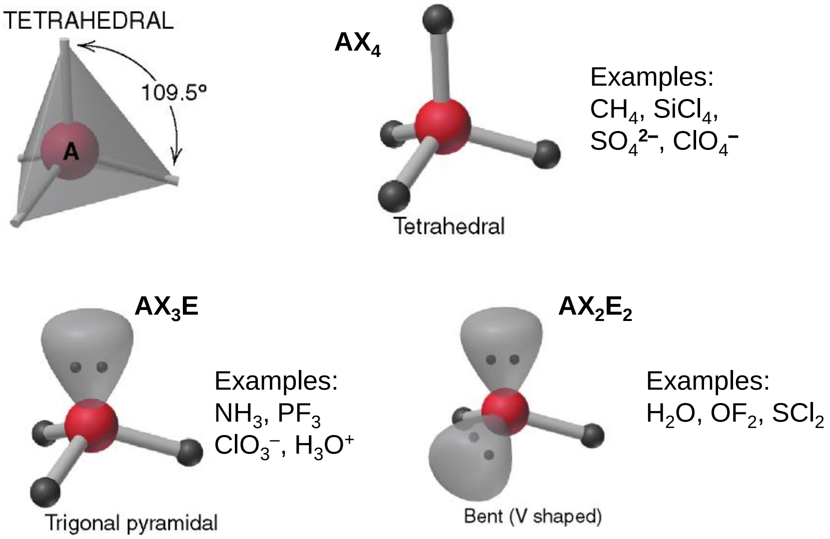
Double Bonds



The ideal angle is 120°.

A double bond has greater electron density than a single bond, and repels the single bond electrons more than they repel each other.

Figure 10.5 **The three molecular shapes of the tetrahedral electron-group arrangement.**



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

Examples:
NH_3, PF_3
ClO_3^-, H_3O^+

Examples:
H_2O, OF_2, SCl_2

Figure 10.6 **Lewis structures do not indicate molecular shape.**

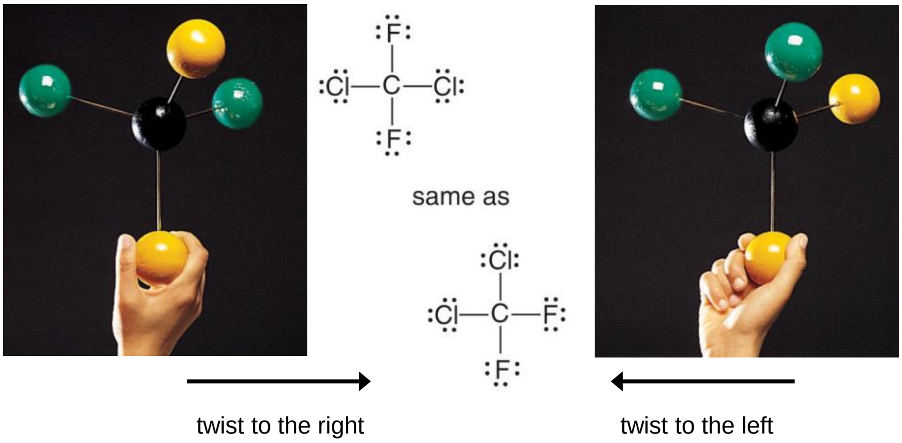
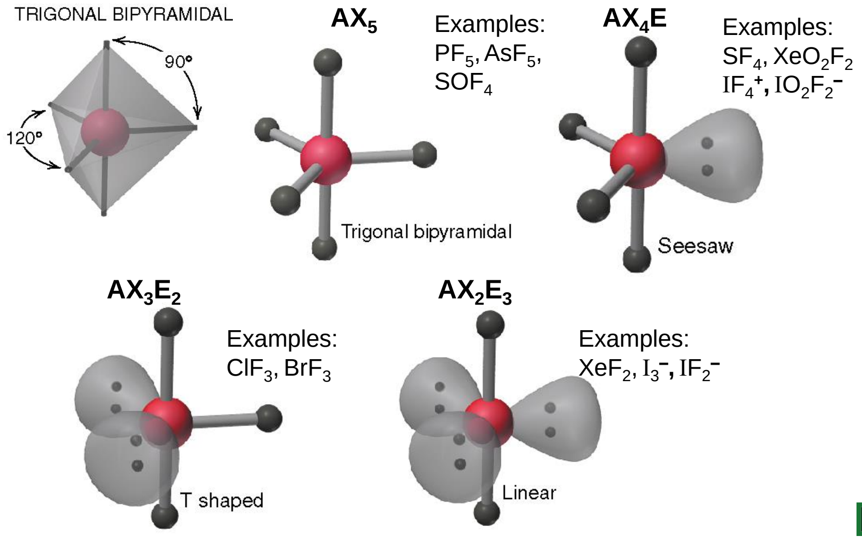


Figure 10.7 The four molecular shapes of the trigonal bipyramidal electron-group arrangement.



AX_5 Examples: PF_5, AsF_5, SOF_4

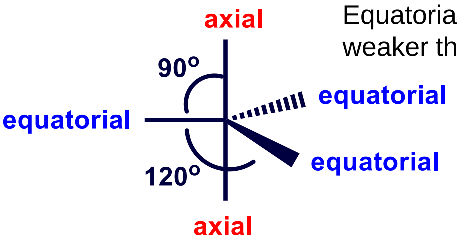
AX_4E Examples: SF_4, XeO_2F_2, IF_4^+, $IO_2F_2^-$

AX_3E_2 Examples: ClF_3, BrF_3

AX_2E_3 Examples: XeF_2, I_3^-, IF_2^-

Axial and Equatorial Positions

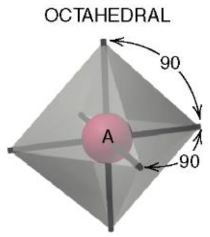
A five electron-group system has two different positions for electron groups, and two ideal bond angles.

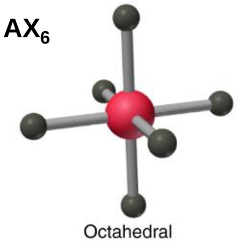


Equatorial-equatorial repulsions are weaker than axial-equatorial repulsions.

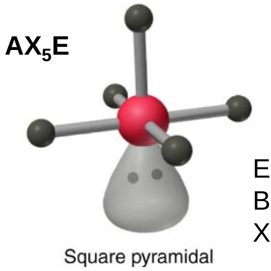
Where possible, lone pairs in a five electron-group system occupy ***equatorial*** positions.

Figure 10.8 **The three molecular shapes of the octahedral electron-group arrangement.**

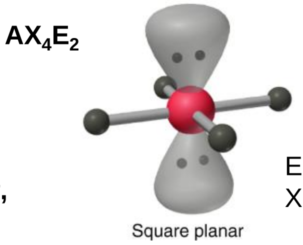




Examples:
SF_6, IOF_5

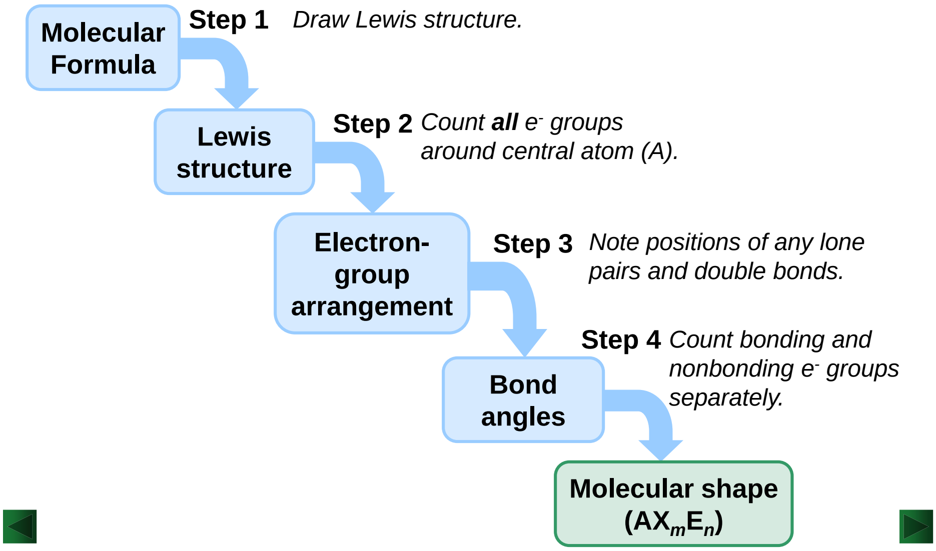


Examples:
BrF_5, TeF_5^-,
$XeOF_4$



Examples:
XeF_4, ICl_4^-

Figure 10.9 **The four steps in converting a molecular formula to a molecular shape**



Molecular Formula

Step 1 *Draw Lewis structure.*

Lewis structure

Step 2 *Count **all** e^- groups around central atom (A).*

Electron-group arrangement

Step 3 *Note positions of any lone pairs and double bonds.*

Bond angles

Step 4 *Count bonding and nonbonding e^- groups separately.*

Molecular shape (AX_mE_n)

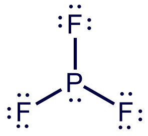
Sample Problem 10.6

Examining 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. The Lewis structure is

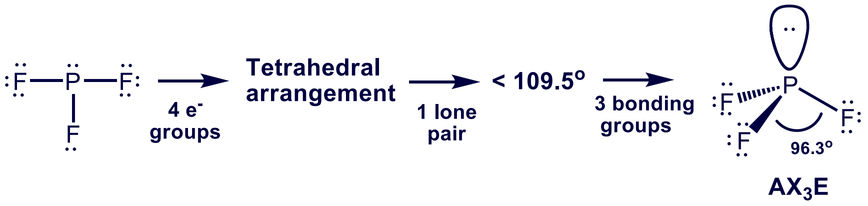


There are four electron groups around P, giving a tetrahedral electron-group arrangement. **The ideal bond angle is therefore 109.5°.**

There is one lone pair and three bonding pairs, so the actual bond angle will be **less than 109.5°.**

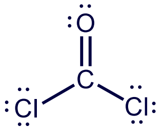
Sample Problem 10.6

The molecular shape for PF_3 is **trigonal pyramidal** (**AX_3E**).

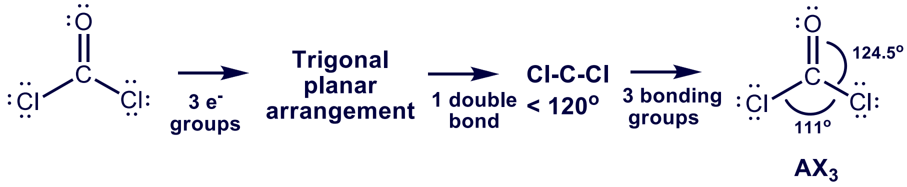


Sample Problem 10.6

(b) For $COCl_2$ there are 24 valence e^-. The Lewis structure is



There are three electron groups around C, giving a trigonal planar electron-group arrangement. **The ideal bond angle is 120°**, but the double bond will compress the Cl-C-Cl angle to **less than 120°.**



3 e^- groups → **Trigonal planar arrangement** → **1 double bond** → **Cl-C-Cl < 120°** → **3 bonding groups** → **AX_3**

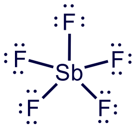
Sample Problem 10.7

Examining Shapes with Five or Six Electron Groups

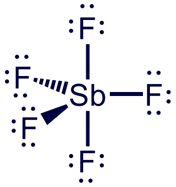
PROBLEM: Draw the molecular shapes and predict the bond angles (relative to the ideal bond angles) of **(a)** SbF_5 and **(b)** BrF_5.

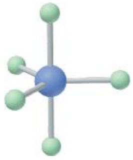
SOLUTION:

(a) SbF_5 has 40 valence e^-. The Lewis structure is



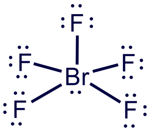
There are five electron groups around Sb, giving a trigonal bipyramidal electron-group arrangement. **The ideal bond angles are 120° between equatorial groups and 90° between axial groups.**





Sample Problem 10.7

(b) BrF_5 has 42 valence e^-.
The Lewis structure is



There are six electron groups around Br, giving an octahedral electron-group arrangement. **The ideal bond angles are 90°**. There is one lone pair, so the bond angles will be **less than 90°** and the molecular shape is **square pyramidal**.

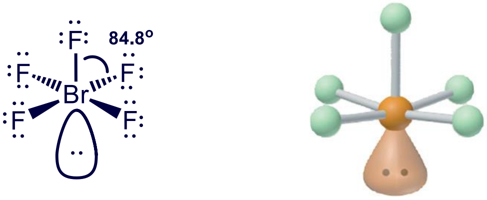
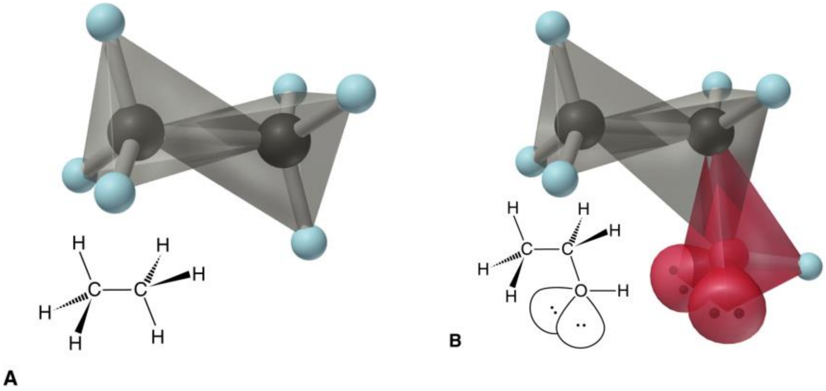


Figure 10.10 **The tetrahedral shapes around the central atoms and the overall shapes of ethane (A) and ethanol (B).**



ethane

CH_3CH_3

ethanol

CH_3CH_2OH

Sample Problem 10.8

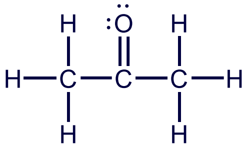
Predicting Molecular Shapes with More Than One Central Atom

PROBLEM: Determine the shape around each of the central atoms in acetone, $(CH_3)_2CO$.

PLAN: There are three central C atoms, two of which are in CH_3– groups. We determine the shape around one central atom at a time.

SOLUTION:

Step 1: The Lewis structure is

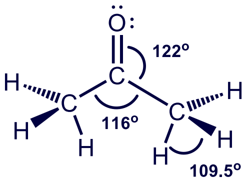


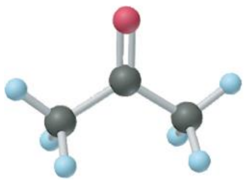
Step 2: Each CH_3– group has four electron groups around its central C, so the electron-group arrangement is *tetrahedral*. The third C atom has three electron groups around it, with a *trigonal planar* arrangement.

Sample Problem 10.8

Step 3: The H-C-H bond angle in each CH_3– group should be near the ideal value of 109.5°. The C=O double bond will compress the C-C-C angle to less than the ideal angle of 120°.

Step 4: The shape around the C in each CH_3– group is **tetrahedral** (**AX_4**). The shape around the middle C is **trigonal planar** (**AX_3**).





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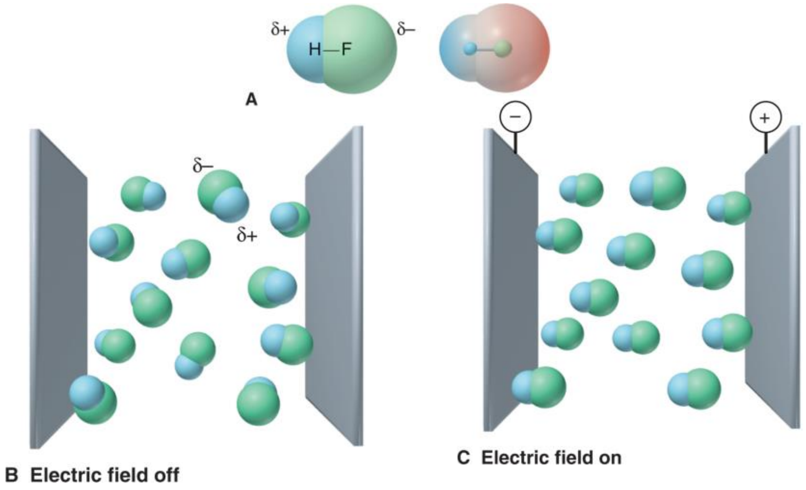
Molecular Shape and Molecular Polarity

Overall ***molecular polarity*** depends on both ***shape*** and ***bond polarity***.

The polarity of a molecule is measured by its ***dipole moment*** (**μ**), which is given in the unit *debye* (D).

A molecule is polar if
- it contains one or more ***polar bonds*** and
- the individual bond dipoles ***do not cancel***.

Figure 10.11 The orientation of polar molecules in an electric field.



Molecules are randomly oriented.

Molecules become oriented when the field is turned on.

Bond Polarity, Bond Angle, and Dipole Moment

Example: CO_2

The ΔEN between C (EN = 2.5) and O (EN = 3.5) makes each C=O bond polar.

CO_2 is linear, the bond angle is 180°, and the individual bond polarities therefore cancel. The molecule has ***no net dipole moment*** (μ = 0 D).

Bond Polarity, Bond Angle, and Dipole Moment

Example: H_2O

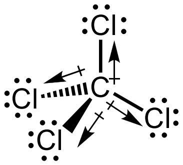
The ΔEN between H (EN = 2.1) and O (EN = 3.5) makes each H-O bond polar.

H_2O has a V shaped geometry and the individual bond polarities do **not** cancel. This molecule has an ***overall molecular polarity***. The O is partially negative while the H atoms are partially positive.

Bond Polarity, Bond Angle, and Dipole Moment

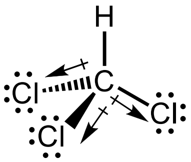
Molecules with the same shape may have different polarities.

CCl_4



Bonds are polar, but individual bond polarities cancel.

$CHCl_3$



Bond polarities do not cancel. This molecule is polar (μ = 1.01 D).

Sample Problem 10.9 **Predicting the Polarity of Molecules**

PROBLEM: For each of the following use the molecular shape and EN values and trends (Figure 9.20, p. 349) to predict the direction of bond and molecular polarity, if present.

(a) Ammonia, NH_3 **(b)** Boron trifluoride, BF_3

(c) Carbonyl sulfide, COS (atom sequence SCO)

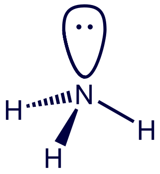
PLAN: We draw and name the molecular shape, and mark each polar bond with a polar arrow pointing toward the atom with the higher EN. If bond polarities balance one another, the molecule is nonpolar. If they reinforce each other, we show the direction of overall molecular polarity.

Sample Problem 10.9

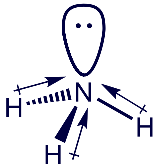
SOLUTION:

(a) NH_3 has 8 valence e^- and a trigonal pyramidal molecular shape.

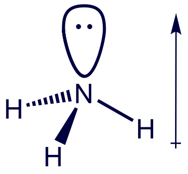
N (EN = 3.0) is more electronegative than H (EN = 2.1) so bond polarities point towards N.



molecular shape



bond polarities



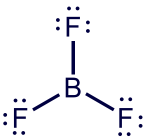
molecular polarity

Ammonia is polar overall.

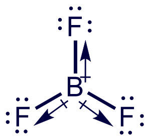
Sample Problem 10.9

(b) BF_3 has 24 valence e^- and a trigonal planar molecular shape.

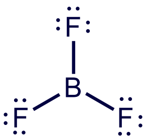
F (EN = 4.0) is more electronegative than B (EN = 2.0) so bond polarities point towards F.



molecular shape



bond polarities



molecular polarity

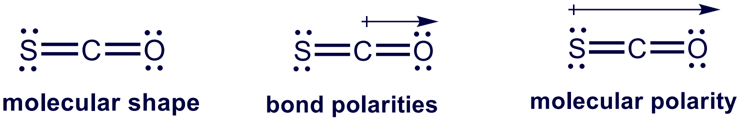
Individual bond polarities balance each other and BF_3 has no molecular polarity.

Boron trifluoride is nonpolar.

Sample Problem 10.9

(c) COS has a linear shape.

C and S have the same EN (2.5) but the C=O bond (ΔEN = 1.0) is quite polar.



Carbonyl sulfide is polar overall.