

10

The Shapes of Molecules

Key Principles

to focus on while studying this chapter

- A *Lewis structure* shows the relative positions of the atoms in a molecule (or polyatomic ion), as well as the placement of all the shared and unshared electron pairs. It is generated from the molecular formula through a series of steps that often apply the octet rule. (**Section 10.1**)
- In many molecules or ions, one electron pair in a double bond spreads over an adjacent single bond, thereby stabilizing the system by *delocalizing* its charge. In such cases, more than one Lewis structure, each called a *resonance form*, can be drawn, and the species exists as a *resonance hybrid*, a mixture of the resonance forms. (**Section 10.1**)
- By assigning to each atom a *formal charge* based on the electrons belonging to the atom and those shared by it, we can select the most important of the various resonance forms, the one that is most like the hybrid. (**Section 10.1**)
- Many compounds do not obey the octet rule, by having either fewer than or more than eight electrons around the central atom. (**Section 10.1**)
- According to VSEPR theory, each group of valence electrons, whether a bonding pair or a lone pair, around a central atom repels the others. These repulsions give rise to five geometric arrangements—*linear*, *trigonal planar*, *tetrahedral*, *trigonal bipyramidal*, and *octahedral*. Various molecular shapes, with characteristic bond angles, arise from these arrangements. (**Section 10.2**)
- A molecule may be polar or nonpolar, depending on its shape and the polarities of its bonds. (**Section 10.3**)



Shape Matters Nearly every biochemical reaction occurs because the shape of one molecule in some way matches the shape of another—only one key fits the lock. In this chapter, you'll learn how the placement of bonded atoms gives rise to a molecule's shape.

Outline

10.1 Depicting Molecules and Ions with Lewis Structures

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Shapes with Four Electron Groups
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10.3 Molecular Shape and Molecular Polarity

Bond Polarity, Bond Angle, and Dipole Moment

In the everyday world, the shapes of interacting objects often reflect their function—cup and saucer, hand and glove, or the complementary shapes of lock and key. The same is true in the molecular world. But, with all the symbols, lines, and dots you’ve been seeing, it’s easy to forget that every molecule has a characteristic minute architecture. Each atom, bonding pair, and lone pair has its own position relative to the others, with angles and distances between them that are determined by the attractive and repulsive forces governing all matter. Molecular shape plays a crucial role in the interactions of reactants, the behavior of synthetic materials, and especially in the life-sustaining processes in cells. In this chapter, we see how to depict molecules, first as two-dimensional drawings and then as three-dimensional objects.

CONCEPTS & SKILLS TO REVIEW before studying this chapter

- electron configurations of main-group elements (Section 8.2)
- electron-dot symbols (Section 9.1)
- octet rule (Section 9.1)
- bond order, bond length, and bond energy (Sections 9.3 and 9.4)
- polar covalent bonds and bond polarity (Section 9.5)

10.1 • DEPICTING MOLECULES AND IONS WITH LEWIS STRUCTURES

The first step toward visualizing a molecule is to convert its molecular formula to its **Lewis structure** (or **Lewis formula***), which shows electron-dot symbols for the atoms, the bonding pairs as lines, and the lone pairs that fill each atom’s outer level (valence shell) as pairs of dots. In many cases, the octet rule (Section 9.1) guides us in allotting electrons to the atoms in a Lewis structure; in many other cases, as you’ll see later in this section, we set the rule aside.

Applying the Octet Rule to Write Lewis Structures

To draw a Lewis structure, we decide on the relative placement of the atoms in the molecule or polyatomic ion and then distribute the total number of valence electrons as bonding and lone pairs. We begin with species that “obey” the octet rule, in which each atom fills its outer level with eight electrons (or two for hydrogen).

Molecules with Single Bonds Figure 10.1 lays out the steps for drawing Lewis structures for species with only single bonds. Let’s use nitrogen trifluoride, NF_3 , to introduce the steps:

Step 1. Place the atoms relative to each other. For compounds with the general molecular formula AB_n , place the atom with the *lower group number* in the center because it needs more electrons to attain an octet; usually, this is also the atom with the *lower electronegativity*. In NF_3 , the N (Group 5A; $\text{EN} = 3.0$) has five electrons and so needs three, whereas each F (Group 7A; $\text{EN} = 4.0$) has seven and needs only one; thus, N goes in the center with the three F atoms around it:



*A Lewis *structure* does **not** indicate the three-dimensional shape, so it may be more correct to call it a Lewis *formula*, but we follow convention and use the term *structure*.

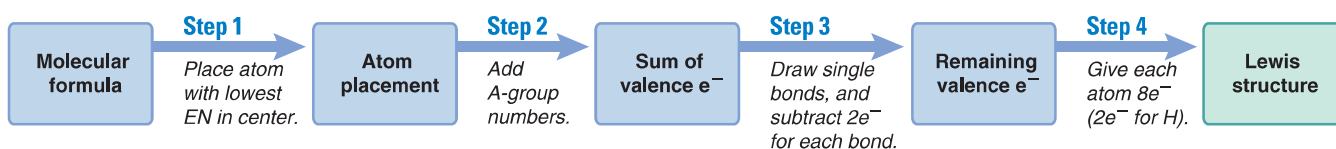


Figure 10.1 The steps in converting a molecular formula into a Lewis structure.

If the atoms have the same group number, as in SO_3 or ClF_3 , place the atom with the *higher period number* (also lower EN) in the center. H can form only one bond, so it is *never* a central atom.

Step 2. Determine the total number of valence electrons.

- For molecules, add up the valence electrons of the atoms. (Recall that the number of valence electrons equals the A-group number.) In NF_3 , N has five valence electrons, and each F has seven:

$$[1 \times \text{N}(5e^-)] + [3 \times \text{F}(7e^-)] = 5e^- + 21e^- = 26 \text{ valence } e^-$$

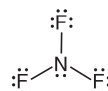
- For polyatomic ions, *add* one e^- for each negative charge, or *subtract* one e^- for each positive charge.

Step 3. Draw a single bond from each surrounding atom to the central atom, and subtract $2e^-$ from the total for each bond to find the number of e^- remaining:



$$3 \text{ N}-\text{F bonds} \times 2e^- = 6e^- \quad \text{so} \quad 26e^- - 6e^- = 20e^- \text{ remaining}$$

Step 4. Distribute the remaining electrons in pairs so that each atom ends up with $8e^-$ (or $2e^-$ for H). First, place lone pairs on the *surrounding (more electronegative) atoms* to give each an octet. If any electrons remain, place them around the central atom—each F gets 3 pairs ($3 \times 6e^- = 18e^-$) and the N gets 1 ($2e^-$), for a total of $20e^-$. Then check that each atom has $8e^-$:

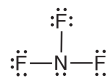


This is the Lewis structure for NF_3 . It is a neutral species, so the total number of electrons (bonds plus lone pairs) equals the sum of the valence electrons:

$$6e^- \text{ in three bonds} + 20e^- \text{ in ten lone pairs} = 26 \text{ valence } e^-$$

If we were writing a Lewis structure for a polyatomic ion, we would also take the charge into account, as described in step 2.

Since Lewis structures do not indicate shape, an equally correct depiction of NF_3 is



or any other that retains the *same connections among the atoms*—a central N atom connected by single bonds to each of three surrounding F atoms.

Using these four steps, you can draw a Lewis structure for any singly bonded species with a central C, N, or O atom, as well as for some species with central atoms from higher periods. In nearly all their compounds,

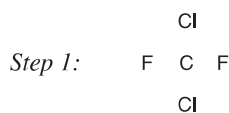
- Hydrogen atoms form one bond.
- Carbon atoms form four bonds.
- Nitrogen atoms form three bonds.
- Oxygen atoms form two bonds.
- Surrounding halogens form one bond; fluorine is *always* a surrounding atom.

Sample Problem 10.1

Drawing Lewis Structures for Molecules with One Central Atom

Problem Draw a Lewis structure for CCl_2F_2 , one of the compounds responsible for the depletion of stratospheric ozone.

Solution *Step 1.* Place the atoms relative to each other. In CCl_2F_2 , carbon has the lowest group number and EN, so it is the central atom (*see margin*). The halogen atoms surround it, but their specific positions are not important.



Step 2. Determine the total number of valence electrons (from A-group numbers): C is in Group 4A; F and Cl are in Group 7A. Therefore, we have

$$[1 \times \text{C}(4e^-)] + [2 \times \text{F}(7e^-)] + [2 \times \text{Cl}(7e^-)] = 32 \text{ valence } e^-$$

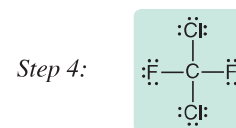
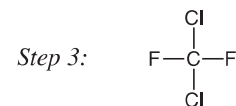
Step 3. Draw single bonds to the central atom (*see margin*) and subtract $2e^-$ for each bond:

$$4 \text{ bonds} \times 2e^- = 8e^- \quad \text{so} \quad 32e^- - 8e^- = 24e^- \text{ remaining}$$

Step 4. Distribute the remaining electrons in pairs, beginning with the surrounding atoms, so that each atom has an octet. Each surrounding halogen gets 3 pairs (*see margin*).

Check Always check that each atom has an octet. Bonding electrons belong to each atom in the bond. The total number in bonds ($8e^-$) and lone pairs ($24e^-$) equals 32 valence e^- . As expected, C has four bonds and the surrounding halogens have one each.

FOLLOW-UP PROBLEM 10.1 Draw a Lewis structure for (a) H_2S ; (b) OF_2 ; (c) SOCl_2 .



In molecules with two or more central atoms bonded to each other, it is usually clear which atoms are surrounding.

Sample Problem 10.2 Drawing Lewis Structures for Molecules with More Than One Central Atom

Problem Draw the Lewis structure for methanol (molecular formula CH_4O), an important industrial alcohol that can be used as a gasoline alternative in cars.

Solution **Step 1.** Place the atoms relative to each other. The H atoms can have only one bond, so C and O must be central and adjacent to each other. C has four bonds and O has two, so we arrange the H atoms accordingly (*see margin*).

Step 2. Find the sum of valence electrons (C is in Group 4A, O is in Group 6A):

$$[1 \times \text{C}(4e^-)] + [1 \times \text{O}(6e^-)] + [4 \times \text{H}(1e^-)] = 14e^-$$

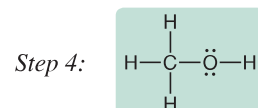
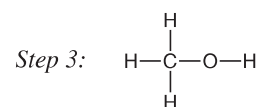
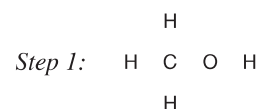
Step 3. Add single bonds (*see margin*) and subtract $2e^-$ for each bond:

$$5 \text{ bonds} \times 2e^- = 10e^- \quad \text{so} \quad 14e^- - 10e^- = 4e^- \text{ remaining}$$

Step 4. Add the remaining electrons in pairs to fill each valence level. C already has an octet, and each H shares $2e^-$ with the C; so the remaining $4e^-$ form two lone pairs on O to give the Lewis structure for methanol (*see margin*).

Check Each H atom has $2e^-$, and C and O each have $8e^-$. The total number of valence electrons is $14e^-$, which equals $10e^-$ in bonds plus $4e^-$ in two lone pairs. Each H has one bond, C has four, and O has two.

FOLLOW-UP PROBLEM 10.2 Draw a Lewis structure for (a) hydroxylamine (NH_3O); (b) dimethyl ether ($\text{C}_2\text{H}_6\text{O}$; no O—H bonds).



Molecules with Multiple Bonds In most cases, if there are not enough electrons for the central atom(s) to attain an octet, a multiple bond is present, and we add the following step to the procedure for drawing a Lewis structure:

Step 5. Cases involving multiple bonds. If a central atom does not end up with an octet, change a lone pair on a surrounding atom into another bonding pair to the central atom, thus forming a multiple bond.

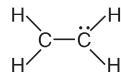
Sample Problem 10.3 Drawing Lewis Structures for Molecules with Multiple Bonds

Problem Draw Lewis structures for the following:

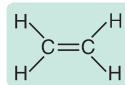
- (a) Ethylene (C_2H_4), the most important reactant in the manufacture of polymers
- (b) Nitrogen (N_2), the most abundant atmospheric gas

Plan We show the structure resulting from steps 1 to 4: placing the atoms, counting the total valence electrons, making single bonds, and distributing the remaining valence electrons in pairs to attain octets. Then we continue with step 5, if needed.

Solution (a) For C_2H_4 . After steps 1 to 4, we have



Step 5. Change a lone pair to a bonding pair. The right C has an octet, but the left C has only $6e^-$, so we change the lone pair to another bonding pair between the two C atoms:



(b) For N_2 . After steps 1 to 4, we have $:\ddot{\text{N}}-\ddot{\text{N}}:$

Step 5. Neither N has an octet, so we change a lone pair to a bonding pair, $:\ddot{\text{N}}=\text{N}:$

In this case, moving one lone pair to make a double bond still does not give the right N an octet, so we move a lone pair from the left N to make a triple bond, $:\text{N}\equiv\text{N}:$

Check (a) Each C has four bonds and counts the $4e^-$ in the double bond as part of its own octet. The valence electron total is $12e^-$, all in six bonds. (b) Each N counts the $6e^-$ in the triple bond as part of its own octet. The valence electron total is $10e^-$, which equals the electrons in three bonds and two lone pairs.

FOLLOW-UP PROBLEM 10.3 Draw Lewis structures for (a) CO (the only common molecule in which C has three bonds); (b) HCN; (c) CO_2 .

Resonance: Delocalized Electron-Pair Bonding

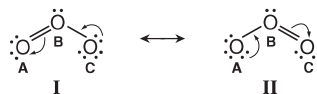
We often find that, for a molecule or polyatomic ion with a *double bond next to a single bond*, we can convert the molecular formula to more than one Lewis structure. Which, if any, is correct?

The Need for Resonance Structures To understand this issue, consider ozone (O_3), an air pollutant at ground level but an absorber of harmful ultraviolet (UV) radiation in the stratosphere. Two Lewis structures (with lettered O atoms for clarity) are



In structure I, oxygen B has a double bond to oxygen A and a single bond to oxygen C. In structure II, the single and double bonds are reversed. You can rotate I to get II, so these are *not* different types of ozone molecules, but different Lewis structures for the *same* molecule.

In fact, *neither* Lewis structure depicts O_3 accurately, because the two oxygen-oxygen bonds in O_3 are actually identical in length and energy. The bonds in O_3 have properties between an $\text{O}-\text{O}$ bond and an $\text{O}=\text{O}$ bond, something like a “one-and-a-half” bond. The molecule is shown more correctly with two Lewis structures, called **resonance structures** (or **resonance forms**), and a two-headed resonance arrow ($\longleftrightarrow$) between them. Resonance structures *have the same relative placement of atoms but different locations of bonding and lone electron pairs*. You can convert one resonance form to another by moving a lone pair to a bonding position, and vice versa:

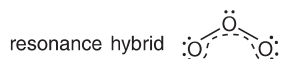


Resonance structures are not real bonding depictions: O_3 does *not* change back and forth quickly from structure I to structure II. The actual molecule is a **resonance hybrid**, an average of the resonance forms.

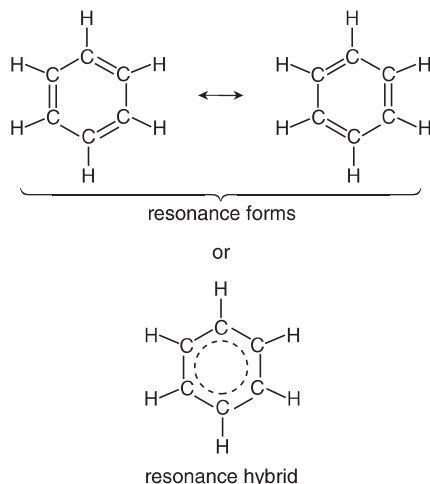
Consider these analogies for a resonance hybrid. A mule is a genetic mix, a hybrid, of a horse and a donkey; it is not a horse one instant and a donkey the next. Similarly, the color purple is a mix of two other colors, red and blue, not red one instant and blue the next. In the same sense, a resonance hybrid is one molecular species, not one resonance form this instant and another resonance form the next. The problem is that we cannot depict the hybrid accurately with a single Lewis structure.

Electron Delocalization Our need for more than one Lewis structure to depict O_3 is due to **electron-pair delocalization**. In a single, double, or triple bond, each electron pair is *localized* between the bonded atoms. In a resonance hybrid, two of the electron pairs (one bonding and one lone pair) are *delocalized*: their density is “spread” over a few adjacent atoms.

In O_3 , the result is two identical bonds, each consisting of a single bond (the localized pair) and a *partial bond* (the contribution from one of the delocalized pairs). We draw the resonance hybrid with a curved dashed line to show the delocalized pairs:



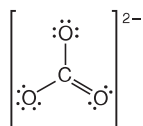
Resonance is very common. For example, benzene (C_6H_6 , shown below) has two important resonance forms in which alternating single and double bonds have different positions. The actual molecule is an average of the two forms with six $C-C$ bonds and three electron pairs delocalized over all six C atoms. The delocalized pairs are often shown as a dashed circle (or sometimes simply a circle):



Fractional Bond Orders Partial bonding, as in resonance hybrids, often leads to fractional bond orders. For the oxygen-oxygen bonds in O_3 , we have

$$\text{Bond order} = \frac{3 \text{ electron pairs}}{2 \text{ bonded-atom pairs}} = 1\frac{1}{2}$$

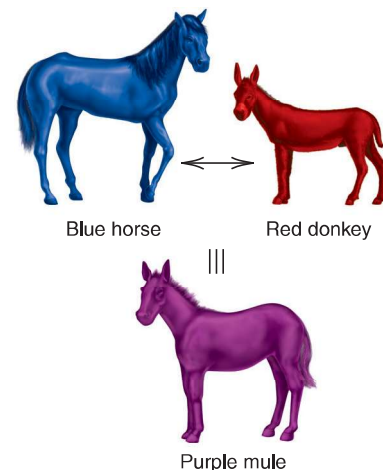
The carbon-carbon bond order in benzene is 9 electron pairs/6 bonded-atom pairs, or $1\frac{1}{2}$ also. For the carbonate ion, CO_3^{2-} , three resonance structures can be drawn. Each has 4 electron pairs shared among 3 bonded-atom pairs, so the bond order is $\frac{4}{3}$, or $1\frac{1}{3}$. One of the three resonance structures for CO_3^{2-} is



Note here (and in Sample Problem 10.4) that the Lewis structure of a polyatomic ion is drawn in *square brackets with the ion charge outside the brackets*.

THINK OF IT THIS WAY

A Purple Mule, Not a Blue Horse and a Red Donkey

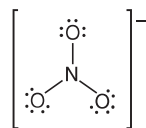


Sample Problem 10.4 Drawing Resonance Structures

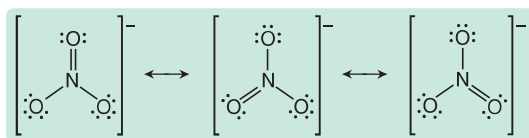
Problem Draw resonance structures for the nitrate ion, NO_3^- , and find the bond order.

Plan We draw a Lewis structure, remembering to add $1e^-$ to the total number of valence electrons because of the $1-$ ionic charge. Then we move lone and bonding pairs to draw other resonance forms and connect them with the resonance arrow. The bond order is the number of shared electron pairs divided by the number of atom pairs.

Solution After steps 1 to 4, we have



Step 5. Since N has only $6e^-$, we change a lone pair on one of the O atoms to a bonding pair to form a double bond, which gives each atom an octet. All the O atoms are equivalent, however, so we can move a lone pair from any one of the three and obtain three resonance structures:



The bond order is

$$\frac{4 \text{ shared electron pairs}}{3 \text{ bonded-atom pairs}} = 1\frac{1}{3}$$

Check Each structure has the same relative placement of atoms, an octet around each atom, and $24e^-$ (the sum of the valence electron total and $1e^-$ from the ionic charge, distributed in four bonds and eight lone pairs).

Comment These three resonance forms contribute equally to the resonance hybrid because all of the surrounding atoms are identical. This is not always the case, as you'll see next.

FOLLOW-UP PROBLEM 10.4 One of the three resonance structures for CO_3^{2-} was shown just before Sample Problem 10.4. Draw the other two.

Formal Charge: Selecting the More Important Resonance Structure

If one resonance form “looks” more like the resonance hybrid than the others, it “weights” the average in its favor. One way to select the more important resonance form is by determining each atom’s **formal charge**, the charge it would have *if the bonding electrons were shared equally*. Let’s examine this concept and then see how formal charge compares with oxidation number.

Determining Formal Charge An atom’s formal charge is its total number of valence electrons minus *all* of its unshared valence electrons and *half* of its shared valence electrons. Thus,

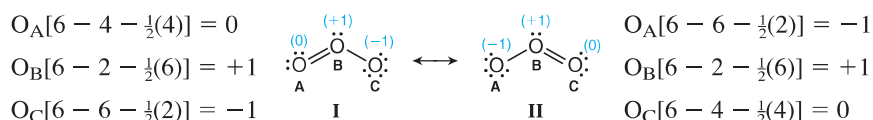
Formal charge of atom =

$$\text{no. of valence } e^- - (\text{no. of unshared valence } e^- + \frac{1}{2} \text{ no. of shared valence } e^-) \quad (10.1)$$

For example, in O_3 , the formal charge of oxygen A in resonance form I is

$$6 \text{ valence } e^- - (4 \text{ unshared } e^- + \frac{1}{2} \text{ of } 4 \text{ shared } e^-) = 6 - 4 - 2 = 0$$

The formal charges of all the atoms in the two O_3 resonance forms are



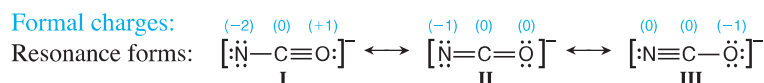
Forms I and II have the same formal charges but on different O atoms, so they contribute equally to the resonance hybrid. *Formal charges must sum to the actual charge on the species:* zero for a molecule or the ionic charge for an ion.

Note that, in I, instead of oxygen's usual two bonds, O_B has three bonds and O_C has one. Only when an atom has a zero formal charge does it have its usual number of bonds; the same holds for C in CO_3^{2-} , N in NO_3^- , and so forth.

Choosing the More Important Resonance Form Three criteria help us choose the more important resonance structure:

- Smaller formal charges (positive *or* negative) are preferable to larger ones.
- The *same* nonzero formal charges on adjacent atoms are not preferred.
- A more negative formal charge should reside on a more electronegative atom.

As in the case of O_3 , the resonance forms for CO_3^{2-} , NO_3^- , and benzene all have identical atoms surrounding the central atom(s) and, thus, have identical formal charges and are equally important contributors to the resonance hybrid. But, let's apply these criteria to the cyanate ion, NCO^- , which has two *different* atoms around the central one. Three resonance forms with formal charges are



Form I is *not* an important contributor to the hybrid because it has a larger formal charge on N and a positive formal charge on the more electronegative O. Forms II and III have the same magnitude of charges, but III has a -1 charge on O, the more electronegative atom. Therefore, II and III are more important than I, and III is more important than II.

Formal Charge Versus Oxidation Number Formal charge (used to examine resonance structures) is *not* the same as oxidation number (used to monitor redox reactions):

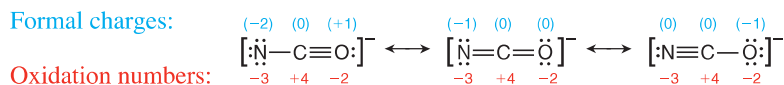
- For a *formal charge*, bonding electrons are *shared equally* by the atoms (as if the bonding were *nonpolar covalent*), so each atom has half of them:

$$\text{Formal charge} = \text{valence } e^- - (\text{lone pair } e^- + \frac{1}{2} \text{ bonding } e^-)$$

- For an *oxidation number*, bonding electrons are *transferred completely* to the more electronegative atom (as if the bonding were *pure ionic*):

$$\text{Oxidation number} = \text{valence } e^- - (\text{lone pair } e^- + \text{bonding } e^-)$$

For the three cyanate ion resonance structures,

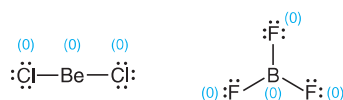


Notice that the oxidation numbers *do not* change from one resonance form to another (because the electronegativities *do not* change), but the formal charges *do* change (because the numbers of bonding and lone pairs *do* change).

Lewis Structures for Exceptions to the Octet Rule

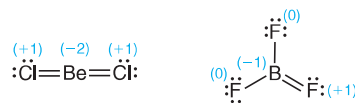
The octet rule applies to most molecules (and ions) with Period 2 central atoms, but not every one, and not to many with central atoms from Period 3 and higher. Three important exceptions occur in molecules with (1) electron-deficient atoms, (2) odd-electron atoms, and (3) atoms with expanded valence shells. In this discussion, you'll also see that formal charge has limitations for selecting the best resonance form.

Molecules with Electron-Deficient Atoms Gaseous molecules containing either beryllium or boron as the central atom are often **electron deficient**: they have *fewer* than eight electrons around the central atom. The Lewis structures, with formal charges, of gaseous beryllium chloride* and boron trifluoride are

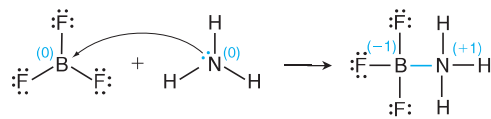


*Even though beryllium is in Group 2A(2), most Be compounds have considerable covalent bonding. For example, molten $BeCl_2$ does not conduct electricity, indicating a lack of ions.

There are only four electrons around Be and six around B. Surrounding halogen atoms don't form multiple bonds to the central atoms to give them an octet, because the halogens are much more electronegative. Formal charges make the following structures unlikely:

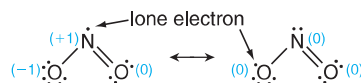


(Some data for BF_3 show a shorter than expected B—F bond. Shorter bonds indicate double-bond character, so the structure with the B=F bond may be a minor contributor to a resonance hybrid.) Electron-deficient atoms often attain an octet by forming additional bonds in reactions. When BF_3 reacts with ammonia, for instance, a compound forms in which boron attains an octet:*

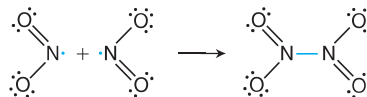


Molecules with Odd-Electron Atoms A few molecules contain a central atom with an odd number of valence electrons, so they cannot have all their electrons in pairs. Most have a central atom from an odd-numbered group, such as N [Group 5A(15)] or Cl [Group 7A(17)]. These are called **free radicals**, species that contain a lone (unpaired) electron, which makes them paramagnetic (Section 8.4) and extremely reactive (such reactivity can be especially harmful to biomolecules).

Consider the free radical nitrogen dioxide, NO_2 , a major contributor to urban smog that is formed when the NO in auto exhaust is oxidized. NO_2 has several resonance forms. Two differ in terms of which O atom is doubly bonded, as in the case of ozone. Two others have the lone electron residing on the N or on an O, so the resonance hybrid has the lone electron delocalized over these two atoms:



But the form with the lone electron on N (*left*) may be more important because of the way NO_2 reacts. Free radicals react with each other to pair up their lone electrons. When two NO_2 molecules react, the lone electrons pair up to form the N—N bond in dinitrogen tetroxide (N_2O_4) and each N attains an octet:



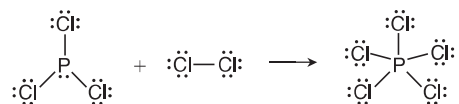
Apparently, in this case, the lone electron spends most of its time on N, so formal charge is not very useful for picking the most important resonance form; we'll see other cases below.

Expanded Valence Shells Many molecules (and ions) have more than eight valence electrons around the central atom. *An atom expands its valence shell to form more bonds, which releases energy.* The central atom must be large and have empty orbitals that can hold the additional pairs. Therefore, **expanded valence shells** (levels) occur only with *nonmetals from Period 3 or higher because they have d orbitals available.* Such a central atom may be bonded to more than four atoms or to four or fewer.

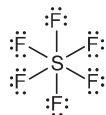
1. *Central atom bonded to more than four atoms.* Phosphorus pentachloride, PCl_5 , is a fuming yellow-white solid used to manufacture lacquers and films. It forms when phosphorus trichloride, PCl_3 , reacts with chlorine gas. The P in PCl_3 has an octet, but two more bonds to chlorine form and P expands its valence shell to 10 electrons in

*Reactions in which one species "donates" an electron pair to another to form a covalent bond are Lewis acid-base reactions, which we discuss fully in Chapter 18.

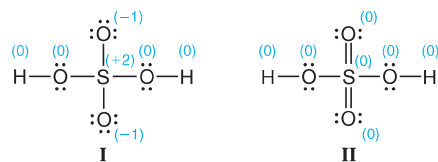
PCl_5 . Note that when PCl_5 forms, *one* Cl—Cl bond breaks (*left side of the equation*), and *two* P—Cl bonds form (*right side*), for a net increase of one bond:



Another example of a central atom with an expanded valence shell is sulfur hexafluoride, SF_6 , a remarkably dense and inert gas used as an insulator in electrical equipment. The central sulfur is surrounded by six single bonds, one to each fluorine, for a total of 12 electrons:



2. *Central atom bonded to four or fewer atoms.* By applying the concept of formal charge, we can draw Lewis structures in which a central atom has an expanded valence shell and is bonded to *four or fewer* atoms. Consider sulfuric acid, the industrial chemical produced in the greatest quantity. Two resonance forms of H_2SO_4 , with formal charges, are



Form I obeys the octet rule, but it has several nonzero formal charges. In form II, sulfur has 12 electrons (6 bonds) around it, but all zero formal charges. Thus, based on the formal charge rules alone, II contributes more than I to the resonance hybrid. More important than whether rules are followed, form II is consistent with observation. In gaseous H_2SO_4 , the two sulfur-oxygen bonds *with* an H atom attached to the O are 157 pm long, whereas the two sulfur-oxygen bonds *without* an H atom are 142 pm long. This shorter bond indicates double-bond character, and other measurements indicate greater electron density in the bonds without the attached H.

3. *Limitations of formal charges.* It's important to realize that determining formal charges is a useful, but not perfect, tool for assessing the importance of contributions to a resonance hybrid. You've already seen that it does not predict an important resonance form of NO_2 . In fact, theoretical calculations indicate that, for many species with central atoms from Period 3 or higher, such as H_2SO_4 , forms with expanded valence shells and zero formal charges (form II above) may actually be *less* important than forms with higher formal charges that follow the octet rule (form I). But we will continue to apply the formal charge rules because it is usually the simplest approach consistent with experimental data.

Sample Problem 10.5 Drawing Lewis Structures for Octet-Rule Exceptions

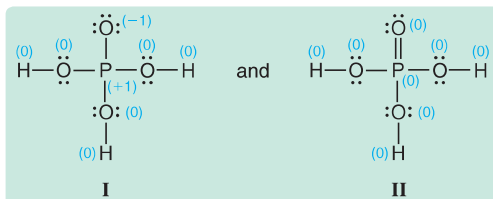
Problem Draw a Lewis structure and identify the octet-rule exception for (a) H_3PO_4 (draw two resonance forms and select the more important); (b) BFCl_2 .

Plan We draw each Lewis structure and examine it for exceptions to the octet rule.

(a) The central atom is in Period 3, so it can have more than an octet.

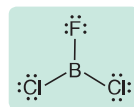
(b) The central atom is B, which can have fewer than an octet of electrons.

Solution (a) H_3PO_4 has two resonance forms. The structures, with formal charges, are



Structure I obeys the octet rule but has nonzero formal charges. Structure II has an expanded valence shell with zero formal charges. According to formal charge rules, **structure II** is the more important form.

(b) BFCl_2 has an *electron-deficient atom*; B has only six electrons surrounding it:



Comment In (a), structure II is consistent with bond-length measurements, which show one shorter (152 pm) phosphorus-oxygen bond and three longer (157 pm) ones. Nevertheless, as for H_2SO_4 , calculations show that structure I may be more important.

FOLLOW-UP PROBLEM 10.5 Draw a Lewis structure with minimal formal charges for (a) POCl_3 ; (b) ClO_2 ; (c) XeF_4 .

Summary of Section 10.1

- A stepwise process converts a molecular formula into a Lewis structure, a two-dimensional representation of a molecule (or ion) that shows the placement of atoms and distribution of valence electrons among bonding and lone pairs.
- When two or more Lewis structures can be drawn for the same relative placement of atoms, the actual molecule (or ion) is a hybrid of those resonance forms.
- Formal charges can be useful for choosing the more important contributor to the hybrid, but experimental data always determine the choice.
- Molecules with an electron-deficient atom (central Be or B) or an odd-electron atom (free radicals) have less than an octet around the central atom but often attain an octet in reactions.
- In a molecule (or ion) with a central atom from Period 3 or higher, that atom can have more than eight valence electrons because it is larger and has empty *d* orbitals for expanding its valence shell.

10.2 • VALENCE-SHELL ELECTRON-PAIR REPULSION (VSEPR) THEORY AND MOLECULAR SHAPE

Virtually every biochemical process hinges to a great extent on the shapes of interacting molecules. Every medicine you take, odor you smell, or flavor you taste depends on part or all of one molecule fitting together with another. Biologists have found that complex behaviors in many organisms, such as mating, defense, navigation, and feeding, often depend on one molecule's shape matching that of another. In this section, we discuss a model for predicting the shape of a molecule.

To obtain the molecular shape, chemists start with the Lewis structure and apply **valence-shell electron-pair repulsion (VSEPR) theory**. Its basic principle is that, *to minimize repulsions, each group of valence electrons around a central atom is located as far as possible from the others*. A “group” of electrons is any number that occupies a localized region around an atom: single bond, double bond, triple bond, lone pair, or even lone electron. (The two electron pairs in a double bond or the three pairs in a triple bond occupy separate orbitals, so they remain near each other and act as one electron group, as you'll see in Chapter 11.) The **molecular shape** is the three-dimensional arrangement of nuclei joined by the bonding groups.

Electron-Group Arrangements and Molecular Shapes

When two, three, four, five, or six objects attached to a central point maximize the space between them, five geometric patterns result, which Figure 10.2A shows with balloons. If the objects are valence-electron groups, repulsions maximize the space each occupies around the central atom, and we obtain the five *electron-group arrangements* seen in the great majority of molecules and polyatomic ions.

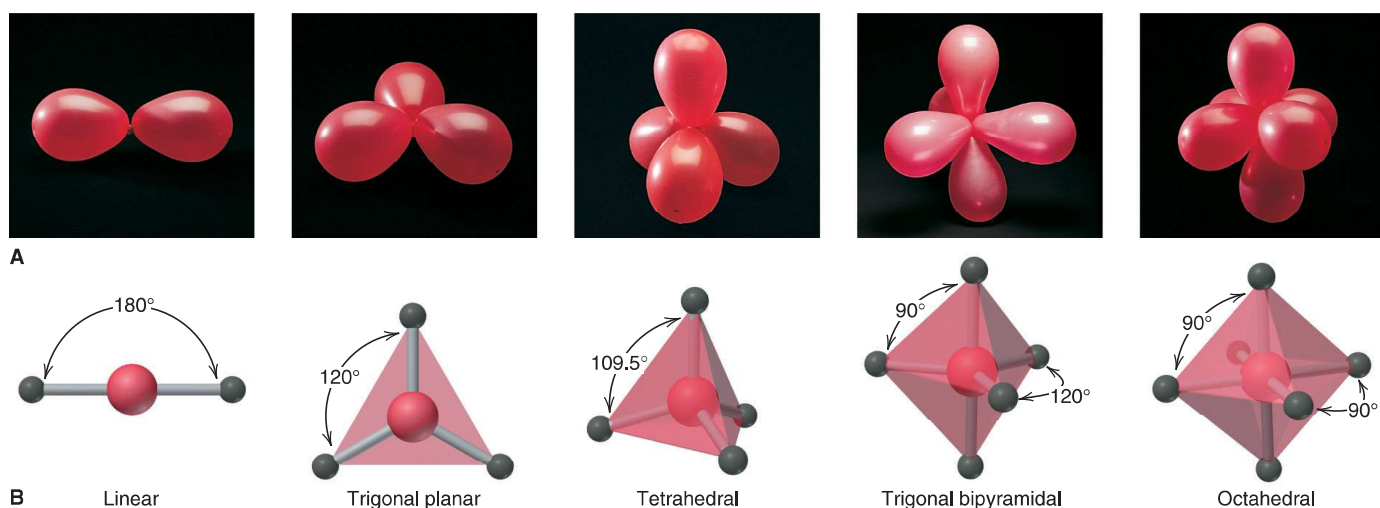
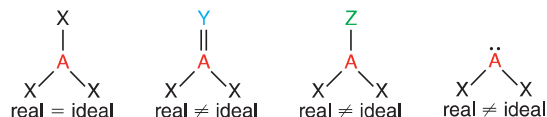


Figure 10.2 Electron-group repulsions and molecular shapes. **A**, Five geometric orientations arise when each balloon occupies as much space as possible. **B**, Mutually repelling bonding groups (gray sticks) attach a surrounding atom (dark gray) to the central atom (red). The name is the electron-group arrangement.

Classifying Molecular Shapes The *electron-group arrangement* is defined by the bonding and nonbonding electron groups, but the *molecular shape* is defined by the relative positions of the nuclei, which are connected by the bonding groups only. Figure 10.2B shows the molecular shapes that occur when *all* the surrounding electron groups are *bonding* groups. When some are *nonbonding* groups, no nucleus is attached so different molecular shapes occur. Thus, *the same electron-group arrangement can give rise to different molecular shapes*: some with all bonding groups (as in Figure 10.2B) and others with bonding and nonbonding groups. To classify molecular shapes, we assign each a specific AX_mE_n designation, where m and n are integers, A is the central atom, X is a surrounding atom, and E is a nonbonding valence-electron group (usually a lone pair).

The Importance of Bond Angle The **bond angle** is the angle formed by the nuclei of two surrounding atoms with the nucleus of the central atom at the vertex. The angles shown for the shapes in Figure 10.2B are *ideal* bond angles determined by basic geometry alone. We observe them when all the bonding groups are the same and connected to the same type of atom. When this is not the case, the *real* bond angles are not equal to the ideal angles:



The Molecular Shape with Two Electron Groups (Linear Arrangement)

Two electron groups attached to a central atom point in opposite directions. This **linear arrangement** of electron groups results in a molecule with a **linear shape** and a bond angle of 180° . Figure 10.3 shows the general form (*top*) and shape (*middle*) with VSEPR shape class (AX_2), and gives the formulas of some linear molecules.

Gaseous beryllium chloride (BeCl_2) is a linear molecule. Recall that the central Be atom is electron deficient, with two electron pairs around it:



In carbon dioxide, the central C atom forms two double bonds with the O atoms:



Each double bond acts as one electron group and is 180° away from the other. The lone pairs on the O atoms of CO_2 or on the Cl atoms of BeCl_2 are *not* involved in the molecular shape: only electron groups around the *central* atom affect shape.

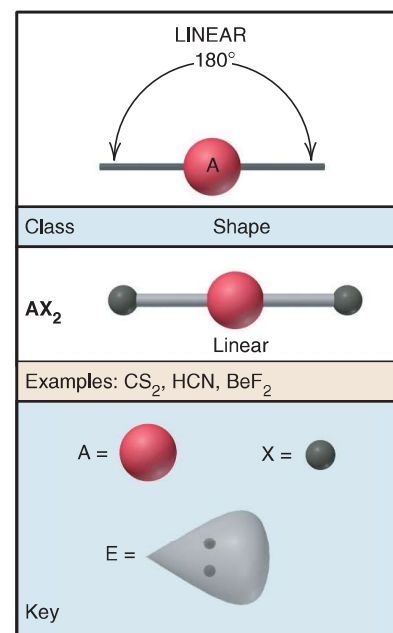


Figure 10.3 The single molecular shape of the linear electron-group arrangement. The key (*bottom*) for A, X, and E also refers to Figures 10.4, 10.5, 10.7, and 10.8.

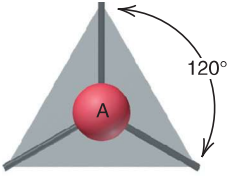
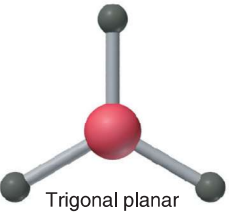
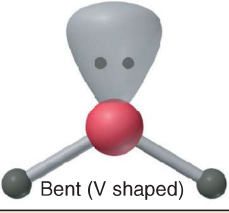
TRIGONAL PLANAR	
	
Class	Shape
AX_3	 Trigonal planar
Examples: SO_3 , BF_3 , NO_3^- , CO_3^{2-}	
AX_2E	 Bent (V shaped)
Examples: SO_2 , O_3 , $PbCl_2$, $SnBr_2$	

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

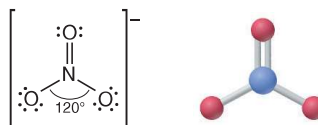
Molecular Shapes with Three Electron Groups (Trigonal Planar Arrangement)

Three electron groups around a central atom point to the corners of an equilateral triangle, which gives the **trigonal planar arrangement** and an ideal bond angle of 120° (Figure 10.4). This arrangement has two molecular shapes—one with all bonding groups and the other with one lone pair. It allows us to see *the effects of lone pairs and double bonds on bond angles*.

1. *All bonding groups: trigonal planar shape (AX_3)*. Boron trifluoride (BF_3), another molecule in which the central atom is electron deficient, is an example. It has six electrons around the central B atom in three single bonds to F atoms. The four nuclei lie in a plane, and each F—B—F angle is 120° :

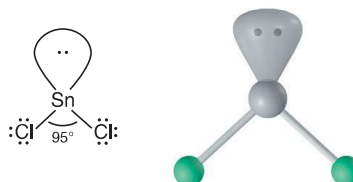


The nitrate ion (NO_3^-) is one of several polyatomic ions with the trigonal planar shape. One of three resonance forms of the nitrate ion (Sample Problem 10.4) is

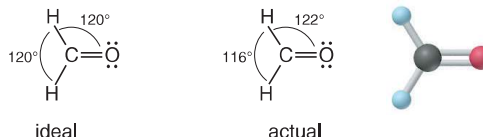


The resonance hybrid has three identical bonds of bond order $1\frac{1}{3}$, so the ideal bond angle is observed.

2. *One lone pair: bent or V shape (AX_2E)*. Gaseous tin(II) chloride is a molecule with a **bent shape**, or **V shape**. The three electron groups are in a trigonal plane with the lone pair at one of the triangle's corners. A lone pair often has a major effect on bond angle. Because it is held by only one nucleus, a lone pair is less confined than a bonding pair and so exerts stronger repulsions. In general, *a lone pair repels bonding pairs more than bonding pairs repel each other, so it decreases the angle between bonding pairs*. Note the 95° bond angle in $SnCl_2$, which is considerably less than the ideal 120° :



Effect of Double Bonds on Bond Angle When the surrounding atoms and electron groups are not identical, the bond angles may also be affected. Consider formaldehyde (CH_2O), whose uses include the manufacture of countertops and the production of methanol. Its trigonal planar shape includes two types of surrounding atoms (O and H) and two types of electron groups (single and double bonds):

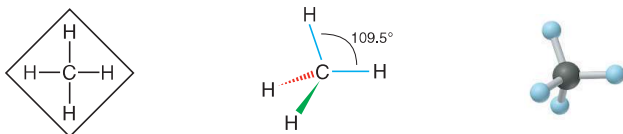


The actual H—C—H bond angle is less than the ideal 120° because *the greater electron density of a double bond repels electrons in single bonds more than the single bonds repel each other*.

Molecular Shapes with Four Electron Groups (Tetrahedral Arrangement)

Shapes based on two or three electron groups lie in a plane, but four electron groups require three dimensions to maximize separation. Consider methane, whose Lewis struc-

ture (*below, left*) shows four bonds pointing to the corners of a square, which suggests 90° bond angles. But, *Lewis structures do not depict shape*. In three dimensions, the four electron groups lie at the corners of a *tetrahedron*, a polyhedron with four faces made of equilateral triangles, giving bond angles of 109.5° (Figure 10.5).



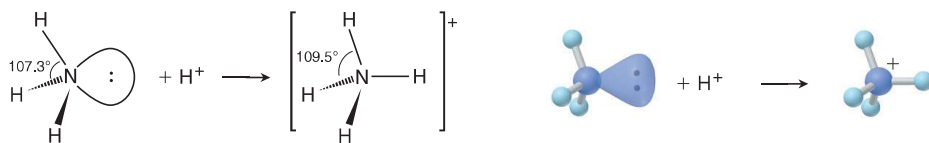
A *wedge-bond perspective drawing* for methane (*above, middle*) indicates depth by using solid and dashed wedges for bonds out of the plane of the page. The normal bond lines (*blue*) are in the plane of the page; the solid wedge (*green*) is the bond from the C atom in the plane of the page to the H above that plane; and the dashed wedge (*red*) is the bond from the C to the H below the plane of the page. The ball-and-stick model (*above, right*) shows the tetrahedral shape more clearly.

All molecules or ions with four electron groups around a central atom adopt the **tetrahedral arrangement**. There are three shapes with this arrangement:

1. *All bonding groups: tetrahedral shape (AX₄)*. Methane has a tetrahedral shape, a very common geometry in organic molecules. In Sample Problem 10.1, we drew the Lewis structure for CCl₂F₂, without regard to relative placement of the four halogen atoms around the carbon atom. Because Lewis structures are flat, it may seem like you can write two different ones for CCl₂F₂, but they represent the same molecule, as a twist of the wrist reveals (Figure 10.6).

2. *One lone pair: trigonal pyramidal shape (AX₃E)*. Ammonia (NH₃) is an example of a molecule with a **trigonal pyramidal shape**, a tetrahedron with one vertex “missing.” Stronger repulsions by the lone pair make the H—N—H bond angle slightly less than the ideal 109.5°. The lone pair forces the N—H pairs closer to each other, and the bond angle is 107.3°.

Picturing shapes is a great way to visualize a reaction. For instance, when ammonia reacts with an acid, the lone pair on N forms a bond to the H⁺ and yields the ammonium ion (NH₄⁺), one of many tetrahedral polyatomic ions. As the lone pair becomes a bonding pair, the H—N—H angle expands from 107.3° to 109.5°:



3. *Two lone pairs: bent or V shape (AX₂E₂)*. Water is the most important V-shaped molecule with the tetrahedral arrangement. [Note that, in the trigonal planar arrangement, the V shape has two bonding groups and *one* lone pair (AX₂E), and its ideal

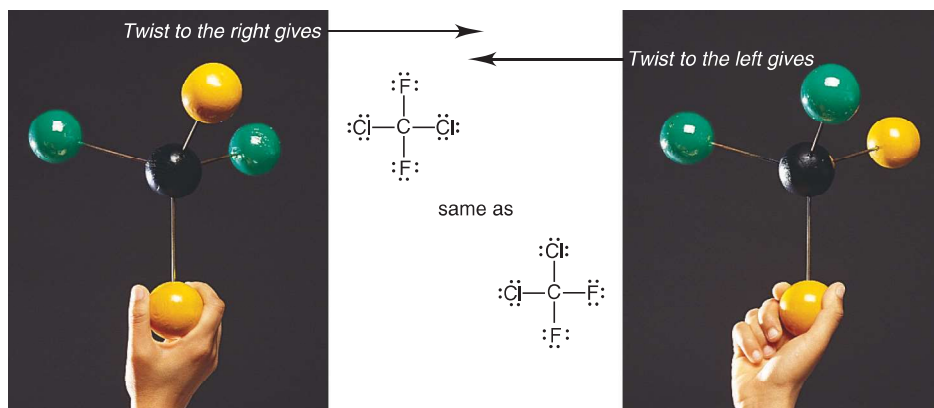


Figure 10.6 Lewis structures do not indicate molecular shape. In this model, Cl is green and F is yellow.

Class	Shape
AX ₄	 Tetrahedral
Examples: CH ₄ , SiCl ₄ , SO ₄ ²⁻ , ClO ₄ ⁻	
AX ₃ E	 Trigonal pyramidal
Examples: NH ₃ , PF ₃ , ClO ₃ ⁻ , H ₃ O ⁺	
AX ₂ E ₂	 Bent (V shaped)
Examples: H ₂ O, OF ₂ , SCl ₂	

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

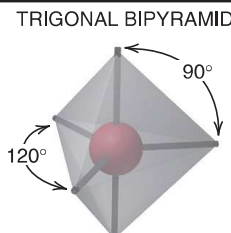
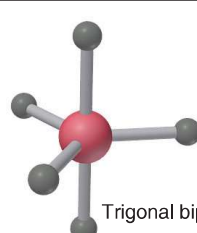
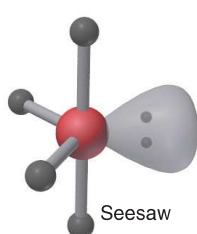
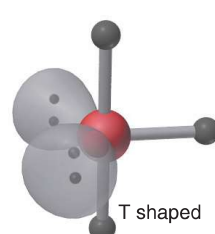
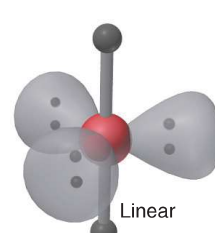
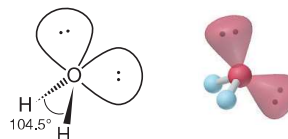
	
Class	Shape
AX_5	 Trigonal bipyramidal
Examples: PF_5 , AsF_5 , SOF_4	
AX_4E	 Seesaw
Examples: SF_4 , XeO_2F_2 , IF_4^+ , $IO_2F_2^-$	
AX_3E_2	 T shaped
Examples: ClF_3 , BrF_3	
AX_2E_3	 Linear
Examples: XeF_2 , I_3^- , IF_2^-	

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

bond angle is 120° , not 109.5° .] Repulsions from two lone pairs are greater than from one, and the $H-O-H$ bond angle is 104.5° , less than the $H-N-H$ angle in NH_3 :



Thus, for similar molecules within a given electron-group arrangement, electron-electron repulsions cause deviations from ideal bond angles in the following order:

$$\text{Lone pair-lone pair} > \text{lone pair-bonding pair} > \text{bonding pair-bonding pair} \quad (10.2)$$

Molecular Shapes with Five Electron Groups (Trigonal Bipyramidal Arrangement)

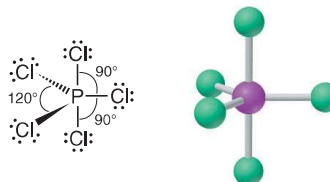
All molecules with five or six electron groups have a central atom from Period 3 or higher because only those atoms have *d* orbitals available to expand the valence shell.

Relative Positions of Electron Groups Five mutually repelling electron groups form the **trigonal bipyramidal arrangement**, in which two trigonal pyramids share a common base (Figure 10.7). This is the only case in which *there are two different positions for electron groups and two ideal bond angles*. Three **equatorial groups** lie in a trigonal plane that includes the central atom, and two **axial groups** lie above and below this plane. Therefore, a 120° bond angle separates equatorial groups, and a 90° angle separates axial from equatorial groups. Two factors come into play:

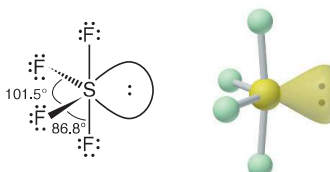
- The greater the bond angle, the weaker the repulsions, so *equatorial-equatorial* (120°) *repulsions are weaker than axial-equatorial* (90°) *repulsions*.
- The stronger repulsions from lone pairs means that, when possible, *lone pairs occupy equatorial positions*.

Shapes for the Trigonal Bipyramidal Arrangement The tendency for lone pairs to occupy equatorial positions, and thus minimize stronger axial-equatorial repulsions, governs three of the four shapes for this arrangement.

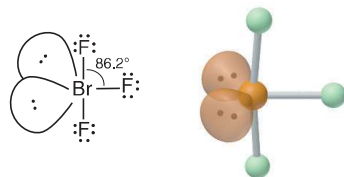
1. *All bonding groups: trigonal bipyramidal shape* (AX_5). Phosphorus pentachloride (PCl_5) has a trigonal bipyramidal shape. With five identical surrounding atoms, the bond angles are ideal:



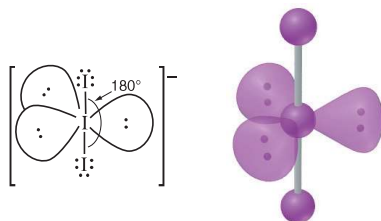
2. *One lone pair: seesaw shape* (AX_4E). Sulfur tetrafluoride (SF_4), a strong fluorinating agent, has the **seesaw shape**; in Figure 10.7, the “seesaw” is tipped on an end. This is the first example of *lone pairs occupying equatorial positions* to minimize repulsions. The lone pair repels all four bonding pairs, reducing the bond angles to 101.5° and 86.8° :



3. *Two lone pairs: T shape (AX_3E_2).* Bromine trifluoride (BrF_3), one of many compounds with fluorine bonded to a larger halogen, has a **T shape**. Since both lone pairs occupy equatorial positions, we see a greater decrease in the axial-equatorial bond angle, down to 86.2° :



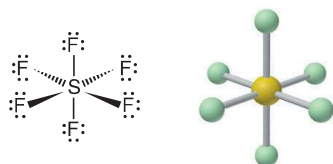
4. *Three lone pairs: linear shape (AX_2E_3).* The triiodide ion (I_3^-), which forms when I_2 dissolves in aqueous I^- solution, is linear. With three equatorial lone pairs and two axial bonding pairs, the three nuclei form a straight line and a 180° X—A—X bond angle:



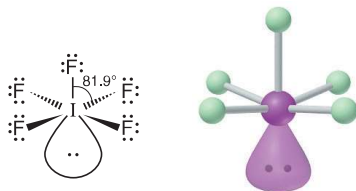
Molecular Shapes with Six Electron Groups (Octahedral Arrangement)

Six electron groups form the **octahedral arrangement**. An *octahedron* is a polyhedron with eight equilateral triangles for faces and six identical vertices (Figure 10.8). Each of the six groups points to a corner, which gives a 90° ideal bond angle.

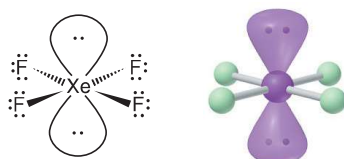
1. *All bonding groups: octahedral shape (AX_6).* When seesaw-shaped SF_4 (discussed above) reacts with more F_2 , the central S atom expands its valence shell further to form octahedral sulfur hexafluoride (SF_6):



2. *One lone pair: square pyramidal shape (AX_5E).* Iodine pentafluoride (IF_5) has a **square pyramidal shape**. Note that it makes no difference where one lone pair resides because all the bond angles are 90° . The lone pair reduces the bond angles to 81.9° :



3. *Two lone pairs: square planar shape (AX_4E_2).* Xenon tetrafluoride (XeF_4) has a **square planar shape**. To avoid stronger 90° lone pair–lone pair repulsions, two lone pairs lie *opposite* each other:



Class	Shape
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 10.8 The three molecular shapes of the octahedral electron-group arrangement.

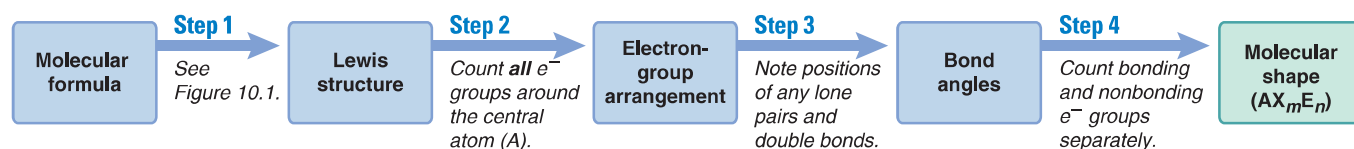


Figure 10.9 The four steps in converting a molecular formula to a molecular shape.

Using VSEPR Theory to Determine Molecular Shape

Let's apply a stepwise method for using VSEPR theory to determine a molecular shape from a molecular formula (Figure 10.9):

Step 1. Write the Lewis structure from the molecular formula (see Figure 10.1) to show the relative placement of atoms and the number of electron groups.

Step 2. Assign an electron-group arrangement by counting *all* electron groups (bonding plus nonbonding) around the central atom.

Step 3. Predict the ideal bond angle from the electron-group arrangement and *the effect of any deviation* caused by lone pairs or double bonds.

Step 4. Draw and name the molecular shape by counting bonding groups and nonbonding groups separately.

The next two sample problems apply these steps.

Sample Problem 10.6

Examining Shapes with Two, Three, or Four Electron Groups

Problem Draw the molecular shapes and predict the bond angles (relative to the ideal angles) of (a) PF_3 and (b) COCl_2 .

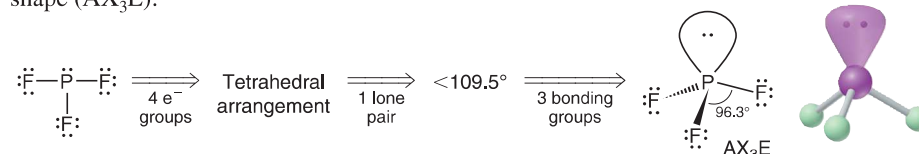
Solution (a) For PF_3 :

Step 1. Write the Lewis structure from the formula (see below, left).

Step 2. Assign the electron-group arrangement: Three bonding groups and one lone pair give four electron groups around P and the *tetrahedral arrangement*.

Step 3. Predict the bond angle: The ideal bond angle is 109.5° . There is one lone pair, so the actual bond angle will be *less than* 109.5° .

Step 4. Draw and name the molecular shape: With one lone pair, PF_3 has a *trigonal pyramidal* shape (AX_3E):



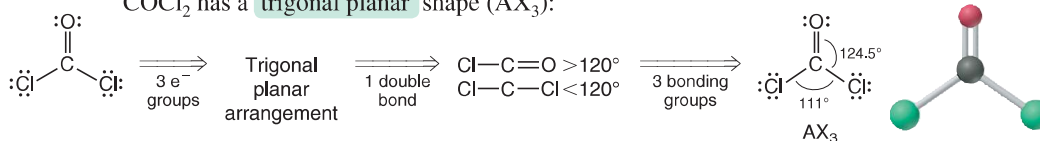
(b) For COCl_2 :

Step 1. Write the Lewis structure from the formula (see below, left).

Step 2. Assign the electron-group arrangement: Two single bonds and one double bond give three electron groups around C and the *trigonal planar arrangement*.

Step 3. Predict the bond angles: The ideal bond angle is 120° , but the double bond between C and O will compress the $\text{Cl} \text{---} \text{C} \text{---} \text{Cl}$ angle to *less than* 120° .

Step 4. Draw and name the molecular shape: With three electron groups and no lone pairs, COCl_2 has a *trigonal planar* shape (AX_3):



Check We compare the answers with the general information in Figures 10.5 and 10.4, respectively.

Comment Be sure the Lewis structure is correct because it determines the other steps.

FOLLOW-UP PROBLEM 10.6 Draw the molecular shapes and predict the bond angles (relative to the ideal angles) of (a) CS_2 ; (b) PbCl_2 ; (c) CBr_4 ; (d) SF_2 .

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 angles) of (a) SbF_5 and (b) BrF_5 .

Plan We proceed as in Sample Problem 10.6, being sure to minimize the number of axial-equatorial repulsions.

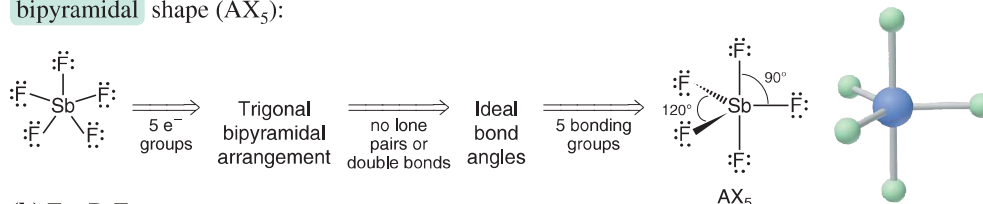
Solution (a) For SbF_5 :

Step 1. Lewis structure (see below, left).

Step 2. Electron-group arrangement: With five electron groups, this is the *trigonal bipyramidal* arrangement.

Step 3. Bond angles: All the groups and surrounding atoms are identical, so the bond angles are ideal: 120° between equatorial groups and 90° between axial and equatorial groups.

Step 4. Molecular shape: Five electron groups and no lone pairs give the *trigonal bipyramidal* shape (AX_5):



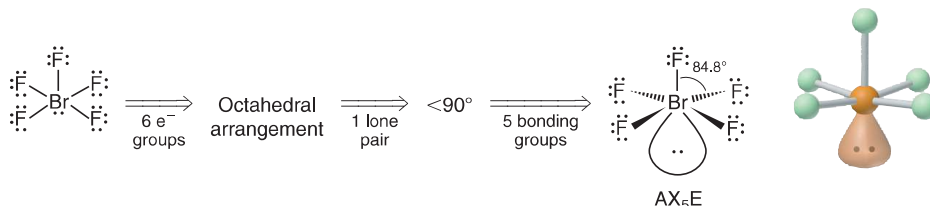
(b) For BrF_5 :

Step 1. Lewis structure (see below, left).

Step 2. Electron-group arrangement: Six electron groups give the *octahedral* arrangement.

Step 3. Bond angles: The lone pair will make all bond angles less than the ideal 90° .

Step 4. Molecular shape: With one lone pair, BrF_5 has the *square pyramidal* shape (AX_5E):



Check We compare our answers with Figures 10.7 and 10.8.

Comment We will also see the linear, tetrahedral, square planar, and octahedral shapes in an important group of substances, called *coordination compounds*, in Chapter 23.

FOLLOW-UP PROBLEM 10.7 Draw the molecular shapes and predict the bond angles (relative to the ideal angles) of (a) ICl_2^- ; (b) ClF_3 ; (c) SOF_4 .

Molecular Shapes with More Than One Central Atom

The shapes of molecules with more than one central atom are composites of the shapes around each of the central atoms. Here are two examples:

1. Ethane (CH_3CH_3 ; molecular formula C_2H_6) is a component of natural gas. With four bonding groups and no lone pairs around the two central carbons, ethane is shaped like two overlapping tetrahedra (Figure 10.10A).

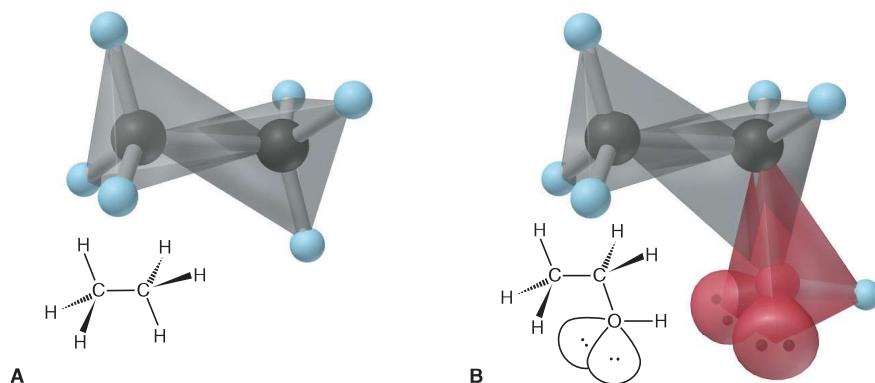


Figure 10.10 The tetrahedral shapes around the central atoms and the overall shapes of ethane (A) and ethanol (B).

2. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$; molecular formula $\text{C}_2\text{H}_6\text{O}$), the intoxicating substance in beer, wine, and whiskey, has three central atoms (Figure 10.10B). The CH_3 — group is tetrahedrally shaped, and the —CH_2 — group has four bonding groups around its central C atom, so it is also tetrahedrally shaped. The O atom has two bonding groups and two lone pairs around it, so the —OH group has a V shape (AX_2E_2).

Sample Problem 10.8

Predicting Molecular Shapes with More Than One Central Atom

Problem Determine the shape around each central atom in acetone, $(\text{CH}_3)_2\text{CO}$.

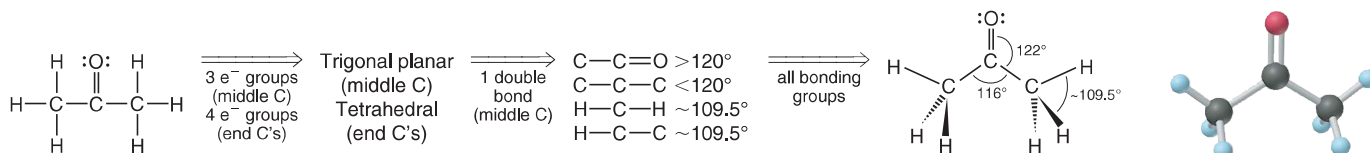
Plan There are three central C atoms, two of which are in CH_3 — groups. We determine the shape around one central atom at a time.

Solution *Step 1.* Lewis structure (see below, left).

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

Step 3. Bond angles: The H—C—H angle in CH_3 — should be near the ideal 109.5° . The C=O double bond will compress the C—C—C angle to less than the ideal 120° .

Step 4. Shapes around central atoms: With four electron groups and no lone pairs, the shape around C in each CH_3 — is **tetrahedral** (AX_4). With three electron groups and no lone pairs, the shape around the middle C is **trigonal planar** (AX_3):



FOLLOW-UP PROBLEM 10.8 Determine the shape around each central atom and predict any deviations from ideal bond angles in the following: (a) H_2SO_4 ; (b) propyne (C_3H_4 ; there is one $\text{C}\equiv\text{C}$ bond); (c) S_2F_2 .

Summary of Section 10.2

- VSEPR theory proposes that each electron group (single bond, multiple bond, lone pair, or lone electron) around a central atom remains as far from the others as possible.
- Five electron-group arrangements are possible when two, three, four, five, or six electron groups surround a central atom. Each arrangement is associated with one or more molecular shapes, depending on the numbers of bonding and lone pairs.
- Ideal bond angles are based on the regular geometric arrangements. Deviations from them occur when surrounding atoms and/or electron groups are not identical.
- Lone pairs and double bonds exert stronger repulsions than single bonds.
- Shapes of larger molecules are composites of the shapes around each central atom.

10.3 • MOLECULAR SHAPE AND MOLECULAR POLARITY

Knowing the shape of its molecules is key to understanding the physical and chemical behavior of a substance. One of the most far-reaching effects of molecular shape is molecular polarity, which can influence melting and boiling points, solubility, reactivity, and even biological function.

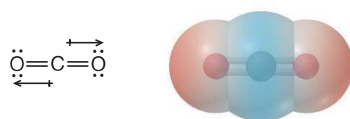
Recall from Chapter 9 that a covalent bond is *polar* when the atoms have different electronegativities and, thus, share the electrons unequally. In diatomic molecules, such as HF, the only bond is polar, so the molecule is polar. In larger molecules, *both shape and bond polarity determine molecular polarity*, an imbalance of charge over the whole molecule or large portion of it. Polar molecules become oriented in an

electric field, with their partially charged ends pointing toward the oppositely charged plates (Figure 10.11). **Dipole moment (μ)** is a measure of molecular polarity, given in the unit *debye* (D) derived from SI units of charge (coulomb, C) and length (m): $1 \text{ D} = 3.34 \times 10^{-30} \text{ C} \cdot \text{m}$. [The unit is named for the Dutch-American scientist Peter Debye (1884–1966) who won the Nobel Prize in 1936 for contributions to the fields of molecular structure and solution behavior.]

Bond Polarity, Bond Angle, and Dipole Moment

The presence of polar bonds does not *always* result in a polar molecule; we must also consider shape and the atoms surrounding the central atom. Here are three cases:

1. CO_2 : *polar bonds, nonpolar molecule*. In carbon dioxide, the electronegativity difference between C (EN = 2.5) and O (EN = 3.5) makes each C=O bond polar. But CO_2 is linear, so the bonds point 180° from each other. The two bond polarities are counterbalanced, and the molecule has *no net dipole moment* ($\mu = 0 \text{ D}$). The electron density model shows regions of high negative charge (*red*) distributed equally on either side of the central region of high positive charge (*blue*):

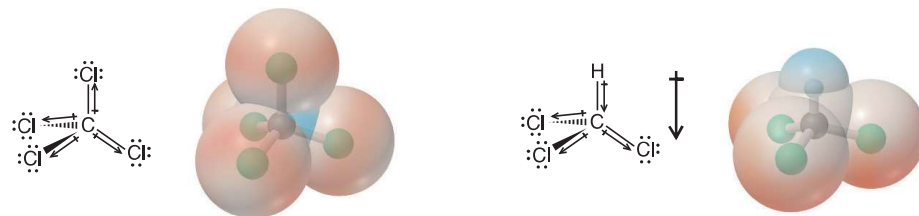


2. H_2O : *polar bonds, polar molecule*. Water also has two polar bonds, but it is polar ($\mu = 1.85 \text{ D}$). In each O—H bond, electron density is pulled from H (EN = 2.1) toward O (EN = 3.5). Bond polarities are *not* counterbalanced because the molecule is V shaped (see also Figure 4.1). The bond polarities are partially reinforced, making the O end partially negative and the other end (the region between the H atoms) partially positive:



(The molecular polarity of water has some amazing effects, from determining the composition of the oceans to supporting life itself, as you'll see in Chapter 12.)

3. *Same shapes, different polarities*. When different molecules have the same shape, the identities of the surrounding atoms affect polarity. Carbon tetrachloride (CCl_4) and chloroform (CHCl_3) are tetrahedral molecules with very different polarities. In CCl_4 , all the surrounding atoms are Cl atoms. Each C—Cl bond is polar ($\Delta\text{EN} = 0.5$), but the molecule is nonpolar ($\mu = 0 \text{ D}$) because the bond polarities counterbalance each other. In CHCl_3 , an H replaces one Cl, disrupting the balance and giving chloroform a significant dipole moment ($\mu = 1.01 \text{ D}$):



Sample Problem 10.9 Predicting the Polarity of Molecules

Problem For each compound, use the molecular shape and EN values and trends (Figure 9.18) 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 point a polar arrow toward the atom with higher EN in each bond. If the bond polarities balance one another, the molecule is nonpolar; if they reinforce each other, we show the direction of the molecular polarity.

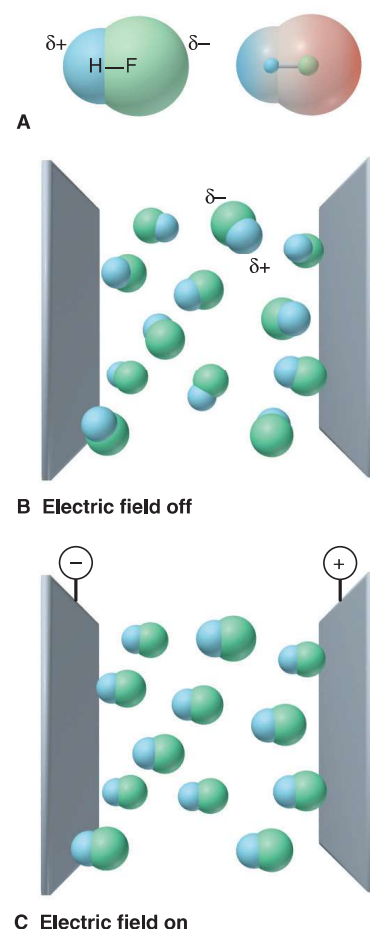
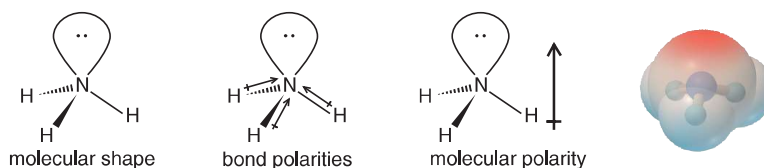


Figure 10.11 The orientation of polar molecules in an electric field.

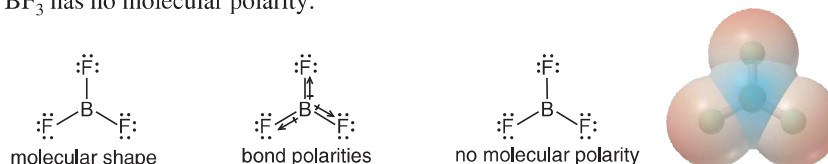
A, Space-filling (*left*) and electron density models (*right*, with red negative and blue positive) of the polar HF molecule. **B**, With the external electric field off, HF molecules are oriented randomly. **C**, With the field on, the molecules, on average, become oriented.

Solution (a) For NH_3 : The molecular shape is trigonal pyramidal. N ($\text{EN} = 3.0$) is more electronegative than H ($\text{EN} = 2.1$), so the bond polarities point toward N and partially reinforce each other; thus the molecular polarity points toward N:



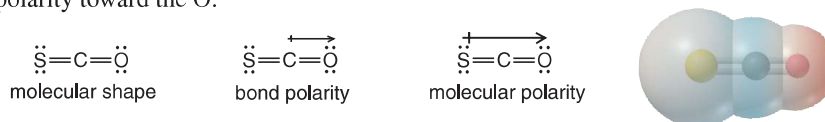
Therefore, **ammonia is polar.**

(b) For BF_3 : The molecular shape is trigonal planar. F ($\text{EN} = 4.0$) is farther to the right in Period 2 than B ($\text{EN} = 2.0$), so it is more electronegative; thus, each bond polarity points toward F. However, the bond angle is 120° , so the three bond polarities balance each other, and BF_3 has no molecular polarity:



Therefore, **boron trifluoride is nonpolar.**

(c) For COS : The molecular shape is linear. With C and S having the same EN, the $\text{C}=\text{S}$ bond is nonpolar, but the $\text{C}=\text{O}$ bond is quite polar ($\Delta\text{EN} = 1.0$), so there is a net molecular polarity toward the O:



Therefore, **carbonyl sulfide is polar.**

Check The electron density models confirm our conclusions. Note that, in (b), the negative (*red*) regions surround the central B atom (*blue*) symmetrically.

FOLLOW-UP PROBLEM 10.9 Show the bond polarities and molecular polarity, if any, for each compound: **(a)** dichloromethane (CH_2Cl_2); **(b)** iodine oxide pentafluoride (IOF_5); **(c)** nitrogen tribromide (NBr_3).

Summary of Section 10.3

- Bond polarity and molecular shape determine molecular polarity, which is measured as a dipole moment.
- A molecule with polar bonds is not necessarily a polar molecule. When bond polarities counterbalance each other, the molecule is nonpolar; when they reinforce each other, the molecule is polar.

CHAPTER REVIEW GUIDE

The following sections provide many aids to help you study this chapter. (Numbers in parentheses refer to pages, unless noted otherwise.)

Learning Objectives

These are concepts and skills to review after studying this chapter.

Related section (§), sample problem (SP), and upcoming end-of-chapter problem (EP) numbers are listed in parentheses.

1. Use the octet rule to write a Lewis structure from a molecular formula (§10.1) (SPs 10.1–10.3) (EPs 10.1, 10.5–10.8)
2. Understand how electron delocalization explains bond properties, and write resonance structures (§10.1) (SP 10.4) (EPs 10.2, 10.9–10.12)
3. Describe the three types of exceptions to the octet rule, draw Lewis structures for such molecules, and use formal charges to select the most important resonance structure (§10.1) (SP 10.5) (EPs 10.3, 10.4, 10.13–10.24)
4. Describe the five electron-group arrangements and associated molecular shapes, predict molecular shapes from Lewis structures, and explain deviations from ideal bond angles (§10.2) (SPs 10.6–10.8) (EPs 10.25–10.50)
5. Understand how a molecule's polarity arises, and use molecular shape and EN values to predict the direction of a dipole (§10.3) (SP 10.9) (EPs 10.51–10.56)

Key Terms

These important terms appear in boldface in the chapter and are defined again in the Glossary.

Section 10.1

Lewis structure (Lewis formula) (303)
 resonance structure (resonance form) (306)
 resonance hybrid (306)
 electron-pair delocalization (307)
 formal charge (308)
 electron deficient (309)

free radical (310)
 expanded valence shell (310)

Section 10.2

valence-shell electron-pair repulsion (VSEPR) theory (312)
 molecular shape (312)
 bond angle (313)
 linear arrangement (313)
 linear shape (313)

trigonal planar arrangement (314)
 bent shape (V shape) (314)
 tetrahedral arrangement (315)
 trigonal pyramidal shape (315)
 trigonal bipyramidal arrangement (316)
 equatorial group (316)
 axial group (316)

seesaw shape (316)
 T shape (317)
 octahedral arrangement (317)
 square pyramidal shape (317)
 square planar shape (317)

Section 10.3

molecular polarity (320)
 dipole moment (μ) (321)

Key Equations and Relationships

Numbered and screened concepts are listed for you to refer to or memorize.

10.1 Calculating the formal charge on an atom (308):

Formal charge of atom

$$= \text{no. of valence } e^-$$

$$- (\text{no. of unshared valence } e^- + \frac{1}{2} \text{ no. of shared valence } e^-)$$

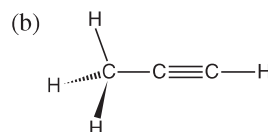
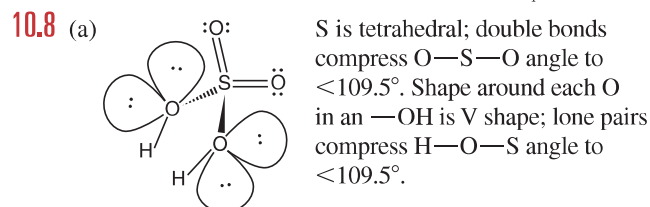
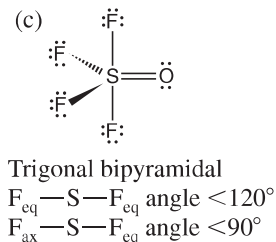
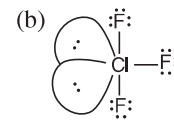
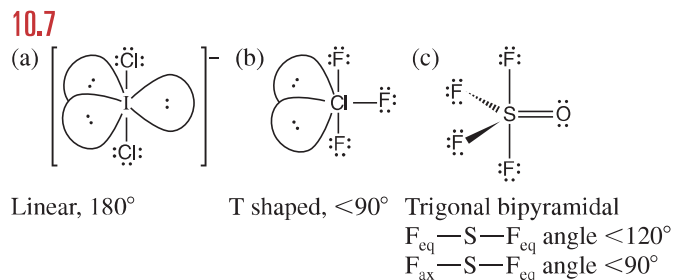
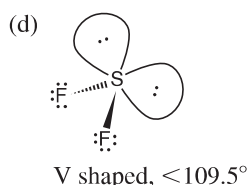
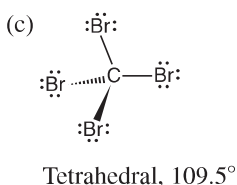
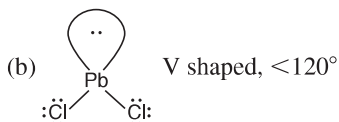
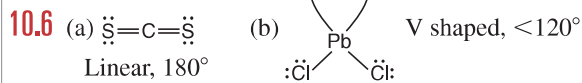
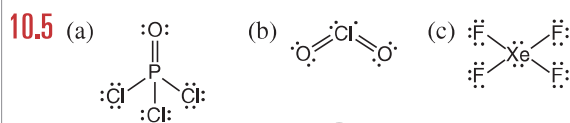
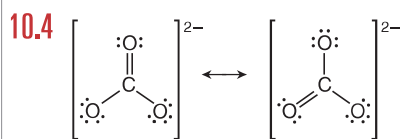
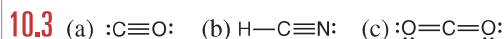
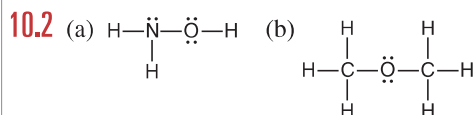
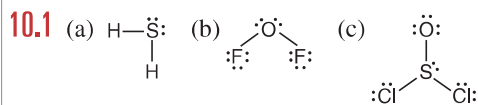
10.2 Ranking the effect of electron-pair repulsions on bond angle (316):

Lone pair–lone pair > lone pair–bonding pair >

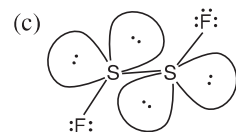
bonding pair–bonding pair

BRIEF SOLUTIONS TO FOLLOW-UP PROBLEMS

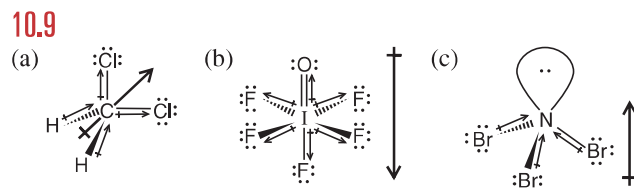
Compare your own solutions to these calculation steps and answers.



Shape around C in CH_3- is tetrahedral, with angles $\sim 109.5^\circ$; other C atoms are linear, 180° .



V shape around each S; $\text{F}-\text{S}-\text{S}$ angle $<109.5^\circ$.



PROBLEMS

Problems with **colored** numbers are answered in Appendix E. Sections match the text and provide the numbers of relevant sample problems. Bracketed problems are grouped in pairs (indicated by a short rule) that cover the same concept. Comprehensive Problems are based on material from any section or previous chapter.

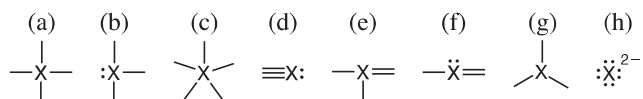
Depicting Molecules and Ions with Lewis Structures

(Sample Problems 10.1 to 10.5)

10.1 Which of these atoms *cannot* serve as a central atom in a Lewis structure: (a) O; (b) He; (c) F; (d) H; (e) P? Explain.

10.2 When is a resonance hybrid needed to adequately depict the bonding in a molecule? Using NO_2 as an example, explain how a resonance hybrid is consistent with the actual bond length, bond strength, and bond order.

10.3 In which of these bonding patterns does X obey the octet rule?



10.4 What is required for an atom to expand its valence shell? Which of the following atoms can expand its valence shell: F, S, H, Al, Se, Cl?

10.5 Draw a Lewis structure for (a) SiF_4 ; (b) SeCl_2 ; (c) COF_2 (C is central).

10.6 Draw a Lewis structure for (a) PH_4^+ ; (b) C_2F_4 ; (c) SbH_3 .

10.7 Draw a Lewis structure for (a) PF_3 ; (b) H_2CO_3 (both H atoms are attached to O atoms); (c) CS_2 .

10.8 Draw a Lewis structure for (a) CH_4S ; (b) S_2Cl_2 ; (c) CHCl_3 .

10.9 Draw Lewis structures of all the important resonance forms of (a) NO_2^+ ; (b) NO_2F (N is central).

10.10 Draw Lewis structures of all the important resonance forms of (a) HNO_3 (HONO_2); (b) HAsO_4^{2-} (HOAsO_3^{2-}).

10.11 Draw Lewis structures of all the important resonance forms of (a) N_3^- ; (b) NO_2^- .

10.12 Draw Lewis structures of all the important resonance forms of (a) HCO_2^- (H is attached to C); (b) HBrO_4 (HOBrO_3).

10.13 Draw the Lewis structure with lowest formal charges, and determine the charge of each atom in (a) IF_5 ; (b) AlH_4^- .

10.14 Draw the Lewis structure with lowest formal charges, and determine the charge of each atom in (a) OCS ; (b) NO .

10.15 Draw a Lewis structure for a resonance form of each ion with the lowest possible formal charges, show the charges, and give oxidation numbers of the atoms: (a) BrO_3^- ; (b) SO_3^{2-} .

10.16 Draw a Lewis structure for a resonance form of each ion with the lowest possible formal charges, show the charges, and give oxidation numbers of the atoms: (a) AsO_4^{3-} ; (b) ClO_2^- .

10.17 These species do not obey the octet rule. Draw a Lewis structure for each, and state the type of octet-rule exception:

(a) BH_3 (b) AsF_4^- (c) SeCl_4

10.18 These species do not obey the octet rule. Draw a Lewis structure for each, and state the type of octet-rule exception:

(a) PF_6^- (b) ClO_3 (c) H_3PO_3 (one P—H bond)

10.19 These species do not obey the octet rule. Draw a Lewis structure for each, and state the type of octet-rule exception:

(a) BrF_3 (b) ICl_2^- (c) BeF_2

10.20 These species do not obey the octet rule. Draw a Lewis structure for each, and state the type of octet-rule exception:

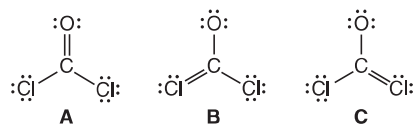
(a) O_3^- (b) XeF_2 (c) SbF_4^-

10.21 Molten beryllium chloride reacts with chloride ion from molten NaCl to form the BeCl_4^{2-} ion, in which the Be atom attains an octet. Show the net ionic reaction with Lewis structures.

10.22 Despite many attempts, the perbromate ion (BrO_4^-) was not prepared in the laboratory until about 1970. (In fact, articles were published explaining theoretically why it could never be prepared!) Draw a Lewis structure for BrO_4^- in which all atoms have lowest formal charges.

10.23 Cryolite (Na_3AlF_6) is an indispensable component in the electrochemical production of aluminum. Draw a Lewis structure for the AlF_6^{3-} ion.

10.24 Phosgene is a colorless, highly toxic gas that was employed against troops in World War I and it is used today as a key reactant in organic syntheses. From the following resonance structures, select the one with the lowest formal charges:



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

(Sample Problems 10.6 to 10.8)

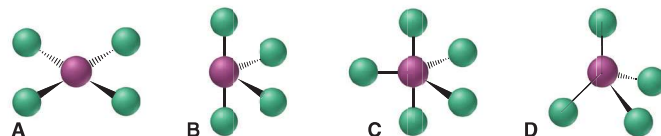
10.25 If you know the formula of a molecule or ion, what is the first step in predicting its shape?

10.26 In what situation is the name of the molecular shape the same as the name of the electron-group arrangement?

10.27 Which of the following numbers of electron groups can give rise to a bent (V-shaped) molecule: two, three, four, five, six? Draw an example for each case, showing the shape classification (AX_mE_n) and the ideal bond angle.

10.28 Name all the molecular shapes that have a tetrahedral electron-group arrangement.

10.29 Consider the following molecular shapes:



(a) Which has the most electron pairs (both shared and unshared) around the central atom?

(b) Which has the most unshared pairs around the central atom?

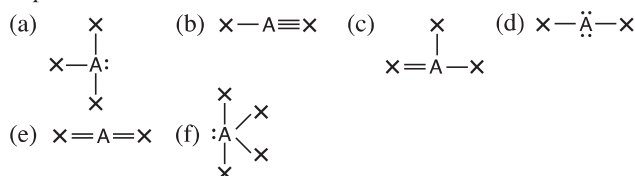
(c) Do any have only shared pairs around the central atom?

10.30 Why aren't lone pairs considered along with surrounding bonding groups when describing the molecular shape?

10.31 Use wedge-bond perspective drawings (if necessary) to sketch the atom positions in a general molecule of formula (not shape class) AX_n that has each of the following shapes:

- (a) V shaped (b) trigonal planar (c) trigonal bipyramidal
(d) T shaped (e) trigonal pyramidal (f) square pyramidal

10.32 What would you expect to be the electron-group arrangement around atom A in each of the following cases? For each arrangement, give the ideal bond angle and the direction of any expected deviation:



10.33 Determine the electron-group arrangement, molecular shape, and ideal bond angle(s) for each of the following:

- (a) O_3 (b) H_3O^+ (c) NF_3

10.34 Determine the electron-group arrangement, molecular shape, and ideal bond angle(s) for each of the following:

- (a) SO_4^{2-} (b) NO_2^- (c) PH_3

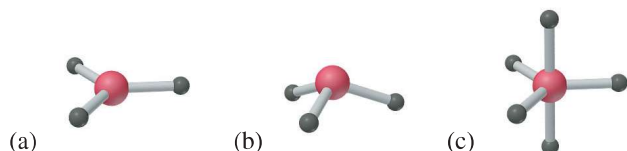
10.35 Determine the electron-group arrangement, molecular shape, and ideal bond angle(s) for each of the following:

- (a) CO_3^{2-} (b) SO_2 (c) CF_4

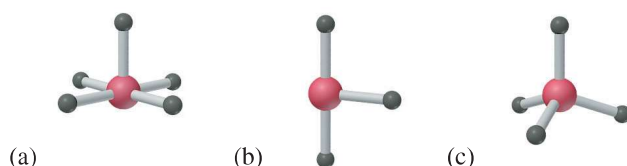
10.36 Determine the electron-group arrangement, molecular shape, and ideal bond angle(s) for each of the following:

- (a) SO_3 (b) N_2O (N is central) (c) CH_2Cl_2

10.37 Name the shape and give the AX_mE_n classification and ideal bond angle(s) for each of the following general molecules:



10.38 Name the shape and give the AX_mE_n classification and ideal bond angle(s) for each of the following general molecules:



10.39 Determine the shape, ideal bond angle(s), and direction of any deviation from the ideal angle(s) for each of the following:

- (a) ClO_2^- (b) PF_5 (c) SeF_4 (d) KrF_2

10.40 Determine the shape, ideal bond angle(s), and direction of any deviation from the ideal angle(s) for each of the following:

- (a) ClO_3^- (b) IF_4^- (c) $SeOF_2$ (d) TeF_5^-

10.41 Determine the shape around each central atom in each molecule, and explain any deviation from ideal bond angles:

- (a) CH_3OH (b) N_2O_4 (O_2NNO_2)

10.42 Determine the shape around each central atom in each molecule, and explain any deviation from ideal bond angles:

- (a) H_3PO_4 (no H—P bond) (b) $CH_3-O-CH_2CH_3$

10.43 Determine the shape around each central atom in each molecule, and explain any deviation from ideal bond angles:

- (a) CH_3COOH (b) H_2O_2

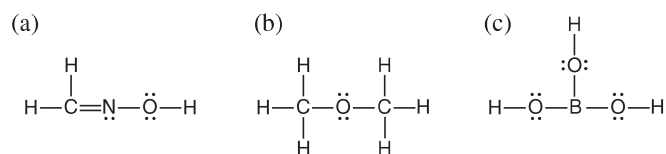
10.44 Determine the shape around each central atom in each molecule, and explain any deviation from ideal bond angles:

- (a) H_2SO_3 (no H—S bond) (b) N_2O_3 ($ONNO_2$)

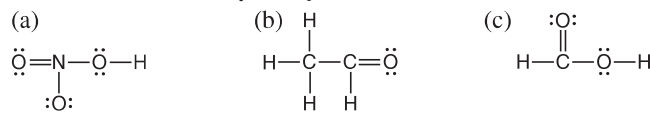
10.45 Arrange the following AF_n species in order of increasing F—A—F bond angles: BF_3 , BeF_2 , CF_4 , NF_3 , OF_2 .

10.46 Arrange the following ACl_n species in order of decreasing Cl—A—Cl bond angles: SCl_2 , OCl_2 , PCl_3 , $SiCl_4$, $SiCl_6^{2-}$.

10.47 State an ideal value for each of the bond angles in each molecule, and note where you expect deviations:



10.48 State an ideal value for each of the bond angles in each molecule, and note where you expect deviations:



10.49 Because both tin and carbon are members of Group 4A(14), they form structurally similar compounds. However, tin exhibits a greater variety of structures because it forms several ionic species. Predict the shapes and ideal bond angles, including any deviations, for the following:

- (a) $Sn(CH_3)_2$ (b) $SnCl_3^-$ (c) $Sn(CH_3)_4$
(d) SnF_5^- (e) SnF_6^{2-}

10.50 In the gas phase, phosphorus pentachloride exists as separate molecules. In the solid phase, however, the compound is composed of alternating PCl_4^+ and PCl_6^- ions. (a) What change(s) in molecular shape occur(s) as PCl_5 solidifies? (b) How does the Cl—P—Cl angle change?

Molecular Shape and Molecular Polarity

(Sample Problem 10.9)

10.51 How can a molecule with polar covalent bonds not be polar? Give an example.

10.52 Consider the molecules SCl_2 , F_2 , CS_2 , CF_4 , and $BrCl$.

- (a) Which has bonds that are the most polar?
(b) Which molecules have a dipole moment?

10.53 Consider the molecules BF_3 , PF_3 , BrF_3 , SF_4 , and SF_6 .

- (a) Which has bonds that are the most polar?
(b) Which molecules have a dipole moment?

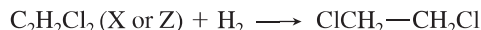
10.54 Which molecule in each pair has the greater dipole moment? Give the reason for your choice.

- (a) SO_2 or SO_3 (b) ICl or IF
(c) SiF_4 or SF_4 (d) H_2O or H_2S

10.55 Which molecule in each pair has the greater dipole moment? Give the reason for your choice.

- (a) ClO_2 or SO_2 (b) HBr or HCl
(c) $BeCl_2$ or SCl_2 (d) AsF_3 or AsF_5

10.56 There are three different dichloroethylenes (molecular formula $C_2H_2Cl_2$), which we can designate X, Y, and Z. Compound X has no dipole moment, but compound Z does. Compounds X and Z each combine with hydrogen to give the same product:



What are the structures of X, Y, and Z? Would you expect compound Y to have a dipole moment?

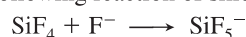
Comprehensive Problems

10.57 In addition to ammonia, nitrogen forms three other hydrides: hydrazine (N_2H_4), diazene (N_2H_2), and tetrazene (N_4H_4).

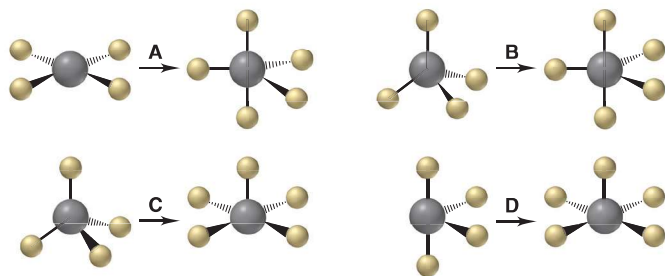
(a) Use Lewis structures to compare the strength, length, and order of the nitrogen-nitrogen bonds in hydrazine, diazene, and N_2 .

(b) Tetrazene (atom sequence H_2NNNNH_2) decomposes above $0^\circ C$ to hydrazine and nitrogen gas. Draw a Lewis structure for tetrazene, and calculate ΔH°_{rxn} for this decomposition.

10.58 Consider the following reaction of silicon tetrafluoride:

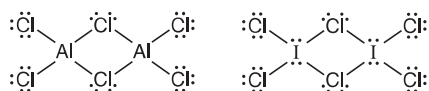


(a) Which depiction below best illustrates the change in molecular shape around Si? (b) Give the name and AX_mE_n designation of each shape in the depiction chosen in part (a).



10.59 Nitrosyl fluoride (NOF) has an atom sequence in which all atoms have formal charges of zero. Write the Lewis structure consistent with this fact.

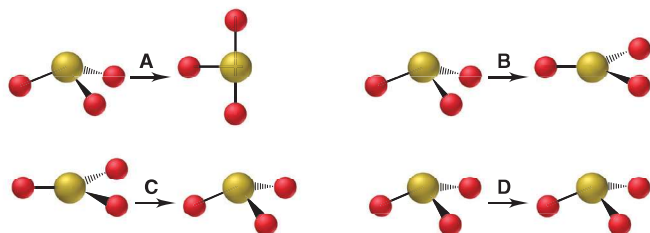
10.60 Both aluminum and iodine form chlorides, Al_2Cl_6 and I_2Cl_6 , with “bridging” Cl atoms. The Lewis structures are



(a) What is the formal charge on each atom? (b) Which of these molecules has a planar shape? Explain.

10.61 The VSEPR model was developed before any xenon compounds had been prepared. Thus, these compounds provided an excellent test of the model’s predictive power. What would you predict for the shapes of XeF_2 , XeF_4 , and XeF_6 ?

10.62 When SO_3 gains two electrons, SO_3^{2-} forms. (a) Which depiction shown below best illustrates the change in molecular shape around S? (b) Does molecular polarity change during this reaction?



10.63 The actual bond angle in NO_2 is 134.3° , and in NO_2^- it is 115.4° , although the ideal bond angle is 120° in both. Explain.

10.64 “Inert” xenon actually forms several compounds, especially with the highly electronegative elements oxygen and fluorine. The simple fluorides XeF_2 , XeF_4 , and XeF_6 are all formed by direct reaction of the elements. As you might expect from the size of the xenon atom, the Xe—F bond is not a strong one. Calculate the Xe—F bond energy in XeF_6 , given that the enthalpy of formation is -402 kJ/mol.

10.65 Chloral, $Cl_3C-CH=O$, reacts with water to form the sedative and hypnotic agent chloral hydrate, $Cl_3C-CH(OH)_2$. Draw Lewis structures for these substances, and describe the change in molecular shape, if any, that occurs around each of the carbon atoms during the reaction.

10.66 Like several other bonds, carbon-oxygen bonds have lengths and strengths that depend on the bond order. Draw Lewis structures for the following species, and arrange them in order of increasing carbon-oxygen bond length and then by increasing carbon-oxygen bond strength: (a) CO; (b) CO_3^{2-} ; (c) H_2CO ; (d) CH_4O ; (e) HCO_3^- (H attached to O).

10.67 The four bonds of carbon tetrachloride (CCl_4) are polar, but the molecule is nonpolar because the bond polarity is canceled by the symmetric tetrahedral shape. When other atoms substitute for some of the Cl atoms, the symmetry is broken and the molecule becomes polar. Use Figure 9.19 (p. 294) to rank the following molecules from the least polar to the most polar: CH_2Br_2 , CF_2Cl_2 , CH_2F_2 , CH_2Cl_2 , CBr_4 , CF_2Br_2 .

10.68 Ethanol (CH_3CH_2OH) is being used as a gasoline additive or alternative in many parts of the world.

(a) Use bond energies to find ΔH°_{rxn} for the combustion of gaseous ethanol. (Assume H_2O forms as a gas.)

(b) In its standard state at $25^\circ C$, ethanol is a liquid. Its vaporization requires 40.5 kJ/mol. Correct the value from part (a) to find the enthalpy of reaction for the combustion of liquid ethanol.

(c) How does the value from part (b) compare with the value you calculate from standard enthalpies of formation (Appendix B)?

(d) “Greener” methods produce ethanol from corn and other plant material, but the main industrial method involves hydrating ethylene from petroleum. Use Lewis structures and bond energies to calculate ΔH°_{rxn} for the formation of gaseous ethanol from ethylene gas with water vapor.

10.69 An oxide of nitrogen is 25.9% N by mass, has a molar mass of 108 g/mol, and contains no nitrogen-nitrogen or oxygen-oxygen bonds. Draw its Lewis structure, and name it.

10.70 An experiment requires 50.0 mL of 0.040 M NaOH for the titration of 1.00 mmol of acid. Mass analysis of the acid shows 2.24% hydrogen, 26.7% carbon, and 71.1% oxygen. Draw the Lewis structure of the acid.

10.71 A major short-lived, neutral species in flames is OH.

(a) What is unusual about the electronic structure of OH?

(b) Use the standard enthalpy of formation of $OH(g)$ (39.0 kJ/mol) and bond energies to calculate the O—H bond energy in $OH(g)$.

(c) From the average value for the O—H bond energy in Table 9.2 (p. 287) and your value for the O—H bond energy in $OH(g)$, find the energy needed to break the first O—H bond in water.

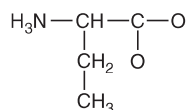
10.72 Pure HN_3 (atom sequence HNNN) is explosive. In aqueous solution, it is a weak acid that yields the azide ion, N_3^- . Draw

resonance structures to explain why the nitrogen-nitrogen bond lengths are equal in N_3^- but unequal in HN_3 .

10.73 Except for nitrogen, the elements of Group 5A(15) all form pentafluorides, and most form pentachlorides. The chlorine atoms of PCl_5 can be replaced with fluorine atoms one at a time to give, successively, PCl_4F , PCl_3F_2 , . . . , PF_5 . (a) Given the sizes of F and Cl, would you expect the first two F substitutions to be at axial or equatorial positions? Explain. (b) Which of the five fluorine-containing molecules have no dipole moment?

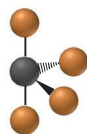
10.74 Dinitrogen monoxide (N_2O) supports combustion in a manner similar to oxygen, with the nitrogen atoms forming N_2 . Draw three resonance structures for N_2O (one N is central), and use formal charges to decide the relative importance of each. What correlation can you suggest between the most important structure and the observation that N_2O supports combustion?

10.75 The Murchison meteorite that landed in Australia in 1969 contained 92 different amino acids, including 21 found in Earth organisms. A skeleton structure (single bonds only) of one of these extraterrestrial amino acids is shown below.

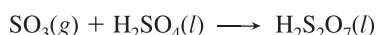


Draw a Lewis structure, and identify any atoms having a nonzero formal charge.

10.76 A student isolates a product with the molecular shape shown at right (F is orange). (a) If the species is a neutral compound, can the black sphere represent selenium (Se)? (b) If the species is an anion, can the black sphere represent N? (c) If the black sphere represents Br, what is the charge of the species?



10.77 When gaseous sulfur trioxide is dissolved in concentrated sulfuric acid, disulfuric acid forms:



Use bond energies (Table 9.2, p. 287) to determine $\Delta H^\circ_{\text{rxn}}$. (The S atoms in $\text{H}_2\text{S}_2\text{O}_7$ are bonded through an O atom. Assume Lewis structures with zero formal charges; BE of $\text{S}=\text{O}$ is 552 kJ/mol.)

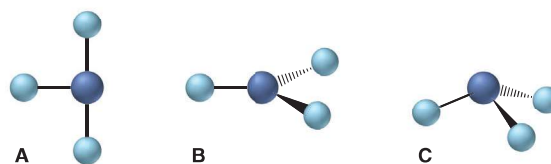
10.78 In addition to propyne (see Follow-up Problem 10.8), there are two other constitutional isomers of formula C_3H_4 . Draw a Lewis structure for each, determine the shape around each carbon, and predict any deviations from ideal bond angles.

10.79 A molecule of formula AY_3 is found experimentally to be polar. Which molecular shapes are possible and which are impossible for AY_3 ?

10.80 In contrast to the cyanate ion (NCO^-), which is stable and found in many compounds, the fulminate ion (CNO^-), with its different atom sequence, is unstable and forms compounds with

heavy metal ions, such as Ag^+ and Hg^{2+} , that are explosive. Like the cyanate ion, the fulminate ion has three resonance structures. Which is the most important contributor to the resonance hybrid? Suggest a reason for the instability of fulminate.

10.81 Consider the following molecular shapes:

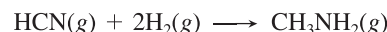


(a) Match each shape with one of the following species: XeF_3^+ , SbBr_3 , GaCl_3 .

(b) Which, if any, is polar?

(c) Which has the most valence electrons around the central atom?

10.82 Hydrogen cyanide can be catalytically reduced with hydrogen to form methylamine. Use Lewis structures and bond energies to determine $\Delta H^\circ_{\text{rxn}}$ for

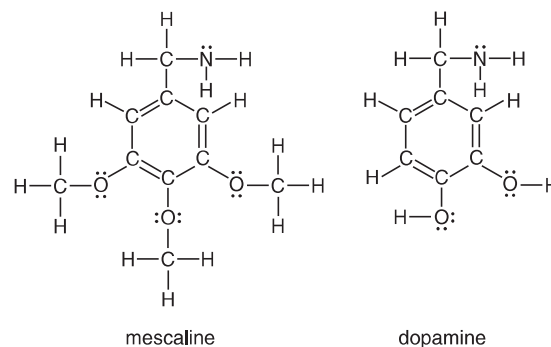


10.83 Ethylene, C_2H_4 , and tetrafluoroethylene, C_2F_4 , are used to make the polymers polyethylene and polytetrafluoroethylene (Teflon), respectively.

(a) Draw the Lewis structures for C_2H_4 and C_2F_4 , and give the ideal $\text{H}-\text{C}-\text{H}$ and $\text{F}-\text{C}-\text{F}$ bond angles.

(b) The actual $\text{H}-\text{C}-\text{H}$ and $\text{F}-\text{C}-\text{F}$ bond angles are 117.4° and 112.4° , respectively. Explain these deviations.

10.84 Lewis structures of mescaline, a hallucinogenic compound in peyote cactus, and dopamine, a neurotransmitter in the mammalian brain, appear below. Suggest a reason for mescaline's ability to disrupt nerve impulses.



10.85 Phosphorus pentachloride, a key industrial compound with annual world production of about 2×10^7 kg, is used to make other compounds. It reacts with sulfur dioxide to produce phosphorus oxychloride (POCl_3) and thionyl chloride (SOCl_2). Draw a Lewis structure, and name the molecular shape of each product.

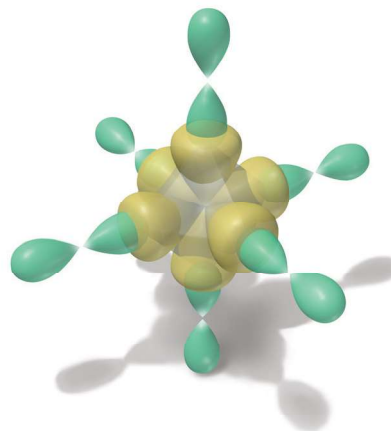
11

Theories of Covalent Bonding

Key Principles

to focus on while studying this chapter

- According to *valence bond (VB) theory*, a covalent bond forms when two electrons with *opposing spins* are localized in the region where orbitals on the bonding atoms *overlap*. Bond strength is related to the *extent* and *direction* of overlap. (**Section 11.1**)
- To account for the shapes of molecules, VB theory proposes that the orbitals of an isolated atom mix together and become *hybrid orbitals*, which have the same orientation in space as the electron-group arrangements of VSEPR theory. Each hybrid orbital has a shape that optimizes overlap and, thus, maximizes bond strength. (**Section 11.1**)
- The *mode* of orbital overlap determines the type of covalent bond: a *sigma (σ) bond* results from *end-to-end* overlap, and a *pi (π) bond* results from *side-to-side* overlap. A single bond is a σ bond, a double bond consists of a σ bond and a π bond, and a triple bond consists of a σ bond and two π bonds. Atoms connected by a σ bond can rotate with respect to each other, but a π bond restricts rotation. (**Section 11.2**)
- According to *molecular orbital (MO) theory*, *atomic orbitals (AOs)* combine to form *molecular orbitals (MOs)*, which spread over the whole molecule. Adding AOs together gives a *bonding MO*; subtracting them gives an *antibonding MO*. Each type of MO has its own shape and energy. A molecule is stabilized when electrons occupy a bonding MO. (**Section 11.3**)
- Like AOs, MOs have specific energy levels and become occupied one electron at a time by a total of two electrons. MO theory proposes that bond strength and length, as well as magnetic properties, depend on the number of electrons in a molecule's orbitals. (**Section 11.3**)



What Is a Covalent Bond? How do molecular shapes, like this model of sulfur hexafluoride, emerge from the orbitals of interacting atoms? And how do bond strength and other properties arise? In this chapter, we examine two theories that rationalize the covalent bond.

Outline

- 11.1 Valence Bond (VB) Theory and Orbital Hybridization**
 - Central Themes of VB Theory
 - Types of Hybrid Orbitals
- 11.2 Modes of Orbital Overlap and the Types of Covalent Bonds**
 - Orbital Overlap in Single and Multiple Bonds
 - Orbital Overlap and Molecular Rotation
- 11.3 Molecular Orbital (MO) Theory and Electron Delocalization**
 - Central Themes of MO Theory
 - Homonuclear Diatomic Molecules of Period 2 Elements