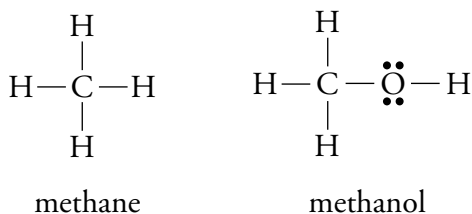




CHAPTER 12

MOLECULAR STRUCTURE

It's Monday morning, and you'd like a cup of coffee, but when you try cranking up the stove to reheat yesterday's brew, nothing happens. Apparently, the city gas line has sprung a leak and been shut down for repairs. The coffee cravings are strong, so you rummage in the garage until you find that can of Sterno left over from your last camping trip. You're saved. Both Sterno and natural gas contain compounds that burn and release heat, but the compounds in each of these substances are different. Natural gas is mostly methane, CH_4 , while Sterno contains several substances, including methanol, CH_3OH .



The oxygen atom in methanol molecules makes methanol's properties very different than methane's. Methane is a colorless, odorless, and tasteless gas. Methanol, or wood alcohol, is a liquid with a distinct odor, and is poisonous in very small quantities.

Chemists have discovered that part of the reason the small difference in structure leads to large differences in properties lies in the nature of covalent bonds and the arrangement of those bonds in space. This chapter provides a model for explaining how covalent bonds form, teaches you how to describe the resulting molecules with Lewis structures, and shows how Lewis structures can be used to predict the three-dimensional geometric arrangement of atoms in molecules.



Methane or methanol? We use both to heat food. How do their molecules—and properties—differ?

- 12.1 A New Look at Molecules and the Formation of Covalent Bonds
- 12.2 Drawing Lewis Structures
- 12.3 Resonance
- 12.4 Molecular Geometry from Lewis Structures

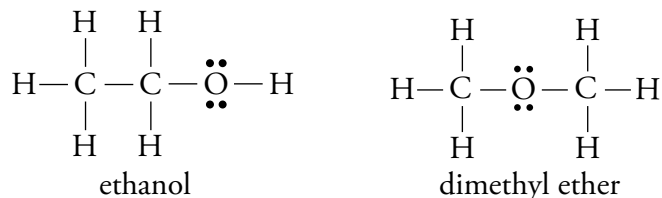
Review Skills

The presentation of information in this chapter assumes that you can already perform the tasks listed below. You can test your readiness to proceed by answering the Review Questions at the end of the chapter. This might also be a good time to read the Chapter Objectives, which precede the Review Questions.

- Given a periodic table, identify the number of the group to which each element belongs. (Section 3.3)
- Given a chemical formula, draw a Lewis structure for it that has the most common number of covalent bonds and lone pairs for each atom. (Section 4.3)
- Write or identify the definitions of valence electrons, electron-dot symbol, lone pairs, Lewis structure, double bond, and triple bond. (Chapter 4 Glossary)
- Write or identify the definition of atomic orbital. (Section 11.1)
- Write electron configurations and orbital diagrams for the nonmetallic elements. (Section 11.2)

12.1 A New Look at Molecules and the Formation of Covalent Bonds

In Chapter 4, you were told that carbon atoms usually have four bonds, oxygen atoms usually have two bonds and two lone pairs, and hydrogen atoms form one bond. Using guidelines such as these, we can predict that there are two possible arrangements of the atoms of C_2H_6O .



In Chapter 4, these bonding characteristics were described without explanation, because you did not yet have the tools necessary for understanding them. Now that you know more about the electron configurations of atoms, you can begin to understand why atoms form bonds as they do. To describe the formation of covalent bonds in molecules, we use a model called the valence-bond model, but before the assumptions of this model are described, let's revisit some of the important issues relating to the use of models for describing the physical world.

The Strengths and Weaknesses of Models

When developing a model of physical reality, scientists take what they think is true and simplify it enough to make it useful. Such is the case with their description of the nature of molecules. Scientific understanding of molecular structure has advanced tremendously in the last few years, but the most sophisticated descriptions are too complex and mathematical to be understood by anyone but the most highly trained chemists and physicists. To be useful to the rest of us, the descriptions have been translated into simplified versions of what scientists consider to be true.

OBJECTIVE 2

Such models have advantages and disadvantages. They help us to visualize, explain, and predict chemical changes, but we need to remind ourselves now and then that they are only models and that as models, they have their limitations. For example, because a model is a simplified version of what we think is true, the processes it depicts are sometimes described using the phrase *as if*. When you read, "It is *as if* an electron were promoted from one orbital to another," the phrase is a reminder that we do not necessarily think this is what really happens. We merely find it *useful* to talk about the process *as if* this is the way it happens.

One characteristic of models is that they change with time. Because our models are simplifications of what we think is real, we are not surprised when they sometimes fail to explain experimental observations. When this happens, the model is altered to fit the new observations.

The valence-bond model for covalent bonds, described below, has its limitations, but it is still extremely useful. For example, you will see in Chapter 14 that it helps us understand the attractions between molecules and predict relative melting points and boiling points of substances. The model is also extremely useful in describing the mechanisms of chemical changes. Therefore, even though it strays a bit from what scientists think is the most accurate description of real molecules, the valence-bond model is the most popular model for explaining covalent bonding.

Every path has its puddle.

English proverb

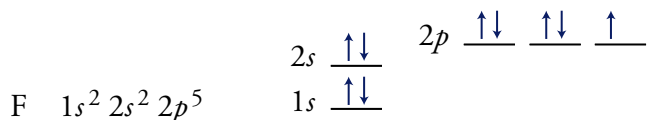
The Valence-Bond Model

The *valence-bond model*, which is commonly used to describe the formation of covalent bonds, is based on the following assumptions:

OBJECTIVE 3

- Only the highest-energy electrons participate in bonding.
- Covalent bonds usually form to pair unpaired electrons.

Fluorine is our first example. Take a look at its electron configuration and orbital diagram.



The first assumption of our model states that only the highest energy electrons of fluorine atoms participate in bonding. There are two reasons why this is a reasonable assumption. First, we know from the unreactive nature of helium atoms that the $1s^2$ electron configuration is very stable, so we assume that these electrons in a fluorine atom are less important than others are for the creation of bonds. The second reason is that the electrons in $2s$ and $2p$ orbitals have larger electron clouds and are therefore more available for interaction with other atoms.

The $2s^2$ and $2p^5$ electrons are the fluorine atom's valence electrons, the important electrons that we learned about in Section 4.3. Now we can define them more precisely.

OBJECTIVE 4

Valence electrons are the highest-energy s and p electrons in an atom. We saw in Chapter 4 that the number of valence electrons in each atom of a representative element is equal to the element's A-group number in the periodic table.

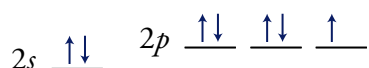
One valence electron ↓ <table border="1" style="display: inline-table; border-collapse: collapse; text-align: center; width: 30px; height: 30px;"><tr><td>1 H</td></tr></table>	1 H	Number of valence electrons equals the A-group number					8A
1 H							
	3A	4A	5A	6A	7A	<table border="1" style="display: inline-table; border-collapse: collapse; text-align: center; width: 30px; height: 30px;"><tr><td>2 He</td></tr></table>	2 He
2 He							
	5 B	6 C	7 N	8 O	9 F	10 Ne	
			15 P	16 S	17 Cl	18 Ar	
			33 As	34 Se	35 Br	36 Kr	
				52 Te	53 I	54 Xe	

Figure 12.1
Valence Electrons

When the columns in the periodic table are numbered by the A-group convention, the number of valence electrons in each atom of a representative element is equal to the element's group number in the periodic table.

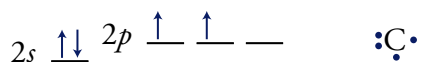
OBJECTIVE 4

Fluorine is in group 7A, so it has seven valence electrons. The orbital diagram for the valence electrons of fluorine is

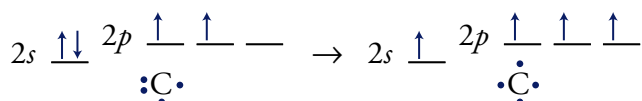


When atoms pair their unpaired electrons by forming chemical bonds, the atoms become more stable. We know that one way for fluorine to pair its one unpaired electron is to gain an electron from another atom and form a fluoride ion, F^- . This

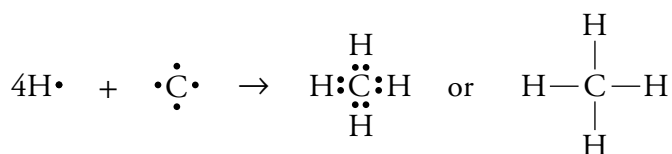
OBJECTIVE 5(A)



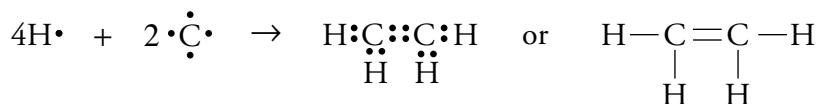
Carbon atoms do exhibit this bonding pattern in very rare circumstances, but in most cases, they form four bonds and have no lone pairs. Methane, CH_4 , is a typical example. When forming four bonds to hydrogen atoms in a methane molecule, each carbon atom behaves as if it has four unpaired electrons. It is *as if* one electron is promoted from the $2s$ orbital to the $2p$ orbital.



The following describes the bond formation in methane using electron-dot symbols.



Carbon atoms also frequently form double bonds, in which they share four electrons with another atom, often another carbon atom. Ethene (commonly called ethylene), C_2H_4 , is an example.



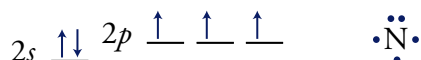
Note that each carbon atom in C_2H_4 has four bonds total, two single bonds to hydrogen atoms and two bonds to the other carbon atom.

The bond between the carbon atoms in ethyne (commonly called acetylene), C_2H_2 , is a triple bond, which can be viewed as the sharing of six electrons between two atoms.

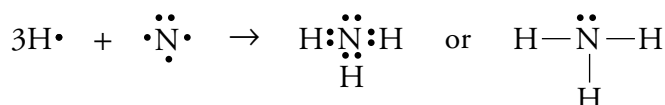


Note that each carbon atom in C_2H_2 has four bonds total, one single bond to a hydrogen atom and three bonds to the other carbon atom.

Nitrogen is in group 5A, so it has five valence electrons. Its orbital diagram and electron-dot symbol are

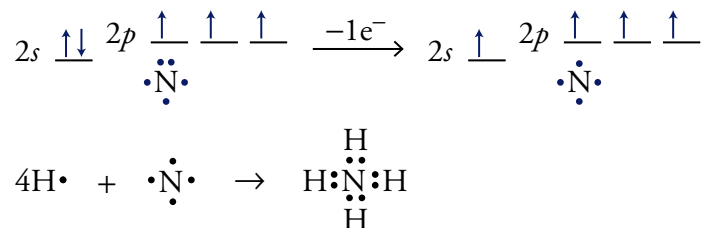


Each nitrogen atom has three unpaired electrons, and as the model predicts, it forms three covalent bonds. For example, a nitrogen atom can bond to three hydrogen atoms to form an ammonia molecule, NH_3 :

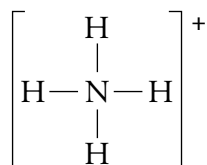


OBJECTIVE 5(E)

Another common bonding pattern for nitrogen atoms is four bonds with no lone pairs. The nitrogen atom in an ammonium polyatomic ion, NH_4^+ , is an example. This pattern and the positive charge on the ion can be explained by the loss of one electron from the nitrogen atom. It is *as if* an uncharged nitrogen atom loses one electron from the $2s$ orbital, leaving it with four unpaired electrons and the ability to make four bonds.

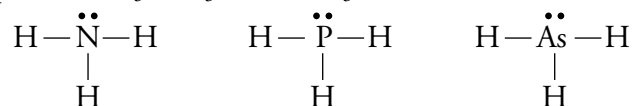


Because nitrogen must lose an electron to form this bonding pattern, the overall structure of the ammonium ion has a +1 charge. The Lewis structures of polyatomic ions are usually enclosed in brackets, with the overall charge written outside the brackets on the upper right.



OBJECTIVE 5(D)

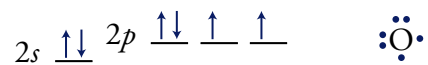
Phosphorus is in group 5A, so its atoms also have five valence electrons, in this case, in the $3s^23p^3$ configuration. Arsenic, also in group 5A, has atoms with a $4s^24p^3$ configuration. Because these valence configurations are similar to nitrogen's, $2s^22p^3$, the model correctly predicts that phosphorus and arsenic atoms will form bonds like nitrogen. For example, they each form three bonds to hydrogen atoms and have one lone pair in NH_3 , PH_3 , and AsH_3 .



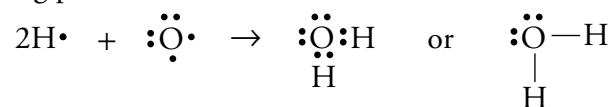
On the other hand, phosphorus and arsenic atoms exhibit bonding patterns that are not possible for nitrogen atoms. For example, molecules such as PCl_5 and AsF_5 have five bonds and no lone pairs. If you take other chemistry courses, you are likely to see compounds with bonding patterns like this, but because they are somewhat uncommon, you will not see them again in this text.

OBJECTIVE 5(F)

The most common bonding pattern for oxygen atoms is two covalent bonds and two lone pairs. Our model explains this in terms of the valence electrons' $2s^22p^4$ electron configuration.

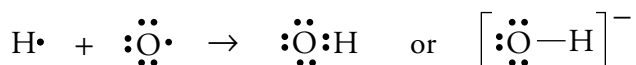
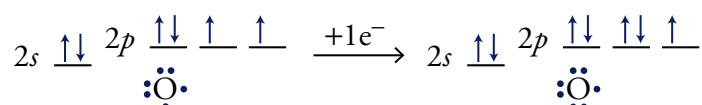


The two unpaired electrons are able to participate in two covalent bonds, and the two pairs of electrons remain two lone pairs. The oxygen atom in a water molecule has this bonding pattern.

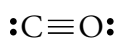


In another common bonding pattern, oxygen atoms gain one electron and form one covalent bond with three lone pairs. The oxygen atom in the hydroxide ion has this bonding pattern.

OBJECTIVE 5(G)

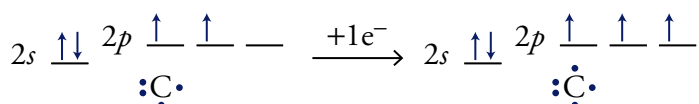
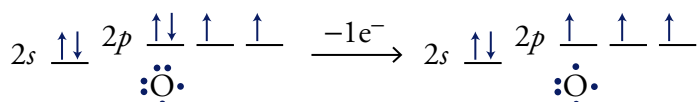


In rare circumstances, carbon and oxygen atoms can form triple bonds, leaving each atom with one lone pair. The carbon monoxide molecule, CO, is an example:



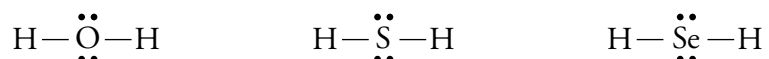
According to the valence-bond model, it is *as if* an electron is transferred from the oxygen atom to the carbon atom as the bonding in CO occurs. This gives each atom three unpaired electrons to form the triple bond, with one lone pair each left over.

OBJECTIVE 5(H)



Like oxygen, sulfur and selenium are in group 6A on the periodic table, so they too have six valence electrons, with $3s^2 3p^4$ and $4s^2 4p^4$ electron configurations, respectively. We therefore expect sulfur atoms and selenium atoms to have bonding patterns similar to oxygen's. For example, they all commonly form two bonds and have two lone pairs, as in molecules such as H_2O , H_2S , and H_2Se .

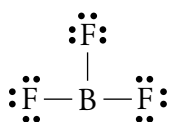
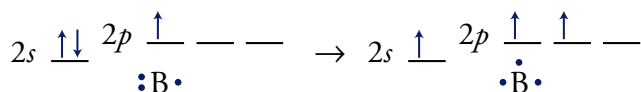
OBJECTIVE 5(F)



Sulfur and selenium atoms have additional bonding patterns that are not possible for oxygen atoms. For example, they can form six bonds in molecules such as SF_6 and SeF_6 . You will not see these somewhat uncommon bonding patterns again in this text.

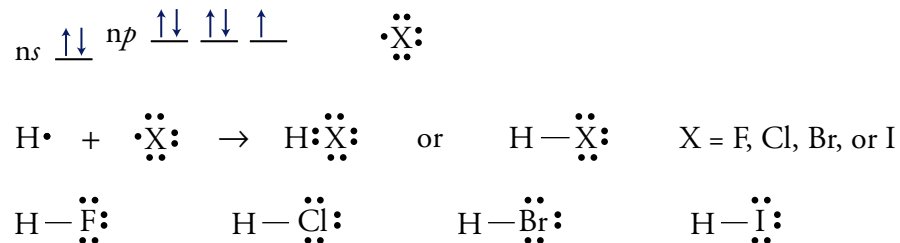
When the three equivalent B–F bonds form in boron trifluoride, BF_3 , it is *as if* one of the boron atom's valence electrons were promoted from its $2s$ orbital to an empty $2p$ orbital. This leaves three unpaired electrons to form three covalent bonds.

OBJECTIVE 5(I)



OBJECTIVE 5(J)

The elements in group 7A all have the ns^2np^5 configuration for their valence electrons. Thus they all commonly form one covalent bond and have three lone pairs. For example, their atoms all form one bond to a hydrogen atom to form HF, HCl, HBr, and HI.



Chlorine, bromine, and iodine atoms have additional, less common bonding patterns that you might see in other chemistry courses.

Table 12.1 summarizes the bonding patterns described in this section. The patterns listed there are not the only possible ones that these elements can have, but any patterns not listed are rare. In Section 12.2, you will be asked to draw Lewis structures from formulas, and knowledge of the common bonding patterns will help you to propose structures and evaluate their stability.

Table 12.1 Covalent Bonding Patterns

Element	Frequency of pattern	Number of bonds	Number of lone pairs	Example
H	always	1	0	H-
B	most common	3	0	$\begin{array}{c} -B- \\ \end{array}$
C	most common	4	0	$\begin{array}{c} \\ -C- \\ \end{array}$ or $\begin{array}{c} -C= \\ \end{array}$ or $-C\equiv$
	rare	3	1	$\equiv C:$
N, P, & As	most common	3	1	$\begin{array}{c} \cdot\ddot{N}- \\ \end{array}$
	common	4	0	$\begin{array}{c} \\ -N- \\ \end{array}$
O, S, & Se	most common	2	2	$\begin{array}{c} \cdot\ddot{O}- \\ \cdot\ddot{O} \end{array}$ or $\begin{array}{c} \cdot\ddot{O} \\ \end{array}$
	common	1	3	$-\ddot{O}:$
	rare	3	1	$\equiv O:$
F, Cl, Br, & I	most common	1	3	$-\ddot{X}:$

12.2 Drawing Lewis Structures

After studying chemistry all morning, you go out to mow the lawn. While adding gasoline to the lawnmower's tank, you spill a bit, so you go off to get some soap and water to clean it up. By the time you get back, the gasoline has all evaporated, which starts you wondering...why does gasoline evaporate so much faster than water? We are not yet ready to explain this, but part of the answer is found by comparing the substances' molecular structures and shapes. Lewis structures provide this information. You will see in Chapter 14 that the ability to draw Lewis structures for the chemical formulas of water, H_2O , and hexane, C_6H_{14} , (one of the major components of gasoline) will help you to explain their relative rates of evaporation. The ability to draw Lewis structures will be important for many other purposes as well, including explaining why the soap would have helped clean up the spill if the gasoline had not evaporated so quickly.

General Procedure

In Chapter 4, you learned to draw Lewis structures for many common molecules by trying to give each atom its most common bonding pattern (Table 12.2). For example, to draw a Lewis structure for methanol, CH_3OH , you would ask yourself how you can get one bond to each hydrogen atom, four bonds to the carbon atom, and two bonds and two lone pairs for the oxygen atom. The structure below shows how this can be done.

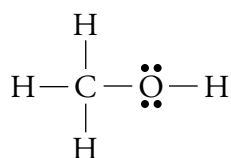


Table 12.2 The Most Common Bonding Patterns for Each Nonmetallic Atom

Elements	Number of Covalent Bonds	Number of Lone Pairs
C	4	0
N, P, & As	3	1
O, S, Se	2	2
F, Cl, Br, & I	1	3

The shortcut described above works well for many simple uncharged molecules, but it does not work reliably for molecules that are more complex or for polyatomic ions. To draw Lewis structures for these, you can use the stepwise procedure described in the following sample study sheet.

Sample Study Sheet 12.1

Drawing Lewis Structures from Formulas

OBJECTIVE 7

TIP-OFF In this chapter, you may be given a chemical formula for a molecule or polyatomic ion and asked to draw a Lewis structure, but there are other, more subtle tip-offs that you will see in later chapters.

GENERAL STEPS See Figure 12.2 for a summary of these steps.

STEP 1 Determine the total number of valence electrons for the molecule or polyatomic ion. (Remember that the number of valence electrons for a representative element is equal to its group number, using the A group convention for numbering groups. For example, chlorine, Cl, is in group 7A, so it has seven valence electrons. Hydrogen has one valence electron.)

- For uncharged molecules, the total number of valence electrons is the sum of the valence electrons of each atom.
- For polyatomic cations, the total number of valence electrons is the sum of the valence electrons for each atom minus the charge.
- For polyatomic anions, the total number of valence electrons is the sum of the valence electrons for each atom plus the charge.

STEP 2 Draw a reasonable skeletal structure, using single bonds to join all the atoms. One or more of the following guidelines might help with this step. (They are clarified in the examples that follow.)

- Try to arrange the atoms to yield the most typical number of bonds for each atom. Table 12.2 lists the most common bonding patterns for the nonmetallic elements.
- Apply the following guidelines in deciding what element belongs in the center of your structure.

Hydrogen and fluorine atoms are never in the center.

Oxygen atoms are rarely in the center.

The element with the fewest atoms in the formula is often in the center.

The atom that is capable of making the most bonds is often in the center.

- Oxygen atoms rarely bond to other oxygen atoms.
- The molecular formula often reflects the molecular structure. (See Example 12.4.)
- Carbon atoms commonly bond to other carbon atoms.

STEP 3 Subtract two electrons from the total for each of the single bonds (lines) described in Step 2 above. This tells us the number of electrons that still need to be distributed.

STEP 4 Try to distribute the remaining electrons as lone pairs to obtain a total of eight electrons around each atom except hydrogen and boron. We saw in Chapter 4 that the atoms in reasonable Lewis structures are often surrounded by an octet of electrons. The following are some helpful observations pertaining to octets.

- In a reasonable Lewis structure, carbon, nitrogen, oxygen, and fluorine always have eight electrons around them.

- Hydrogen will always have a total of two electrons from its one bond.
- Boron can have fewer than eight electrons but never more than eight.
- The nonmetallic elements in periods beyond the second period (P, S, Cl, Se, Br, and I) usually have eight electrons around them, but they can have more. (In this text, they will always have eight electrons around them, but if you go on to take other chemistry courses, it will be useful to know that they can have more.)
- The bonding properties of the metalloids arsenic, As, and tellurium, Te, are similar to those of phosphorus, P, and sulfur, S, so they usually have eight electrons around them but can have more.

STEP 5 Do one of the following.

- If in Step 4 you were able to obtain an octet of electrons around each atom other than hydrogen and boron, and if you used all of the remaining valence electrons, go to step 6.
- If you have electrons remaining after each of the atoms other than hydrogen and boron have their octet, you can put more than eight electrons around elements in periods beyond the second period. (You will not need to use this procedure for any of the structures in this text, but if you take more advanced chemistry courses, it will be useful.)
- If you do not have enough electrons to obtain octets of electrons around each atom (other than hydrogen and boron), convert one lone pair into a multiple bond for each two electrons that you are short. (See Example 12.2.)

If you would need two more electrons to get octets, convert one lone pair in your structure to a second bond between two atoms.

If you would need four more electrons to get octets, convert two lone pairs into bonds. This could mean creating a second bond in two different places or creating a triple bond in one place.

If you would need six more electrons to get octets, convert three lone pairs into bonds.

Etc.

STEP 6 Check your structure to see if all of the atoms have their most common bonding pattern (Table 12.2).

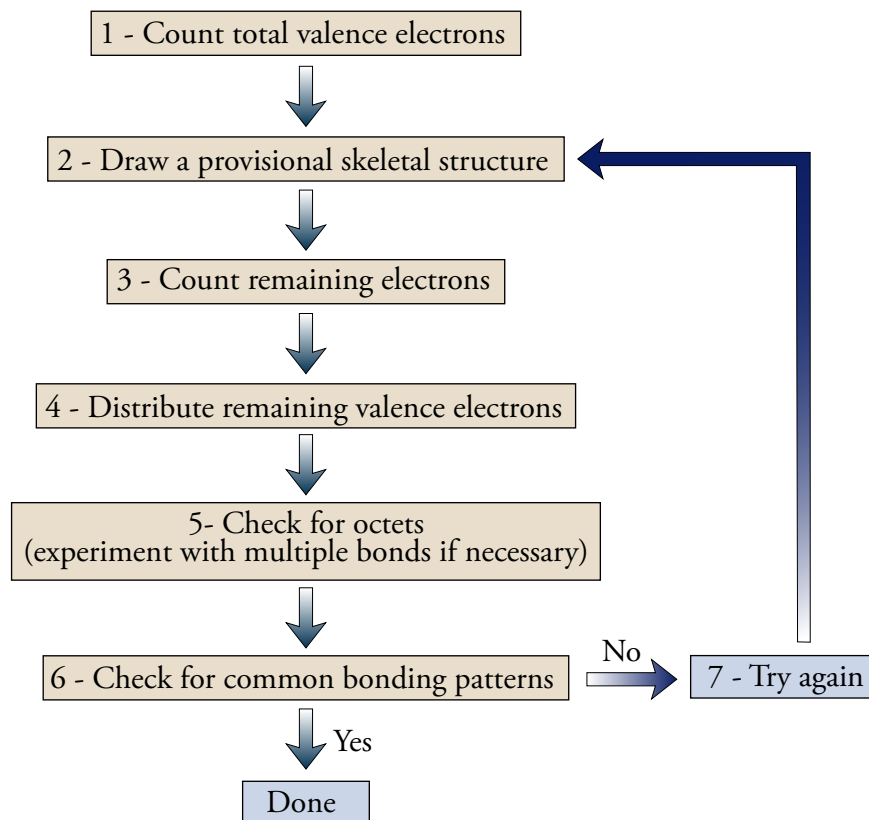
- If each atom has its most common bonding pattern, your structure is a reasonable structure. Skip Step 7.
- If one or more atoms are without their most common bonding pattern, continue to Step 7.

STEP 7 If necessary, try to rearrange your structure to give each atom its most common bonding pattern. One way to do this is to return to Step 2 and try another skeleton. (This step is unnecessary if all of the atoms in your structure have their most common bonding pattern.)

EXAMPLE See Examples 12.1 to 12.4.

Figure 12.2
Lewis Structure Procedure

OBJECTIVE 7



EXAMPLE 12.1 - Drawing Lewis Structures

OBJECTIVE 7

Draw a reasonable Lewis structure for methyl bromide, CH_3Br , which is an ozone depleting gas used as a fumigant.

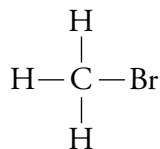
Solution

Let's start with the stepwise procedure for drawing Lewis structures.

STEP 1 To determine the number of valence electrons for CH_3Br , we note that carbon is in group 4A, so its atoms have four valence electrons; hydrogen has one valence electron; bromine is in group 7A, so its atoms have seven valence electrons.

$$\text{CH}_3\text{Br} \quad \text{Number of valence } e^- = \overset{\text{C}}{1(4)} + \overset{\text{H}}{3(1)} + \overset{\text{Br}}{1(7)} = 14$$

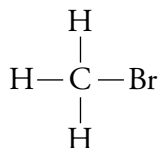
STEP 2 Before setting up the skeleton for CH_3Br , we check Table 12.2, which reminds us that carbon atoms usually have four bonds, hydrogen atoms always have one bond, and bromine atoms most commonly have one bond. Thus the following skeleton is most reasonable.



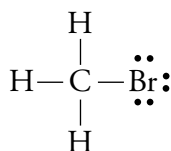
STEP 3 We started with 14 total valence electrons for CH_3Br , and we have used eight of them for the four bonds in the skeleton we drew in Step 2.

$$\begin{aligned} \text{Number } e^- \text{ remaining} &= \text{total valence } e^- - \text{number of bonds} \left(\frac{2 e^-}{1 \text{ bond}} \right) \\ &= 14 - 4(2) = 6 \end{aligned}$$

STEP 4 After Step 3, we have the following skeleton for CH_3Br and six valence electrons still to distribute.

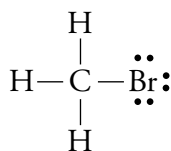


Hydrogen atoms never have lone pairs, and the carbon atom has an octet of electrons around it from its four bonds. In contrast, the bromine atom needs six more electrons to obtain an octet, so we put the remaining six electrons around the bromine atom as three lone pairs.



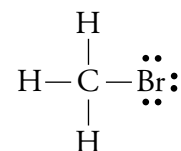
STEP 5 The structure drawn in Step 4 for CH_3Br has an octet of electrons around the carbon and bromine atoms. Hydrogen has its one bond. We have also used all of the valence electrons. Thus we move on to Step 6.

STEP 6 All of the atoms in the structure drawn for CH_3Br have their most common bonding pattern, so we have a reasonable Lewis structure.



STEP 7 Because the atoms in our structure for CH_3Br have their most common bonding pattern, we skip this step.

Shortcut The shortcut to drawing Lewis structures described in Section 4.3 can often be used for uncharged molecules such as CH_3Br . Carbon atoms usually have four bonds and no lone pairs, hydrogen atoms always have one bond, and bromine atoms most commonly have one bond and three lone pairs. The only way to give these atoms their most common bonding patterns is with the following Lewis structure, which is the same Lewis structure we arrived at with the stepwise procedure.



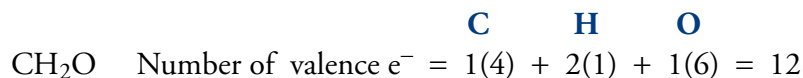
EXAMPLE 12.2 - Drawing Lewis Structures

OBJECTIVE 7

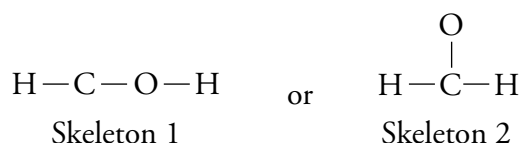
Formaldehyde, CH_2O , has many uses, including the preservation of biological specimens. Draw a reasonable Lewis structure for formaldehyde.

Solution

STEP 1 Carbon is in group 4A, so its atoms have four valence electrons. Hydrogen has one valence electron. Oxygen is in group 6A, so its atoms have six valence electrons.

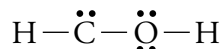


STEP 2 There are two possible skeletons for this structure. We will work with skeleton 1 first.

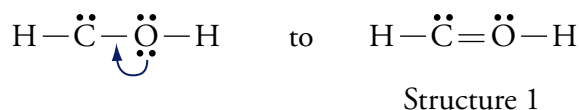


STEP 3 (Skeleton 1) Number of e^- remaining = $12 - 3(2) = 6$

STEP 4 (Skeleton 1) The most common bonding pattern for oxygen atoms is two bonds and two lone pairs. It is possible for carbon atoms to have one lone pair, although that is rare. Thus we might use our six remaining electrons as two lone pairs on the oxygen atom and one lone pair on the carbon atom.



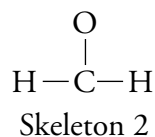
STEP 5 (Skeleton 1) The structure above leaves the carbon atom without its octet. Because we are short two electrons for octets, we convert one lone pair to another bond. Converting the lone pair on the carbon to a multiple bond would still leave the carbon with only six electrons around it and would put ten electrons around the oxygen atom. Carbon and oxygen atoms always have eight electrons around them in a reasonable Lewis structure. Thus we instead try converting one of the lone pairs on the oxygen atom to another C–O bond.



STEP 6 In structure 1, the carbon atom and the oxygen atom have rare bonding patterns. This suggests that there might be a better way to arrange the atoms. We proceed to Step 7.

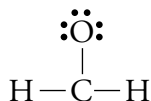
STEP 7 To attempt to give each atom its most common bonding pattern, we return to Step 2 and try another skeleton.

STEP 2 The only alternative to skeleton 1 for CH_2O is

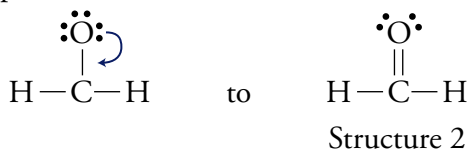


STEP 3 (Skeleton 2) Number of e^- remaining = $12 - 3(2) = 6$

STEP 4 (Skeleton 2) Oxygen atoms commonly have one bond and three lone pairs, so we might use our remaining electrons as three lone pairs on the oxygen atom.



STEP 5 (Skeleton 2) In Step 4, we used all of the remaining electrons but left the carbon atom with only six electrons around it. Because we are short two electrons needed to obtain octets of electrons around each atom, we convert one lone pair into another bond.



STEP 6 (Skeleton 2) All of the atoms have their most common bonding pattern, so we have a reasonable Lewis structure.

STEP 7 (Skeleton 2) Because each atom in Structure 2 has its most common bonding pattern, we skip this step.

Because Structure 2 is the only arrangement that gives each atom its most common bonding pattern, we could have skipped the stepwise procedure and used the shortcut for this molecule.

EXAMPLE 12.3 - Drawing Lewis Structures

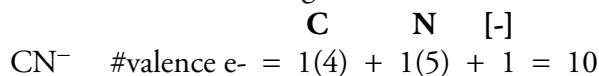
The cyanide polyatomic ion, CN^- is similar in structure to carbon monoxide, CO . Although they work by different mechanisms, they are both poisons that can disrupt the use of oxygen, O_2 , in organisms. Draw a reasonable Lewis structure for the cyanide ion.

OBJECTIVE 7

Solution

The shortcut does not work for polyatomic ions, so we use the stepwise procedure for CN^- .

STEP 1 Carbon is in group 4A, so its atoms have four valence electrons. Nitrogen is in group 5A, so its atoms have five valence electrons. Remember to add one electron for the -1 charge.

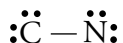


STEP 2 There is only one way to arrange two atoms.

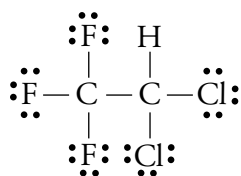


STEP 3 Number e^- remaining = $10 - 1(2) = 8$

STEP 4 Both the carbon atom and the nitrogen atom need six more electrons. We do not have enough electrons to provide octets by the formation of lone pairs. You will see in the next step that we will make up for this lack of electrons with multiple bonds. For now, we might put two lone pairs on each atom.

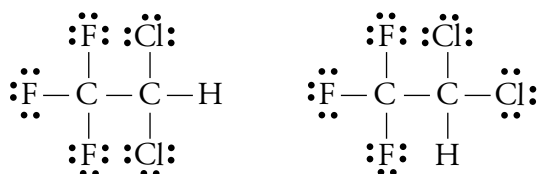


STEP 4 We expect halogen atoms to have three lone pairs, so we can use the 30 remaining electrons to give us three lone pairs for each fluorine and chlorine atom.



Structure 1

We could also represent CF_3CHCl_2 , with the following Lewis structures:



Structure 2

Structure 3

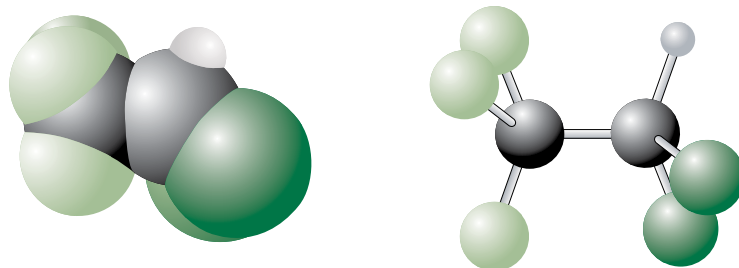
Structures 2 and 3 might look like they represent different molecules, but they actually represent the same molecule as Structure 1. To confirm that this is true, picture yourself sitting on the hydrogen atom in either the space filling or the ball-and-stick model shown in Figure 12.3 for CF_3CHCl_2 . Atoms connected to each other by single bonds, such as the two carbon atoms in this molecule, are constantly rotating with respect to each other. Thus your hydrogen atom is sometimes turned toward the top of the molecule (somewhat like in Structure 1), sometimes toward the bottom of the structure (somewhat like Structure 3), and sometimes in one of the many possible positions in between. (Section 12.4 describes how you can predict molecular shapes. If you do not see at this point why Structures 1, 2, and 3 all represent the same molecule, you might return to this example after reading that section.)

STEP 5 We have used all of the valence electrons, and we have obtained octets of electrons around each atom other than hydrogen. Thus we move to Step 6.

STEP 6 All of the atoms in our structure have their most common bonding pattern, so we have a reasonable Lewis structure.

STEP 7 Because each atom in our structure has its most common bonding pattern, we skip this step.

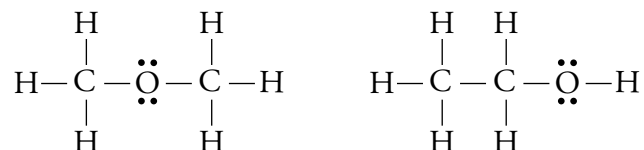
Figure 12.3
Models of CF_3CHCl_2



More Than One Possible Structure

OBJECTIVE 7

It is possible to generate more than one reasonable Lewis structure for some formulas. When this happens, remember that the more common the bonding pattern is (as summarized in Table 12.1), the more stable the structure. Even after you apply this criterion, you may still be left with two or more Lewis structures that are equally reasonable. For example, the following Lewis structures for C_2H_6O both have the most common bonding pattern for all of their atoms.



In fact, both these structures describe actual compounds. The first structure is dimethyl ether, and the second is ethanol. Substances that have the same molecular formula but different structural formulas are called **isomers**. We can write the formulas for these two isomers so as to distinguish between them: CH_3OCH_3 represents dimethyl ether, and CH_3CH_2OH represents ethanol.

EXAMPLE 12.5 - Drawing Lewis Structures

OBJECTIVE 7

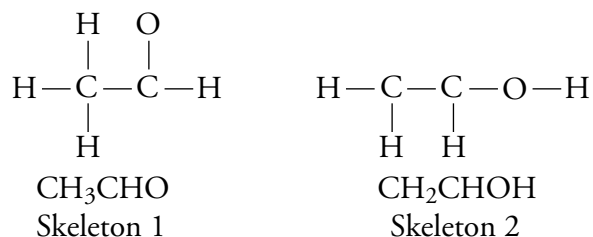
Acetaldehyde can be converted into the sedative chloral hydrate (the “Mickey Finn” or knockout drops often mentioned in detective stories). In the first step of the reaction that forms chloral hydrate, acetaldehyde, CH_3CHO , changes to its isomer, CH_2CHOH . Draw a reasonable Lewis structures for each of these isomers.

Solution

STEP 1 Both molecules have the molecular formula C_2H_4O .

$$\begin{array}{ccc}
 \text{C} & \text{H} & \text{O} \\
 \text{Number valence } e^- = & 2(4) + & 4(1) + & 1(6) = 18
 \end{array}$$

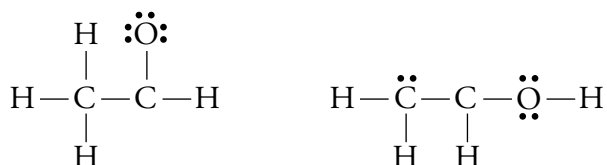
STEP 2 Because we expect carbon atoms to bond to other carbon atoms, we can link the two carbon atoms together to start each skeleton, which is then completed to try to match each formula given.



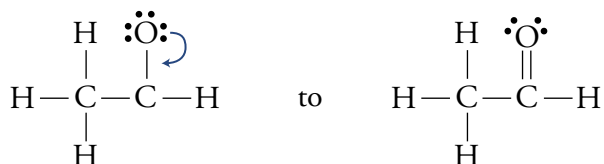
STEP 3 Number of e^- remaining = $18 - 6(2) = 6$

STEP 4 For Skeleton 1, we can add three lone pairs to the oxygen atom to give it its octet. For Skeleton 2, we can add two lone pairs to the oxygen atom to get its most common bonding pattern of two bonds and two lone pairs. We can place

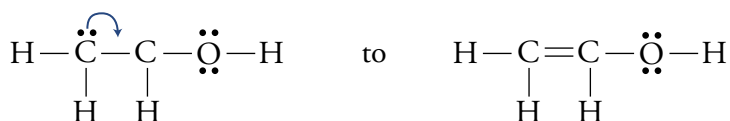
the remaining two electrons on one of the carbon atoms as a lone pair.



STEP 5 In each case, we have one carbon atom with only six electrons around it, so we convert one lone pair into another bond.



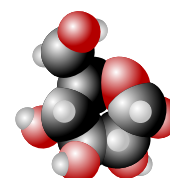
Structure 1



Structure 2

STEP 6 All of the atoms in both structures have their most common bonding pattern, so we have two reasonable Lewis structures representing isomers. Structure 1 is acetaldehyde (or ethanal) and structure 2 is ethenol.

STEP 7 Because each atom in our structures has its most common bonding pattern, we skip this step.



Web
Molecules

EXERCISE 12.1 - Lewis Structures

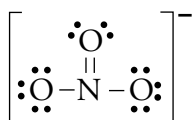
Draw a reasonable Lewis structure for each of the following formulas.

- | | |
|----------------------------|---------------------------|
| a. CCl_4 | f. N_2H_4 |
| b. Cl_2O | g. H_2O_2 |
| c. COF_2 | h. NH_2OH |
| d. C_2Cl_6 | i. NCl_3 |
| e. BCl_3 | |

OBJECTIVE 7

12.3 Resonance

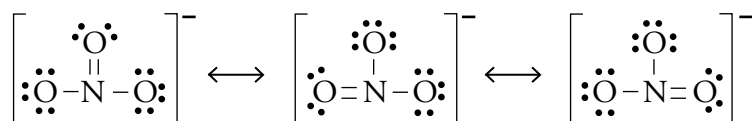
As the valence-bond model was being developed, chemists came to recognize that it did not always describe all molecules and polyatomic ions adequately. For example, if we follow the procedures in Section 12.2 to draw a Lewis structure for the nitrate ion, NO_3^- , we would obtain a structure that chemists have discovered is not an accurate description of the ion's bonds:



This Lewis structure shows two different types of bonds, single and double. Because more energy is required to break a double bond than to break a single bond, we say that a double bond is stronger than a single bond. Double bonds also have a shorter bond length (the distance between the nuclei of the two atoms in the bond) than single bonds do. Thus, if the above Lewis structure for nitrate were correct, the nitrate polyatomic ion would have one bond that is shorter and stronger than the other two.

This is not the case. Laboratory analyses show all three of the bonds in the nitrate ion to be the same strength and the same length. Interestingly, analysis of the bonds suggests they are longer than double bonds and shorter than single bonds. They are also stronger than single bonds but not as strong as double bonds. In order to explain how these characteristics are possible for the nitrate ion and for molecules and polyatomic ions like it, the valence-bond model had to be expanded.

The model now allows us to view certain molecules and polyatomic ions *as if* they were able to resonate—to switch back and forth—between two or more different structures. For example, the nitrate ion can be viewed *as if* it resonates between the three different structures below. Each of these structures is called a **resonance structure**. The hypothetical switching from one resonance structure to another is called **resonance**. In chemical notation, the convention is to separate the resonance structures with double headed arrows.



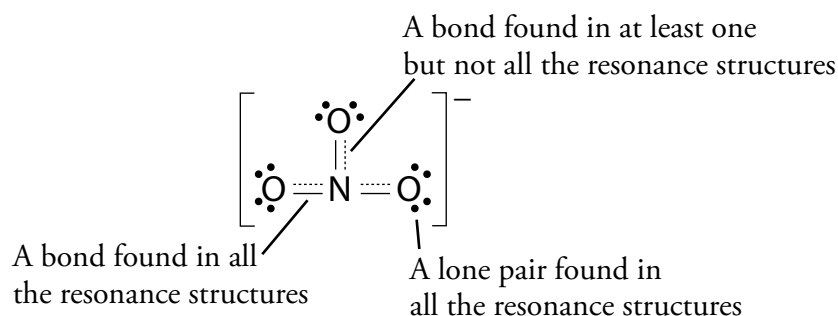
It is important to stress that the nitrate ion is not really changing from one resonance structure to another, but chemists find it useful, as an intermediate stage in the process of developing a better description of the nitrate ion, to think of it as if it were doing so. In actuality, the ion behaves as if it were a blend of the three resonance structures.

OBJECTIVE 8

We can draw a Lewis-like structure that provides a better description of the actual character of the nitrate ion by blending the resonance structures into a single **resonance hybrid**:

- STEP 1** Draw the skeletal structure, using solid lines for the bonds that are found in all of the resonance structures.
- STEP 2** Where there is sometimes a bond and sometimes not, draw a dotted line.
- STEP 3** Draw only those lone pairs that are found on every one of the resonance structures. (Leave off the lone pairs that are on one or more resonance structure but not on all of them.)

The resonance hybrid for the nitrate polyatomic ion is

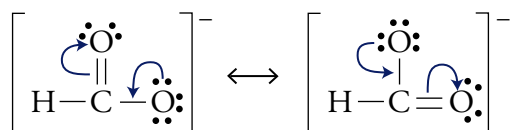


OBJECTIVE 8

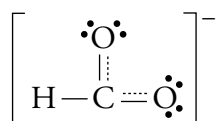
Resonance is possible whenever a Lewis structure has a multiple bond and an adjacent atom with at least one lone pair. The arrows in the following generalized structures show how you can think of the electrons shifting as one resonance structure changes to another.



For example, the two resonance structures for the formate ion, HCO_2^- are

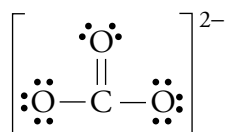


To generate the second resonance structure from the first, we imagine one lone pair dropping down to form another bond, and pushing an adjacent bond off to form a lone pair. The arrows show this *hypothetical* shift of electrons, which leads to the resonance hybrid below.



EXERCISE 12.2 - Resonance

Draw all of the reasonable resonance structures and the resonance hybrid for the carbonate ion, CO_3^{2-} . A reasonable Lewis structure for the carbonate ion is



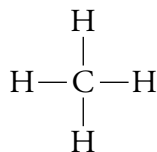
You can find a more comprehensive description of resonance at the textbook's Web site.

OBJECTIVE 8

12.4 Molecular Geometry from Lewis Structures

The shapes of molecules play a major role in determining their function. For example, Special Topic 4.1 describes how the shape of ethanol molecules allows them to attach to specific sites on nerve cell membranes and slow the transfer of information from one neuron to another. Special Topic 6.2 describes how the shapes of the molecules in our food determine whether they taste sweet or bitter. You will find out in Special Topic 17.2 that the fat substitute Olestra is indigestible because it does not fit into the enzyme that digests natural fat. The purpose of this section is to show you how to use Lewis structures to predict three-dimensional shapes of simple molecules and polyatomic ions. Let's start with a review of some of the information from Section 4.1, where this topic was first introduced.

The carbon atoms in methane, CH_4 , molecules are surrounded by four electron groups, each composed of a two electron covalent bond to a hydrogen atom.



OBJECTIVE 9

Because each electron group is negatively charged and because negative charges repel each other, the most stable arrangement for the electron groups is one in which they are as far apart as possible. In Chapter 4, we saw that the geometric arrangement in which four electron groups are as far apart as possible is a tetrahedral arrangement, with bond angles of 109.5° . A tetrahedron is a four sided solid for which each side is an equilateral triangle, and a **bond angle** is the angle formed by any three adjacent atoms in a molecule. The carbon in a methane molecule can be viewed as sitting in the center of a tetrahedron with a hydrogen atom at each of the four corners.

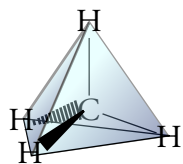
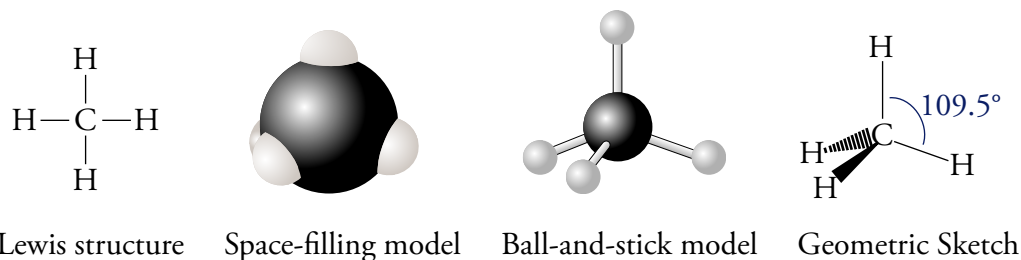


Figure 12.4 shows four ways to describe the methane molecule. The space filling model in that figure is probably the best representation of the actual structure of the CH_4 molecule, but when scientists are focusing on the bonds in a molecule, they often prefer to think of the structure as represented by the ball-and-stick model, the Lewis structure, and the geometric sketch. Notice that the Lewis structure for CH_4 does not show the correct bond angles. In order to display bond angles correctly with a Lewis-like structure, chemists use geometric sketches, such as the last image in Figure 12.4. Remember that in a geometric sketch, a solid line represents a bond whose central axis lies in the plane of the paper, a solid wedge shape represents a bond whose axis is extending out of the plane of the paper toward you, and a dashed wedge shape represents a bond whose axis extends out behind the plane of the paper, away from you.

Figure 12.4Four Ways to Describe a Methane, CH_4 , Molecule

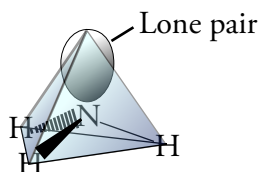
OBJECTIVE 9



The tetrahedral arrangement is very common and important in chemistry, so be sure that you have a clear image in your mind of the relationship between the geometric sketch in Figure 12.4 and the three-dimensional shape of a molecule such as methane. You can make a ball-and-stick model of this molecule using a firm piece of fruit such as an apple or a green tomato for the carbon atom, four toothpicks to represent the axes through each of the four bonds, and four grapes to represent the hydrogen atoms. Try

to arrange the toothpicks and grapes so that each grape is an equal distance from the other three. When you think you have successfully constructed a CH_4 fruit molecule, turn your model over and over, so that a different grape is on top each time. If your model is really tetrahedral, it will always look the same, no matter which grape is on top (Figure 12.5).

The nitrogen atom in each ammonia molecule, NH_3 , has four electron groups around it (three bond groups and one lone pair), and, like with methane molecules, the best way to get these four groups as far apart as possible is in a tetrahedral arrangement. The electrons in the lone pair exert a greater repulsive force than the electrons in the bonds, however, so the bond groups are pushed a little closer together. As a result, the bond angles for ammonia are 107° , rather than the 109.5° found in the methane molecule.



There are two ways to describe the geometry of the ammonia molecule. We can describe the arrangement of all the electron groups, including the lone pair, and call the shape tetrahedral. Or we can describe the arrangement of the atoms only, without considering the lone pair, and call ammonia's shape a **trigonal pyramid** (Figure 12.6). The three hydrogen atoms represent the corners of the pyramid's base, and the nitrogen atom forms the peak. In this book, we will call the geometry that describes all of the electron groups, including the lone pairs, the **electron group geometry**. The shape that describes the arrangement of the atoms only—treating the lone pairs as invisible—will be called the **molecular geometry**.

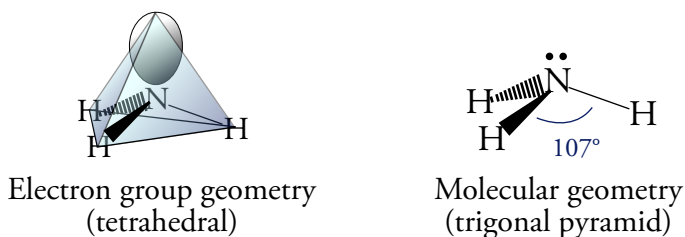


Figure 12.6
Geometry of an
Ammonia Molecule

OBJECTIVE 9

The water molecule's electron group geometry, which is determined by the arrangement of its four electron groups around the oxygen atom, is tetrahedral (Figure 12.7).

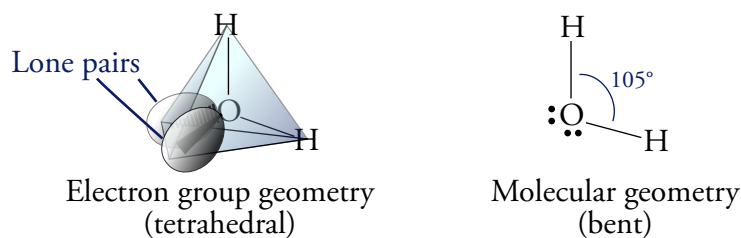


Figure 12.7
Geometry of a Water
Molecule

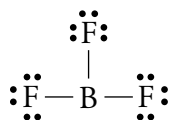
OBJECTIVE 9

Its molecular geometry, which describes the arrangement of the atoms only, is called **bent**. The two lone pairs on the oxygen atom exert a stronger repulsion than the two bond groups and push the bond groups closer together than they would be if all of the electron groups around the oxygen atom were identical. The bond angle becomes 105° instead of the 109.5° predicted for four identical electron groups.



Figure 12.5
A Green Tomato-Grape
Ball-and-Stick Model for
the CH_4 Molecule

The boron atom in the center of a BF_3 molecule is surrounded by three electron groups, which are each composed of a two-electron covalent bond to a fluorine atom.



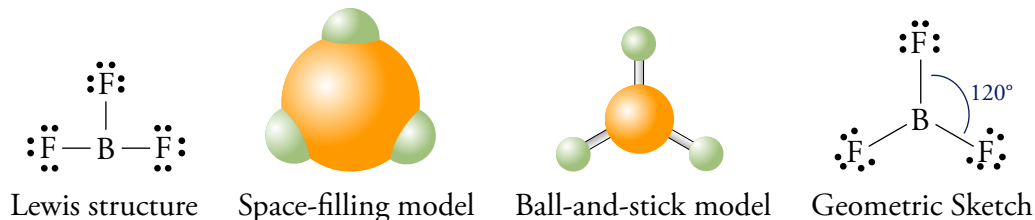
OBJECTIVE 9

The geometric arrangement that keeps three electron groups as far apart as possible is called **trigonal planar** (often called **triangular planar**) and leads to angles of 120° between the groups. Therefore, the B–F bonds in BF_3 molecules have a trigonal planar arrangement with 120° angles between any two fluorine atoms (Figure 12.8).

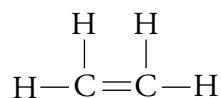
Figure 12.8

Four Ways to Describe a Boron Trifluoride, BF_3 , Molecule

OBJECTIVE 9



Molecules quite often have more than one central atom (an atom with two or more atoms bonded to it). To describe the arrangement of atoms in such molecules, we need to consider the central atoms one at a time. Let's look at the ethene, C_2H_4 , molecule:



There are three electron groups around each of ethene's carbon atoms (two single bonds to hydrogen atoms and the double bond to the other carbon). Because these groups repel each other, the most stable arrangement around each carbon atom—with the electron groups as far apart as possible—is a triangle with all three groups in the same plane and with angles of about 120° between the groups. That is, ethene has a trigonal planar arrangement of atoms around each carbon.

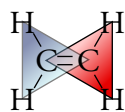
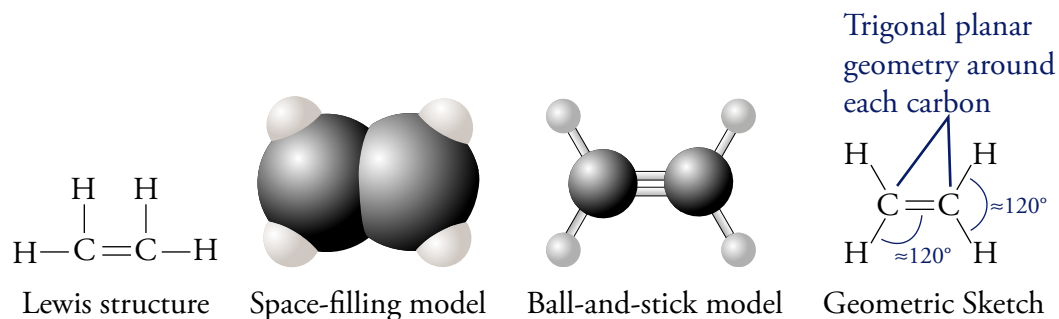


Figure 12.9 shows four ways to describe a C_2H_4 molecule. Because the bond groups around each carbon are not identical (two are single bonds and one is a double bond), the angles are only approximately 120° .



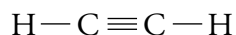
OBJECTIVE 9

Figure 12.9
Four Ways to Describe an Ethene (Ethylene), C_2H_4 , Molecule

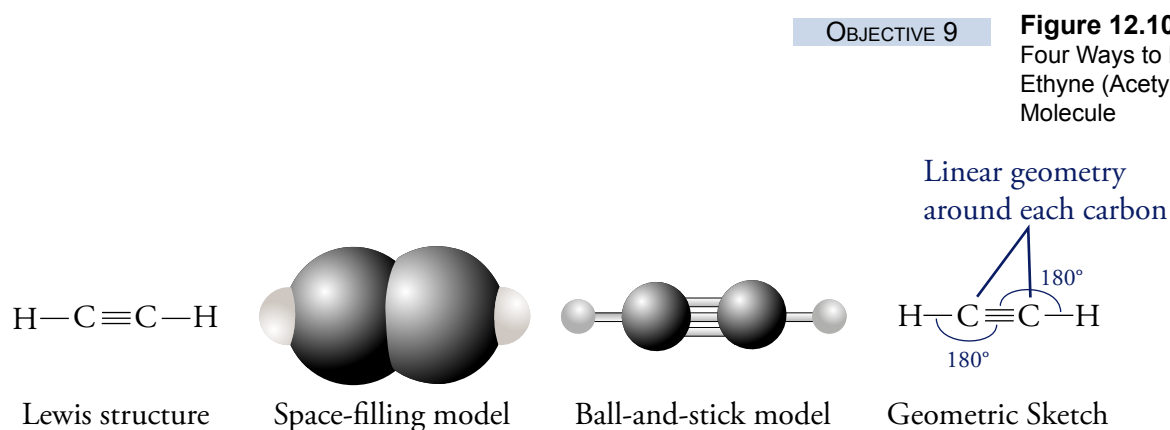
When atoms have only two electron groups around them, the groups are arranged in a line, with bond angles of 180° . This arrangement is called **linear**. For example, the carbon atom in HCN has two electron groups around it (one single bond and one triple bond), and the best way to keep these groups apart is in a linear shape.



There are two central atoms in an acetylene, C_2H_2 , molecule.



Because each of acetylene's central atoms has two electron groups around it, the arrangement of atoms around each is linear. Figure 12.10 shows four ways to describe a C_2H_2 molecule.



OBJECTIVE 9

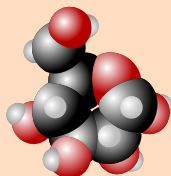
Figure 12.10
Four Ways to Describe an Ethyne (Acetylene), C_2H_2 , Molecule

The following sample study sheet summarizes a systematic procedure for predicting electron group geometries, drawing geometric sketches, and describing molecular geometries.

Sample Study Sheet 12.2

Predicting Molecular Geometry

OBJECTIVE 9



Web Molecules

TIP-OFF In this chapter, you are given a Lewis structure for a molecule or polyatomic ion (or a formula from which you can draw a Lewis structure), and asked to (1) name the electron group geometry around one or more atoms in the structure, (2) draw a geometric sketch of the structure, and/or (3) name the molecular geometry around one or more of the atoms in the structure. You will find in later chapters that there are other tip-offs for these tasks.

GENERAL STEPS Follow these steps.

STEP 1 To determine the name of the electron group geometry around each atom that is attached to two or more other atoms, count the number of electron groups around each “central” atom and apply the guidelines found on Table 12.3. An electron group can be a single bond, a lone pair, or a multiple bond. (Double and triple bonds count as one group.)

STEP 2 Use one or more of the geometric sketches shown on Table 12.3 as models for the geometric sketch of your molecule. If the groups around the central atom are identical, the bond angle is exact. If the groups are not identical, the angles are approximate.

STEP 3 To determine the name of the molecular geometry around each atom that has two or more atoms attached to it, count the number of bond groups and lone pairs, and then apply the guidelines found on Table 12.3. Single, double, and triple bonds all count as one bond group. Notice that if all of the electron groups attached to the atom are bond groups (no lone pairs), the name of the molecular geometry is the same as the name of the electron group geometry.

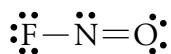
EXAMPLE See Examples 12.6 and 12.7.

Table 12.3 Electron Group and Molecular Geometry

e^- groups	e^- group geometry	General geometric sketch	Bond angles	Bond groups	Lone pairs	molecular geometry
2	linear		180°	2	0	linear
3	trigonal planar		120°	3	0	trigonal planar
				2	1	bent
4	tetrahedral		109.5°	4	0	tetrahedral
				3	1	trigonal pyramid
				2	2	bent

EXAMPLE 12.6 - Predicting Molecular Geometry

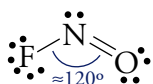
Nitrosyl fluoride, NOF, is used as an oxidizer in rocket fuels.



Using its Lewis structure, (a) write the name of the electron group geometry around the nitrogen atom, (b) draw a geometric sketch of the molecule, including bond angles, and (c) write the name of the molecular geometry around the nitrogen atom.

Solution

1. Table 12.3 tells us that because there are three electron groups around the nitrogen in nitrosyl fluoride (two bond groups and one lone pair), the electron group geometry around the nitrogen atom is **trigonal planar**.
2. The geometric sketch for NOF is

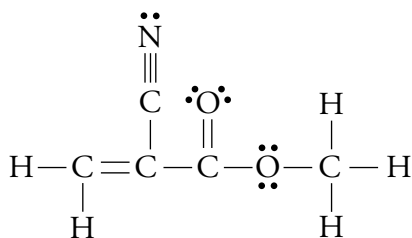


3. The nitrogen atom in NOF has one single bond, one double bond, and one lone pair. According to Table 12.3, an atom with two bond groups and one lone pair has the molecular geometry called **bent**.

OBJECTIVE 9

EXAMPLE 12.7 - Predicting Molecular Geometry

Methyl cyanoacrylate is the main ingredient in Super Glue.

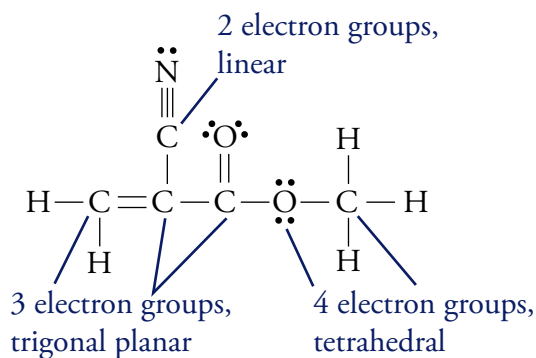


Using the Lewis structure above, (a) write the name of the electron group geometry around each atom that has two or more atoms attached to it, (b) draw a geometric sketch of the molecule, including bond angles, and (c) write the name of the molecular geometry around each atom that has two or more atoms attached to it. (This example was chosen because it contains several different types of electron groups and molecular shapes. The structures in the exercises and problems that accompany this chapter are much simpler.)

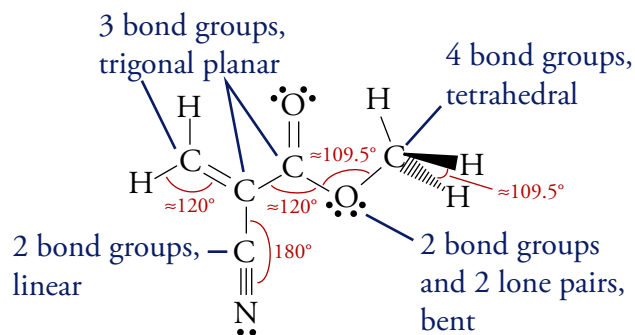
OBJECTIVE 9

Solution

a.



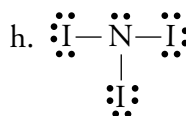
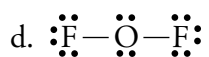
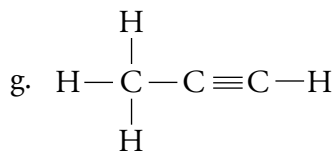
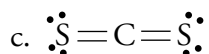
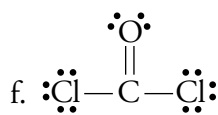
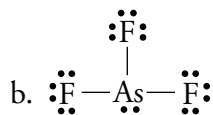
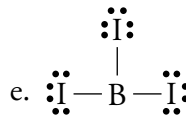
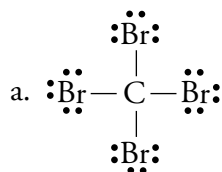
b and c. There are many ways to sketch the molecule and still show the correct geometry. The following is just one example. (Remember that your assigned exercises will be simpler than this one.)



EXERCISE 12.3 - Molecular Geometry

OBJECTIVE 9

For each of the Lewis structures given below, (a) write the name of the electron group geometry around each atom that has two or more atoms attached to it, (b) draw a geometric sketch of the molecule, including bond angles, and (c) write the name of the molecular geometry around each atom that has two or more atoms attached to it.



Valence electrons The highest energy *s* and *p* electrons for an atom.

Isomers Compounds that have the same molecular formula but different molecular structures.

Resonance structures Two or more Lewis structures for a single molecule or polyatomic ion that differ in the positions of lone pairs and multiple bonds but not in the positions of the atoms in the structure. It is as if the molecule or ion were able to shift from one of these structures to another by shifting pairs of electrons from one position to another.

Resonance The hypothetical switching from one resonance structure to another.

Resonance hybrid A structure that represents the average of the resonance structures for a molecule or polyatomic ion.

Bond angle The angle between any three adjacent atoms in a molecule.

Trigonal pyramid The molecular geometry formed around an atom with three bonds and one lone pair.

Electron group geometry A description of the arrangement of all the electron groups around a central atom in a molecule or polyatomic ion, including the lone pairs.

Molecular geometry The description of the arrangement of all the atoms around a central atom in a molecule or polyatomic ion. This description does not consider lone pairs.

Bent The molecular geometry formed around an atom with two bond groups and two lone pairs or two bond groups and one lone pair.

Trigonal planar (often called triangular planar) The geometric arrangement that keeps three electron groups as far apart as possible. It leads to angles of 120° between the groups.

Linear geometry The geometric arrangement that keeps two electron groups as far apart as possible. It leads to angles of 180° between the groups.

You can test yourself on the glossary terms at the textbook's Web site.

The goal of this chapter is to teach you to do the following.

1. Define all of the terms in the Chapter Glossary.

Section 12.1 A New Look at Molecules and the Formation of Covalent Bonds

2. Describe the advantages and disadvantages of using models to describe physical reality.
3. Describe the assumptions that lie at the core of the valence-bond model.
4. Write or identify the number of valence electrons in an atom of any representative element.

5. Use the valence-bond model to explain how (a) fluorine atoms form one covalent bond and have three lone pairs in molecules such as F_2 , (b) hydrogen atoms can form one covalent bond and have no lone pairs in molecules such as HF, (c) carbon atoms can form four covalent bonds and have no lone pairs in molecules such as CH_4 , (d) nitrogen, phosphorus, and arsenic atoms can form three covalent bonds and have one lone pair in molecules such as NH_3 , PH_3 , and AsH_3 , (e) nitrogen atoms can form four covalent bonds and have no lone pairs in structures such as NH_4^+ , (f) oxygen, sulfur, and selenium atoms can form two covalent bonds and have two lone pairs in molecules such as H_2O , H_2S , and H_2Se (g) oxygen atoms can form one covalent bond and have three lone pairs in structures such as OH^- , (h) carbon and oxygen atoms can form three covalent bonds and have one lone pair in molecules such as CO, (i) boron atoms can form three covalent bonds and have no lone pairs in molecules such as BF_3 , (j) halogen atoms can form one covalent bond and have three lone pairs in molecules such as HF, HCl, HBr, and HI.
6. Write electron-dot symbols for the representative elements.

Section 12.2 Drawing Lewis Structures

7. Given a formula for a molecule or polyatomic ion, draw a reasonable Lewis structure for it.

Section 12.3 Resonance

8. Given a Lewis structure or enough information to draw one, predict whether it is best described in terms of resonance, and if it is, draw all of the reasonable resonance structures and the resonance hybrid for the structure.

Section 12.4 Molecular Geometry from Lewis Structures

9. Given a Lewis structure or enough information to write one, do the following.
 - a. Write the name of the electron group geometry around each atom that has two or more atoms attached to it.
 - b. Draw a geometric sketch of the molecule, including bond angles (or approximate bond angles).
 - c. Write the name of the molecular geometry around each atom that has two or more atoms attached to it.

Review Questions

1. Using the A-group convention, what is the group number of the column on the periodic table that includes the element chlorine, Cl?
2. Draw Lewis structures for CH_4 , NH_3 , and H_2O .
3. Write the definition of orbital.
4. Write a complete electron configuration and an orbital diagram for each of the following.
 - a. oxygen, O
 - b. phosphorus, P

Complete the following statements by writing one of these words or phrases in each blank.

109.5°	most
A-group	most common
anions	never
as far apart	oxygen
as if	pair unpaired
cations	polyatomic ions
change	predict
eight	rarely
electron group	<i>s</i> and <i>p</i>
explain	structural
fewest	triple
four	true
function	two
highest-energy	uncharged
lone pairs	useful
molecular	visualize
more	

5. When developing a model of physical reality, scientists take what they think is _____ and simplify it enough to make it _____.
6. Models have advantages and disadvantages. They help us to _____, _____, and _____ chemical changes, but we need to remind ourselves now and then that they are only models and that as models, they have their limitations.
7. One characteristic of models is that they _____ with time.
8. The valence-bond model, which is commonly used to describe the formation of covalent bonds, is based on the assumptions that only the _____ electrons participate in bonding, and covalent bonds usually form to _____ electrons.
9. Valence electrons are the highest-energy _____ electrons in an atom.
10. When the columns in the periodic table are numbered by the _____ convention, the number of valence electrons in each atom of a representative element is equal to the element's group number in the periodic table.
11. Paired valence electrons are called _____.
12. When forming four bonds to hydrogen atoms in a methane molecule, each carbon atom behaves _____. One electron is promoted from the $2s$ orbital to the $2p$ orbital.
13. Carbon atoms frequently form double bonds, in which they share _____ electrons with another atom, often another carbon atom.
14. A(n) _____ bond can be viewed as the sharing of six electrons between two atoms.

15. The shortcut for drawing Lewis structures for which we try to give each atom its _____ bonding pattern works well for many simple uncharged molecules, but it does not work reliably for molecules that are more complex or for _____.
16. For _____ molecules, the total number of valence electrons is the sum of the valence electrons of each atom.
17. For polyatomic _____, the total number of valence electrons is the sum of the valence electrons for each atom minus the charge.
18. For polyatomic _____, the total number of valence electrons is the sum of the valence electrons for each atom plus the charge.
19. Hydrogen and fluorine atoms are _____ in the center of a Lewis structure.
20. Oxygen atoms are _____ in the center of a Lewis structure.
21. The element with the _____ atoms in the formula is often in the center of a Lewis structure.
22. The atom that is capable of making the _____ bonds is often in the center of a Lewis structure.
23. Oxygen atoms rarely bond to other _____ atoms.
24. In a reasonable Lewis structure, carbon, nitrogen, oxygen, and fluorine always have _____ electrons around them.
25. In a reasonable Lewis structure, hydrogen will always have a total of _____ electrons from its one bond.
26. Boron can have fewer than eight electrons around it in a reasonable Lewis structure but never _____ than eight.
27. Substances that have the same molecular formula but different _____ formulas are called isomers.
28. The shapes of molecules play a major role in determining their _____.
29. The most stable arrangement for electron groups is one in which they are _____ as possible.
30. The geometric arrangement in which four electron groups are as far apart as possible is a tetrahedral arrangement, with bond angles of _____.
31. In this book, we call the geometry that describes all of the electron groups, including the lone pairs, the _____ geometry. The shape that describes the arrangement of the atoms only—treating the lone pairs as invisible—is called the _____ geometry.

Chapter Problems

OBJECTIVE 2

OBJECTIVE 3

OBJECTIVE 4

Section 12.1 A New Look at Molecules and the Formation of Covalent Bonds

32. Describe the advantages and disadvantages of using models to describe physical reality.
33. Describe the assumptions that lie at the core of the valence-bond model.
34. How many valence electrons do the atoms of each of the following elements have? Write the electron configuration for these electrons. (For example, fluorine has seven valence electrons, which can be described as $2s^2 2p^5$.)
 - a. nitrogen, N
 - b. sulfur, S
 - c. iodine, I
 - d. argon, Ar

35. How many valence electrons do the atoms of each of the following elements have? Write the electron configuration for these electrons. (For example, fluorine has seven valence electrons, which can be described as $2s^2 2p^5$.)
- a. oxygen, O b. boron, B c. neon, Ne d. phosphorus, P e. carbon, C
36. Draw electron-dot symbols for each of the following elements.
- a. nitrogen, N b. sulfur, S c. iodine, I d. argon, Ar
37. Draw electron-dot symbols for each of the following elements.
- a. oxygen, O b. boron, B c. neon, Ne d. phosphorus, P e. carbon, C
38. To which group on the periodic table would atoms with the following electron-dot symbols belong? List the group numbers using the 1-18 convention and using the A-group convention.
- a. $\cdot\ddot{X}\cdot$ b. $\cdot\ddot{X}\cdot$ c. $\cdot\ddot{X}\cdot$
39. To which group on the periodic table would atoms with the following electron-dot symbols belong? List the group numbers using the 1-18 convention and using the A-group convention.
- a. $\cdot\ddot{X}\cdot$ b. $\cdot\ddot{X}\cdot$ c. $\cdot\ddot{X}\cdot$
40. For each of the following elements, sketch all of the ways mentioned in Section 12.1 that their atoms could look in a Lewis structure. For example, fluorine has only one bonding pattern, and it looks like $\text{—}\ddot{F}\cdot$.
- a. nitrogen, N b. boron, B c. carbon, C
41. For each of the following elements, sketch all of the ways mentioned in Section 12.1 that their atoms could look in a Lewis structure. For example, fluorine has only one bonding pattern, and it looks like $\text{—}\ddot{F}\cdot$.
- a. hydrogen, H b. oxygen, O c. chlorine, Cl
42. Use the valence-bond model to explain the following.
- a. Fluorine atoms have one bond and three lone pairs in F_2 .
 b. Carbon atoms have four bonds and no lone pairs in CH_4 .
 c. Nitrogen atoms have three bonds and one lone pair in NH_3 .
 d. Sulfur atoms have two bonds and two lone pairs in H_2S .
 e. Oxygen atoms have one bond and three lone pairs in OH^- .
43. Use the valence-bond model to explain the following.
- a. Phosphorus atoms have three bonds and one lone pair in PH_3 .
 b. Nitrogen atoms have four bonds and no lone pairs in NH_4^+ .
 c. Oxygen atoms have two bonds and two lone pairs in H_2O .
 d. Boron atoms have three bonds and no lone pair in BF_3 .
 e. Chlorine atoms have one bond and three lone pairs in HCl .
44. Based on your knowledge of the most common bonding patterns for the nonmetallic elements, predict the formulas with the lowest subscripts for the compounds that would form from the following pairs of elements. (For example, hydrogen and oxygen can combine to form H_2O and H_2O_2 , but H_2O has lower subscripts.)
- a. C and H b. S and H c. B and F

OBJECTIVE 4

OBJECTIVE 6

OBJECTIVE 6

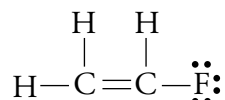
OBJECTIVE 5

OBJECTIVE 5

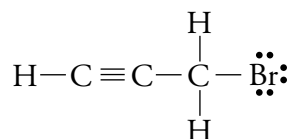
45. Based on your knowledge of the most common bonding patterns for the nonmetallic elements, predict the formulas with the lowest subscripts for the compounds that would form from the following pairs of elements. (For example, hydrogen and oxygen can combine to form H_2O and H_2O_2 , but H_2O has lower subscripts.)
- a. P and I b. O and Br c. N and Cl

Section 12.2 Drawing Lewis Structures

46. Copy the following Lewis structure and identify the single bonds, the double bond, and the lone pairs.



47. Copy the following Lewis structure and identify the single bonds, the triple bond, and the lone pairs.



48. For each of the following molecular compounds, identify the atom that is most likely to be found in the center of its Lewis structure. Explain why.
- a. CBr_4 b. SO_2 c. H_2S d. NOF
49. For each of the following molecular compounds, identify the atom that is most likely to be found in the center of its Lewis structure. Explain why.
- a. BI_3 b. SO_3 c. AsH_3 d. HCN
50. Calculate the total number of valence electrons for each of the following formulas.
- a. HNO_3 b. CH_2CHF
51. Calculate the total number of valence electrons for each of the following formulas.
- a. H_3PO_4 b. $\text{HC}_2\text{H}_3\text{O}_2$

OBJECTIVE 7

52. Draw a reasonable Lewis structure for each of the following formulas.
- a. Cl_4 b. O_2F_2 c. HC_2F d. NH_2Cl
 e. PH_3 f. S_2F_2 g. HNO_2 h. N_2F_4
 i. CH_2CHCH_3

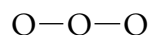
OBJECTIVE 7

53. Draw a reasonable Lewis structure for each of the following formulas.
- a. H_2S b. CHBr_3 c. NF_3 d. Br_2O
 e. H_2CO_3 f. H_2S_2 g. HOCl h. BBr_3
 i. $\text{CH}_3\text{CH}_2\text{CHCH}_2$

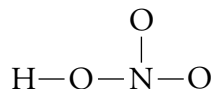
Section 12.3 Resonance

OBJECTIVE 8

54. Draw a reasonable Lewis structure for the ozone molecule, O_3 , using the skeleton below. The structure is best described in terms of resonance, so draw all of its reasonable resonance structures and the resonance hybrid that summarizes these structures.



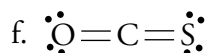
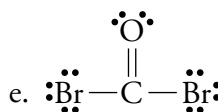
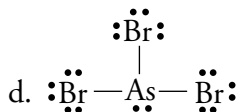
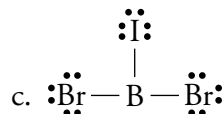
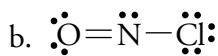
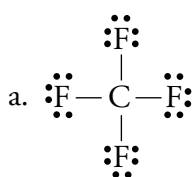
55. Draw a reasonable Lewis structure for a nitric acid, HNO_3 , using the skeleton below. The structure is best described in terms of resonance, so draw all of its reasonable resonance structures and the resonance hybrid that summarizes these structures.



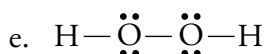
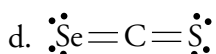
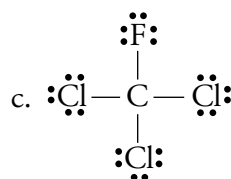
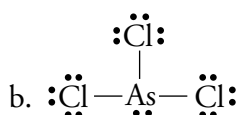
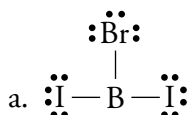
OBJECTIVE 8

Section 12.4 Molecular Geometry from Lewis Structures

56. Although both CO_2 molecules and H_2O molecules have three atoms, CO_2 molecules are linear, and H_2O molecules are bent. Why?
57. Although both BF_3 molecules and NH_3 molecules have four atoms, the BF_3 molecules are planar, and NH_3 molecules are pyramidal. Why?
58. Using the symbol X for the central atom and Y for the outer atoms, draw the general geometric sketch for a three-atom molecule with linear geometry.
59. Using the symbol X for the central atom and Y for the outer atoms, draw the general geometric sketch for a molecule with trigonal planar geometry.
60. Using the symbol X for the central atom and Y for the outer atoms, draw the general geometric sketch for a molecule with tetrahedral geometry.
61. For each of the Lewis structures given below, (1) write the name of the electron group geometry around each atom that has two or more atoms attached to it, (2) draw a geometric sketch of the molecule, including bond angles (or approximate bond angles), and (3) write the name of the molecular geometry around each atom that has two or more atoms attached to it.



62. For each of the Lewis structures given below, (1) write the name of the electron group geometry around each atom that has two or more atoms attached to it, (2) draw a geometric sketch of the molecule, including bond angles (or approximate bond angles), and (3) write the name of the molecular geometry around each atom that has two or more atoms attached to it.



OBJECTIVE 9

OBJECTIVE 9