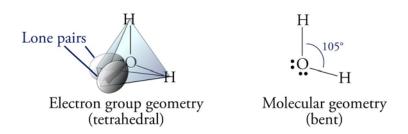
# Chapter 12 Molecular Structure



- ♦ Review Skills
- 12.1 A New Look at Molecules and the Formation of Covalent Bonds
  - The Strengths and Weaknesses of Models
  - The Valence-Bond Model
- 12.2 Drawing Lewis Structures
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Internet: Resonance

- 12.4 Molecular Geometry from Lewis Structures
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♦ Chapter Objectives

**Review Questions** 

**Key Ideas** 

**Chapter Problems** 

#### **Section Goals and Introductions**

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

- *To describe the strengths and weaknesses of scientific models.*
- To introduce a model, called the valence-bond model, which is very useful for describing the formation of covalent bonds.
- To explain the most common covalent bonding patterns for the nonmetallic atoms in terms of the valence-bond model.

This section shows how the information learned in Chapter 11 can be combined with a model for covalent bonding called the valence-bond model to explain the common bonding patterns of the nonmetallic atoms. The most common of these bonding patterns were listed in Chapter 3, but now you have the background necessary for understanding why atoms have the bonding patterns that they do. It's important to recognize that although the valence bond model is only

a model (and therefore a simplification of reality), it is extremely useful. You will find the information in *Table 12.1: Covalent Bonding Patterns* very helpful when drawing Lewis structures (the task described in Section 12.2).

#### **Section 12.2 Drawing Lewis Structures**

Goal: To show how Lewis structures can be drawn from chemical formulas.

In Chapter 3, you learned to draw simple Lewis structures by arranging the atoms to yield the most common bonding pattern for each atom. This technique works very well for many molecules, but it is limited. For example, it does not work for polyatomic ions. This section describes a procedure for drawing Lewis structures from chemical formulas that works for a broader range of molecules and polyatomic ions.

#### Section 12.3 Resonance

Goal: To introduce a concept called resonance and show how it can be used to explain the characteristics of certain molecules and polyatomic ions.

The Lewis structures derived for some molecules and polyatomic ions by the technique described in Section 12.2 do not explain their characteristics adequately. One way that the valence-bond model has been expanded to better explain some of these molecules and polyatomic ions is by introducing the concept of resonance described in this section. See the related section on our Web site:

Internet: Resonance

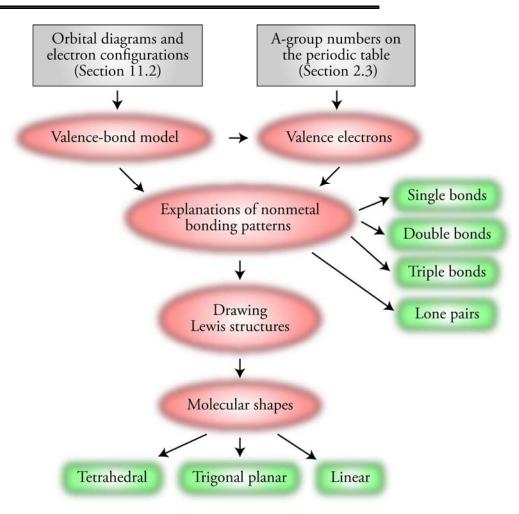
#### **Section 12.4 Molecular Geometry from Lewis Structures**

Goals

- To show how you can predict the arrangement of atoms in molecules and polyatomic ions (called molecular geometry).
- To show how to make sketches of the molecular geometry of atoms in molecules and polyatomic ions.

The arrangement of atoms in a molecule or polyatomic ion (that is, its molecular geometry) plays a significant role in determining its properties. This section explains why molecules and polyatomic ions have the geometry that they do, and *Sample Study Sheet 12.2: Predicting Molecular Geometry* and *Table 12.3: Electron Group and Molecular Geometry* show you how to predict and sketch these geometries.

## **Chapter 12 Map**



## **Chapter Checklist**

ш	Read the Review Skins section. If there is any skill mentioned that you have not yet
	mastered, review the material on that topic before reading this chapter.
	Read the chapter quickly before the lecture that describes it.
	Attend class meetings, take notes, and participate in class discussions.
	Work the Chapter Exercises, perhaps using the Chapter Examples as guides.
	Study the Chapter Glossary and test yourself on our Web site:
	Internet: Glossary Quiz
	Study all of the Chapter Objectives. You might want to write a description of how you
	will meet each objective. (Although it is best to master all of the objectives, the following
	objectives are especially important because they pertain to skills that you will need while
	studying other chapters of this text: 7 and 9.)

Reread the Study Sheets in this chapter and decide whether you will use them or some
variation on them to complete the tasks they describe.
Sample Study Sheet 12.1: Drawing Lewis Structures from Formulas
Sample Study Sheet 12.2: Predicting Molecular Geometry
Memorize the following.
Be sure to check with your instructor to determine how much you are expected to know
of the following.

• The most common bonding patterns for the nonmetallic elements.

Elements	Number of covalent bonds	Number of lone pairs
С	4	0
N, P, & As	3	1
O, S, Se	2	2
F, Cl, Br, & I	1	3

• Although it's not absolutely necessary, it will help you to draw Lewis structures to know the expanded list of bonding patterns listed below.

Element	Frequency of pattern	Number of bonds	Number of lone pairs	Example
Н	always	1	0	H-
В	most common	3	0	-B-
С	most common	4	0	$-\stackrel{\mid}{C}$ or $-\stackrel{\mid}{C}$ or $-C\equiv$
	rare	3	1	≡C <b>:</b>
N, P, & As	most common	3	1	- <u>N</u> -
	common	4	0	-N-
O, S, & Se	most common	2	2	-Ö− or Ö
	common	1	3	-Ö:
	rare	3	1	≡O <b>:</b>
F, Cl, Br, & I	most common	1	3	− <b>∷</b> :

• The information found in the table below.

e <sup>-</sup> groups	e <sup>–</sup> group geometry	General Geometric Sketch	Bond angles	Bond groups	Lone pairs	molecular geometry
2	linear	180°	180°	2	0	linear
				3	0	trigonal planar
3		120°	120°	2	1	bent
		100.5°		4	0	tetrahedral
4	tetrahedral	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	109.5°	3	1	trigonal pyramid
		•		2	2	bent

Ш	To get a review of the most important topics in the chapter, fill in the blanks in the Key
	Ideas section.
	Work all of the selected problems at the end of the chapter, and check your answers with

the solutions provided in this chapter of the study guide.

☐ Ask for help if you need it.

## **Web Resources**

<u>Internet: Resonance</u> <u>Internet: Glossary Quiz</u>

## **Exercises Key**

**Exercise 12.1 - Lewis Structures:** Draw a reasonable Lewis structure for each of the following formulas. (06; 7)

ing formulas. (b) 
$$7$$

i. Cl:

i. Cl-C-Cl:

i. Cl:

i. Cl-Ö-Cl:

i. Cl-Ö-Cl:

i. Cl-C-C-C-Cl:

i. Cl-C-C-C-Cl:

i. Cl-C-C-C-Cl:

i. Cl-C-C-C-Cl:

i. Cl-C-C-C-Cl:

i. Cl-B-Cl:

i. H-N-N-H

i. H

i. N2H4

i. H-Ö-Ö-H

i. NH2OH

i. NCl3

**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 (06; 8)

$$\begin{bmatrix} \dot{\mathbf{O}} \\ \vdots \ddot{\mathbf{O}} - \ddot{\mathbf{C}} - \ddot{\mathbf{O}} \end{bmatrix}^{2-} \\ \vdots \ddot{\mathbf{O}} - \ddot{\mathbf{C}} - \ddot{\mathbf{O}} \end{bmatrix}^{2-} \longleftrightarrow \begin{bmatrix} \dot{\mathbf{O}} \\ \vdots \ddot{\mathbf{O}} - \ddot{\mathbf{C}} - \ddot{\mathbf{O}} \end{bmatrix}^{2-} \longleftrightarrow \begin{bmatrix} \dot{\mathbf{O}} \\ \vdots \ddot{\mathbf{O}} - \ddot{\mathbf{C}} - \ddot{\mathbf{O}} \end{bmatrix}^{2-} \\ \vdots \ddot{\mathbf{O}} - \ddot{\mathbf{C}} - \ddot{\mathbf{O}} \end{bmatrix}^{2-} \begin{bmatrix} \dot{\mathbf{O}} \\ \vdots \ddot{\mathbf{O}} - \ddot{\mathbf{C}} - \ddot{\mathbf{O}} \end{bmatrix}^{2-} \\ \vdots \ddot{\mathbf{O}} - \ddot{\mathbf{C}} - \ddot{\mathbf{O}} \end{bmatrix}^{2-} \end{bmatrix}$$

**Exercise 12.3 - Molecular Geometry:** For each of the Lewis structures that follow, (a) write the name of the electron group geometry around each atom that has two or more atoms attached to it, (b) draw the 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. (Obj 9)

100/11	
 Br:	Electron Group Geometry - tetrahedral
Br: 	Br. Br.
a. Br	Br.
	Molecular Geometry - tetrahedral
	Electron Group Geometry - <b>tetrahedral</b>
b. :F—As—F:	F. 109.5° F
	Molecular Geometry <b>– trigonal pyramid</b>
	Electron Group Geometry - linear
c. <b>:</b> \$=C= <b>\$</b> :	\$ _C=\$
	Molecular Geometry - linear
	Electron Group Geometry - tetrahedral
	:F:
d. F. Ö-F:	109.5° F.
	Molecular Geometry - bent
	Electron Group Geometry - trigonal planar
:Ï: e. :Ï.─B.─Ï:	
e. :1—B—1:	•••
	Molecular Geometry – trigonal planar
f. *Cl-C-Cl:	Electron Group Geometry - trigonal planar
	Molecular Geometry – trigonal planar

## **Review Questions Key**

- 1. Using the A-group convention, what is the group number of the column in the periodic table that includes the element chlorine, Cl? (See Section 2.3.) **7A**
- 2. Draw Lewis structures for CH<sub>4</sub>, NH<sub>3</sub>, and H<sub>2</sub>O. (See Section 3.3.)

3. Define the term *orbital*. (See Section 11.1.)

Orbital can be defined as the volume that contains a high percentage of the electron charge generated by an electron in an atom. It can also be defined as the volume within which an electron has a high probability of being found.

4. Write a complete electron configuration and an orbital diagram for each of the following. (See Section 11.2.)

a. oxygen, O
$$1s^{2} 2s^{2} 2p^{4}$$

$$2s \xrightarrow{\uparrow \downarrow} 2p \xrightarrow{\uparrow \downarrow} \xrightarrow{\uparrow} \xrightarrow{\uparrow}$$

$$1s \xrightarrow{\uparrow \downarrow}$$

## **Key Ideas Answers**

- 5. When developing a model of physical reality, scientists take what they think is **true** and simplify it enough to make it **useful**.
- 7. One characteristic of models is that they **change** with time.
- 9. Valence electrons are the highest-energy s and p electrons in an atom.
- 11. Paired valence electrons are called **lone pairs**.
- 13. Carbon atoms frequently form double bonds, in which they share **four** electrons with another atom, often another carbon atom.
- 15. The shortcut for drawing Lewis structures for which we try to give each atom its **most common** bonding pattern works well for many simple uncharged molecules, but it does not work reliably for molecules that are more complex or for **polyatomic ions**.
- 17. For polyatomic **cations**, the total number of valence electrons is the sum of the valence electrons for each atom minus the charge.
- 19. Hydrogen and fluorine atoms are **never** in the center of a Lewis structure.
- 21. The element with the **fewest** atoms in the formula is often in the center of a Lewis structure.
- 23. Oxygen atoms rarely bond to other **oxygen** atoms.
- 25. In a reasonable Lewis structure, hydrogen will always have a total of **two** electrons from its one bond.
- 27. Substances that have the same molecular formula but different **structural** formulas are called isomers.
- 29. The most stable arrangement for electron groups is one in which they are **as far apart** as possible.
- 31. In this book, we 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—is called the **molecular** geometry.

## **Problems Key**

#### 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. (Obj 2)

Our models come with 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 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 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 a simplification of what we think is real, we are not surprised when they sometimes fail to explain experimental observation. When this happens, the model is altered to fit the new observations.

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 7 valence electrons, which can be described as  $2s^2 2p^5$ .) (04)

a.	nitrogen, N	five valence electrons – $2s^2 2p^3$
b.	sulfur, S	six valence electrons $-3s^2 3p^4$
c.	iodine, I	seven valence electrons – $5s^2 5p^5$
a.	argon, Ar	eight valence electrons – $3s^2 3p^6$

36. Draw electron-dot symbols for each of the following elements. (Obj. 4 & 6)

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.

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 —.

42. Use the valence-bond model to explain the following observations. (Obj 5)

The answers to each of these problems is based on the following assumptions of the valence bond model.

- Only the highest energy electrons participate in bonding.
- Covalent bonds usually form to pair unpaired electrons.
- a. Fluorine atoms have one bond and three lone pairs in  $F_2$ .

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

$$2s \xrightarrow{\uparrow\downarrow} 2p \xrightarrow{\uparrow\downarrow} \xrightarrow{\uparrow\downarrow} \uparrow$$
 :F.

The one unpaired electron leads to one bond, and the three pairs of electrons give fluorine atoms three lone pairs.

b. Carbon atoms have four bonds and no lone pairs in CH<sub>4</sub>.

Carbon is in group 4A, so it has four valence electrons per atom. It is as if one electron is promoted from the 2s orbital to the 2p orbital.

$$2s \xrightarrow{\uparrow\downarrow} \stackrel{2p}{\longrightarrow} \stackrel{\uparrow}{\longleftarrow} \longrightarrow 2s \xrightarrow{\uparrow} \stackrel{2p}{\longrightarrow} \stackrel{\uparrow}{\longleftarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow}$$

The four unpaired electrons lead to four covalent bonds. Because there are no pairs of electrons, carbon atoms have no lone pairs when they form four bonds.

$$4H^{\bullet} + {}^{\bullet}\dot{C}^{\bullet} \rightarrow H^{\bullet}\dot{C}^{\bullet}\dot{H} \text{ or } H^{-}C^{-}H$$

c. Nitrogen atoms have three bonds and one lone pair in NH<sub>3</sub>.

Nitrogen is in group 5A, so it has five valence electrons per atom. The orbital diagram for the valence electrons of nitrogen is below.

$$_{2s} \xrightarrow{\uparrow\downarrow} ^{2p} \xrightarrow{\uparrow} \xrightarrow{\uparrow} \xrightarrow{\uparrow}$$
 ·N·

The three unpaired electrons lead to three bonds, and the one pair of electrons gives nitrogen atoms one lone pair.

d. Sulfur atoms have two bonds and two lone pairs in H<sub>2</sub>S.

Sulfur is in group 6A, so it has six valence electrons per atom. The orbital diagram for the valence electrons of sulfur is below.

$$3s \stackrel{\uparrow}{\downarrow} 3p \stackrel{\uparrow}{\downarrow} \stackrel{\uparrow}{\downarrow} \stackrel{\uparrow}{\downarrow}$$
 :

The two unpaired electrons lead to two bonds, and the two pairs of electrons give sulfur atoms two lone pairs.

$$H-S-H$$

e. Oxygen atoms have one bond and three lone pairs in OH<sup>-</sup>.

Oxygen is in group 6A, so it has six valence electrons per atom. If it gains one electron, it will have a total of seven.

$$2s \xrightarrow{\uparrow \downarrow} 2p \xrightarrow{\uparrow \downarrow} \xrightarrow{\uparrow} \xrightarrow{\uparrow} \xrightarrow{+1e^{-}} 2s \xrightarrow{\uparrow \downarrow} 2p \xrightarrow{\uparrow \downarrow} \xrightarrow{\uparrow \downarrow} \xrightarrow{\uparrow} \xrightarrow{\uparrow}$$

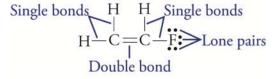
The one unpaired electron leads to one bond, and the three pairs of electrons give oxygen atoms with an extra electron three lone pairs.

$$H \cdot + \cdot O : \rightarrow [H : O :]^- \text{ or } [H - O :]^-$$

- 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<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, but H<sub>2</sub>O has lower subscripts.)
  - a. C and H CH<sub>4</sub>
  - b. S and H  $H_2S$
  - c. B and F **BF**<sub>3</sub>

#### **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. 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<sub>4</sub> **Carbon** –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. Carbon atoms usually form four bonds, and bromine atoms usually form one bond.
  - b. SO<sub>2</sub> Sulfur The element with the fewest atoms in the formula is often in the center. Oxygen atoms are rarely in the center. Oxygen atoms rarely bond to other oxygen atoms.
  - c. H<sub>2</sub>S **Sulfur** –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. Sulfur atoms usually form two bonds, and hydrogen atoms form one bond. Hydrogen atoms are never in the center.
  - d. NOF **Nitrogen** –The atom that is capable of making the most bonds is often in the center. Nitrogen atoms usually form three bonds, oxygen atoms usually form two bonds, and fluorine atoms form one bond. Fluorine atoms are never in the center.
- 50. Calculate the total number of valence electrons for each of the following formulas.
  - a.  $HNO_3$  1 + 5 + 3(6) = 24 valence electrons
  - b.  $CH_2CHF \ 2(4) + 3(1) + 7 = 18$  valence electrons
- 52. Draw a reasonable Lewis structure for each of the following formulas. (06) 7.

a. 
$$CI_4$$

b.  $O_2F_2$ 

c.  $HC_2F$ 
 $H-N-CI:$ 
 $H-N-CI:$ 

d.  $NH_2CI$ 
 $H-P-H$ 

e.  $PH_3$ 

f.  $S_2F_2$ 

g.  $HNO_2$ 
 $H-O-N-O$ 
 $F-N-N-F:$ 

h.  $N_2F_4$ 
 $H-C=C-C-H$ 

i.  $CH_2CHCH_3$ 

#### Section 12.3 Resonance

54. Draw a reasonable Lewis structure for the ozone molecule, O<sub>3</sub>, using the skeleton that follows. 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.

(064 8)

#### **Section 12.4 Molecular Geometry from Lewis Structures**

56. Although both CO<sub>2</sub> molecules and H<sub>2</sub>O molecules have three atoms, CO<sub>2</sub> molecules are linear, and H<sub>2</sub>O molecules are bent. Why?

Atoms are arranged in molecules to keep the electron groups around the central atom as far apart as possible. An electron group is either (1) a single bond, (2) a multiple bond (double or triple), or (3) a lone pair. The Lewis structure for  $CO_2$  shows that the carbon atom has two electron groups around it. The best way to get two things as far apart as possible is in a linear arrangement.

$$o = c = o$$

The Lewis structure for  $H_2O$  shows that the oxygen atom has four electron groups around it. The best way to get four things as far apart as possible is in a tetrahedral arrangement.



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.

$$Y - X - Y$$

### 61. For each of the Lewis structures that follows, (06; 9)

- Write the name of the electron group geometry around each atom that has two or more atoms attached to it.
- Draw the geometric sketch of the molecule, including bond angles (or approximate bond angles).
- Write the name of the molecular geometry around each atom that has two or more atoms attached to it.

