

8

Covalent Bonding

INSIDE:

- 8.1 Molecular Compounds
- 8.2 The Nature of Covalent Bonding
- 8.3 Bonding Theories
- 8.4 Polar Bonds and Molecules

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Water droplets result from attractions between water molecules.

BIG IDEA

BONDING AND INTERACTIONS

Essential Questions:

1. How is the bonding in molecular compounds different from the bonding in ionic compounds?
2. How do electrons affect the shape of a molecule?
3. What factors affect molecular properties?

CHEMYSTERY



What's That Alarm?

A family woke up in the middle of the night to the sound of a piercing alarm. The family thought it must be the fire alarm. They quickly evacuated the house and called 9-1-1. While they waited for the fire department to arrive, they didn't see smoke or any other signs of fire coming from the house.

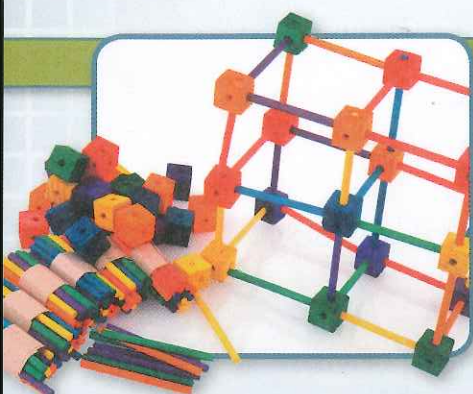
The fire department inspected the home and told the family that a compound containing carbon and oxygen atoms caused the alarm. Carbon dioxide (CO_2) is made of carbon and oxygen, but the fire department confirmed that it wasn't carbon dioxide. Are other molecules besides carbon dioxide made of carbon and oxygen? What was this mystery substance, and why would it set off an alarm?

► Connect to the **BIG IDEA** As you read about covalent bonding, think about how there could be different molecules made of carbon and oxygen atoms.

NATIONAL SCIENCE EDUCATION STANDARDS

B-2, B-4

8.1 Molecular Compounds



CHEMISTRY & YOU

Q: How are atoms joined together to make compounds with different structures? This toy model is made from cubes joined together in units by sticks. Although the types of pieces are limited, you can make many different toy models depending on how many pieces you use and how they are arranged. In this lesson, you will learn how atoms are joined together to form units called molecules.

Key Questions

Key What information does a molecular formula provide?

Key What representative units define molecular compounds and ionic compounds?

Vocabulary

- covalent bond
- molecule
- diatomic molecule
- molecular compound
- molecular formula

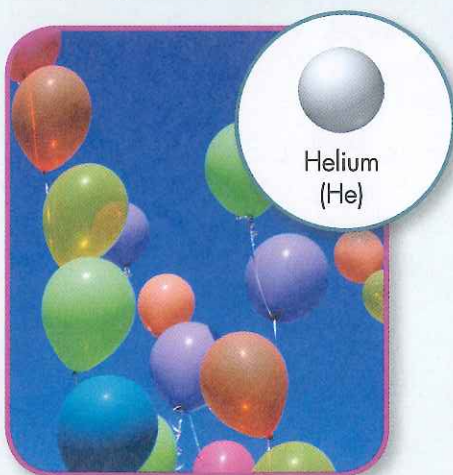
Molecules and Molecular Compounds

Key What information does a molecular formula provide?

In nature, only the noble gas elements, such as helium and neon, exist as uncombined atoms. They are monatomic; that is they consist of single atoms, as shown in Figure 8.1. But not all elements are monatomic. For example, a key component of the air you breathe is oxygen gas, O_2 . As you might guess from the chemical formula, O_2 represents two oxygen atoms that are bonded together.

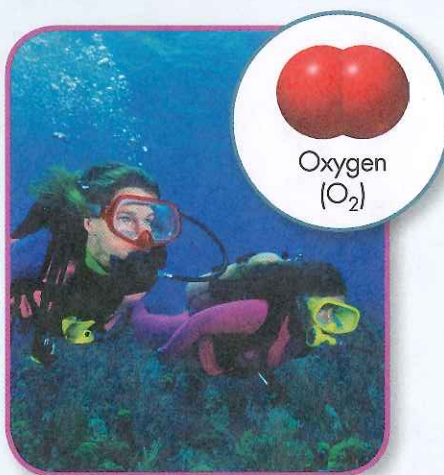
In Chapter 7, you learned about ionic compounds, which are generally crystalline solids with high melting points. Other compounds, however, have very different properties. For example, water (H_2O) is a liquid at room temperature. Carbon dioxide (CO_2) and nitrous oxide (N_2O) are both gases at room temperature. The attractions that hold together the atoms in O_2 , H_2O , CO_2 , and N_2O cannot be explained by ionic bonding. These bonds do not involve the transfer of electrons.

Figure 8.1
Comparing Gas Particles



Helium
(He)

Helium, which is less dense than air, is often used to inflate balloons.



Oxygen
(O_2)

Scuba divers breathe compressed air, a mixture that contains oxygen gas.




Nitrous oxide
(N_2O)

Nitrous oxide (also known as laughing gas) is sometimes used as a mild anesthetic in dental procedures.

Sharing Electrons Recall that ionic bonds form when the combining atoms give up or accept electrons. Another way that atoms can combine is by sharing electrons. Atoms that are held together by sharing electrons are joined by a **covalent bond**. In a covalent bond, a “tug of war” for electrons takes place between the atoms, bonding the atoms together. In Lesson 8.2, you will learn about the different types of covalent bonds.

In Figure 8.1, the representative units shown for oxygen and nitrous oxide are called molecules. A **molecule** is a neutral group of atoms joined together by covalent bonds. Oxygen gas consists of oxygen molecules; each oxygen molecule consists of two covalently bonded oxygen atoms. An oxygen molecule is an example of a **diatomic molecule**—a molecule that contains two atoms. Other elements found in nature in the form of diatomic molecules include hydrogen, nitrogen, and the halogens. Molecules can also be made of atoms of different elements. A compound composed of molecules is called a **molecular compound**. Water is an example of a molecular compound. The molecules in water are all the same; each water molecule is a tightly bound unit of two hydrogen atoms and one oxygen atom.

Representing Molecules A **molecular formula** is the chemical formula of a molecular compound.  A **molecular formula shows how many atoms of each element a substance contains**. The molecular formula of water is H_2O . Notice that a subscript written after an element’s symbol indicates the number of atoms of each element in the molecule. If there is only one atom, the subscript 1 is omitted. The molecular formula of carbon dioxide is CO_2 . This formula represents a molecule containing one carbon atom and two oxygen atoms.

Butane, shown in Figure 8.2, is also a molecular compound. The molecular formula for butane is C_4H_{10} . According to this formula, one molecule of butane contains four carbon atoms and ten hydrogen atoms. A molecular formula reflects the actual number of atoms in each molecule. The subscripts are not necessarily lowest whole-number ratios. Note that molecular formulas also describe molecules consisting of atoms of one element. For example, an oxygen molecule consists of two oxygen atoms bonded together; its molecular formula is O_2 .

A molecular formula does not tell you about a molecule’s structure. In other words, it does not show either the arrangement of the various atoms in space or which atoms are covalently bonded to one another. A variety of diagrams and molecular models, some of them illustrated in Figure 8.3, can be used to show the arrangement of atoms in a molecule. Diagrams and models like these will be used throughout this textbook.



Figure 8.2 Butane
Butane (C_4H_{10}) is commonly used in lighters and household torches. The butane torch shown here is being used to caramelize sugar on a dessert.

Figure 8.3 Representations of an Ammonia Molecule
The formula NH_3 tells you the composition of an ammonia molecule, but it does not reveal the arrangement of the atoms. Molecular models and structural formulas specify the bonds between atoms and the arrangement of those atoms.

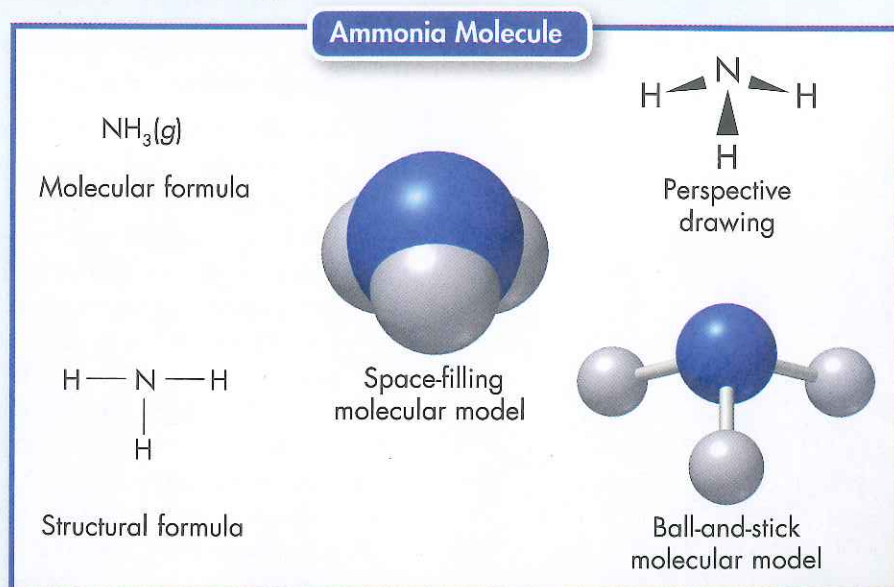


Figure 8.4 Molecular Formulas and Structures

The formula of a molecular compound indicates the numbers and kinds of atoms in each molecule of the compound.

Use Models Which of these molecules has the greatest number of oxygen atoms?

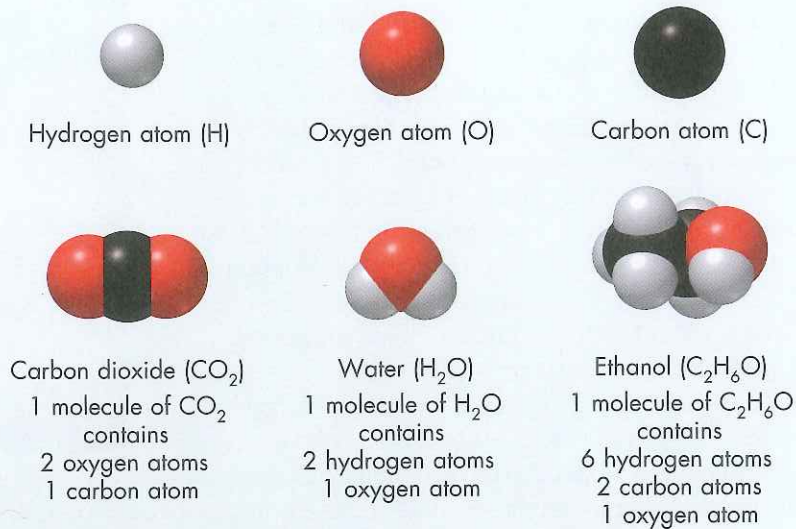


Figure 8.4 shows the chemical formulas and structures of some other molecular compounds. The arrangement of the atoms within a molecule is called its molecular structure. Carbon dioxide, for example, is a gas produced by the complete burning of carbon. It is found in Earth's atmosphere and is dissolved in seawater. The molecular structure of carbon dioxide shows how the three atoms are arranged in a row. It also shows how the carbon atom in each molecule is in the middle between the two oxygen atoms. The molecular structure of water shows how the oxygen atom is in the middle between the hydrogen atoms. However, the atoms in water are not arranged in a row. Instead, the hydrogen atoms are mainly on one side of the water molecule. The molecular structure of ethanol (C₂H₆O) is more complicated. As you can see in the model, each carbon is bonded to four atoms, each hydrogen is bonded to one atom, and the one oxygen is bonded to two atoms.

CHEMISTRY & YOU

Q: Similar to how you can make different types of toy models, there are thousands of different types of molecular structures. How are atoms joined together to make compounds with different structures?

Comparing Molecular and Ionic Compounds

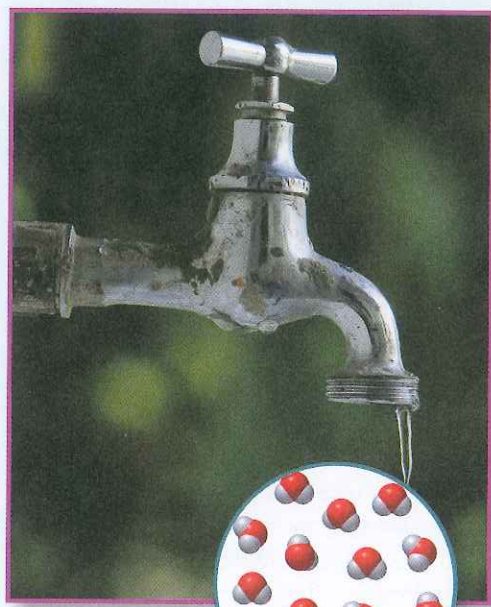
Key Question What representative units define molecular compounds and ionic compounds?

You have now seen how formulas can be used to describe molecular compounds and ionic compounds. Each type of compound contains atoms of different elements that are combined chemically. However, the formulas describe different representative units. **The representative unit of a molecular compound is a molecule. For an ionic compound, the representative unit is a formula unit.** Recall that a formula unit is the lowest whole-number ratio of ions in an ionic compound. It is important not to confuse formula units with molecules. A molecule is made up of two or more atoms that act as a unit. No such discrete units exist in an ionic compound, which consists of a continuous array of ions. So there is no such thing as a molecule of sodium chloride or a molecule of magnesium chloride. Instead, these compounds exist as collections of positively and negatively charged ions arranged in repeating three-dimensional patterns.

Molecular compounds tend to have relatively lower melting and boiling points than ionic compounds. Many molecular compounds are gases or liquids at room temperature. In contrast to ionic compounds, which are formed from a metal combined with a nonmetal, most molecular compounds are composed of atoms of two or more nonmetals. For example, one atom of carbon can combine with one atom of oxygen to produce one molecule of a compound known as carbon monoxide. Carbon monoxide is a poisonous gas produced by burning gasoline in internal combustion engines or in household gas appliances and furnaces. Figure 8.5 illustrates some differences between molecular and ionic compounds, using water and sodium chloride as examples.

Figure 8.5 Molecular and Ionic Compounds Water, which is a molecular compound, and sodium chloride, which is an ionic compound, are compared here.

Interpret Diagrams How do molecular compounds differ from ionic compounds?

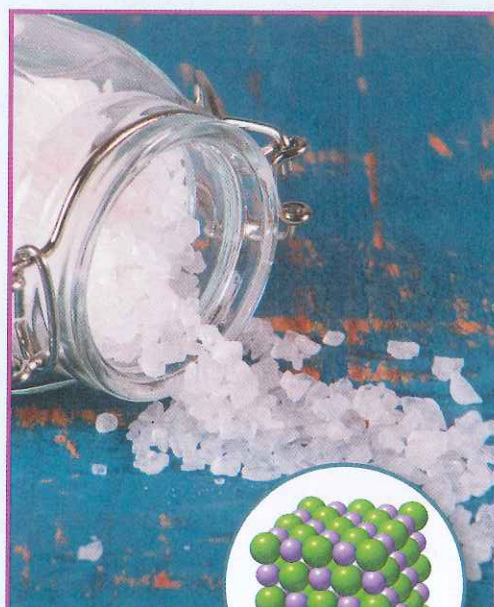


Collection of water molecules

Molecule of water:



Chemical formula:



Array of sodium ions and chloride ions

Formula unit of sodium chloride:



Chemical formula:



8.1 LessonCheck

- Identify** What information does a molecular formula provide?
- Compare** How is the representative unit of a molecular compound different from the representative unit of an ionic compound?
- Identify** What are the only elements that exist in nature as uncombined atoms? What term is used to describe such elements?
- Compare and Contrast** Describe how the molecule whose formula is NO is different from the molecule whose formula is N_2O .
- Apply Concepts** Give an example of a diatomic molecule found in Earth's atmosphere.
- Identify** What information does a molecular structure give?

8.2 The Nature of Covalent Bonding



CHEMISTRY & YOU

Q: What is the difference between the oxygen you breathe and the oxygen in ozone in the atmosphere? Our atmosphere contains two different molecules that are both made of oxygen atoms. One is the oxygen that our cells need to survive. The other molecule containing only oxygen atoms is the ozone that protects us from the sun but also contributes to smog. The colors in this map indicate the concentrations of ozone in various parts of Earth's atmosphere. In this lesson, you will learn how oxygen atoms can join to form the oxygen you breathe and can also join to form ozone.

Key Questions

Key What is the result of electron sharing in covalent bonds?

Key How are coordinate covalent bonds different from other covalent bonds?

Key What are some exceptions to the octet rule?

Key How is the strength of a covalent bond related to its bond dissociation energy?

Key How are resonance structures used?

Vocabulary

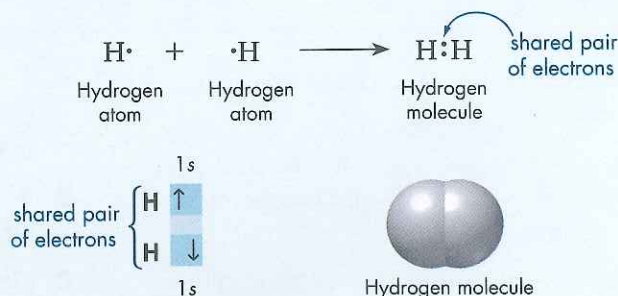
- single covalent bond
- structural formula
- unshared pair
- double covalent bond
- triple covalent bond
- coordinate covalent bond
- polyatomic ion
- bond dissociation energy
- resonance structure

The Octet Rule in Covalent Bonding

Key What is the result of electron sharing in covalent bonds?

Recall that when ionic compounds form, electrons tend to be transferred so that each ion acquires a noble gas configuration. A similar rule applies for covalent bonds. **Key** In covalent bonds, electron sharing usually occurs so that atoms attain the electron configurations of noble gases. For example, a single hydrogen atom has one electron. But a pair of hydrogen atoms shares electrons to form a covalent bond in a diatomic hydrogen molecule. Each hydrogen atom, thus, attains the electron configuration of helium, a noble gas with two electrons. Combinations of atoms of the nonmetals and metalloids in Groups 4A, 5A, 6A, and 7A of the periodic table are likely to form covalent bonds. The combined atoms usually acquire a total of eight electrons, or an octet, by sharing electrons, so that the octet rule applies.

Single Covalent Bonds The hydrogen atoms in a hydrogen molecule are held together mainly by the attraction of the shared electrons to the positive nuclei. Two atoms held together by sharing one pair of electrons are joined by a **single covalent bond**. Hydrogen gas consists of diatomic molecules whose atoms share only one pair of electrons, forming a single covalent bond.

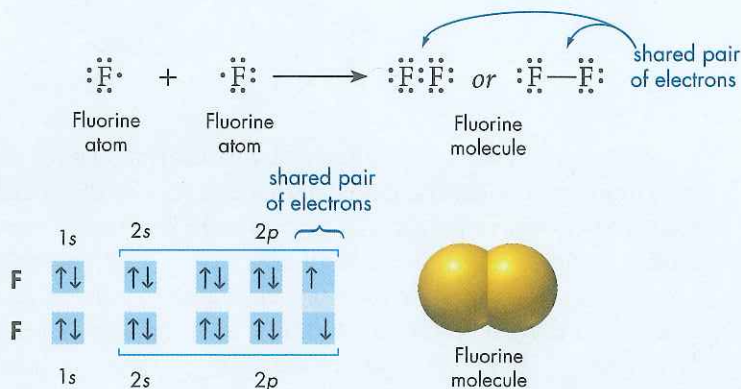


An electron dot structure such as H:H represents the shared pair of electrons of the covalent bond by two dots. The pair of shared electrons forming the covalent bond is also often represented as a dash, as in H—H for hydrogen. A **structural formula** represents the covalent bonds as dashes and shows the arrangement of covalently bonded atoms. In contrast, the molecular formula of hydrogen, H₂, indicates only the number of hydrogen atoms in each molecule.

See covalent bonding animated online.

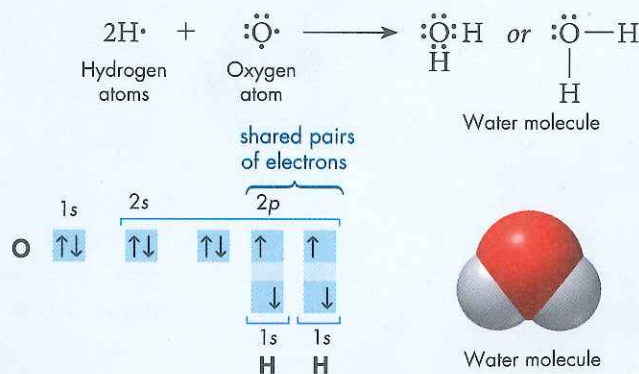


The halogens also form single covalent bonds in their diatomic molecules. Fluorine is one example. Because a fluorine atom has seven valence electrons, it needs one more to attain the electron configuration of a noble gas. By sharing electrons and forming a single covalent bond, two fluorine atoms each achieve the electron configuration of neon.

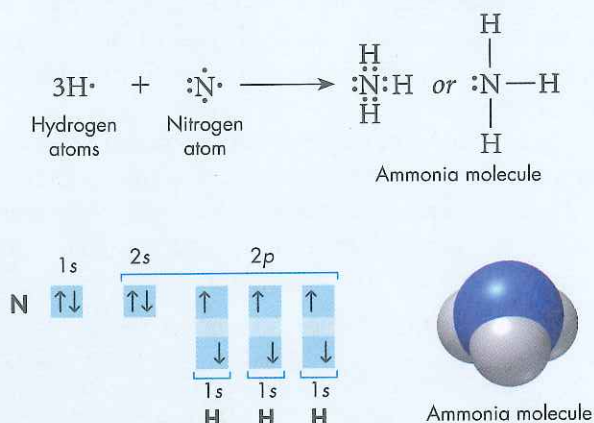


In the F₂ molecule, each fluorine atom contributes one electron to complete the octet. Notice that the two fluorine atoms share only one pair of valence electrons. A pair of valence electrons that is not shared between atoms is called an **unshared pair**, also known as a lone pair or a nonbonding pair. In F₂, each fluorine atom has three unshared pairs of electrons.

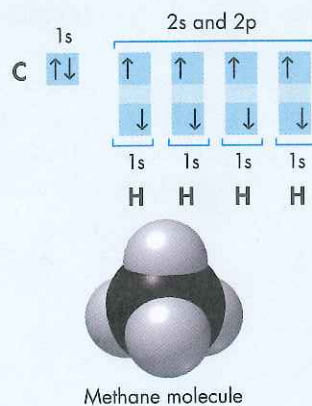
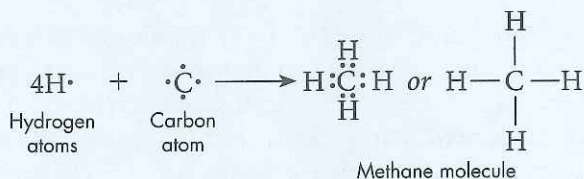
You can draw electron dot structures for molecules of compounds in much the same way that you draw them for molecules of diatomic elements. Water (H₂O) is a molecule containing three atoms with two single covalent bonds. Two hydrogen atoms share electrons with one oxygen atom. The hydrogen and oxygen atoms attain noble-gas configurations by sharing electrons. As you can see in the electron dot structures below, the oxygen atom in water has two unshared pairs of valence electrons.



You can draw the electron dot structure for ammonia (NH_3), a suffocating gas, in a similar way. The ammonia molecule has one unshared pair of electrons.



The stove in Figure 8.6 is fueled by natural gas. The principal component of natural gas is methane (CH_4). Methane contains four single covalent bonds. The carbon atom has four valence electrons and needs four more valence electrons to attain a noble-gas configuration. Each of the four hydrogen atoms contributes one electron to share with the carbon atom, forming four identical carbon-hydrogen bonds. As you can see in the electron dot structure below, methane has no unshared pairs of electrons.



When carbon forms bonds with other atoms, it usually forms four bonds, as in methane. You would not predict this pattern based on carbon's electron configuration, shown below.

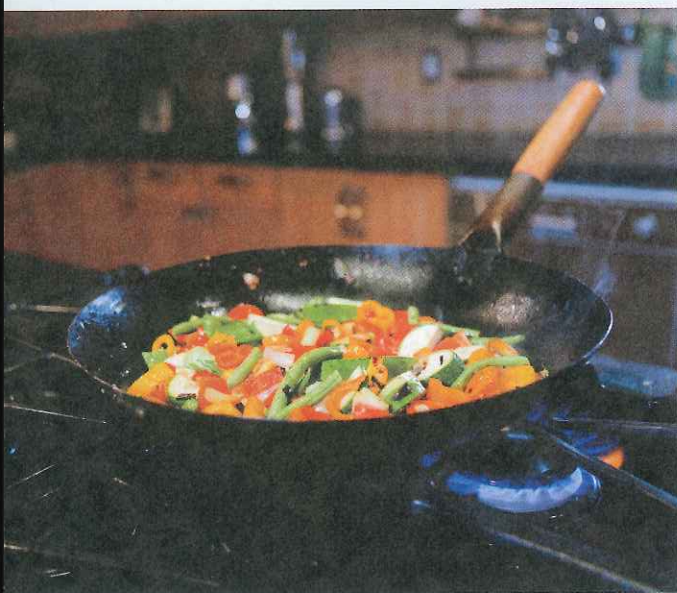


Figure 8.6 Methane
Methane is the principal component of natural gas. Natural gas is commonly used as a fuel for household gas appliances such as gas stoves, water heaters, dryers, and furnaces.

If you tried to form covalent C—H bonds for methane by combining the two $2p$ electrons of the carbon with two $1s$ electrons of hydrogen atoms, you would incorrectly predict a molecule with the formula CH_2 (instead of CH_4). The formation of four bonds by carbon can be explained by the fact that one of carbon's $2s$ electrons is promoted to the vacant $2p$ orbital to form the following electron configuration:



This electron promotion requires only a small amount of energy. The promotion provides four electrons of carbon that are capable of forming covalent bonds with four hydrogen atoms. Methane, the carbon compound formed by electron sharing of carbon with four hydrogen atoms, is much more stable than CH_2 . The stability of the resulting methane more than compensates for the small energy cost of the electron promotion. Therefore, formation of methane (CH_4) is more energetically favored than the formation of CH_2 .



Sample Problem 8.1

Drawing an Electron Dot Structure

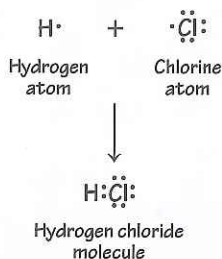
Hydrochloric acid (HCl (aq)) is prepared by dissolving gaseous hydrogen chloride (HCl (g)) in water. Hydrogen chloride is a diatomic molecule with a single covalent bond. Draw the electron dot structure for HCl .

1 Analyze Identify the relevant concepts. In a single covalent bond, a hydrogen and a chlorine atom must share a pair of electrons. Each must contribute one electron to the bond. Then show the electron sharing in the compound they produce.

2 Solve Apply concepts to the problem.

Draw the electron dot structures for the hydrogen and chlorine atoms.

Draw the electron dot structure for the hydrogen chloride molecule.



Through electron sharing, the hydrogen and chlorine atoms attain the electron configurations of the noble gases helium and argon, respectively.



7. Draw electron dot structures for each molecule.


- chlorine
- bromine
- iodine

8. The following molecules have single covalent bonds. Draw an electron dot structure for each.

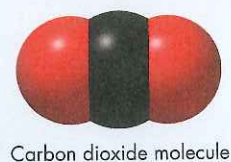
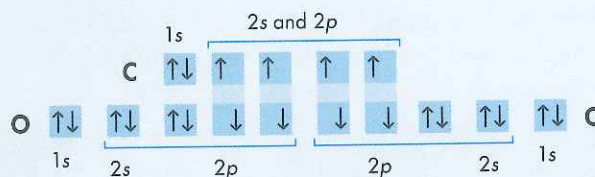
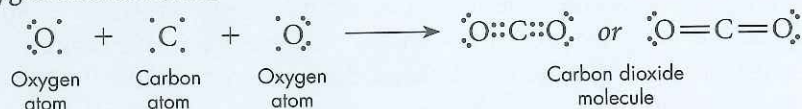
- H_2O_2
- PCl_3



Figure 8.7 Carbon Dioxide
Carbon dioxide gas is soluble in water and is used to carbonate many beverages. A carbon dioxide molecule has two carbon–oxygen double bonds.

Double and Triple Covalent Bonds Sometimes atoms bond by sharing more than one pair of electrons.  **Atoms form double or triple covalent bonds if they can attain a noble gas structure by sharing two pairs or three pairs of electrons.** A **double covalent bond** is a bond that involves two shared pairs of electrons. Similarly, a bond formed by sharing three pairs of electrons is a **triple covalent bond**.

Carbon dioxide (CO₂) is used to carbonate many soft drinks like the one shown in Figure 8.7. The carbon dioxide molecule contains two oxygens, each of which shares two electrons with carbon to form a total of two carbon–oxygen double bonds.



The two double bonds in the carbon dioxide molecule are identical to each other. Carbon dioxide is an example of a triatomic molecule, which is a molecule consisting of three atoms.

An example of an element whose molecules contain triple bonds is nitrogen (N₂), a major component of Earth's atmosphere, illustrated in Figure 8.8. A single nitrogen atom has five valence electrons. Each nitrogen atom in the nitrogen molecule must share three electrons to have the electron configuration of neon. In the nitrogen molecule, each nitrogen atom has one unshared pair of electrons.

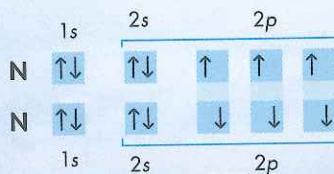
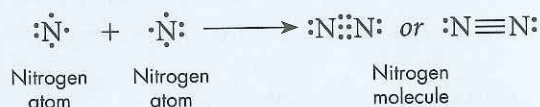
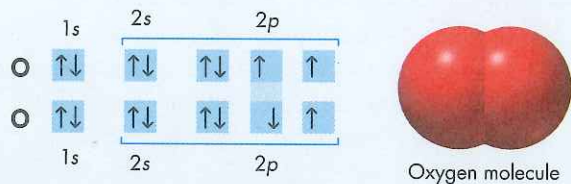
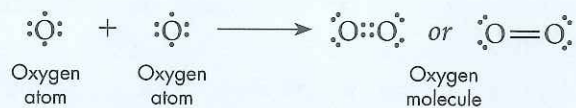


Figure 8.8 Oxygen and Nitrogen
Oxygen and nitrogen are the main components of Earth's atmosphere. The oxygen molecule is an exception to the octet rule. It has two unpaired electrons. Three pairs of electrons are shared in a nitrogen molecule.

You might think that an oxygen atom, with six valence electrons, would form a double bond by sharing two of its electrons with another oxygen atom.



In such an arrangement, all the electrons within the molecule would be paired. Experimental evidence, however, indicates that two of the electrons in O_2 are still unpaired. Thus, the bonding in the oxygen molecule (O_2) does not obey the octet rule. You cannot draw an electron dot structure that adequately describes the bonding in the oxygen molecule.

Nitrogen and oxygen are both diatomic molecules. Table 8.1 lists the properties and uses of these elements and some others that exist as diatomic molecules.

Table 8.1

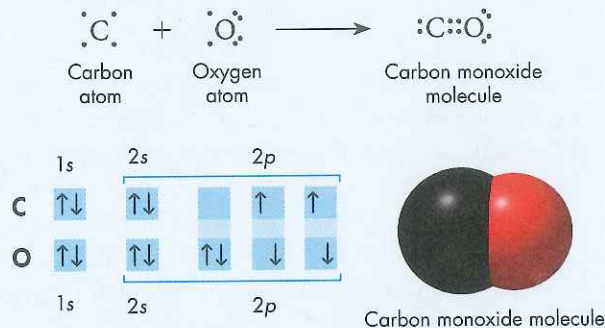
The Diatomic Elements

Name	Chemical formula	Electron dot structure	Properties and uses
Fluorine	F_2	$\text{:}\ddot{\text{F}}\text{—}\ddot{\text{F}}\text{:}$	Greenish-yellow reactive toxic gas. Compounds of fluorine, a halogen, are added to drinking water and toothpaste to promote healthy teeth.
Chlorine	Cl_2	$\text{:}\ddot{\text{Cl}}\text{—}\ddot{\text{Cl}}\text{:}$	Greenish-yellow reactive toxic gas. Chlorine is a halogen used in household bleaching agents.
Bromine	Br_2	$\text{:}\ddot{\text{Br}}\text{—}\ddot{\text{Br}}\text{:}$	Dense red-brown liquid with pungent odor. Compounds of bromine, a halogen, are used in the preparation of photographic emulsions.
Iodine	I_2	$\text{:}\ddot{\text{I}}\text{—}\ddot{\text{I}}\text{:}$	Dense gray-black solid that produces purple vapors; a halogen. A solution of iodine in alcohol (tincture of iodine) is used as an antiseptic.
Hydrogen	H_2	H—H	Colorless, odorless, tasteless gas. Hydrogen is the lightest known element.
Nitrogen	N_2	$\text{:}\text{N}\equiv\text{N}\text{:}$	Colorless, odorless, tasteless gas. Air is almost 80% nitrogen by volume.
Oxygen	O_2	Inadequate	Colorless, odorless, tasteless gas that is vital for life. Air is about 20% oxygen by volume.

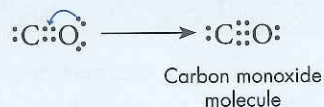
Coordinate Covalent Bonds

🔑 How are coordinate covalent bonds different from other covalent bonds?

Carbon monoxide (CO) is an example of a type of covalent bonding different from that seen in water, ammonia, methane, and carbon dioxide. A carbon atom needs to gain four electrons to attain the electron configuration of neon. An oxygen atom needs two electrons. Yet it is possible for both atoms to achieve noble-gas electron configurations by a type of bonding called coordinate covalent bonding. To see how, begin by looking at the double covalent bond between carbon and oxygen.



With the double bond in place, the oxygen has a stable configuration, but the carbon does not. As shown below, the dilemma is solved if the oxygen also donates one of its unshared pairs of electrons for bonding.



A covalent bond in which one atom contributes both bonding electrons is a **coordinate covalent bond**. In a structural formula, you can show coordinate covalent bonds as arrows that point from the atom donating the pair of electrons to the atom receiving them. The structural formula of carbon monoxide, with two covalent bonds and one coordinate covalent bond, is $\text{C}\equiv\text{O}$. **🔑** In a coordinate covalent bond, the shared electron pair comes from one of the bonding atoms. Once formed, a coordinate covalent bond is like any other covalent bond.

The ammonium ion (NH_4^+), which is often found in fertilizers like the one in Figure 8.9, consists of atoms joined by covalent bonds, including a coordinate covalent bond. A **polyatomic ion**, such as NH_4^+ , is a tightly bound group of atoms that has a positive or negative charge and behaves as a unit. The ammonium ion forms when a positively charged hydrogen ion (H^+) attaches to the unshared electron pair of an ammonia molecule (NH_3).

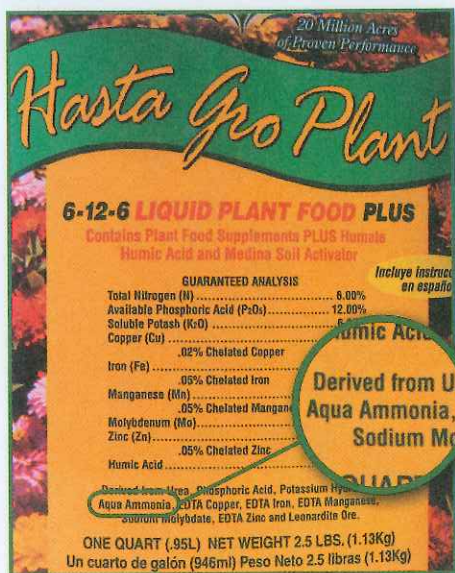
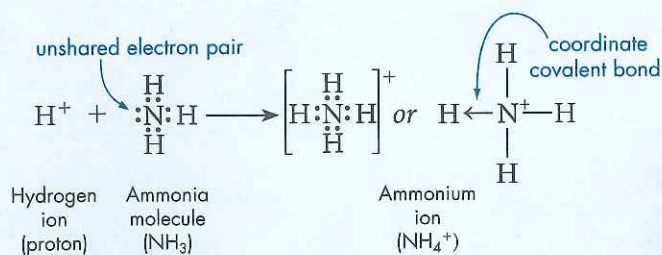
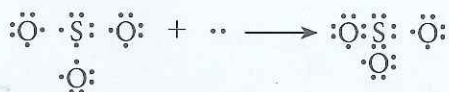


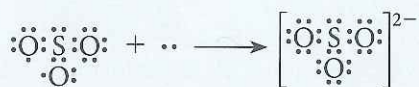
Figure 8.9 Ammonia Fertilizers

Most plants need nitrogen that is already combined in a compound rather than molecular nitrogen (N_2) to grow. The polyatomic ammonium ion (NH_4^+), present in ammonia hydroxide, also called aqua ammonia, is an important component of fertilizer for field crops, home gardens, and potted plants.

Most polyatomic cations and anions contain covalent and coordinate covalent bonds. Therefore, compounds containing polyatomic ions include both ionic and covalent bonding. As another example, draw the electron dot structure of the polyatomic ion SO_3^{2-} . First, draw the electron dot structures for the oxygen and sulfur atoms, and the two extra electrons indicated by the charge. Then, join two of the oxygens to sulfur by single covalent bonds.



Next, join the remaining oxygen by a coordinate covalent bond, with sulfur donating one of its unshared pairs to oxygen, and add the two extra electrons. Put brackets around the structure and indicate the $2-$ charge.



Each of the atoms now has eight valence electrons, satisfying the octet rule. Without the extra electrons, two of the oxygens would be electron-deficient.

Table 8.2 lists electron dot structures of some common compounds with covalent bonds.

Remember, the charge of a negative polyatomic ion is equal to the number of electrons that are in addition to the valence electrons of the atoms present. Since a negatively charged polyatomic ion is part of an ionic compound, the positive charge of the cation of the compound balances the additional electrons.



Sample Problem 8.2

Drawing the Electron Dot Structure of a Polyatomic Ion

The H_3O^+ ion forms when a hydrogen ion is attracted to an unshared electron pair in a water molecule. Draw the electron dot structure of the hydronium ion.

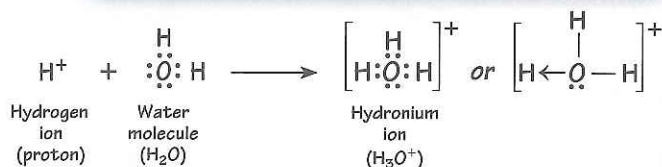
1 Analyze Identify the relevant concepts. Each atom must share electrons to satisfy the octet rule.

2 Solve Apply the concepts to the problem.

Draw the electron dot structure of the water molecule and the hydrogen ion. Then, draw the electron dot structure of the hydronium ion. The oxygen must share a pair of electrons with the added hydrogen ion to form a coordinate covalent bond.

Check that all the atoms have the electrons they need and that the charge is correct.

Remember to always include the charge when drawing electron dot structures of polyatomic ions.



The oxygen in the hydronium ion has eight valence electrons, and each hydrogen shares two valence electrons, satisfying the octet rule. The water molecule is neutral, and the hydrogen ion has a positive charge, giving the hydronium ion a charge of $1+$.

9. Draw the electron dot structure of the hydroxide ion (OH^-).

10. Draw the electron dot structures for sulfate (SO_4^{2-}) and carbonate (CO_3^{2-}). Sulfur and carbon are the central atoms, respectively.

Table 8.2

Some Common Molecular Compounds

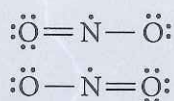
Name	Chemical formula	Structure	Properties and uses
Carbon monoxide	CO	$\text{:C}\equiv\text{O:}$	Colorless, highly toxic gas. It is a major air pollutant present in cigarette smoke and exhaust.
Carbon dioxide	CO ₂	$\text{:O}=\text{C}=\text{O:}$	Colorless unreactive gas. This normal component of the atmosphere is exhaled in the breath of animals and is essential for plant growth.
Hydrogen peroxide	H ₂ O ₂	$\text{H}-\ddot{\text{O}}-\ddot{\text{O}}-\text{H}$	Colorless, unstable liquid when pure. It is used as rocket fuel. A 3% solution is used as a bleach and antiseptic.
Sulfur dioxide	SO ₂	$\text{:O}=\text{S}^{\cdot\cdot}-\ddot{\text{O}}$	Oxides of sulfur are produced in the combustion of petroleum products and coal. They are major air pollutants in industrial areas. Oxides of sulfur can lead to respiratory problems.
Sulfur trioxide	SO ₃	$\text{:O}=\text{S}^{\cdot\cdot}-\ddot{\text{O}}$	
Nitric oxide*	NO	$\text{:O}=\ddot{\text{N}}^{\cdot}$	Oxides of nitrogen are major air pollutants produced by the combustion of fossil fuels in automobile engines. They irritate the eyes, throat, and lungs. Nitrogen dioxide, a dark-brown gas, readily converts to colorless dinitrogen tetroxide. Dinitrogen tetroxide is used as a rocket fuel.
Nitrogen dioxide*	NO ₂	$\text{:O}=\ddot{\text{N}}-\ddot{\text{O}}$	
Dinitrogen tetroxide	N ₂ O ₄	$\text{:O}=\ddot{\text{N}}-\ddot{\text{N}}=\ddot{\text{O}}$	
Nitrous oxide	N ₂ O	$\text{:O}^{\cdot\cdot}-\text{N}\equiv\text{N:}$	Colorless, sweet-smelling gas. It is used as an anesthetic commonly called laughing gas.
Hydrogen cyanide	HCN	$\text{H}-\text{C}\equiv\text{N:}$	Colorless, toxic gas with the smell of almonds.
Hydrogen fluoride	HF	$\text{H}-\ddot{\text{F}}:$	Four hydrogen halides, all extremely soluble in water. Hydrogen chloride, a colorless gas with a pungent odor, readily dissolves in water to give a solution called hydrochloric acid.
Hydrogen chloride	HCl	$\text{H}-\ddot{\text{Cl}}:$	
Hydrogen bromide	HBr	$\text{H}-\ddot{\text{Br}}:$	
Hydrogen iodide	HI	$\text{H}-\ddot{\text{I}}:$	

*Does not obey the octet rule

Exceptions to the Octet Rule

Key What are some exceptions to the octet rule?

The octet rule provides guidance for drawing electron dot structures. For some molecules or ions, however, it is impossible to draw structures that satisfy the octet rule. **Key** The octet rule cannot be satisfied in molecules whose total number of valence electrons is an odd number. There are also molecules in which an atom has less, or more, than a complete octet of valence electrons. The nitrogen dioxide (NO_2) molecule, for example, contains a total of seventeen, an odd number, of valence electrons. Each oxygen contributes six electrons and the nitrogen contributes five. Two plausible electron dot structures can be drawn for the NO_2 molecule.



Nitrogen dioxide molecule

An unpaired electron is present in each of these structures, both of which fail to follow the octet rule. It is impossible to draw an electron dot structure for NO_2 that satisfies the octet rule for all atoms. Yet, NO_2 does exist as a stable molecule. In fact, it is produced naturally by lightning strikes of the sort shown in Figure 8.10.

A number of other molecules also have an odd number of electrons. In these molecules, as in NO_2 , complete pairing of electrons is not possible. It is not possible to draw an electron dot structure that satisfies the octet rule. Examples of such molecules include chlorine dioxide (ClO_2) and nitric oxide (NO).

Several molecules with an even number of valence electrons, such as some compounds of boron, also fail to follow the octet rule. This outcome may occur because an atom acquires less than an octet of eight electrons. The boron atom in boron trifluoride (BF_3), for example, is deficient by two electrons and, therefore, is an exception to the octet rule. Boron trifluoride readily reacts with ammonia to make the compound $\text{BF}_3 \cdot \text{NH}_3$. In doing so, the boron atom accepts the unshared electron pair from ammonia and completes the octet.

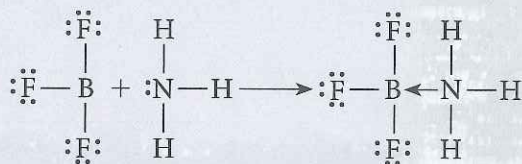


Figure 8.10
Nitrogen Dioxide
Lightning is one means by which nitrogen and oxygen in the atmosphere produce nitrogen dioxide.

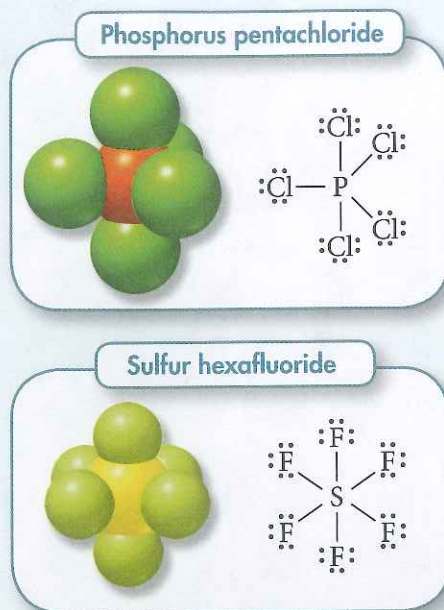


Figure 8.11

Exceptions to the Octet Rule

Phosphorus pentachloride and sulfur hexafluoride, are exceptions to the octet rule.

Interpret Diagrams

How many valence electrons does the sulfur in sulfur hexafluoride (SF_6) have for the structure shown in the figure?

A few atoms, especially phosphorus and sulfur, sometimes expand the octet to ten or twelve electrons. Consider phosphorus trichloride (PCl_3) and phosphorus pentachloride (PCl_5). Both are stable compounds in which all of the chlorine atoms are bonded to a single phosphorus atom. Covalent bonding in PCl_3 follows the octet rule because all the atoms have eight valence electrons. However, as shown in Figure 8.11, the electron dot structure for PCl_5 can be written so that phosphorus has ten valence electrons. The octet is also expanded in sulfur hexafluoride (SF_6). The electron dot structure for SF_6 can be written so that sulfur has twelve valence electrons.

Bond Dissociation Energies

🔑 *How is the strength of a covalent bond related to its bond dissociation energy?*

A large quantity of heat is released when hydrogen atoms combine to form hydrogen molecules. This release of heat suggests that the product is more stable than the reactants. The covalent bond in the hydrogen molecule (H_2) is so strong that it would take 435 kJ of energy to break apart all of the bonds in 1 mole (6.02×10^{23} bonds or about 2 grams) of H_2 . (You will study the mole, abbreviated mol, in Chapter 12.) The energy required to break the bond between two covalently bonded atoms is the **bond dissociation energy**. The units for this energy are often given in kJ/mol, which is the energy needed to break one mole of bonds. For example, the bond dissociation energy for the H_2 molecule is 435 kJ/mol.

Table 8.3

Bond Dissociation Energies and Bond Lengths for Covalent Bonds		
Bond	Bond dissociation energy (kJ/mol)	Bond length (pm)
H—H	435	74
C—H	393	109
C—O	356	143
C=O	736	121
C≡O	1074	113
C—C	347	154
C=C	657	133
C≡C	908	121
C—N	305	147
Cl—Cl	243	199
N—N	209	140
O—H	464	96
O—O	142	132

Key A large bond dissociation energy corresponds to a strong covalent bond. A typical carbon-carbon single bond has a bond dissociation energy of 347 kJ/mol. Typical carbon-carbon double and triple bonds have bond dissociation energies of 657 kJ/mol and 908 kJ/mol, respectively. Strong carbon-carbon bonds help explain the stability of carbon compounds. Compounds with only C—C and C—H single covalent bonds, such as methane, tend to be quite unreactive. They are unreactive partly because the dissociation energy for each of these bonds is high. Bond dissociation energies of some common bonds are shown in Table 8.3.

Resonance

Key How are resonance structures used?

Ozone in the upper atmosphere blocks harmful ultraviolet radiation from the sun. At lower elevations, as shown in Figure 8.12, it contributes to smog. The ozone molecule has two possible electron dot structures. Notice that the structure on the left can be converted to the one on the right by shifting electron pairs without changing the positions of the oxygen atoms.



As drawn, these electron dot structures suggest that the bonding in ozone consists of one single coordinate covalent bond and one double covalent bond. Because earlier chemists imagined that the electron pairs rapidly flip back and forth, or resonate, between the different electron dot structures, they used double-headed arrows to indicate that two or more structures are in resonance.

Double covalent bonds are usually shorter than single covalent bonds, so it was believed that the bond lengths in ozone were unequal. Experimental measurements show, however, that this is not the case. The two bonds in ozone are the same length. This result can be explained if you assume that the actual bonding in the ozone molecule is the average of the two electron dot structures. The electron pairs do not actually resonate back and forth. The actual bonding is a hybrid, or mixture, of the extremes represented by the resonance forms.

The two electron dot structures for ozone are examples of what are still referred to as resonance structures. **Resonance structures** are structures that occur when it is possible to draw two or more valid electron dot structures that have the same number of electron pairs for a molecule or ion. **Key** Chemists use resonance structures to envision the bonding in molecules that cannot be adequately described by a single structural formula. Although no back-and-forth changes occur, double-headed arrows are used to connect resonance structures.

CHEMISTRY & YOU

Q: What is the difference between the oxygen you breathe and the oxygen in ozone in the atmosphere?

Learn more about oxygen in the air online.

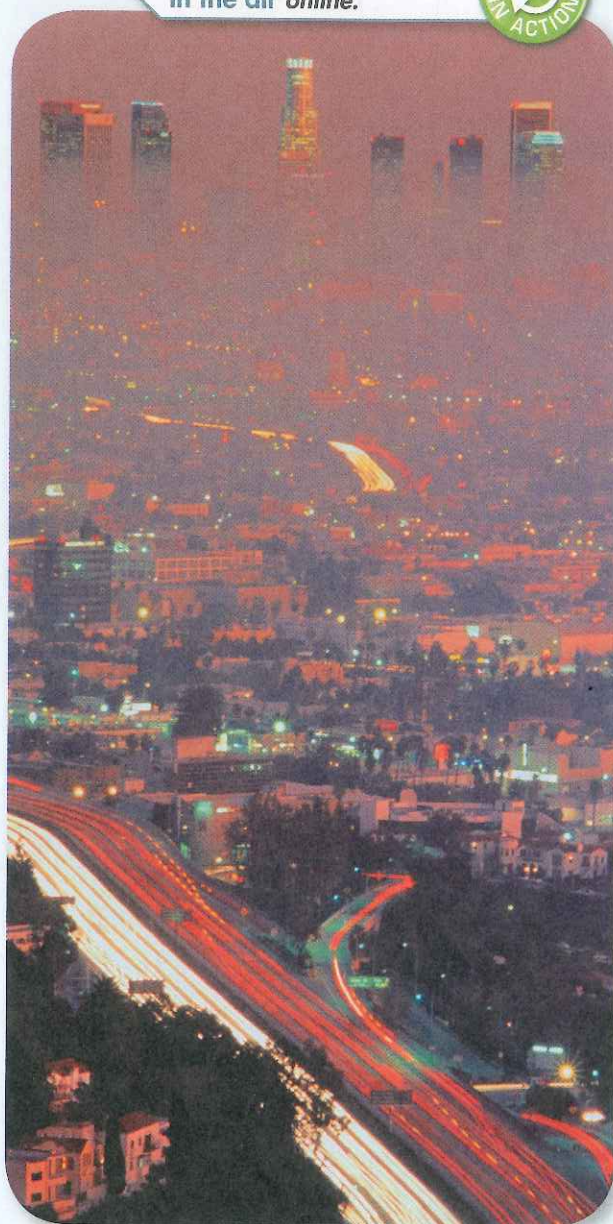


Figure 8.12 Ozone Smog

Although ozone high above the ground forms a protective layer that absorbs ultraviolet radiation from the sun, at lower elevations ozone is a pollutant that contributes to smog. The smog shown here in Los Angeles, California, makes it difficult to see the city skyline.

Quick Lab

Purpose To compare and contrast the stretching of rubber bands and the dissociation energy of covalent bonds

Materials

- 1 170-g (6-oz) can of food
- 2 454-g (16-oz) cans of food
- 3 No. 25 rubber bands
- metric ruler
- coat hanger
- plastic grocery bag
- paper clip
- graph paper
- motion detector (optional)



Strengths of Covalent Bonds

Procedure

1. Bend the coat hanger to fit over the top of a door. The hook should hang down on one side of the door. Measure the length of the rubber bands (in cm). Hang a rubber band on the hook created by the coat hanger.
2. Place the 170-g can in the plastic bag. Use the paper clip to fasten the bag to the end of the rubber band. Lower the bag gently until it is suspended from the end of the rubber band. Measure and record the length of the stretched rubber band. Using different combinations of food cans, repeat this process three times with the following masses: 454 g, 624 g, and 908 g.

3. Repeat Step 2, first using two rubber bands to connect the hanger and the paper clip, and then using three.

4. Graph the length difference: (stretched rubber band) – (unstretched rubber band) on the y -axis versus mass (kg) on the x -axis for one, two, and three rubber bands. Draw the straight line that you estimate best fits the points for each set of data. (Your graph should have three separate lines.) The x -axis and y -axis intercepts of the lines should pass through zero, and the lines should extend past 1 kg on the x -axis. Determine the slope of each line in cm/kg.

Analyze and Conclude

1. **Analyze Experimental Results** Assuming the rubber bands are models for covalent bonds, what can you conclude about the relative strengths of single, double, and triple bonds?
2. **Evaluate** How does the behavior of the rubber bands differ from that of covalent bonds?



8.2 LessonCheck

11. **Identify** What electron configurations do atoms usually achieve by sharing electrons to form covalent bonds?
12. **Compare** How is a coordinate covalent bond different from other covalent bonds?
13. **List** List three ways in which the octet rule can sometimes fail to be obeyed.
14. **Explain** How is the strength of a covalent bond related to its bond dissociation energy?
15. **Identify** How are resonance structures used?
16. **Explain** How is an electron dot structure used to represent a covalent bond?
17. **Infer** When are two atoms likely to form a double bond between them? A triple bond?
18. **Identify** What kinds of information does a structural formula reveal about the compound it represents?
19. **Compare** Use the bond dissociation energies of H_2 and of a typical carbon-carbon bond to decide which bond is stronger. Explain your reasoning.
20. **Use Models** Draw electron dot structures for the following molecules, which have only single covalent bonds:
 - a. H_2S
 - b. PH_3
 - c. ClF

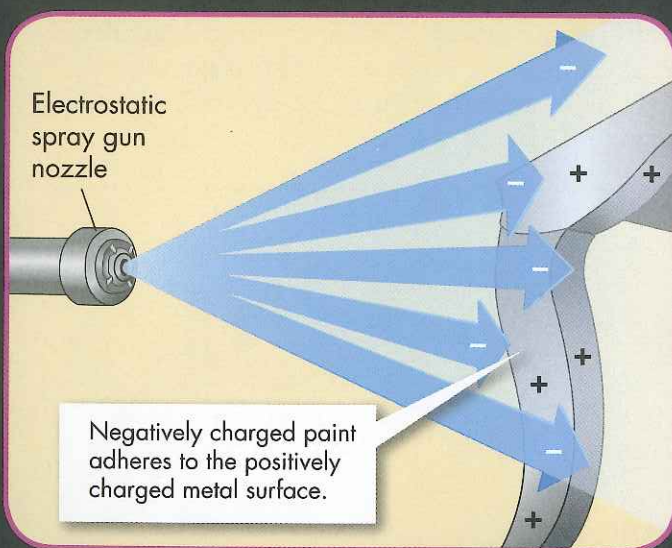
Powder Coating

Have you ever admired a new car with its glossy, smooth paint? Car manufacturers use a special process to apply paint to a car. This process is called powder coating or electrostatic spray painting.

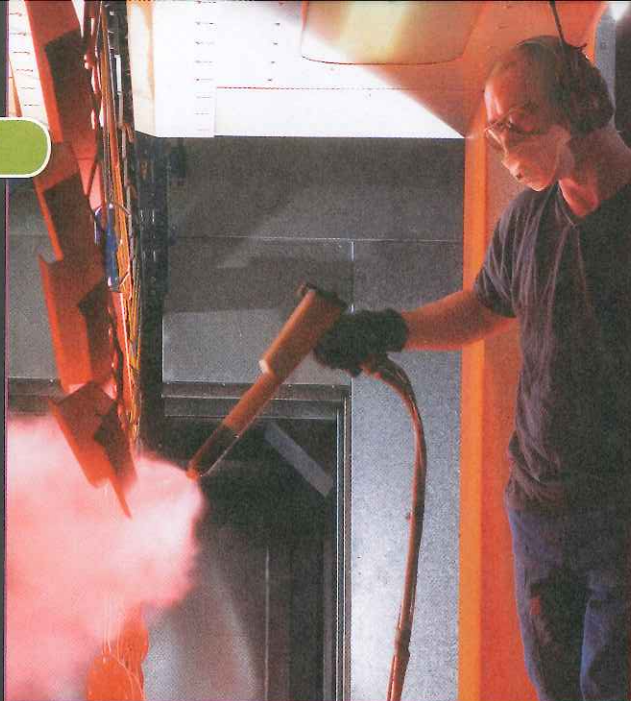
In powder coating, a custom-designed spray nozzle wired up to an electric power supply imparts a negative charge to the paint droplets as they exit the spray gun. The negatively charged droplets are attracted to the grounded, positively-charged, metal surface. Painting with attractive forces is very efficient, because almost all the paint is applied to the car body and very little is wasted.

Powder coating isn't just for cars. The process has many different applications, including the painting of motorcycles, outdoor furniture, exercise equipment, office furniture, and metal fencing.

An eye-catching paint finish isn't the only benefit of powder coating, however. This process is also environmentally friendly. Since the paint is actually attracted to its intended surface, the amount of wasted paint is much lower compared to traditional spray painting. Also, the amount of toxic volatile organic compounds (VOCs) released is minimal, if there are any at all.



ATTRACTIVE PAINT The paint almost wraps around the metal, sticking to any available charged surface.



APPLYING THE POWDER This worker is using an electrostatic spray gun to apply powder to the metal. Any powder that does not stick to the part can be collected and reused. Once the powder is applied, the part is baked in an oven to cure the paint.

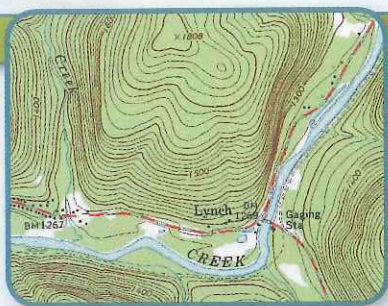


GLOSSY FINISH Powder coating can produce a smooth, glossy paint finish.

Take It Further

- 1. Analyze Benefits** Powder coating is being used for more and more applications, partly because of its many benefits. Research other advantages of powder coating that are not mentioned here.
- 2. Infer** Powder coating results in a smooth surface, usually without drips and runs. Given what you have learned about attractive forces, why do you think drips and runs are avoided during powder coating?

8.3 Bonding Theories



CHEMISTRY & YOU

Q: How can you predict where an electron is most likely to be found in a molecule? If you ever go hiking in a hilly area, you might see a topographic map like the one shown here. The lines on a topographic map show you where elevations change. In this lesson, you will learn how to interpret electron “maps” that show where you are most likely to find electrons.

Key Questions

🔑 How are atomic and molecular orbitals related?

🔑 What do scientists use the VSEPR theory for?

🔑 In what ways is orbital hybridization useful in describing molecules?

Vocabulary

- molecular orbital
- bonding orbital
- sigma bond
- pi bond
- tetrahedral angle
- VSEPR theory
- hybridization

Molecular Orbitals

🔑 How are atomic and molecular orbitals related?

The model you have been using for covalent bonding assumes the orbitals are those of the individual atoms. There is a quantum mechanical model of bonding, however, that describes the electrons in molecules using orbitals that exist only for groupings of atoms. When two atoms combine, this model assumes that their atomic orbitals overlap to produce **molecular orbitals**, or orbitals that apply to the entire molecule.

In some ways, atomic orbitals and molecular orbitals are similar.

🔑 Just as an atomic orbital belongs to a particular atom, a molecular orbital belongs to a molecule as a whole. Each atomic orbital is filled if it contains two electrons. Similarly, two electrons are required to fill a molecular orbital. A molecular orbital that can be occupied by two electrons of a covalent bond is called a **bonding orbital**.

Sigma Bonds When two atomic orbitals combine to form a molecular orbital that is symmetrical around the axis connecting two atomic nuclei, a **sigma bond** is formed, as illustrated in Figure 8.13. The symbol for this bond is the Greek letter sigma (σ).

⊕ represents the nucleus.

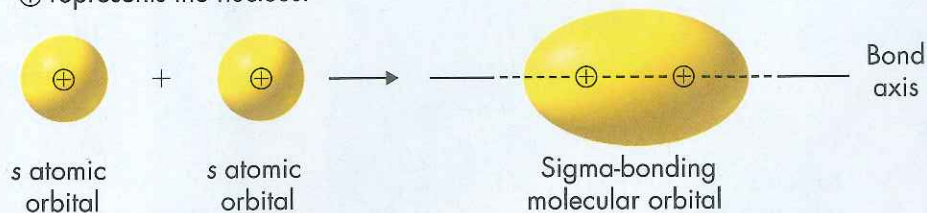


Figure 8.13 s Orbital Sigma Bonds

Two s atomic orbitals can combine to form a molecular orbital, as in the case of hydrogen (H_2). In a bonding molecular orbital, the electron density between the nuclei is high.

⊕ represents the nucleus.

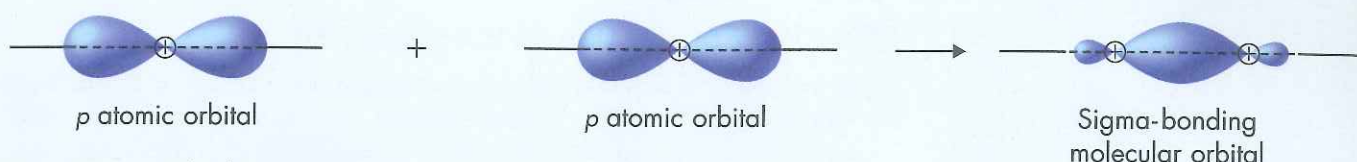


Figure 8.14 *p* Orbital Sigma Bonds

Two *p* atomic orbitals can combine to form a sigma-bonding molecular orbital, as in the case of fluorine (F_2). Notice that the sigma bond is symmetrical around the bond axis connecting the nuclei.

In general, covalent bonding results from an imbalance between the attractions and repulsions of the nuclei and electrons involved. Because their charges have opposite signs, the nuclei and electrons attract each other. Conversely, nuclei repel other nuclei and electrons repel other electrons because their charges have the same sign. In a hydrogen molecule, the nuclei repel each other, as do the electrons. In a bonding molecular orbital of hydrogen, however, the attractions between the hydrogen nuclei and the electrons are stronger than the repulsions. The balance of all the interactions between the hydrogen atoms is thus tipped in favor of holding the atoms together. The result is a stable diatomic molecule of H_2 .

Atomic *p* orbitals can also overlap to form molecular orbitals. A fluorine atom, for example, has a half-filled $2p$ orbital. When two fluorine atoms combine, as shown in Figure 8.14, the *p* orbitals overlap to produce a bonding molecular orbital. There is a high probability of finding a pair of electrons between the positively charged nuclei of the two fluorines. The fluorine nuclei are attracted to this region of high electron density. This attraction holds the atoms together in the fluorine molecule (F_2). The overlap of the $2p$ orbitals produces a bonding molecular orbital that is symmetrical when viewed around the F—F bond axis connecting the nuclei. Therefore, the F—F bond is a sigma bond.

Pi Bonds In the sigma bond of the fluorine molecule, the *p* atomic orbitals overlap end to end. In some molecules, however, orbitals can overlap side by side. As shown in Figure 8.15, the side-by-side overlap of atomic *p* orbitals produces what are called pi molecular orbitals. When a pi molecular orbital is filled with two electrons, a pi bond results. In a **pi bond** (symbolized by the Greek letter π), the bonding electrons are most likely to be found in sausage-shaped regions above and below the bond axis of the bonded atoms. Atomic orbitals in pi bonding overlap less than in sigma bonding. Therefore, pi bonds tend to be weaker than sigma bonds.

⊕ represents the nucleus.

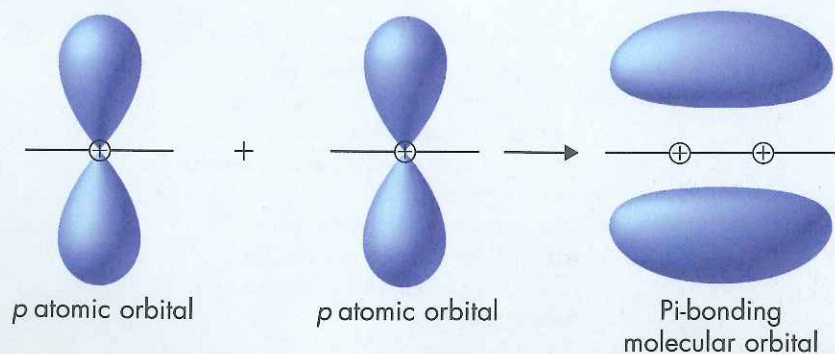


Figure 8.15
p Orbital Pi Bonds

The side-by-side overlap of two *p* atomic orbitals produces a pi-bonding molecular orbital. Together, the two sausage-shaped regions in which the bonding electron pair is most likely to be found constitute one pi-bonding molecular orbital.

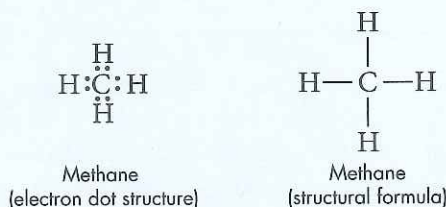
CHEMISTRY & YOU

Q: Models and drawings are often used to help you visualize where something can be found. How can a drawing show you where an electron is most likely to be found?

VSEPR Theory

What do scientists use the VSEPR theory for?

A photograph or sketch may fail to do justice to your appearance. Similarly, electron dot structures fail to reflect the three-dimensional shapes of the molecules illustrated in Figure 8.16. The electron dot structure and structural formula of methane (CH_4), for example, show the molecule as if it were flat and merely two-dimensional.



READING SUPPORT

BUILD VOCABULARY: Word Origins *Tetrahedral* comes from the Greek *tetra-*, meaning “four,” and *hedra*, meaning “face.” *How do these word origins help you understand the shapes of molecules?*

In reality, methane molecules are three-dimensional. As Figure 8.16a shows, the hydrogens in a methane molecule are at the four corners of a geometric solid called a regular tetrahedron. In this arrangement, all of the $\text{H}-\text{C}-\text{H}$ angles are 109.5° , the **tetrahedral angle**.

In order to explain the three-dimensional shape of molecules, scientists use valence-shell electron-pair repulsion theory (VSEPR theory). **VSEPR theory** states that the repulsion between electron pairs causes molecular shapes to adjust so that the valence-electron pairs stay as far apart as possible. The methane molecule has four bonding electron pairs and no unshared pairs. The bonding pairs are farthest apart when the angle between the central carbon and its attached hydrogens is 109.5° . This measurement is the $\text{H}-\text{C}-\text{H}$ bond angle found experimentally.

Unshared pairs of electrons are also important in predicting the shapes of molecules. The nitrogen in ammonia (NH_3) is surrounded by four pairs of valence electrons, so you might predict the tetrahedral angle of 109.5° for the $\text{H}-\text{N}-\text{H}$ bond angle. However, one of the valence-electron pairs shown in Figure 8.16b is an unshared pair. No bonding atom is vying for these unshared electrons. Thus, they are held closer to the nitrogen than are the bonding pairs. The unshared pair strongly repels the bonding pairs, pushing them together. The measured $\text{H}-\text{N}-\text{H}$ bond angle is only 107° .

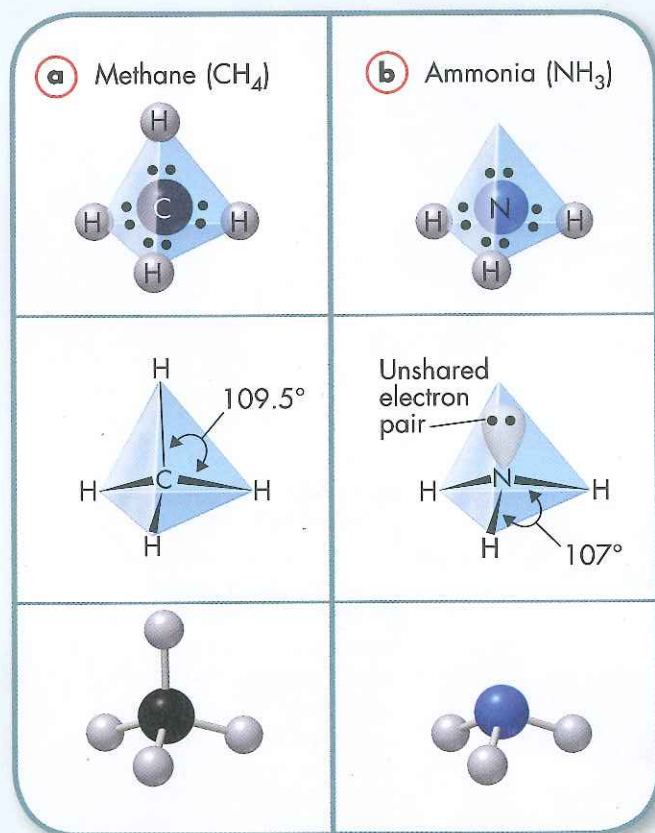


Figure 8.16 Three-Dimensional Molecules

a. Methane is a tetrahedral molecule. The hydrogens in methane are at the four corners of a regular tetrahedron, and the bond angles are all 109.5° . **b.** An ammonia molecule is pyramidal. The unshared pair of electrons repels the bonding pairs.

Use Models *How do the resulting $\text{H}-\text{N}-\text{H}$ bond angles compare to the tetrahedral angle?*

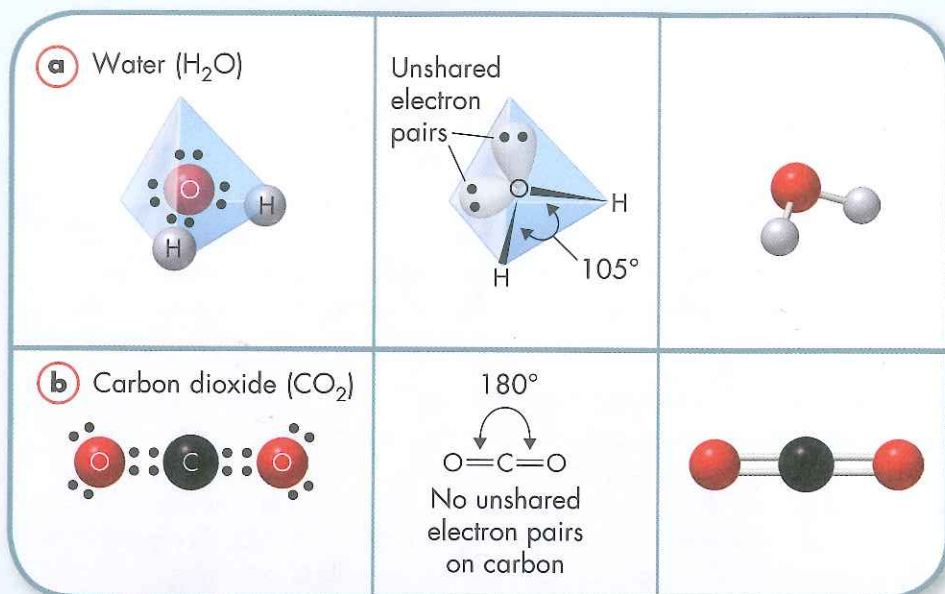


Figure 8.17
Planar and Linear Molecules
This comparison of water and carbon dioxide illustrates how unshared pairs of electrons can affect the shape of a molecule made of three atoms. **a.** The water molecule is bent because the two unshared pairs of electrons on oxygen repel the bonding electrons. **b.** In contrast, the carbon dioxide molecule is linear. The carbon atom has no unshared electron pairs.

In a water molecule, oxygen forms single covalent bonds with two hydrogen atoms. The two bonding pairs and the two unshared pairs of electrons form a tetrahedral arrangement around the central oxygen. Thus, the water molecule is planar (flat) but bent. With two unshared pairs repelling the bonding pairs, the $\text{H}-\text{O}-\text{H}$ bond angle is compressed in comparison with the $\text{H}-\text{C}-\text{H}$ bond angle in methane. The experimentally measured bond angle in water is about 105° , as shown in Figure 8.17a.

In contrast, the carbon in a carbon dioxide molecule has no unshared electron pairs. As illustrated in Figure 8.17b, the double bonds joining the oxygens to the carbon are farthest apart when the $\text{O}=\text{C}=\text{O}$ bond angle is 180° . Thus, CO_2 is a linear molecule. Nine of the possible molecular shapes are shown in Figure 8.18.

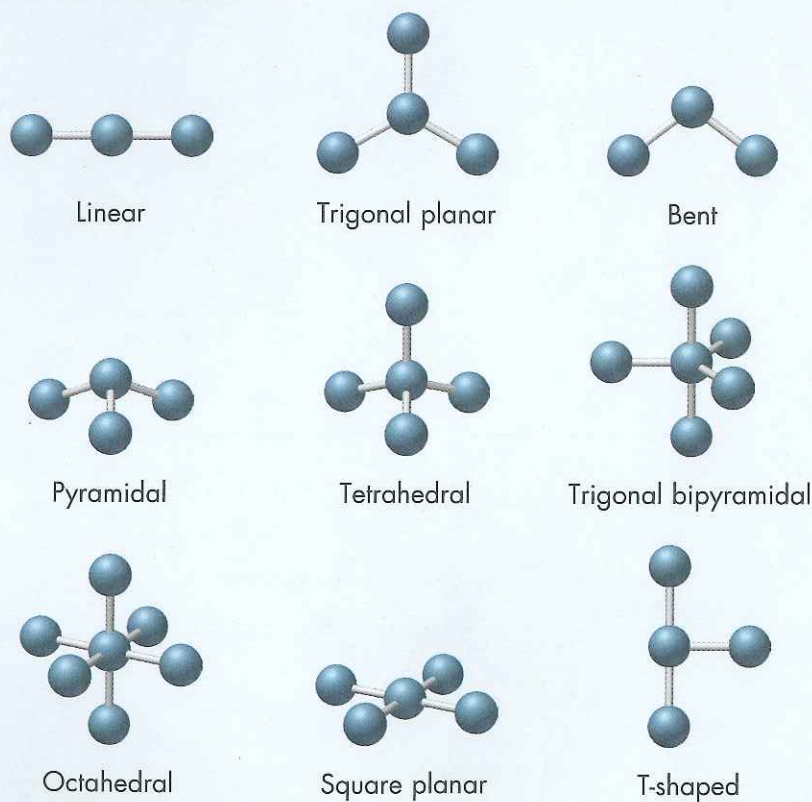


Figure 8.18
Molecular Shapes
Shown here are common molecular shapes.
Infer What is the shape of an ammonium ion?

Hybrid Orbitals

Key In what ways is orbital hybridization useful in describing molecules?

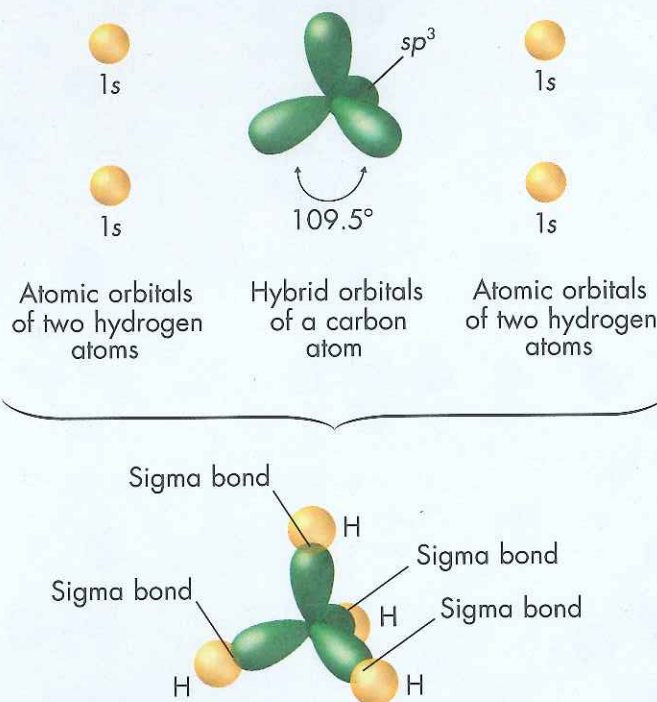
The VSEPR theory works well when accounting for molecular shapes, but it does not help much in describing the types of bonds formed. **Key** Orbital hybridization provides information about both molecular bonding and molecular shape. In hybridization, several atomic orbitals mix to form the same total number of equivalent hybrid orbitals.

Hybridization Involving Single Bonds Recall that the carbon atom's outer electron configuration is $2s^2 2p^2$, but one of the $2s$ electrons is promoted to a $2p$ orbital to give one $2s$ electron and three $2p$ electrons, allowing it to bond to four hydrogen atoms in methane. You might suspect that one bond would be different from the other three. In fact, all the bonds are identical. This fact is explained by orbital hybridization.

The one $2s$ orbital and three $2p$ orbitals of a carbon atom mix to form four sp^3 hybrid orbitals. These are at the tetrahedral angle of 109.5° . As you can see in Figure 8.19, the four sp^3 orbitals of carbon overlap with the $1s$ orbitals of the four hydrogen atoms. The sp^3 orbitals extend farther into space than either s or p orbitals, allowing a great deal of overlap with the hydrogen $1s$ orbitals. The eight available valence electrons fill the molecular orbitals to form four C—H sigma bonds. The extent of overlap results in unusually strong covalent bonds.

Figure 8.19 Methane Molecule

In methane, each of the four sp^3 hybrid orbitals of carbon overlaps with a $1s$ orbital of hydrogen.



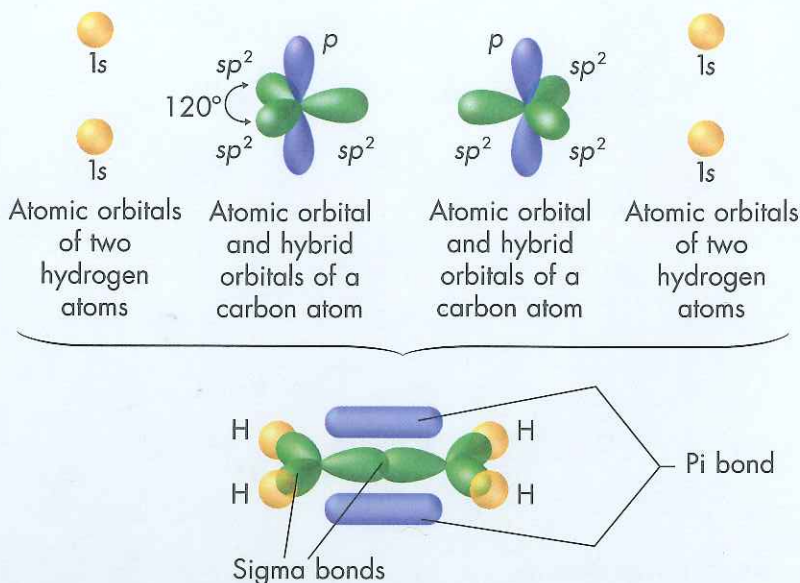
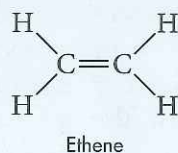


Figure 8.20 Ethene Molecule

In an ethene molecule, two sp^2 hybrid orbitals from each carbon overlap with a $1s$ orbital of hydrogen to form a sigma bond. The other sp^2 orbitals overlap to form a carbon-carbon sigma bond. The p atomic orbitals overlap to form a pi bond.

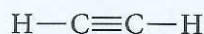
Infer What region of space does the pi bond occupy relative to the carbon atoms?

Hybridization Involving Double Bonds Hybridization is also useful in describing double covalent bonds. Ethene is a relatively simple molecule that has one carbon-carbon double bond and four carbon-hydrogen single bonds.



Experimental evidence indicates that the H—C—H bond angles in ethene are about 120° . In ethene, sp^2 hybrid orbitals form from the combination of one $2s$ and two $2p$ atomic orbitals of carbon. As you can see in Figure 8.20, each hybrid orbital is separated from the other two by 120° . Two sp^2 hybrid orbitals of each carbon form sigma-bonding molecular orbitals with the four available hydrogen $1s$ orbitals. The third sp^2 orbitals of each of the two carbons overlap to form a carbon-carbon sigma-bonding orbital. The nonhybridized $2p$ carbon orbitals overlap side by side to form a pi-bonding orbital. A total of twelve electrons fill six bonding molecular orbitals. Thus, five sigma bonds and one pi bond hold the ethene molecule together. Although they are drawn alike in structural formulas, pi bonds are weaker than sigma bonds. In chemical reactions that involve breaking one bond of a carbon-carbon double bond, the pi bond is more likely to break than the sigma bond.

Hybridization Involving Triple Bonds A third type of covalent bond is a triple bond, which is found in ethyne (C_2H_2), also called acetylene.



As with other molecules, the hybrid orbital description of ethyne is guided by an understanding of the properties of the molecule. Ethyne is a linear molecule. The best hybrid orbital description is obtained if a $2s$ atomic orbital of carbon mixes with only one of the three $2p$ atomic orbitals. The result is two sp hybrid orbitals for each carbon.

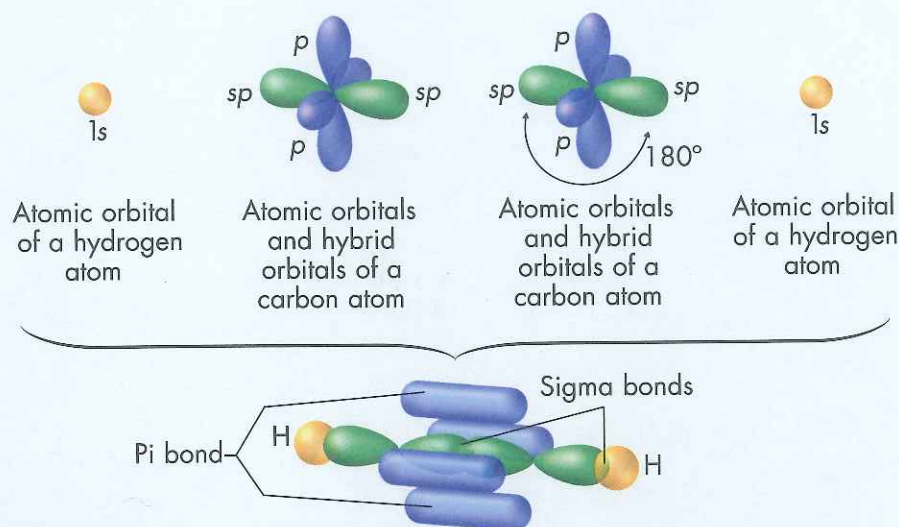


Figure 8.21 Ethyne Molecule

In an ethyne molecule, one sp hybrid orbital from each carbon overlaps with a $1s$ orbital of hydrogen to form a sigma bond. The other sp hybrid orbital of each carbon overlaps to form a carbon-carbon sigma bond. The two p atomic orbitals from each carbon also overlap.

Interpret Diagrams How many pi bonds are formed in an ethyne molecule?

The carbon-carbon sigma-bonding molecular orbital of the ethyne molecule shown in Figure 8.21 forms from the overlap of one sp orbital from each carbon. The other sp orbital of each carbon overlaps with the $1s$ orbital of each hydrogen, also forming sigma-bonding molecular orbitals. The remaining pair of p atomic orbitals on each carbon overlap side by side. They form two pi-bonding molecular orbitals that surround the central carbons. The ten available electrons completely fill five bonding molecular orbitals. The bonding of ethyne consists of three sigma bonds and two pi bonds.



8.3 LessonCheck

- Review** How are atomic and molecular orbitals related?
- Identify** What do scientists use VSEPR theory for?
- Describe** How is orbital hybridization useful in describing molecules?
- Classify** What shape would you expect a simple carbon-containing compound to have if the carbon atom has the following hybridizations?
a. sp^2 b. sp^3 c. sp
- Describe** What is a sigma bond? Describe, with the aid of a diagram, how the overlap of two half-filled $1s$ orbitals produces a sigma bond.
- Explain** Use VSEPR theory to predict bond angles in the following covalently bonded molecules. Explain your predictions.
a. methane b. ammonia c. water
- Identify** How many sigma and how many pi bonds are in an ethyne molecule (C_2H_2)?
- Classify** The BF_3 molecule is planar. The attachment of a fluoride ion to the boron in BF_3 , through a coordinate covalent bond, creates the BF_4^- ion. What is the geometric shape of this ion?

8.4 Polar Bonds and Molecules



CHEMISTRY & YOU

Q: How does a snowflake get its shape? Snow covers approximately 23 percent of Earth's surface. Each individual snowflake is formed from as many as 100 snow crystals. The size and shape of each crystal depends mainly on the air temperature and amount of water vapor in the air at the time the snow crystal forms. In this lesson, you will see how polar covalent bonds in water molecules influence the distinctive geometry of snowflakes.

Key Questions

How do electronegativity values determine the charge distribution in a polar bond?

How do the strengths of intermolecular attractions compare with the strengths of ionic and covalent bonds?

Why are the properties of covalent compounds so diverse?

Vocabulary

- nonpolar covalent bond
- polar covalent bond
- polar bond
- polar molecule
- dipole
- van der Waals forces
- dipole interaction
- dispersion force
- hydrogen bond
- network solid

Bond Polarity

How do electronegativity values determine the charge distribution in a polar bond?

Covalent bonds involve electron sharing between atoms. However, covalent bonds differ in terms of how the bonded atoms share the electrons. The character of the molecule depends on the kind and number of atoms joined together. These features, in turn, determine the molecular properties.

The bonding pairs of electrons in covalent bonds are pulled, as in the tug of war in Figure 8.22, between the nuclei of the atoms sharing the electrons. When the atoms in the bond pull equally (as occurs when identical atoms are bonded), the bonding electrons are shared equally, and each bond formed is a **nonpolar covalent bond**. Molecules of hydrogen (H_2), oxygen (O_2), and nitrogen (N_2) have nonpolar covalent bonds. Diatomic halogen molecules, such as Cl_2 , are also nonpolar.

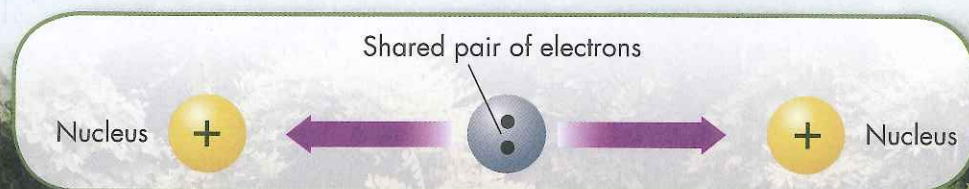


Figure 8.22
Electron Tug of War
The nuclei of atoms pull on the shared electrons, much as the knot in the rope is pulled toward opposing sides in a tug of war.




Cl

H

Figure 8.23 Electron Cloud Model of a Polar Bond

This electron-cloud picture of hydrogen chloride shows that the chlorine atom attracts the electron cloud more than the hydrogen atom does.

Infer Which atom is more electronegative, a chlorine atom or a hydrogen atom?

A **polar covalent bond**, known also as a **polar bond**, is a covalent bond between atoms in which the electrons are shared unequally.  The more-electronegative atom attracts electrons more strongly and gains a slightly negative charge. The less-electronegative atom has a slightly positive charge. Refer back to Table 6.2 in Chapter 6 to see the electronegativities of some common elements. The higher the electronegativity value, the greater the ability of an atom to attract electrons to itself.

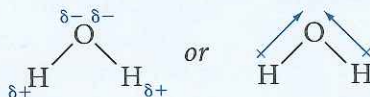
Describing Polar Covalent Bonds In the hydrogen chloride molecule (HCl), hydrogen has an electronegativity of 2.1 and chlorine has an electronegativity of 3.0. These values are significantly different, so the covalent bond in hydrogen chloride is polar. The chlorine atom, with its higher electronegativity, acquires a slightly negative charge. The hydrogen atom acquires a slightly positive charge. The lowercase Greek letter delta (δ) denotes that the atoms in the covalent bond acquire only partial charges, less than $1+$ or $1-$.



The minus sign in this notation shows that chlorine has acquired a slightly negative charge. The plus sign shows that hydrogen has acquired a slightly positive charge. These partial charges are shown as clouds of electron density as illustrated in Figure 8.23. The polar nature of the bond may also be represented by an arrow pointing to the more electronegative atom, as shown here:



The O—H bonds in a water molecule are also polar. The highly electronegative oxygen partially pulls the bonding electrons away from hydrogen. The oxygen acquires a slightly negative charge. The hydrogen is left with a slightly positive charge.



As shown in Table 8.4, the electronegativity difference between two atoms tells you what kind of bond is likely to form. There is no sharp boundary between ionic and covalent bonds. As the electronegativity difference between two atoms increases, the polarity of the bond increases. If the difference is more than 2.0, the electrons will likely be pulled away completely by one of the atoms. In that case, an ionic bond will form.

Table 8.4

Electronegativity Differences and Bond Types		
Electronegativity difference range	Most probable type of bond	Example
0.0–0.4	Nonpolar covalent	H—H (0.0)
0.4–1.0	Moderately polar covalent	$\overset{\delta+}{\text{H}}-\overset{\delta-}{\text{Cl}}$ (0.9)
1.0–2.0	Very polar covalent	$\overset{\delta+}{\text{H}}-\overset{\delta-}{\text{F}}$ (1.9)
≥ 2.0	ionic	Na^+Cl^- (2.1)



Sample Problem 8.3

Identifying Bond Type

Which type of bond (nonpolar covalent, moderately polar covalent, very polar covalent, or ionic) will form between each of the following pairs of atoms?

- a. N and H c. Ca and Cl
b. F and F d. Al and Cl

1 Analyze Identify the relevant concepts. In each case, the pairs of atoms involved in the bonding pair are given. The types of bonds depend on the electronegativity differences between the bonding elements.

2 Solve Apply concepts to this problem.

The electronegativity difference between two atoms is expressed as the absolute value. So, you will never express the difference as a negative number.

- Identify the electronegativities of each atom using Table 6.2.
- Calculate the electronegativity difference between the two atoms.
- Based on the electronegativity difference, determine the bond type using Table 8.4.

N (3.0), H (2.1); 0.9; moderately polar covalent

F (4.0), F (4.0); 0.0; nonpolar covalent

Ca (1.0), Cl (3.0); 2.0; ionic

Al (1.5), Cl (3.0); 1.5; very polar covalent

29. Identify the bonds between atoms of each pair of elements as nonpolar covalent, moderately polar covalent, very polar covalent, or ionic.

- a. H and Br d. Cl and F
b. K and Cl e. Li and O
c. C and O f. Br and Br

30. Place the following covalent bonds in order from least to most polar:

- a. H—Cl c. H—S₂
b. H—Br d. H—C₂

Describing Polar Covalent Molecules The presence of a polar bond in a molecule often makes the entire molecule polar. In a **polar molecule**, one end of the molecule is slightly negative, and the other end is slightly positive. For example, in the hydrogen chloride molecule the partial charges on the hydrogen and chlorine atoms are electrically charged regions, or poles. A molecule that has two poles is called a dipolar molecule, or **dipole**. The hydrogen chloride molecule is a dipole. Look at Figure 8.24. When polar molecules are placed between oppositely charged plates, they tend to become oriented with respect to the positive and negative plates.

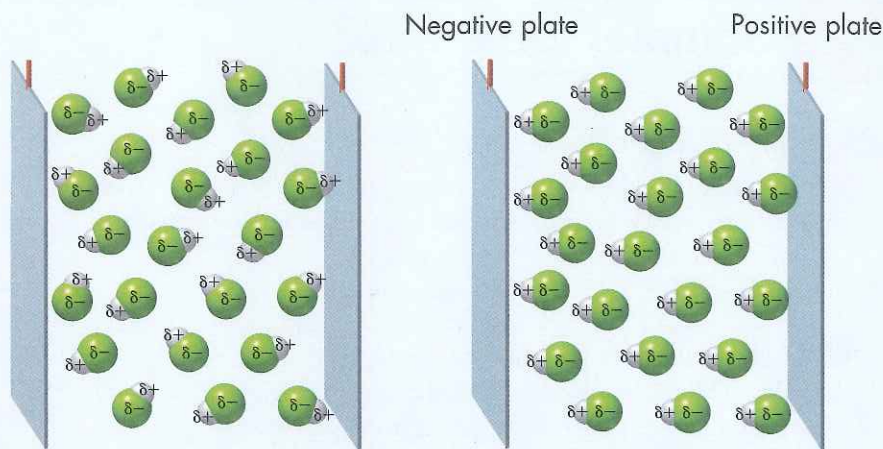
Figure 8.24
Polar Molecules in an Electric Field

When polar molecules, such as HCl, are placed in an electric field, the slightly negative ends of the molecules become oriented toward the positively charged plate, and the slightly positive ends of the molecules become oriented toward the negatively charged plate.

Predict What would happen if, instead, carbon dioxide molecules were placed between the plates? Why?



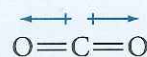
See Polar Molecules animated online.



Electric field is absent.
Polar molecules orient randomly.

Electric field is on.
Polar molecules line up.

The effect of polar bonds on the polarity of an entire molecule depends on the shape of the molecule and the orientation of the polar bonds. A carbon dioxide molecule, for example, has two polar bonds and is linear.



Note that the carbon and oxygens lie along the same axis. Therefore, the bond polarities cancel because they are in opposite directions. Carbon dioxide is thus a nonpolar molecule, despite the presence of two polar bonds.

The water molecule also has two polar bonds. However, the water molecule is bent rather than linear. Therefore, the bond polarities do not cancel and a water molecule is polar.

Attractions Between Molecules

Key How do the strengths of intermolecular attractions compare with ionic and covalent bonds?

Molecules can be attracted to each other by a variety of different forces. **Key** Intermolecular attractions are weaker than either ionic or covalent bonds. Nevertheless, you should not underestimate the importance of these forces. Among other things, these attractions are responsible for determining whether a molecular compound is a gas, a liquid, or a solid at a given temperature.

Van der Waals Forces The two weakest attractions between molecules are collectively called **van der Waals forces**, named after the Dutch chemist Johannes van der Waals (1837–1923). Van der Waals forces consist of dipole interactions and dispersion forces.

Dipole interactions occur when polar molecules are attracted to one another. The electrical attraction involved occurs between the oppositely charged regions of polar molecules, as shown in Figure 8.25. The slightly negative region of a polar molecule is weakly attracted to the slightly positive region of another polar molecule. Dipole interactions are similar to, but much weaker than, ionic bonds.

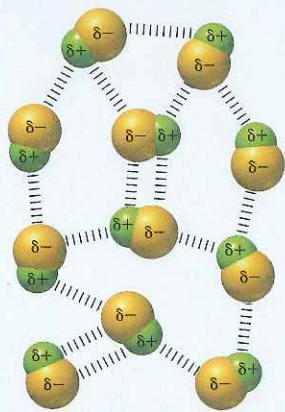


Figure 8.25 Dipole Interactions
Polar molecules are attracted to one another by dipole interactions, a type of van der Waals force.

Dispersion forces, the weakest of all molecular interactions, are caused by the motion of electrons. They occur even between nonpolar molecules. When the moving electrons happen to be momentarily more on the side of a molecule closest to a neighboring molecule, their electric force influences the neighboring molecule's electrons to be momentarily more on the opposite side. This shift causes an attraction between the two molecules similar to, but much weaker than, the force between permanently polar molecules. The strength of dispersion forces generally increases as the number of electrons in a molecule increases. The halogen diatomic molecules, for example, attract each other mainly by means of dispersion forces. Fluorine and chlorine have relatively few electrons and are gases at ordinary room temperature and pressure because of their especially weak dispersion forces. The larger number of electrons in bromine generates larger dispersion forces. Bromine molecules therefore attract each other sufficiently to make bromine a liquid at ordinary room temperature and pressure. Iodine, with a still larger number of electrons, is a solid at ordinary room temperature and pressure.

Hydrogen Bonds The dipole interactions in water produce an attraction between water molecules. Each O—H bond in the water molecule is highly polar, and the oxygen acquires a slightly negative charge because of its greater electronegativity. The hydrogens in water molecules acquire a slightly positive charge. The positive region of one water molecule attracts the negative region of another water molecule, as illustrated in Figure 8.26. This attraction between the hydrogen of one water molecule and the oxygen of another water molecule is strong compared to other dipole interactions. This relatively strong attraction, which is also found in hydrogen-containing molecules other than water, is called a hydrogen bond. Figure 8.26 illustrates hydrogen bonding in water.

Hydrogen bonds are attractive forces in which a hydrogen covalently bonded to a very electronegative atom is also weakly bonded to an unshared electron pair of another electronegative atom. This other atom may be in the same molecule or in a nearby molecule. Hydrogen bonding always involves hydrogen. It is the only chemically reactive element with valence electrons that are not shielded from the nucleus by other electrons.

Remember that for a hydrogen bond to form, a covalent bond must already exist between a hydrogen atom and a highly electronegative atom, such as oxygen, nitrogen, or fluorine. The combination of this strongly polar bond and the lack of shielding effect in a hydrogen atom is responsible for the relative strength of hydrogen bonds. A hydrogen bond has about 5 percent of the strength of an average covalent bond. Hydrogen bonds are the strongest of the intermolecular forces. They are extremely important in determining the properties of water and biological molecules such as proteins. Figure 8.27 shows how the relatively strong attractive forces between water molecules allows the water strider to sit on the surface of the water.

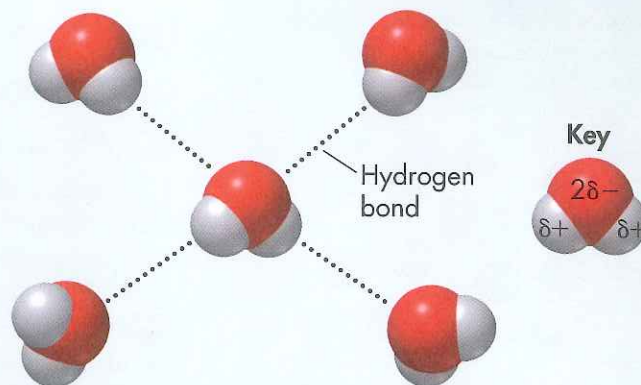


Figure 8.26
Hydrogen Bonds in Water
The strong hydrogen bonding between water molecules accounts for many properties of water, such as the fact that water is a liquid rather than a gas at room temperature.

CHEMISTRY & YOU

Q: How does a snowflake get its shape?

Figure 8.27 Walking on Water
The strong attractions between water molecules allow this water strider to “walk” on water instead of sinking into the water.



Intermolecular Attractions and Molecular Properties

Key Why are the properties of covalent compounds so diverse?

At room temperature, some compounds are gases, some are liquids, and some are solids. The physical properties of a compound depend on the type of bonding it displays—in particular, on whether it is ionic or covalent.

A great range of physical properties occurs among covalent compounds.

Key The diversity of physical properties among covalent compounds is mainly because of widely varying intermolecular attractions.

The melting and boiling points of most compounds composed of molecules are low compared with those of ionic compounds. In most solids formed from molecules, only the weak attractions between molecules need to be broken. However, a few solids that consist of molecules do not melt until the temperature reaches 1000°C or higher, or they decompose without melting at all. Most of these very stable substances are **network solids** (or network crystals), solids in which all of the atoms are covalently bonded to each other. Melting a network solid would require breaking covalent bonds throughout the solid.

Diamond is an example of a network solid. As shown in Figure 8.28, each carbon atom in a diamond is covalently bonded to four other carbons, interconnecting carbon atoms throughout the diamond. Cutting a diamond requires breaking a multitude of these bonds. Diamond does not melt; rather, it vaporizes to a gas at 3500°C and above.

Silicon carbide, with the formula SiC and a melting point of about 2700°C, is also a network solid. Silicon carbide is so hard that it is used in grindstones and as an abrasive. It is also used as a coating on materials that are exposed to high temperatures, as in Figure 8.29. The molecular structures of silicon carbide and diamond are similar to each other. You can think of samples of diamond, silicon carbide, and other network solids as single molecules.

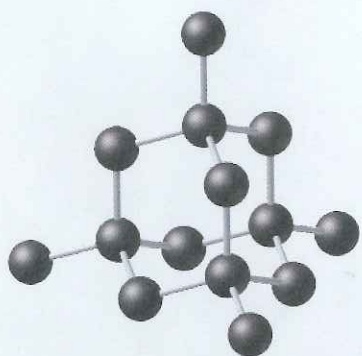


Figure 8.28 Diamond

Diamond is a network-solid form of carbon. Diamond has a three-dimensional structure, with each carbon at the center of a tetrahedron.

Figure 8.29 Silicon Carbide

Surfaces are coated with silicon carbide to make products that are non-adhesive and resistant to extreme temperature, abrasions, and corrosion.

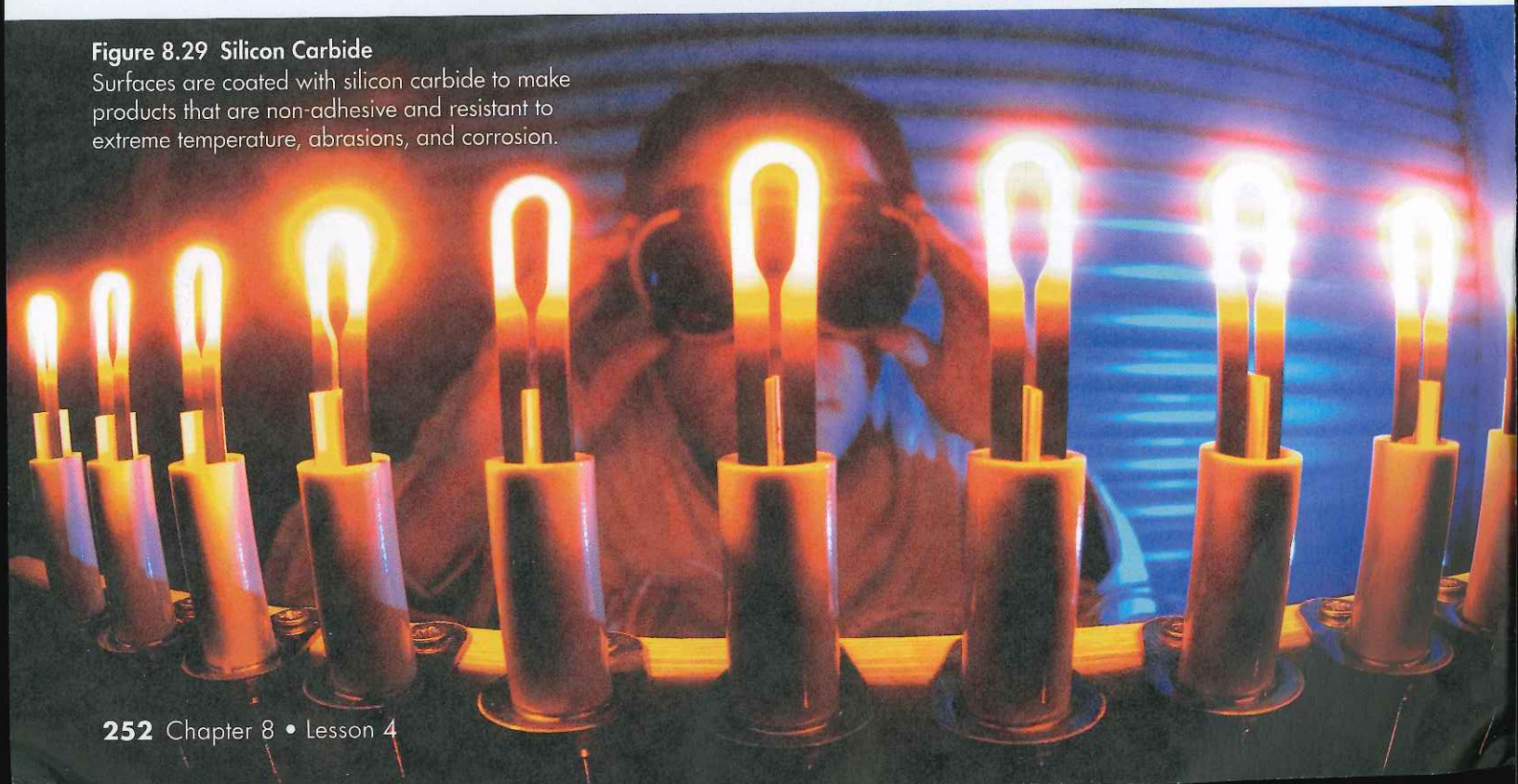


Table 8.5 summarizes some of the characteristic differences between ionic and covalent (molecular) substances. Note that ionic compounds have higher melting points than molecular compounds. Ionic compounds also tend to be soluble in water.

Table 8.5

Characteristics of Ionic and Molecular Compounds		
Characteristic	Ionic compound	Molecular compound
Representative unit	Formula unit	Molecule
Bond formation	Transfer of one or more electrons between atoms	Sharing of electron pairs between atoms
Type of elements	Metallic and nonmetallic	Nonmetallic
Physical state	Solid	Solid, liquid, or gas
Melting point	High (usually above 300°C)	Low (usually below 300°C)
Solubility in water	Usually high	High to low
Electrical conductivity of aqueous solution	Good conductor	Poor to nonconducting



8.4 LessonCheck

- 31. Explain** How do electronegativity values determine the charge distribution in a polar covalent bond?
- 32. Compare** How do the strengths of intermolecular attractions compare to the strengths of ionic bonds and covalent bonds?
- 33. Explain** Why are the properties of covalent compounds so diverse?
- 34. Explain** Explain this statement: Not every molecule with polar bonds is polar. Use CCl_4 as an example.
- 35. Draw** Draw the electron dot structure for each molecule. Identify polar covalent bonds by assigning slightly positive ($\delta+$) and slightly negative ($\delta-$) symbols to the appropriate atoms.
- a. HOOH c. HBr
 b. BrCl d. H_2O
- 36. Compare** How does a network solid differ from most other covalent compounds?
- 37.** What happens when polar molecules are between oppositely charged metal plates?

BIG IDEA BONDING AND INTERACTIONS

- 38.** Explain how dipole interactions and dispersion forces are related. First, explain what produces the attractions between polar molecules. Then, explain what produces dispersion forces between molecules. Identify what is similar and what is different in the two mechanisms of intermolecular attraction.

Small-Scale Lab

Paper Chromatography of Food Dyes

Purpose

To use paper chromatography to separate and identify food dyes in various samples

Materials

- pencil
- ruler
- scissors
- toothpicks
- 4 different colors of food coloring
- plastic cup
- 0.1% NaCl solution
- chromatography paper

Procedure



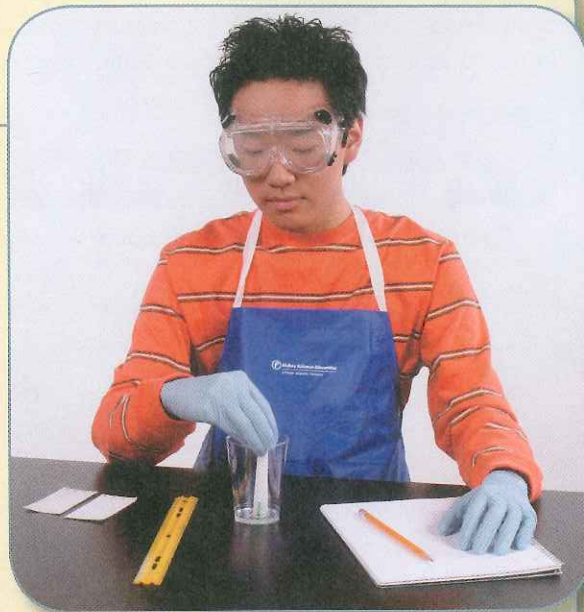
Cut a 5 cm × 10 cm strip of chromatography paper and label it with a pencil, as shown below. Use a different toothpick to place a spot of each of the four food colors on the Xs on your chromatography paper. Allow the spots to dry for a few minutes. Fill the plastic cup so its bottom is just covered with the solvent (0.1% NaCl solution). Wrap the chromatography paper around a pencil. Remove the pencil and place the chromatography paper, color-spot side down, in the solvent. When the solvent reaches the top of the chromatography paper, remove the paper and allow it to dry.

Analysis

Using your experimental data, record the answers to the following questions below your data table.

1. If a food-color sample yields a single streak or spot, it is usually a pure compound. Which food colors consist of pure compounds?
2. Which food colors are mixtures of compounds?
3. Food colors often consist of a mixture of three colored dyes: Red No. 40, Yellow No. 5, and Blue No. 1. Read the label on the food-color package. Which dyes do your food-color samples contain?

Food Color Samples	Your name		
0.1% NaCl solution			
X			
X			
X			
X			
Red	Yellow	Green	Blue



4. Identify each spot or streak on your chromatogram as Red No. 40, Yellow No. 5, or Blue No. 1.
5. Paper chromatography separates polar covalent compounds on the basis of their relative polarities. The dyes that are the most polar migrate the fastest and appear at the top of the paper. Which dye is the most polar? Which dye is the least polar?

You're the Chemist

The following small-scale activities allow you to develop your own procedures and analyze the results.

1. **Design an Experiment** Design and carry out an experiment to identify the dyes in various colored candies.
2. **Design an Experiment** Design and carry out an experiment to identify the dyes in various colored markers using the paper chromatography method.
3. **Design an Experiment** Design and carry out an experiment to identify the dyes in various colored powdered drinks using the paper chromatography method.
4. **Analyze Data** Use different solvents, such as 2-propanol (rubbing alcohol), vinegar, and ammonia, to separate food colors. Does the choice of solvent affect the results?
5. **Analyze Data** Explore the effect of different papers on your results. Try paper towels, notebook paper, and coffee filters. Report your results. Examine the relative positions of Blue No. 1 and Yellow No. 5. What do you observe?

8 Study Guide

BIG IDEA

BONDING AND INTERACTIONS

In molecular compounds, bonding occurs when atoms share electrons. In ionic compounds, bonding occurs when electrons are transferred between atoms. Shared electrons and the valence electrons that are not shared affect the shape of a molecular compound, as the valence electrons stay as far apart from each other as possible. The molecular properties of a molecule are affected by intermolecular attractions.

8.1 Molecular Compounds

Key A molecular formula shows how many atoms of each element a substance contains.

Key The representative unit of a molecular compound is a molecule. For an ionic compound, the representative unit is a formula unit.

- covalent bond (223)
- molecule (223)
- diatomic molecule (223)
- molecular compound (223)
- molecular formula (223)

8.2 The Nature of Covalent Bonding

Key In covalent bonds, electron sharing occurs so that atoms attain the configurations of noble gases.

Key In a coordinate covalent bond, the shared electron pair comes from a single atom.

Key The octet rule is not satisfied in molecules with an odd number of valence electrons and in molecules in which an atom has less, or more, than a complete octet of valence electrons.

Key A large bond dissociation energy corresponds to a strong covalent bond.

Key Chemists use resonance structures to envision the bonding in molecules that cannot be adequately described by a single structural formula.

- single covalent bond (226)
- structural formula (227)
- unshared pair (227)
- double covalent bond (230)
- triple covalent bond (230)
- coordinate covalent bond (232)
- polyatomic ion (232)
- bond dissociation energy (236)
- resonance structure (237)

8.3 Bonding Theories

Key Just as an atomic orbital belongs to a particular atom, a molecular orbital belongs to a molecule as a whole.

Key In order to explain the three-dimensional shape of molecules, scientists use the valence-shell electron-pair repulsion theory (VSEPR theory).

Key Orbital hybridization provides information about both molecular bonding and molecular shape.

- molecular orbital (240)
- bonding orbital (240)
- sigma bond (240)
- pi bond (241)
- tetrahedral angle (242)
- VSEPR theory (242)
- hybridization (244)



8.4 Polar Bonds and Molecules

Key When different atoms bond, the more-electronegative atom attracts electrons more strongly and acquires a slightly negative charge.

Key Intermolecular attractions are weaker than either an ionic or covalent bond.

Key The diversity of physical properties among covalent compounds is mainly because of widely varying intermolecular attractions.

- nonpolar covalent bond (247)
- polar covalent bond (248)
- polar bond (248)
- polar molecule (249)
- dipole (249)
- van der Waals forces (250)
- dipole interaction (250)
- dispersion force (251)
- hydrogen bond (251)
- network solid (252)

Lesson by Lesson

8.1 Molecular Compounds

39. The melting point of a compound is 1240°C . Is this compound most likely an ionic compound or a molecular compound?
40. Identify the number and kinds of atoms present in a molecule of each compound.
- ascorbic acid (vitamin C), $\text{C}_6\text{H}_8\text{O}_6$
 - sucrose (table sugar), $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
 - trinitrotoluene (TNT), $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$
41. Which of the following gases in Earth's atmosphere would you expect to find as molecules and which as individual atoms? Explain.
- nitrogen
 - oxygen
 - argon
42. Describe the differences between molecular formulas and structural formulas for molecular compounds.
43. Identify the phrases that generally apply to molecular compounds.
- contain metals and nonmetals
 - are often gases or liquids
 - have low melting points
 - contain ionic bonds
 - use covalent bonding

8.2 The Nature of Covalent Bonding

44. Explain why neon is monatomic but chlorine is diatomic.
45. Classify the following compounds as ionic or covalent:
- | | |
|--------------------------|-------------------------|
| a. MgCl_2 | c. H_2O |
| b. Na_2S | d. H_2S |
46. Describe the difference between an ionic and a covalent bond.
47. How many electrons do two atoms in a double covalent bond share? How many in a triple covalent bond?
- *48. Characterize a coordinate covalent bond and give an example.

49. Draw plausible electron dot structures for the following substances. Each substance contains only single covalent bonds.
- | | |
|------------------|-------------------------|
| a. I_2 | c. H_2S |
| b. OF_2 | d. NI_3 |
- *50. Explain why compounds containing C—N and C—O single bonds can form coordinate covalent bonds with H^+ but compounds containing only C—H and C—C single bonds cannot.
51. Draw the electron dot structure of the polyatomic thiocyanate anion (SCN^-).
52. Draw the electron dot structure for the hydrogen carbonate ion (HCO_3^-). Carbon is the central atom, and hydrogen is attached to oxygen in this polyatomic anion.
53. Using electron dot structures, draw at least two resonance structures for the nitrite ion (NO_2^-). The oxygens in NO_2^- are attached to the nitrogen.
- *54. Which of these compounds contain elements that do not follow the octet rule? Explain.
- | | |
|-----------------------------|-------------------|
| a. NF_3 | c. SF_4 |
| b. PCl_2F_3 | d. SCl_2 |
55. Explain what is meant by *bond dissociation energy*.
56. What is the relationship between the magnitude of a molecule's bond dissociation energy and its expected chemical reactivity?
57. How many electrons must the atoms of the elements below share with other atoms in covalent bonding to achieve an octet of electrons?
- | | | |
|------|-------|------|
| a. S | c. N | e. I |
| b. C | d. Br | |
- *58. Draw the electron dot structures for each of these molecules.
- | | |
|------------------|---------------------------|
| a. NH_3 | c. H_2O_2 |
| b. BrCl | d. SiH_4 |

8.3 Bonding Theories

59. What is a pi bond? Describe, with the aid of a diagram, how the overlap of two half-filled *p* atomic orbitals produces a pi bond.

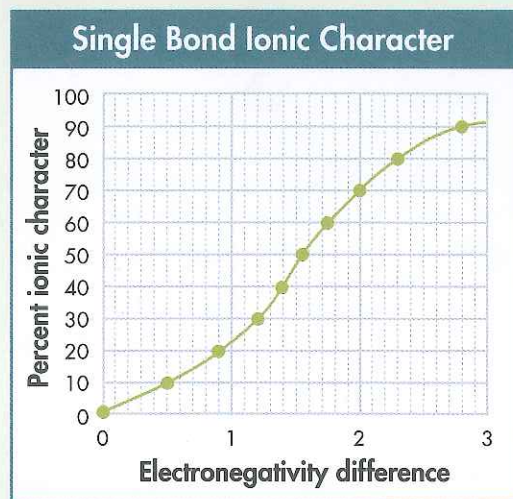
- *60. Use VSEPR theory to predict the shapes of the following compounds:
- | | | |
|----------------------|---------------------|----------------------|
| a. CO ₂ | c. SO ₃ | e. CO |
| b. SiCl ₄ | d. SCl ₂ | f. H ₂ Se |
61. The molecule CO₂ has two carbon–oxygen double bonds. Describe the bonding in the CO₂ molecule, which involves hybridized orbitals for carbon and oxygen.
62. What type of bonding orbital is always formed between hydrogen and another atom in a covalent compound?
- *63. What types of hybrid orbitals are involved in the bonding of the carbon atoms in the following molecules?
- | |
|-------------------------------------|
| a. CH ₄ |
| b. H ₂ C=CH ₂ |
| c. HC≡CH |
| d. N≡C—C≡N |

8.4 Polar Bonds and Molecules

64. How must the electronegativities of two atoms compare if a covalent bond between them is to be polar?
- *65. The bonds between the following pairs of elements are covalent. Arrange them according to polarity, listing the most polar bond first.
- | | | |
|---------|--------|---------|
| a. H—Cl | c. H—F | e. H—H |
| b. H—C | d. H—O | f. S—Cl |
66. What is a hydrogen bond?
67. Depict the hydrogen bonding between two ammonia molecules and between one ammonia molecule and one water molecule.
68. Why do compounds with strong intermolecular attractive forces have higher boiling points than compounds with weak intermolecular attractive forces?
- *69. Use Table 8.3 to determine how many kilojoules are required to dissociate all the C—H bonds in 1 mol of methane (CH₄).
70. Which of these molecules is least likely to form a hydrogen bond with a water molecule?
- | | |
|-----------------------|----------------------------------|
| a. NH ₃ | c. HF |
| b. CH ₃ Cl | d. H ₂ O ₂ |

Understand Concepts

- *71. Devise a hybridization scheme for PCl₃ and predict the molecular shape based on this scheme.
72. The chlorine and oxygen atoms in thionyl chloride (SOCl₂) are bonded directly to the sulfur. Draw an acceptable electron dot structure for thionyl chloride.
73. Explain why each electron dot structure is incorrect. Replace each structure with one that is more acceptable.
- | |
|--|
| a. $[:C::\ddot{N}:]^-$ |
| b. $:\ddot{F}:\ddot{P}::\ddot{F}:$
$:\ddot{F}:$ |
74. Use VSEPR theory to predict the geometry of each of the following:
- | | |
|----------------------------------|---------------------|
| a. SiCl ₄ | c. CCl ₄ |
| b. CO ₃ ²⁻ | d. SCl ₂ |
75. The following graph shows how the percent ionic character of a single bond varies according to the difference in electronegativity between the two elements forming the bond. Answer the following questions, using this graph and Table 6.2.

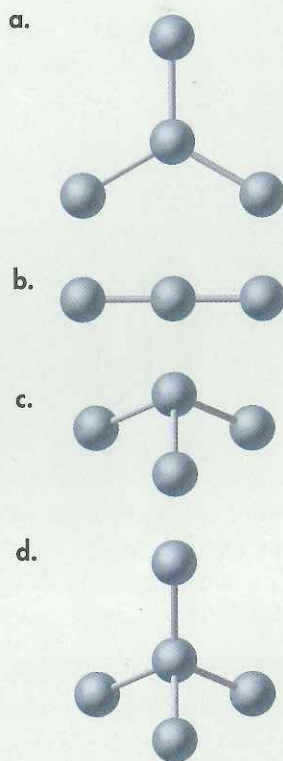


- a. What is the relationship between the percent ionic character of single bonds and the electronegativity difference?
- b. What electronegativity difference will result in a bond with a 50 percent ionic character?
- c. Estimate the percent ionic character of the bonds formed between (1) lithium and oxygen, (2) nitrogen and oxygen, (3) magnesium and chlorine, and (4) nitrogen and fluorine.

76. Give the angles between the orbitals of each hybrid.

- sp^3 hybrids
- sp^2 hybrids
- sp hybrids

77. What is the geometry around the central atom in each of these simple molecules?



*78. Which of the following molecules contains a central atom that does not obey the octet rule?

- PBr_5
- AlI_3
- PF_3
- $SiCl_4$

79. Vinegar contains the compound ethanoic acid, whose molecular formula is CH_3COOH .

- Draw the electron dot structure of ethanoic acid. (*Hint*: The two carbon atoms are bonded to each other, and the two oxygens are bonded to the same carbon.)
- Is the bonding between each of the oxygen atoms and the carbon the same?
- Is the bonding between the carbon atom and each oxygen atom a polar or nonpolar bond?
- Is ethanoic acid a polar molecule?

Think Critically

80. **Compare** Make a list of the elements in the compounds found in Table 8.2 on page 234. What do the elements that form covalent bonds have in common?

81. **Explain** Is there a clear difference between a very polar covalent bond and an ionic bond? Explain.

*82. **Explain** Ethyl alcohol (CH_3CH_2OH) and dimethyl ether (CH_3OCH_3) each have the same molecular formula, C_2H_6O . Ethyl alcohol has a much higher boiling point ($78^\circ C$) than dimethyl ether ($-25^\circ C$). Propose an explanation for this difference.

83. **Evaluate** Although the relative positions of the atoms are correct in each of these molecules, there are one or more incorrect bonds in each of the electron dot structures. Identify the incorrect bonds. Draw the correct electron dot structure for each molecule.

- $H=C=C=H$
- $:F-O-H$
- $:I::Cl:$
- $H-N::N-H$

*84. **Predict** What shape do you expect for a molecule with a central atom and the following pairings?

- two bonding pairs of electrons and two nonbonding pairs of electrons
- four bonding pairs and zero nonbonding pairs
- three bonding pairs and one nonbonding pair

85. **Interpret Tables** Is this statement true or false? "As the electronegativity difference between covalently bonded atoms increases, the strength of the bond increases." Use the table below to justify your answer.

Bond	Electronegativity difference	Bond dissociation energy (kJ/mol)
$C-C$	$2.5 - 2.5 = 0.0$	347
$C-H$	$2.5 - 2.1 = 0.4$	393
$C-N$	$3.0 - 2.5 = 0.5$	305
$C-O$	$3.5 - 2.5 = 1.0$	356

Enrichment

86. **Explain** There are some compounds in which one atom has more electrons than the corresponding noble gas. Examples are PCl_5 , SF_6 , and IF_7 . Draw the electron dot structures of P, S, and I atoms and of these compounds. Considering the outer shell configuration of P, S, and I, develop an orbital hybridization scheme to explain the existence of these compounds.
87. **Use Models** Draw the electron dot structure of formic acid, H_2CO_2 . The carbon is the central atom, and all the atoms are attached to the carbon except for a hydrogen bonded to an oxygen.
88. **Predict** The electron structure and geometry of the methane molecule (CH_4) can be described by a variety of models, including electron dot structure, simple overlap of atomic orbitals, and orbital hybridization of carbon. Draw the electron dot structure of CH_4 . Sketch two molecular orbital pictures of the CH_4 molecule. For your first sketch, assume that one of the paired $2s^2$ electrons of carbon has been promoted to the empty $2p$ orbital. Overlap each half-filled atomic orbital of carbon to a half-filled $2s$ orbital of hydrogen. What is the predicted geometry of the CH_4 molecule, using this simple overlap method? In your second sketch, assume hybridization of the $2s$ and $2p$ orbitals of carbon. Now what geometry would you predict for CH_4 ? Which picture is preferable based on the facts that all $\text{H}-\text{C}-\text{H}$ bond angles in CH_4 are 109.5° and all $\text{C}-\text{H}$ bond distances are identical?
89. **Use Models** Oxalic acid, $\text{C}_2\text{H}_2\text{O}_4$, is used in polishes and rust removers. Draw the electron dot structure for oxalic acid given that the two carbons are bonded together but neither of the hydrogen atoms is bonded to a carbon atom.
90. **Use Models** Draw as many resonance structures as you can for HN_3 . (*Hint:* The three nitrogen atoms are bonded in a row, and the hydrogen atom is bonded to a nitrogen atom at the end of the row of nitrogens.)
- *91. **Explain** Draw an electron dot structure for each molecule and explain why it fails to obey the octet rule.
- | | | |
|-------------------|-------------------|-------------------|
| a. BeF_2 | c. ClO_2 | e. XeF_2 |
| b. SiF_6 | d. BF_3 | |

Write About Science

92. **Explain** Describe what a molecular compound is. Explain how a molecular formula is the chemical formula of a molecular compound.
93. **Research a Problem** Research how chemists know that an oxygen molecule has unpaired electrons. Write a brief report on what you find.

CHEMISTRY

What's That Alarm?

The family realized that the alarm was caused by carbon monoxide (CO). In carbon monoxide, the carbon and oxygen atom are joined by a triple covalent bond. Although carbon monoxide and carbon dioxide are both made of carbon and oxygen atoms, they have very different properties.



Carbon monoxide is an odorless, tasteless gas. When it gets into the bloodstream, it causes the hemoglobin to convert to a form that is unable to transport oxygen. Symptoms of carbon monoxide poisoning include headaches, nausea, vomiting, and mental confusion. Exposure to high levels of carbon monoxide can result in death.

Fuel-burning appliances, such as water heaters, fireplaces, furnaces, and gas stoves, produce carbon monoxide. If the appliance is not functioning properly, it may release unsafe amounts of carbon monoxide. If a home contains one of these appliances, then the homeowners should install carbon monoxide detectors, since the gas cannot be detected by sight or smell.

94. **Use Models** Draw the electron dot structures of carbon monoxide and carbon dioxide. Describe the structural differences between these two molecules.
95. **Connect to the BIG IDEA** How does covalent bonding allow there to be different molecular compounds composed of the same kinds of atoms?

Cumulative Review

96. Name three indicators of chemical change.
- *97. Make the following conversions:
- 66.5 mm to micrometers
 - 4×10^{-2} g to centigrams
 - 5.62 mg/mL to decigrams per liter
 - 85 km/h to meters per second
98. How many significant figures are in each measurement?
- 0.00052 m
 - 9.8×10^4 g
 - 5.050 mg
 - 8.700 mL
99. How many neutrons are in each atom?
- silicon-30
 - magnesium-24
 - nitrogen-15
 - chromium-50
100. How do isotopes of an atom differ?
- *101. In a neutral atom, the number of which two subatomic particles must always be equal?
102. How many electrons are in the $2p$ sublevel of an atom of each element?
- aluminum
 - carbon
 - fluorine
 - lithium
103. What happens to the wavelength of light as the frequency increases?
104. What does the 5 in $3d^5$ represent?
105. Write correct electron configurations for atoms of the following elements:
- sodium
 - sulfur
 - phosphorus
 - nitrogen
106. How does the ionic radius of a typical anion compare with the radius for the corresponding neutral atom?
107. What criteria did Mendeleev and Moseley use to arrange the elements on the periodic table?
108. Give the electron configuration of the element found at each location in the periodic table.
- Group 1A, period 4
 - Group 3A, period 3
 - Group 6A, period 3
 - Group 2A, period 6
- *109. Identify the larger atom of each pair.
- calcium and barium
 - silicon and sulfur
 - sodium and nitrogen
110. Which of these statements about the periodic table is correct?
- Elements are arranged in order of increasing atomic mass.
 - A period is a horizontal row.
 - Nonmetals are located on the right side of the table.
- I only
 - I and II only
 - I, II, and III
 - I and III only
 - II and III only
- *111. Which of the following ions has the same number of electrons as a noble gas?
- Al^{3+}
 - O^{2-}
 - Br^-
 - N^{3-}
112. Which element is likely to form an ionic compound with chlorine?
- iodine
 - cesium
 - helium
113. How many valence electrons does each atom have?
- argon
 - aluminum
 - selenium
 - beryllium
114. Write the electron configuration of each ion.
- oxide ion
 - magnesium ion
 - nitride ion
 - potassium ion
115. An alloy is composed of two or more elements. Is an alloy a compound? Explain your answer.

If You Have Trouble With . . .

Question	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115
See Chapter	2	3	3	4	4	4	5	5	5	5	6	6	6	6	6	7	7	7	7	7

Standardized Test Prep

Select the choice that best answers each question or completes each statement.

- A bond in which two atoms share a pair of electrons is not
 - a coordinate covalent bond.
 - a polar covalent bond.
 - an ionic bond.
 - a nonpolar covalent bond.
- How many valence electrons are in a molecule of phosphoric acid, H_3PO_4 ?
 - 7
 - 16
 - 24
 - 32
- Which of these molecules can form a hydrogen bond with a water molecule?
 - N_2
 - NH_3
 - O_2
 - CH_4
- Which substance contains both covalent and ionic bonds?
 - NH_4NO_3
 - CH_3OCH_3
 - LiF
 - CaCl_2
- Which of these bonds is most polar?
 - $\text{H}-\text{Cl}$
 - $\text{H}-\text{Br}$
 - $\text{H}-\text{F}$
 - $\text{H}-\text{I}$

Use the description and data table below to answer Questions 6–9.

The table relates molecular shape to the number of bonding and nonbonding electron pairs in molecules.

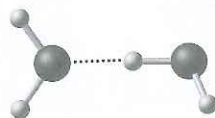
Bonding pairs	Non-bonding pairs	Arrangement of electron pairs	Molecular shape	Example
4	0	tetrahedral	tetrahedral	CH_4
3	1	tetrahedral	pyramidal	NCl_3
2	2	tetrahedral	bent	H_2S
1	3	tetrahedral	linear	HF

- Draw the electron dot structure for each example molecule.

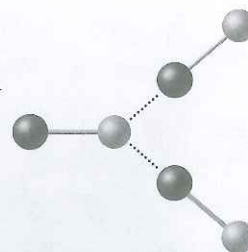
- Explain why the arrangement of electron pairs is tetrahedral in each molecule.
- H_2S has two hydrogen atoms bonded to a sulfur atom. Why isn't the molecule linear?
- What is the arrangement of electron pairs in PBr_3 ? Predict the molecular shape of a PBr_3 molecule.

For Questions 10–11, identify the type of intermolecular bonding represented by the dotted lines in the drawings.

- H_2O



- BrCl



Tips for Success

Connectors Sometimes two phrases in a true/false question are connected by a word such as *because*. The word implies that one thing caused another thing to happen. Statements that include such words can be false even if both parts of the statement are true by themselves.

In Questions 12–14, a statement is followed by an explanation. Decide if each statement is true, and then decide if the explanation given is correct.

- A carbon monoxide molecule has a triple covalent bond because carbon and oxygen atoms have an unequal number of valence electrons.
- Xenon has a lower boiling point than neon because dispersion forces between xenon atoms are stronger than those between neon atoms.
- The nitrate ion has three resonance structures because the nitrate ion has three single bonds.

If You Have Trouble With . . .

Question	1	2	3	4	5	6	7	8	9	10	11	12	13	14
See Lesson	8.2	8.2	8.4	8.3	8.1	8.3	8.2	8.2	8.2	8.2	8.4	8.4	8.4	8.2