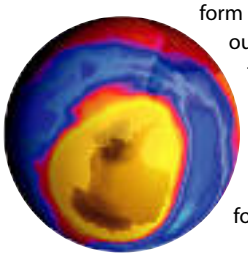
8.2 The Nature of Covalent Bonding

Connecting to Your World You know that without oxygen to breathe, you could not live. But did you know that oxygen plays another important role in your life? High in the atmosphere, a different form of oxygen, called ozone, forms a layer that filters out harmful radiation from the sun. The colors in this map indicate the concentrations of ozone in various parts of Earth's atmosphere. In this section, you will learn how oxygen atoms can join in pairs to form the oxygen you breathe and can also join in groups of three oxygen atoms to form ozone.

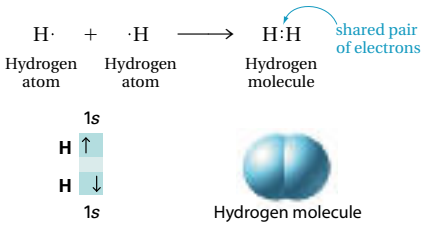


The Octet Rule in Covalent Bonding

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. **In covalent bonds, electron sharing usually occurs so that atoms attain the electron configurations of noble gases.** For example, each hydrogen atom has one electron. But a pair of hydrogen atoms share these two electrons when they form a covalent bond in a 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. In this case the 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 a 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.



Guide for Reading

Key Concepts

- What is the result of electron sharing in covalent bonds?
- How do electron dot structures represent shared electrons?
- How do atoms form double or triple covalent bonds?
- How are coordinate covalent bonds different from other covalent bonds?
- How is the strength of a covalent bond related to its bond dissociation energy?
- How are oxygen atoms bonded in ozone?
- What are some exceptions to the octet rule?

Vocabulary

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

Reading Strategy

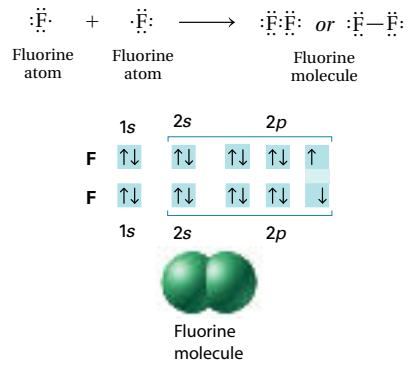
Identifying Main Idea/Details List the main idea in the paragraph following the heading *The Octet Rule in Covalent Bonding*. As you read, list examples of how this rule is followed when a single covalent bond, a double covalent bond, and a triple covalent bond form.

Go Online NSTA SCI LINKS

For: Links on Valence Electrons
Visit: www.SciLinks.org
Web Code: cdn-1082

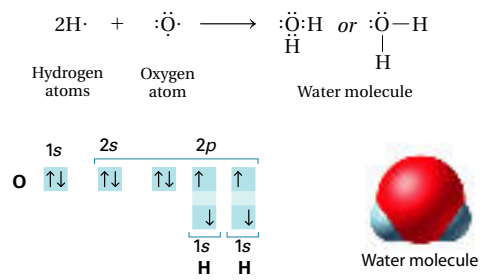
An electron dot structure such as H:H represents the shared pair of electrons of the covalent bond by two dots. The pair of shared electrons forming the covalent bond is also often represented as a dash, as in H—H for hydrogen. A **structural formula** represents the covalent bonds by dashes and shows the arrangement of covalently bonded atoms. In contrast, the molecular formula of hydrogen, H_2, indicates only the number of hydrogen atoms in each molecule.

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 F_2 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.

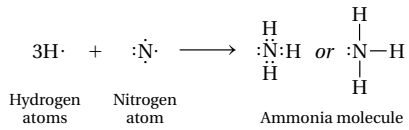
You can draw electron dot structures for molecules of compounds in much the same way that you draw them for molecules of diatomic elements. Water (H_2O) is a molecule containing three atoms with two single covalent bonds. Two hydrogen atoms share electrons with one oxygen atom. The hydrogen and oxygen 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.

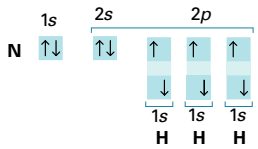


Checkpoint ***What does a structural formula represent?***

218 Chapter 8

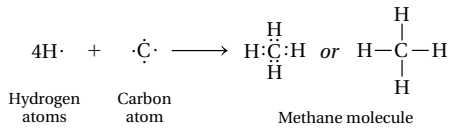
You can draw the electron dot structure for ammonia (NH_3), a suffocating gas, in a similar way. The ammonia molecule has one unshared pair of electrons.

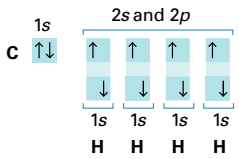




Ammonia molecule

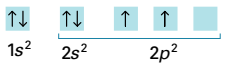
Methane (CH_4) contains four single covalent bonds. The carbon atom has four valence electrons and needs four more valence electrons to attain a noble-gas configuration. Each of the four hydrogen atoms contributes one electron to share with the carbon atom, forming four identical carbon-hydrogen bonds.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





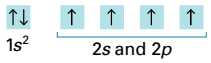
Methane molecule

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



Checkpoint ***What is the electron dot structure of a methane molecule?***

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 simply explained. 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.

CONCEPTUAL PROBLEM 8.1

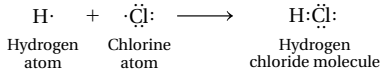
Drawing an Electron Dot Structure

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. First, draw the electron dot structures for the two atoms. Then show the electron sharing in the compound they produce.

2 Solve ***Apply concepts to the situation.***



In the electron dot structures, the hydrogen atom and the chlorine atom are each correctly shown to have an unpaired electron. Through electron sharing, the hydrogen and chlorine atoms are shown to attain the electron configurations of the noble gases helium and argon, respectively.

Practice Problems

7. Draw electron dot structures for each molecule.
a. chlorine **b.** bromine **c.** iodine

8. The following molecules have single covalent bonds. Draw an electron dot structure for each.
a. H_2O_2 **b.** PCl_3

Interactive Textbook

Problem Solving 8.8 Solve Problem 8 with the help of an interactive guided tutorial.

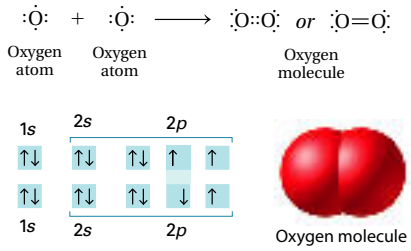
with ChemASAP

220 Chapter 8

Double and Triple Covalent Bonds

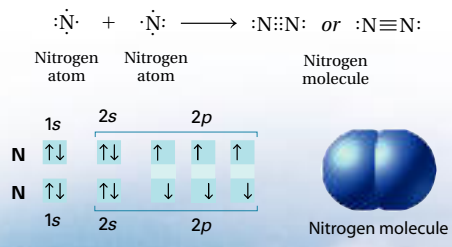
Sometimes atoms bond by sharing more than one pair of electrons. **Atoms form double or triple covalent bonds if they can attain a noble gas structure by sharing two pairs or three pairs of electrons.** A bond that involves two shared pairs of electrons is a **double covalent bond.** A bond formed by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

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.

An element whose molecules contain triple bonds is nitrogen (N_2), a major component of Earth's atmosphere illustrated in Figure 8.7. In the nitrogen molecule, each nitrogen atom has one unshared pair of electrons. A single nitrogen atom has five valence electrons. Each nitrogen atom in the nitrogen molecule must gain three electrons to have the electron configuration of neon.



Interactive Textbook

Simulation 6 Simulate the covalent bonding between molecules.

with ChemASAP

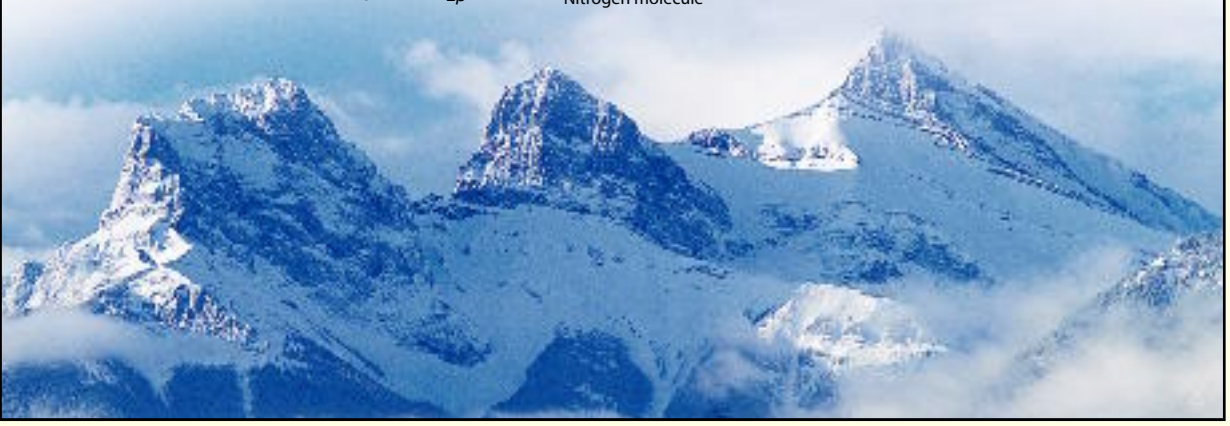


Figure 8.7 Oxygen and nitrogen are the main components of Earth's atmosphere. The oxygen molecule is an exception to the octet rule. It has two unpaired electrons. Three pairs of electrons are shared in a nitrogen molecule.

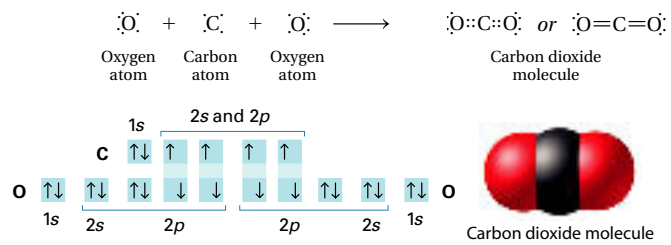
Table 8.1

The Diatomic Elements

Name	Chemical formula	Electron dot structure	Properties and uses
Fluorine	F_2	:F̈—F̈:	Greenish-yellow reactive toxic gas. Compounds of fluorine, a halogen, are added to drinking water and toothpaste to promote healthy teeth.
Chlorine	Cl_2	:C̈l—C̈l:	Greenish-yellow reactive toxic gas. Chlorine is a halogen used in household bleaching agents.
Bromine	Br_2	:B̈r—B̈r:	Dense red-brown liquid with pungent odor. Compounds of bromine, a halogen, are used in the preparation of photographic emulsions.
Iodine	I_2	:Ï—Ï:	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	:N≡N:	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.

Figure 8.8 Carbon dioxide gas is soluble in water and is used to carbonate many beverages. A carbon dioxide molecule has two carbon–oxygen double bonds.

Up to this point in your textbook, the examples of single and triple covalent bonds have involved diatomic molecules. Table 8.1 lists the properties and uses of the elements that exist as diatomic molecules. Single, double, and triple covalent bonds can also exist between unlike atoms. For example, consider carbon dioxide (CO_2), which is present in the atmosphere and is used to carbonate many soft drinks as shown in Figure 8.8. 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.

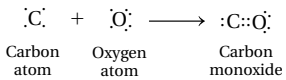


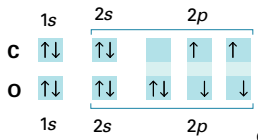
The two double bonds in the carbon dioxide molecule are identical to each other. Carbon dioxide is an example of a triatomic molecule, which is a molecule consisting of three atoms.

222 Chapter 8

Coordinate Covalent Bonds

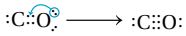
Carbon monoxide (CO) is an example of a type of covalent bonding different from that seen in water, ammonia, methane, and carbon dioxide. A carbon atom needs to gain four electrons to attain the electron configuration of neon. An oxygen atom needs two electrons. Yet it is possible for both atoms to achieve 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.





Carbon monoxide molecule

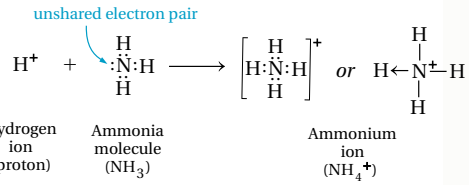
With the double bond in place, the oxygen has a stable configuration but the carbon does not. As shown below, the dilemma is solved if the oxygen also donates one of its unshared pairs of electrons for bonding.



Carbon monoxide molecule

A **coordinate covalent bond** is a covalent bond in which one atom contributes both bonding electrons. 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 C≡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^+) 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). Most plants need nitrogen that is already combined in a compound rather than molecular nitrogen (N_2) to grow. The fertilizer shown in Figure 8.9 contains the nitrogen compound ammonium sulfate.

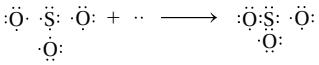


Checkpoint ***What is a polyatomic ion?***

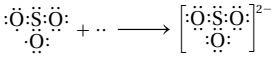
Figure 8.9 The polyatomic ammonium ion (NH_4^+), present in ammonium sulfate, is an important component of fertilizer for field crops, home gardens, and potted plants.

Most polyatomic cations and anions contain both 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-}. Start by drawing 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.



Then 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 about the structure and indicate the 2− charge, giving the result shown.

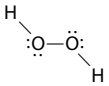


Each of the atoms of the completed structure has eight valence electrons, satisfying the octet rule. Without the two extra electrons, two of the oxygens would be electron-deficient.

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

Table 8.2

Some Common Molecular Compounds

Name	Chemical formula	Structure	Properties and uses
Hydrogen peroxide	H_2O_2		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		Oxides of sulfur are produced in 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		
Nitric oxide	NO		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	NO_2		
Nitrous oxide	N_2O		Colorless, sweet-smelling gas. It is used as an anesthetic commonly called laughing gas.
Hydrogen cyanide	HCN		Colorless, toxic gas with the smell of almonds.
Hydrogen fluoride	HF		Two hydrogen halides, all extremely soluble in water. Hydrogen chloride, a colorless gas with pungent odor, readily dissolves in water to give a solution called hydrochloric acid.
Hydrogen chloride	HCl		

224 Chapter 8

Remember, the electron dot structure for a neutral molecule contains the same number of electrons as the total number of valence electrons in the combining atoms. The negative charge of a polyatomic ion shows the number of electrons in addition to the valence electrons of the atoms present. Because a negatively charged polyatomic ion is part of an ionic compound, the positive charge of the cation of the compound balances these additional electrons.

CONCEPTUAL PROBLEM 8.2

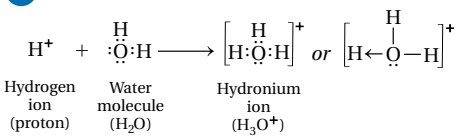
Drawing the Electron Dot Structure of a Polyatomic Ion

The polyatomic hydronium ion (H_3O^+), which is found in acidic mixtures such as lemon juice, contains a coordinate covalent bond. 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.***

H_3O^+ forms by the addition of a hydrogen ion to a water molecule. Draw the electron dot structure of the water molecule. Then, add the hydrogen ion. Oxygen must share a pair of electrons with the added hydrogen ion to form a coordinate covalent bond.

2 Solve ***Apply the concepts to this situation.***



The oxygen in the hydronium ion has eight valence electrons, and each hydrogen shares two valence electrons. This satisfies the needs of both hydrogen and oxygen for valence electrons. The water molecule is electrically neutral, and the hydrogen ion has a positive charge. The combination of these two species must have a charge of 1+, as is found in the hydronium ion.

Practice Problems

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

10. Draw the electron dot structure of the polyatomic boron tetrafluoride anion (BF_4^-).

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

12. 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.

Interactive Textbook

Problem-Solving 8.10 Solve Problem 10 with the help of an interactive guided tutorial.

with ChemASAP

Quick LAB

Strengths of Covalent Bonds

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
- pencil
- motion detector (optional)

Procedure

Sensor version available in the Probeware Lab Manual.

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

Bond Dissociation Energies

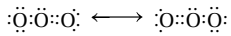
A large quantity of heat is released when hydrogen atoms combine to form hydrogen molecules. This suggests that the product is more stable than the reactants. The covalent bond in the hydrogen molecule (H_2) is so strong that it would take 435 kJ of energy to break apart all of the bonds in 1 mole (about 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 known as the **bond dissociation energy.** This is usually expressed as the energy needed to break one mole of bonds, or 6.02×10^{23} bonds. The bond dissociation energy for the H_2 molecule is 435 kJ/mol.

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.

226 Chapter 8

Resonance

Ozone in the upper atmosphere blocks harmful ultraviolet radiation from the sun. At the lower elevations shown in Figure 8.10, 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 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 of oxygen atoms in ozone is a hybrid, or mixture, of the extremes represented by the resonance forms.**

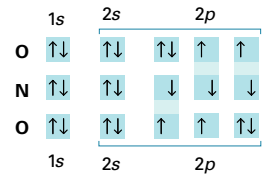
The two electron dot structures for ozone are examples of what are still referred to as resonance structures. A **resonance structure** is a structure that occurs when it is possible to draw two or more valid electron dot structures that have the same number of electron pairs for a molecule or ion. Resonance structures are simply a way to envision the bonding in certain molecules. Although no back-and-forth changes occur, double-headed arrows are used to connect resonance structures.

Checkpoint ***What notation is used to show that the two covalent bonds in O_3 are the same?***

Figure 8.10 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.

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. **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 fewer, 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.

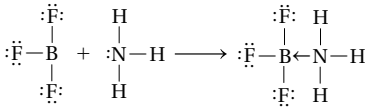


Nitrogen dioxide molecule

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 8.11.

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 may happen 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 $BF_3 \cdot NH_3$. In doing so, the boron atom accepts the unshared electron pair from ammonia and completes the octet.

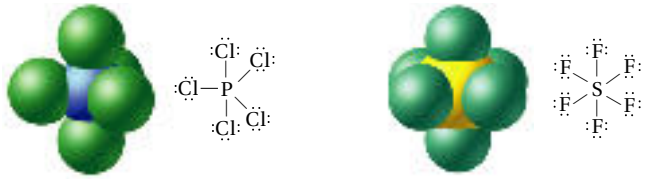


Checkpoint ***Give two examples of exceptions to the octet rule.***

Figure 8.11 Lightning is one means by which nitrogen and oxygen in the atmosphere produce nitrogen dioxide.

228 Chapter 8

Figure 8.12 Phosphorus pentachloride, used as a chlorinating and dehydrating agent, and sulfur hexafluoride, used as an insulator for electrical equipment, are exceptions to the octet rule. **Interpreting Diagrams** ***How many valence electrons does the sulfur in sulfur hexafluoride (SF_6) have for the structure shown in the figure?***



Phosphorus pentachloride Sulfur hexafluoride

A few atoms, especially phosphorus and sulfur, sometimes expand the octet to include ten or twelve electrons. Consider phosphorus trichloride (PCl_3) and phosphorus pentachloride (PCl_5). Both are stable compounds in which all of the chlorines 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 8.12, the electron dot structure for PCl_5 can be written so that phosphorus has ten valence electrons.

8.2 Section Assessment

13. **Key Concept** What electron configurations do atoms usually achieve by sharing electrons to form covalent bonds?

14. **Key Concept** How is an electron dot structure used to represent a covalent bond?

15. **Key Concept** When are two atoms likely to form a double bond between them? A triple bond?

16. **Key Concept** How is a coordinate covalent bond different from other covalent bonds?

17. **Key Concept** How is the strength of a covalent bond related to its bond dissociation energy?

18. **Key Concept** Draw the electron dot resonance structures for ozone and explain how they describe its bonding.

19. **Key Concept** List three ways in which the octet rule can sometimes fail to be obeyed.

20. What kinds of information does a structural formula reveal about the compound it represents?

21. Draw electron dot structures for the following molecules, which have only single covalent bonds.
a. H_2S **b.** PH_3 **c.** ClF

22. Use the bond dissociation energies of H_2 (435 kJ/mol) and of a typical carbon–carbon bond (347 kJ/mol) to decide which bond is stronger. Explain your reasoning.

Elements Handbook

Ozone Read the feature on ozone on page R31 of the Elements Handbook. Describe the effect of CFCs on the ozone layer. Explain why the United States has banned the use of CFCs in aerosols.

Interactive Textbook

Assessment 8.2 Test yourself on the important concepts of Section 8.2.

with **ChemASAP**