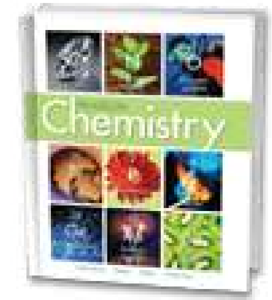


Chapter 8
Covalent Bonding

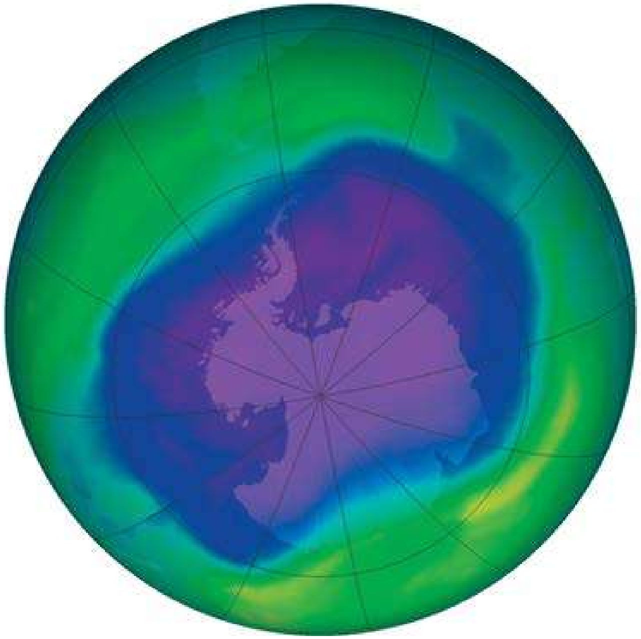
8.1 Molecular Compounds

8.2 The Nature of Covalent Bonding

8.3 Bonding Theories
8.4 Polar Bonds and Molecules

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.



The Octet Rule in Covalent Bonding

What is the result of electron sharing in covalent bonds?

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

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.

The Octet Rule in Covalent Bonding

- 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.

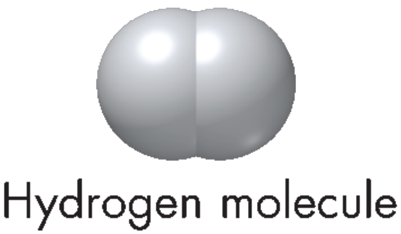
Single Covalent Bonds

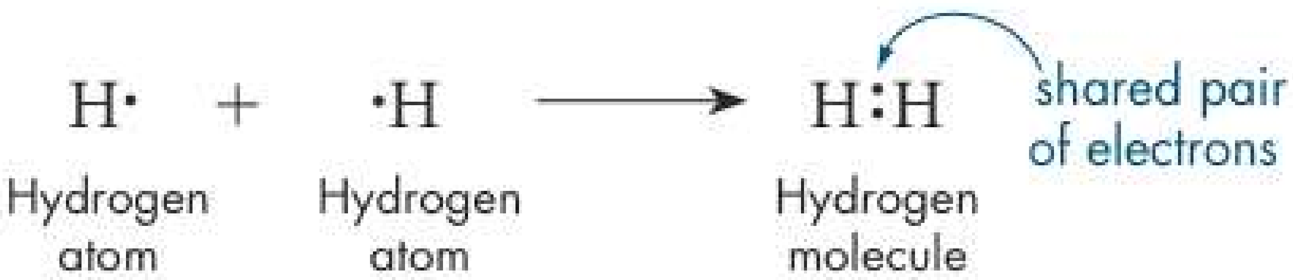
- The hydrogen atoms in a hydrogen molecule are held together mainly by the attraction of the shared electrons to the positive nuclei.

- Two atoms held together by sharing one pair of electrons are joined by a **single covalent bond**.

Single Covalent Bonds

Hydrogen gas consists of diatomic molecules whose atoms share only one pair of electrons, forming a single covalent bond.





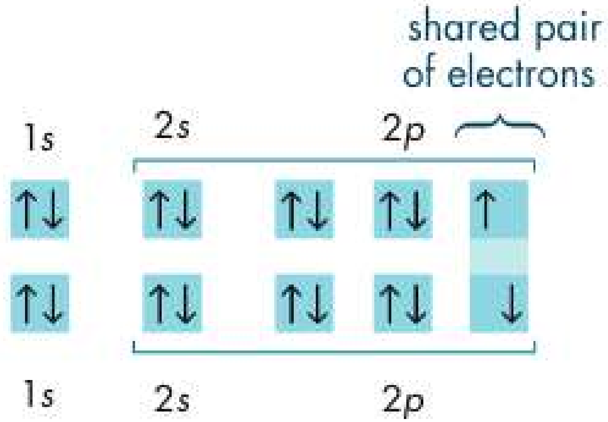
Single Covalent Bonds

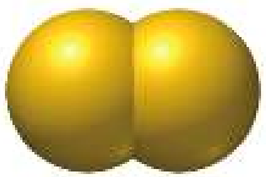
- An electron dot structure such as H:H represents the shared pair of electrons of the covalent bond by two dots.
- The pair of shared electrons forming the covalent bond is also often represented as a dash, as in H—H for hydrogen.
- A **structural formula** represents the covalent bonds as dashes and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

Single Covalent Bonds

- The halogens also form single covalent bonds in their diatomic molecules. Fluorine is one example.

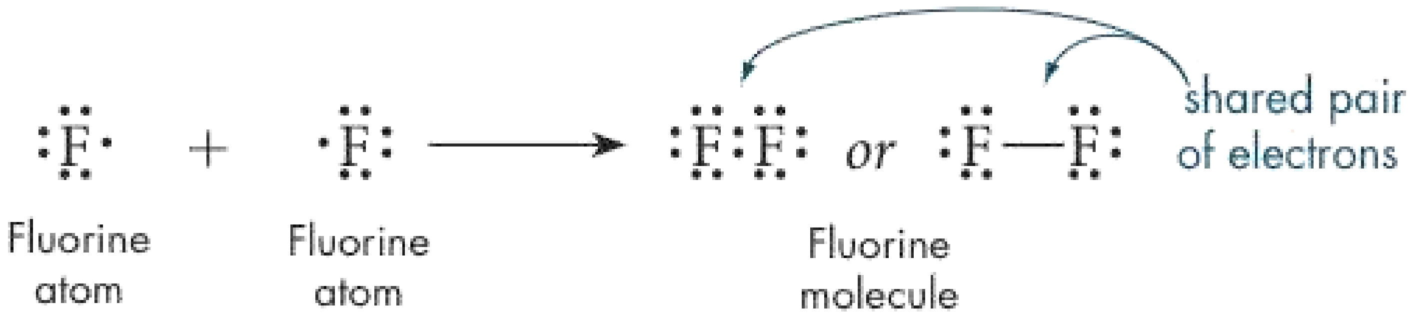
- By sharing electrons and forming a single covalent bond, two fluorine atoms each achieve the electron configuration of neon.





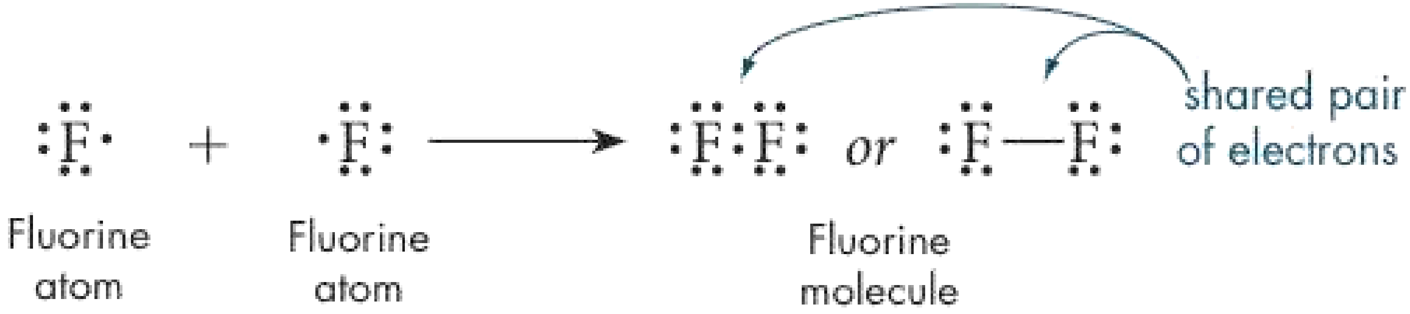
Single Covalent Bonds

- 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.



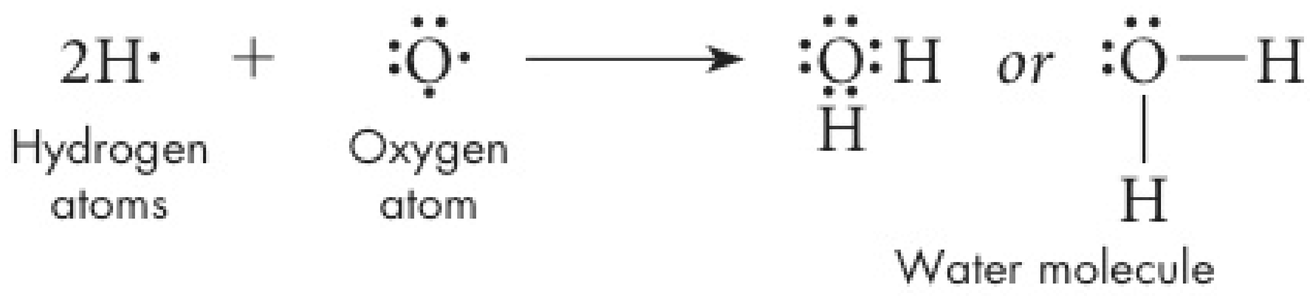
Single Covalent Bonds

- A pair of valence electrons that is not shared between atoms is called an **unshared pair**, also known as a lone pair or a nonbinding pair.
  - In F_2, each fluorine atom has three unshared pairs of electrons.



Single Covalent Bonds

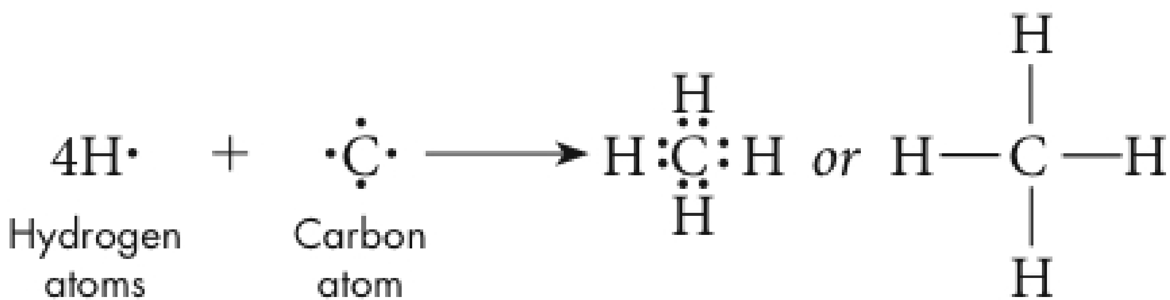
As you can see in the electron dot structures below, the oxygen atom in water has two unshared pairs of valence electrons.



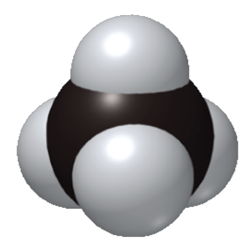
Single Covalent Bonds

- 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.

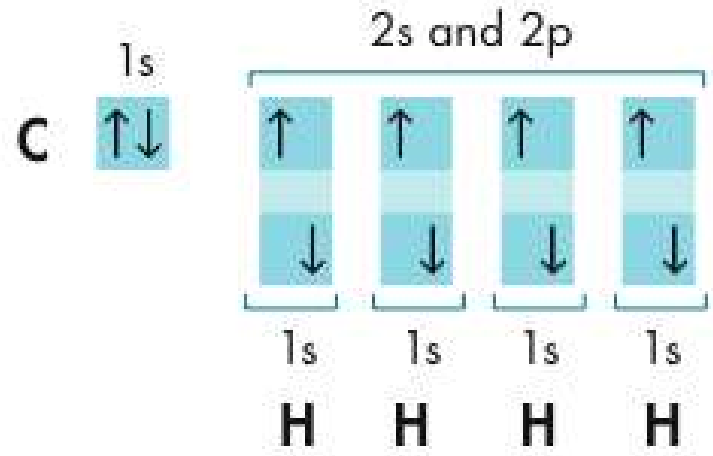


Methane molecule


Methane molecule

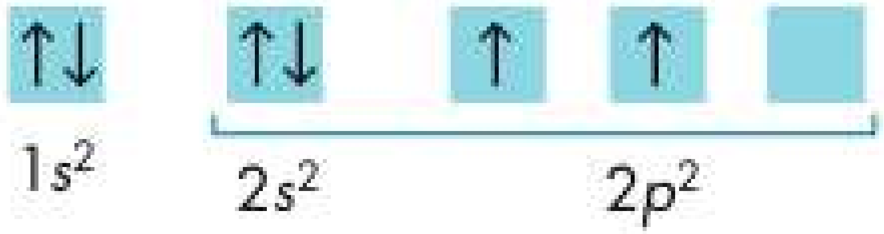
Single Covalent Bonds

Each of the four hydrogen atoms contributes one electron to share with the carbon atom, forming four identical carbon–hydrogen bonds.



Single Covalent Bonds

- 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.



Single Covalent Bonds

The formation of four bonds by carbon can be explained by the fact that one of carbon's 2*s* electrons is promoted to the vacant 2*p* orbital to form the following electron configuration.

- This electron promotion requires only a small amount of energy, and the stability of the resulting methane more than compensates for the small energy cost.

Drawing an Electron Dot Structure

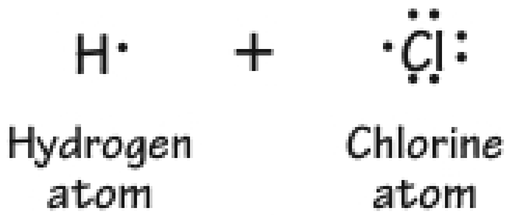
Hydrochloric acid (HCl (*aq*)) is prepared by dissolving gaseous hydrogen chloride (HCl (*g*)) in water. Hydrogen chloride is a diatomic molecule with a single covalent bond. Draw the electron dot structure for HCl.

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.

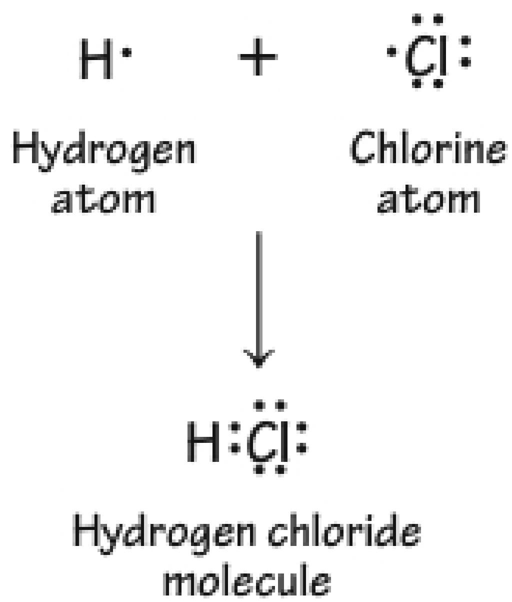
2 Solve Apply concepts to the problem.

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



2 Solve Apply concepts to the problem.

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.

Double and Triple Covalent Bonds

Atoms form double or triple covalent bonds if they can attain a noble gas structure by sharing two or three pairs of electrons.

Double and Triple Covalent Bonds

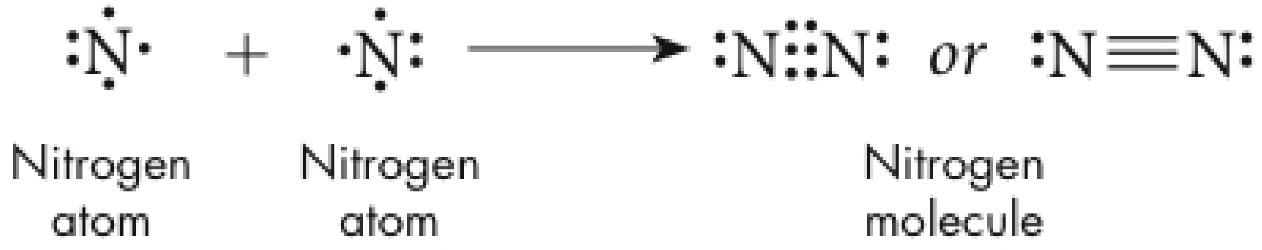
- A **double covalent bond** is a bond that involves two shared pairs of electrons.
- Similarly, a bond formed by sharing three pairs of electrons is a **triple covalent bond**.

Double and Triple Covalent Bonds

The carbon dioxide (CO_2) molecule contains two oxygens, each of which shares two electrons with carbon to form a total of two carbon–oxygen double bonds.

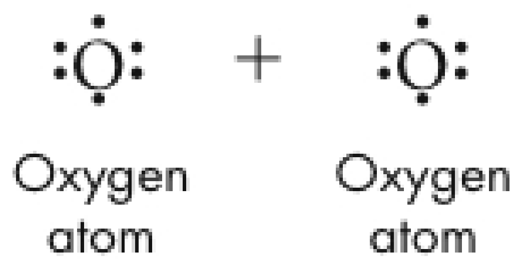
Double and Triple Covalent Bonds

- Nitrogen (N_2), a major component of Earth's atmosphere, contains triple bonds.
- A single nitrogen atom has five valence electrons; each nitrogen atom in the molecule must share three electrons to have the electron configuration of neon.



Double and Triple Covalent Bonds

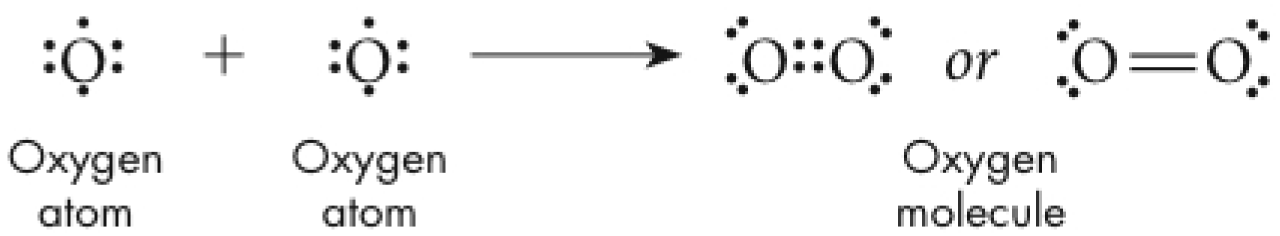
- You might think that an oxygen atom, with six valence electrons, would form a double bond by sharing two of its electrons with another oxygen atom.



- In such an arrangement, all the electrons within the molecule would be paired.

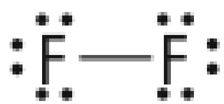
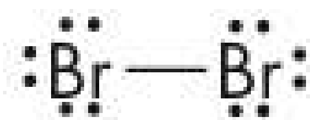
Double and Triple Covalent Bonds

- 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.



Nitrogen and oxygen are both diatomic molecules; the table below lists some other diatomic molecules.

Diatomic Elements

Name	Chemical formula	Electron dot structure	Properties and uses
Fluorine	F_2		Greenish-yellow reactive toxic gas. Compounds of fluorine, a halogen, are added to drinking water and toothpaste to promote healthy teeth.
Bromine	Br_2		Dense red-brown liquid with pungent odor. Compounds of bromine, a halogen, are used in the preparation of photographic emulsions.
Hydrogen	H_2	H—H	Colorless, odorless, tasteless gas. Hydrogen is the lightest known element.

The “octet” in the octet rule refers to eight of what?

The “octet” in the octet rule refers to eight of what?

Each of the atoms joined by a covalent bond usually acquires eight electrons in its valence shell. Most noble gases have eight valence electrons.

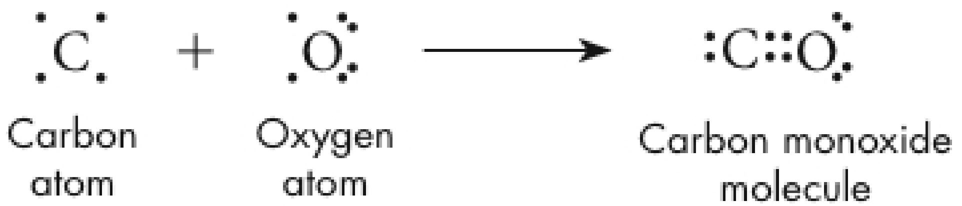
Coordinate Covalent Bonds

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.

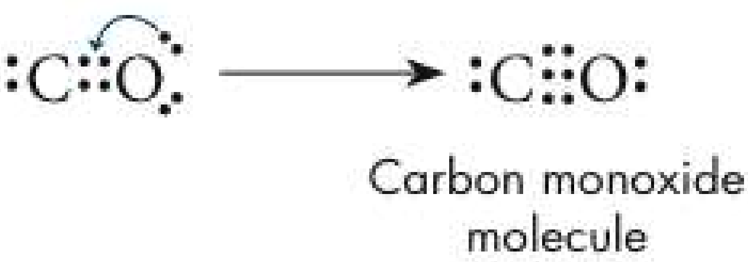
- It is possible for both carbon (which needs to gain four electrons) and oxygen (which needs to gain two electrons) to achieve noble-gas electron configurations by a type of bonding called coordinate covalent bonding.

Look at the double covalent bond between carbon and oxygen.



With the double bond in place, the oxygen had a stable electron 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.



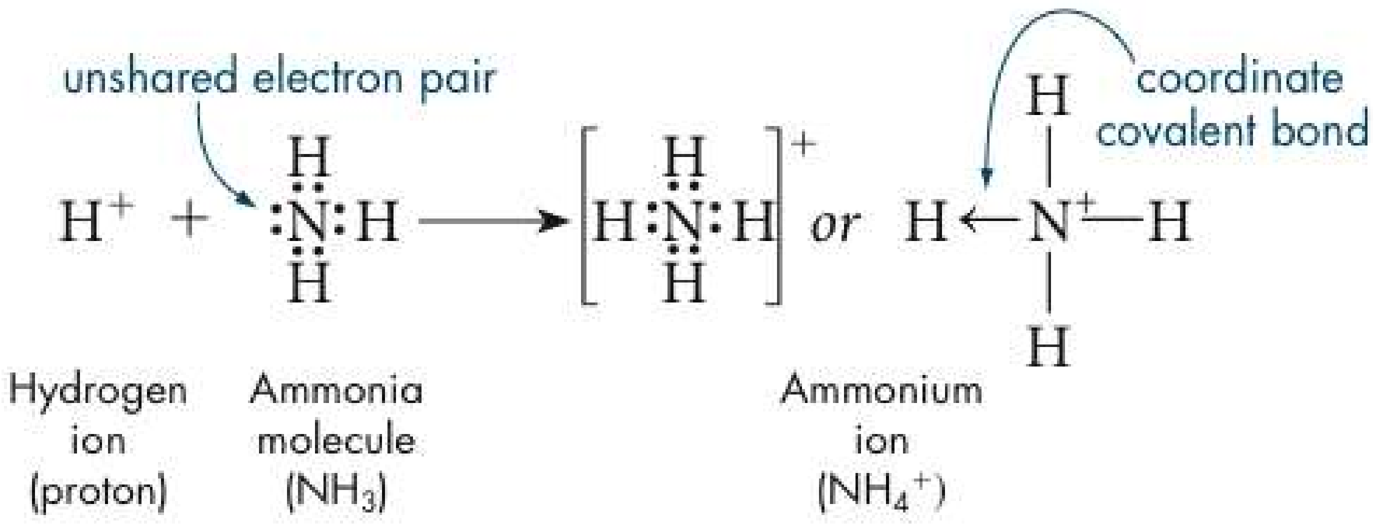
- A covalent bond in which one atom contributes both bonding electrons is a **coordinate covalent bond**.

In a coordinate covalent bond, the shared electron pair comes from one of the bonding atoms.

- 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 polyatomic cations and anions contain covalent and coordinate covalent bonds.
- Therefore, compounds containing polyatomic ions include both ionic and covalent bonding.

Drawing the Electron Dot Structure of a Polyatomic Ion

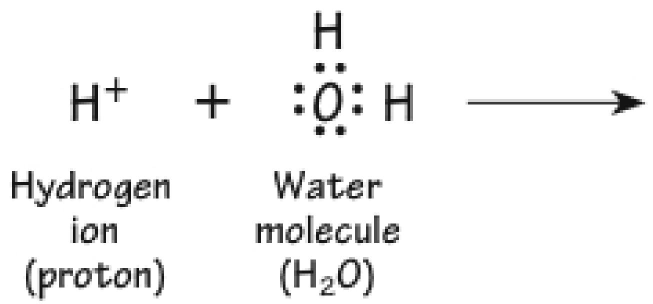
The H_3O^+ ion forms when a hydrogen ion is attracted to an unshared electron pair in a water molecule. Draw the electron dot structure of the hydronium ion.

1 Analyze **Identify the relevant concepts.**

Each atom must share electrons to satisfy the octet rule.

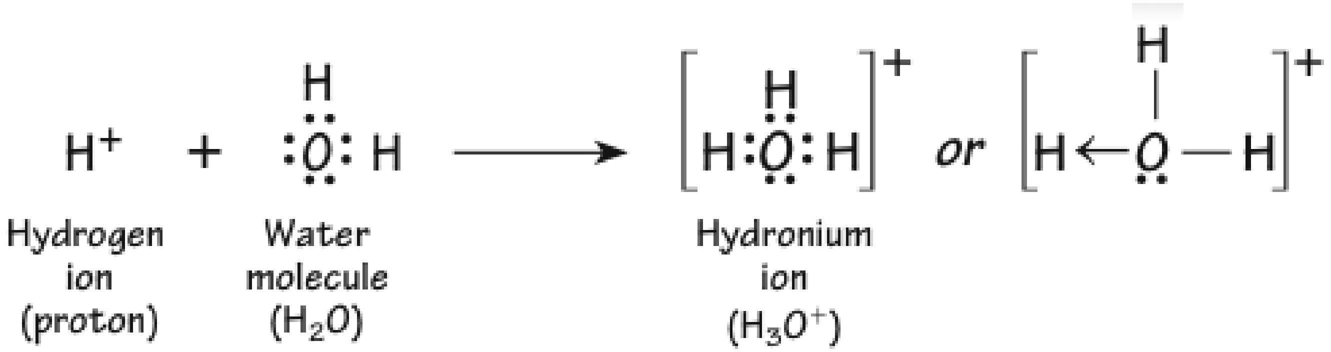
2 Solve Apply the concepts to the problem.

Draw the electron dot structure of the water molecule and the hydrogen ion. Then draw the electron dot structure of the hydronium ion.



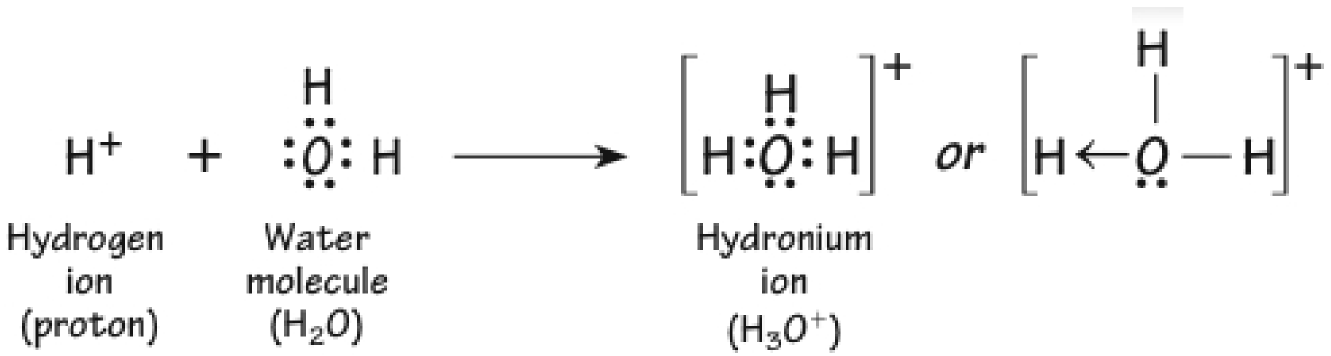
2 Solve Apply the concepts to the problem.

The oxygen must share a pair of electrons with the added hydrogen ion to form a coordinate covalent bond.



2 Solve Apply the concepts to the problem.

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



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+.

Do all atoms joined in covalent bonds donate electrons to the bond?

Do all atoms joined in covalent bonds donate electrons to the bond?

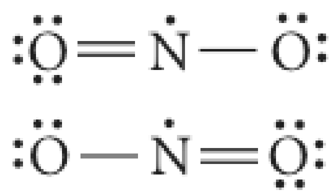
No. In coordinate covalent bonds, the shared electron pair comes from one of the bonding atoms.

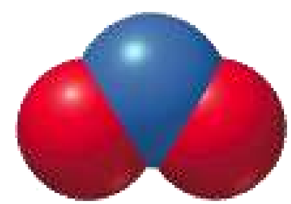
Exceptions to the Octet Rule

What are some exceptions to 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 less, or more, than a complete octet of valence electrons.

- Two plausible electron dot structures can be drawn for the NO_2 molecule, which has a total of seventeen valence electrons.

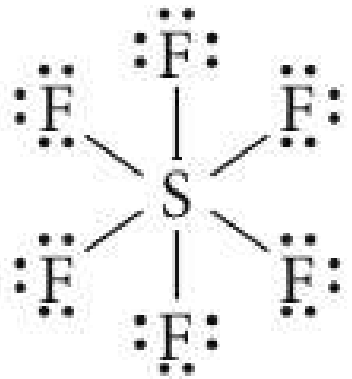




Nitrogen dioxide molecule

- 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.

- Some molecules with an even number of valence electrons, such as some compounds of boron, also fail to follow the octet rule.
- A few atoms, especially phosphorus and sulfur, expand the octet to ten or twelve electrons.
  - Sulfur hexafluoride (SF6) is an example.



Are molecules that do not obey the octet rule necessarily unstable?

Are molecules that do not obey the octet rule necessarily unstable?

No. There are molecules like NO_2 *that do not obey the octet rule, but that are stable, naturally occurring molecules.*

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 (about 2 grams) of H_2.
- The energy required to break the bond between two covalently bonded atoms is known as 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.

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.
- Strong carbon–carbon bonds help explain the stability of carbon compounds.
  - They are unreactive partly because the dissociation energy is high.

True or False: A strong covalent bond has a low bond dissociation energy.

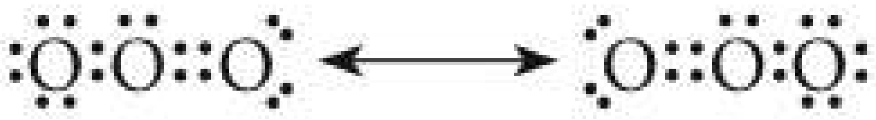
True or False: A strong covalent bond has a low bond dissociation energy.

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

Resonance

How are resonance structures used?

- 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.

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 the two bonds in ozone are the same length.
- 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.

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.

Do resonance structures accurately represent actual bonding?

Do resonance structures accurately represent actual bonding?

No. Resonance structures are a way to envision the bonding in certain molecules. The actual bonding is a hybrid, or mixture, of the extremes represented by the resonance forms.

- In covalent bonds, electron sharing occurs so that atoms attain the configurations of noble gases.
- In a coordinate covalent bond, the shared electron pair comes from a single atom.
- The octet rule is not satisfied in molecules with an odd number of electrons and in molecules in which an atom has less, or more, than a complete octet of valence electrons.

- A large bond dissociation energy corresponds to a strong covalent bond.
- In ozone, the bonding of oxygen atoms is a hybrid of the extremes represented by the resonance forms.

- **single covalent bond:** a bond formed when two atoms share a pair of electrons
- **structural formula:** a chemical formula that shows the arrangement of atoms in a molecule or a polyatomic ion; each dash between a pair of atoms indicates a pair of shared electrons
- **unshared pair:** a pair of valence electrons that is not shared between atoms

- **double covalent bond:** a bond in which two atoms share two pairs of electrons
- **triple covalent bond:** a covalent bond in which three pairs of electrons are shared by two atoms
- **coordinate covalent bond:** a covalent bond in which one atom contributes both bonding electrons

- **polyatomic ion:** a tightly bound group of atoms that behaves as a unit and has a positive or negative charge

- **bond dissociation energy:** the energy required to break the bond between two covalently bonded atoms; this value is usually expressed in kJ per mol of substance

- **resonance structure:** one of the two or more equally valid electron dot structures of a molecule or polyatomic ion

END OF 8.2