

# Bonding

## Lewis (Electron Dot) Diagrams

### Lesson Vocabulary

- **octet rule:** States that elements tend to form compounds in ways that give each atom eight valence electrons.
- **Lewis electron dot structure:** A diagram for a chemical substance in which each element is represented by its symbol and each valence electron is represented by a single dot.
- **isoelectronic:** Two atoms or ions with the same number of electrons.
- **cation:** A positively charged ion.
- **anion:** A negatively charged ion.

### Introduction

As we studied in our chapter on the periodic table, we saw that elements share a number of important properties with other elements found in the same group. The chemical behavior of a given element is largely dictated by the configuration of its valence electrons. Many elements have a tendency to gain or lose electrons in order to achieve a more stable configuration. When a neutral atom gains or loses electrons, it becomes an ion. In this lesson, we will look at ways to predict what type of ion a given element is likely to form.

### Octet Rule

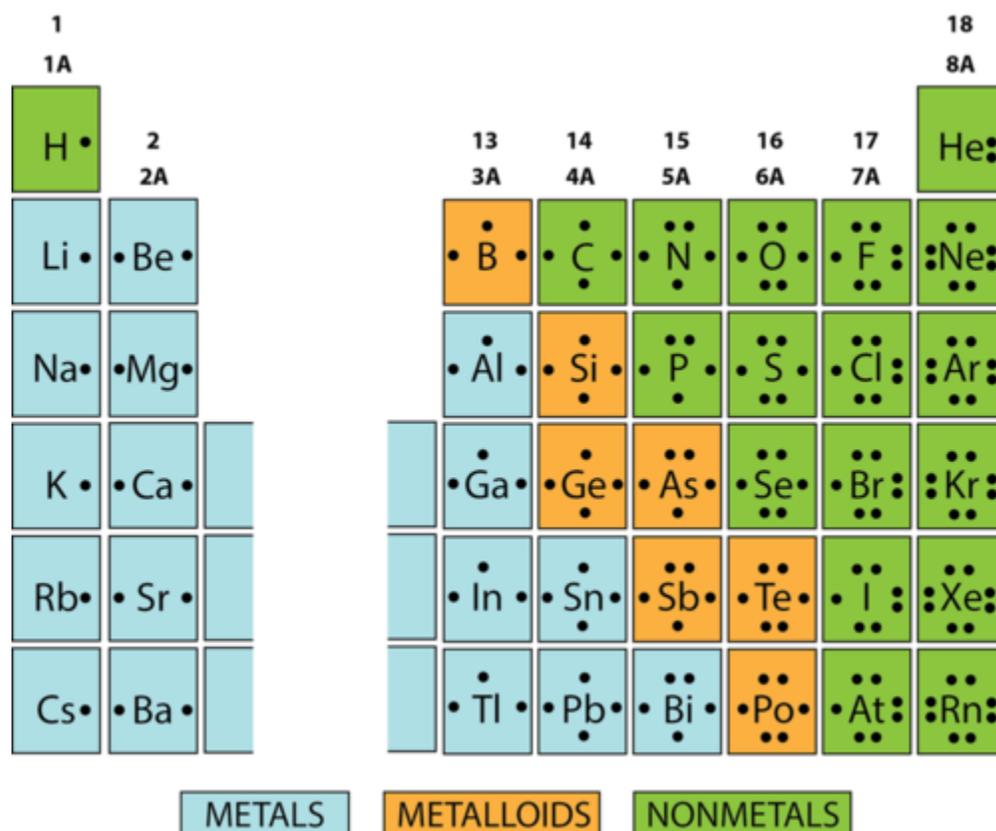
The noble gases are unreactive because of their electron configurations. American chemist Gilbert Lewis (1875-1946) used this observation to explain the types of ions and molecules that are formed by other elements. He called his explanation the octet rule. The **octet rule** states that elements tend to form compounds in ways that give each atom eight valence electrons. An exception to this rule is the elements in the first period, which are particularly stable when they have two valence electrons. A broader statement that encompasses both the octet rule and this exception is that atoms react in order to achieve the same valence electron configuration as that of the nearest noble gas. Most noble gases have eight valence electrons, but because the first principal energy level can hold a maximum of two electrons, the first noble gas (helium) needs only two valence electrons to fill its outermost energy level. As a result, the nearby elements hydrogen, lithium, and beryllium tend to form stable compounds by achieving a total of two valence electrons.

There are two ways in which atoms can satisfy the octet rule. One way is by sharing their valence electrons with other atoms. The second way is by transferring valence electrons from one atom to another. Atoms of metallic elements tend to lose all of their valence electrons, which leaves them with an octet from the next lowest principal energy level. Atoms of nonmetallic elements tend to gain electrons in order to fill their outermost principal energy level with an octet.

### Electron Dot Diagrams

A common way to keep track of valence electrons is with **Lewis electron dot structures**. In an electron dot structure, each atom is represented by its chemical symbol, and each valence electron is represented by a single dot. Note that only valence electrons are shown explicitly in these diagrams. For the main group elements, the number of valence electrons for a neutral atom can be determined by looking at which group the element belongs to. In the s block, Group 1 elements have one valence electron, while Group 2 elements have two valence electrons. In the p block, the number of valence electrons is equal to the group number minus ten. Group 13 elements have three valence electrons, Group 14

elements have four, and so on. The noble gases in Group 18 have eight valence electrons, and the full outer s and p sublevels are what give these elements their special stability. Representative dot diagrams are shown in the **Figure** below:

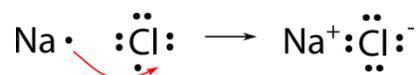


The image shown here displays dots circling each elemental symbol. Elements will typically gain, lose or share electrons to achieve an octet. Only one group of elements (the noble gases) has a complete octet as neutral atoms.

### Ionic Compounds and Their Electron Dot Diagrams

Metals will typically lose electrons to achieve stability, while non-metals typically gain electrons to achieve stability. Two atoms or ions with the same number of electrons are referred to as **isoelectronic**.

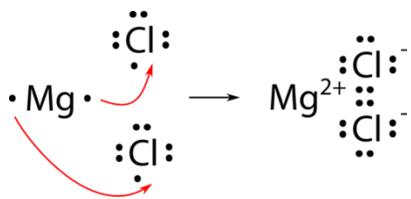
We will use sodium chloride as an example to demonstrate the nature of the ionic bond and how it forms. As you know, sodium is a metal, and it can lose its one valence electron to become a cation. Chlorine is a nonmetal, and it gains one electron to become an anion. By forming ions in this way, both atoms achieve a noble gas electron configuration. However, electrons cannot be simply "lost" to nowhere in particular, nor can they be "gained" without a source. In the case of sodium chloride, a single electron is transferred from the sodium atom to the chlorine atom, as shown below.



The ionic bond is the attraction between the  $\text{Na}^+$  ion and the  $\text{Cl}^-$  ion. It is conventional to show the cation without any dots around the symbol, since the energy level that originally contained the valence electron(s) is now empty. The anion is now shown with a complete octet of electrons.

For a compound such as magnesium chloride, the two elements are not combined in a 1:1 ratio. Because magnesium has two valence electrons, it needs to lose both to achieve a noble gas configuration. Since chlorine only has room for

one more electron in its valence level, two chlorine atoms must be present as electron acceptors in order to form each  $\text{Mg}^{2+}$  ion.



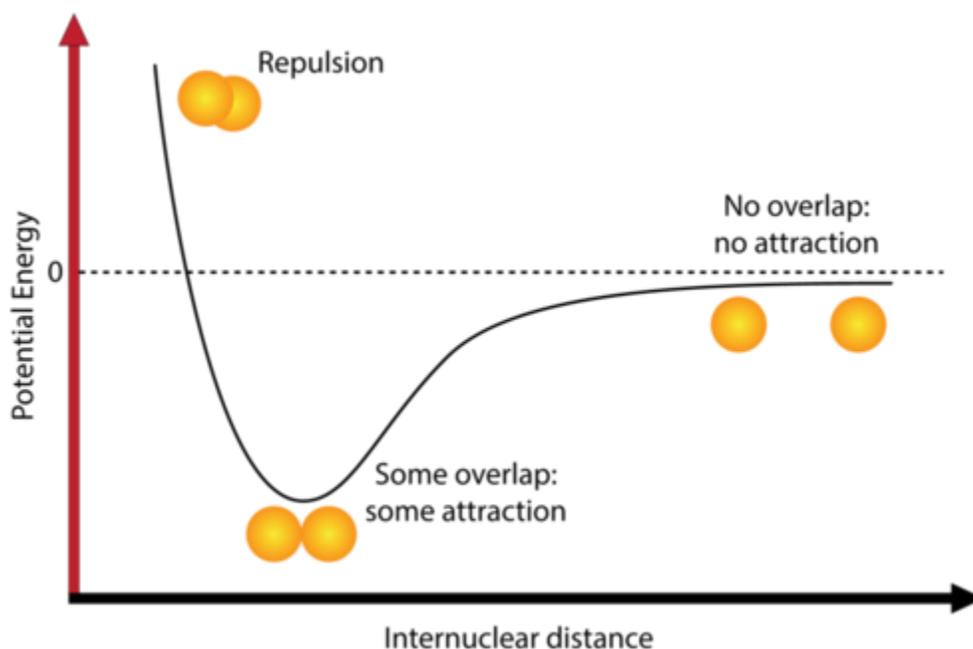
The final formula for magnesium chloride is  $\text{MgCl}_2$ .

## The Covalent Bond

### Energy and Bond Formation

Molecular compounds are those that take the form of individual molecules. A molecule is generally comprised of two or more nonmetal atoms. Familiar examples include water ( $\text{H}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), and ammonia ( $\text{NH}_3$ ). Recall that a molecular formula shows the quantity of each atom that occurs in a single molecule of that compound. One molecule of water contains two hydrogen atoms and one oxygen atom. Hydrogen ( $\text{H}_2$ ) is an example of an element that exists naturally as a diatomic molecule. A **diatomic molecule** is a molecule that contains exactly two atoms.

Nature favors chemical bonding because most atoms attain a lower potential energy when they are bonded to other atoms than when they are isolated. Consider two hydrogen atoms that are separated by a distance large enough to prevent any interaction between them. At this distance, the potential energy of the system is said to be equal to zero (**Figure** below).



The graph shows how the potential energy of two hydrogen atoms changes as a function of their separation distance. The potential energy is zero when they are completely isolated from one another. The energy reaches its minimum at the ideal bond distance and increases rapidly when the atoms come closer because of nuclear repulsion.

As the atoms approach one another, their electron clouds gradually begin to overlap, giving rise to several new interactions. For example, the single electrons possessed by each hydrogen atom begin to repel each other, causing the

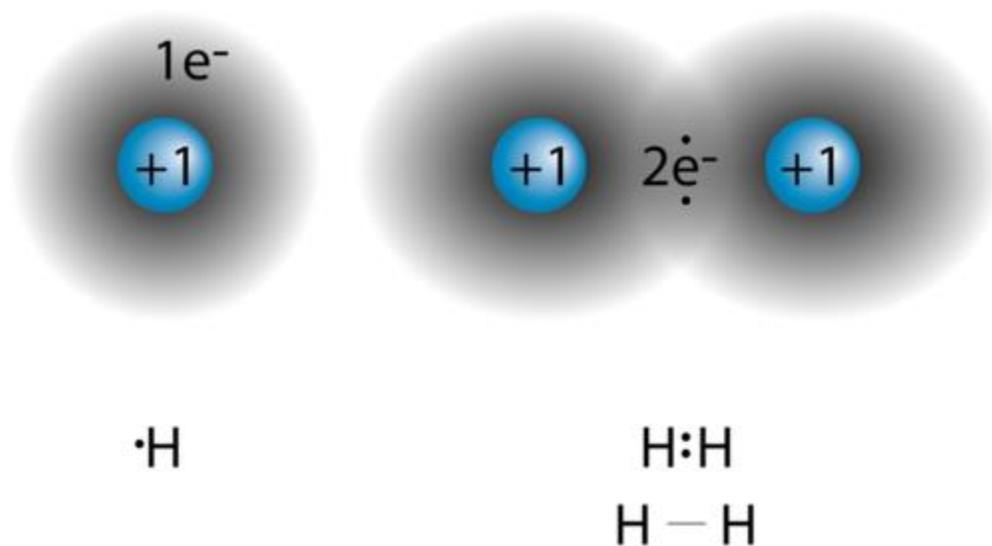
potential energy of the system to increase. However, attractive forces also begin to develop between each electron and the positively charged nucleus of the other atom, causing a decrease in potential energy.

As the atoms first begin to interact, the attractive force is stronger than the repulsive force, so the potential energy of the system decreases, as pictured above (**Figure** above). Remember, a lower potential energy is indicative of a more stable system. As the two hydrogen atoms move closer and closer together, the potential energy continues to decrease. Eventually, a position is reached where the potential energy is at its lowest possible point. If the hydrogen atoms move any closer together, the repulsive force between the two positively charged nuclei (a third type of interaction) begins to dominate. When like charges are forced this close together, the resulting repulsive force is very strong, as can be seen by the sharp rise in energy at the far left of the diagram.

The point at which the potential energy reaches its minimum represents the ideal distance between hydrogen atoms for a stable chemical bond to occur. This type of chemical bond is called a covalent bond. A **covalent bond** is a bond in which two atoms share one or more pairs of electrons. The single electrons from each of the two hydrogen atoms are shared when the atoms come together to form a hydrogen molecule ( $H_2$ ).

## Lewis Electron-Dot Structures

In a previous chapter, you learned that the valence electrons of an atom can be shown in a simple way with an electron dot diagram. A hydrogen atom is shown as  $H\bullet$  because of its one valence electron. *The structures of molecules that are held together by covalent bonds can be diagrammed by Lewis electron-dot structures.* The hydrogen molecule is pictured below (**Figure** below).



On the left is a single hydrogen atom with one electron. On the right is an  $H_2$  molecule showing the electron cloud overlap. The shared pair of electrons in the covalent bond can be shown in a Lewis structure by either a pair of dots or a dash.

The shared pair of electrons is shown as two dots in between the two H symbols ( $H:H$ ). This is called a **single covalent bond**, when *two atoms are joined by the sharing of one pair of electrons*. The single covalent bond can also be shown by a dash in between the two symbols ( $H-H$ ). A **structural formula** is a formula that shows the arrangement of atoms in a molecule and represents covalent bonds between atoms by dashes.

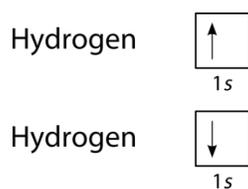
## The Octet Rule and Covalent Bonds

When ions form, they conform to the octet rule by either losing or gaining electrons in order to achieve the electron configuration of the nearest noble gas. Similarly, nonmetal atoms share electrons by forming covalent bonds in such a way that each of the atoms involved in the bond can attain a noble-gas electron configuration. The shared electrons are “counted” for each of the atoms involved in the sharing. For hydrogen ( $H_2$ ), the shared pair of electrons means that each of the atoms is able to attain the electron configuration of the noble gas, helium, which has two electrons.

For atoms other than hydrogen, the sharing of electrons will usually provide each of the atoms with eight valence electrons.

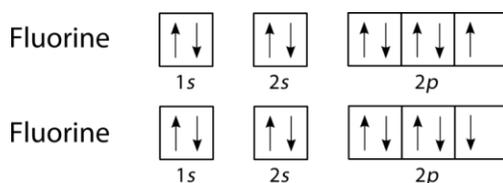
### Single Covalent Bonds

A covalent bond forms when two singly occupied orbitals overlap with each other. For the hydrogen molecule, this can be shown as:

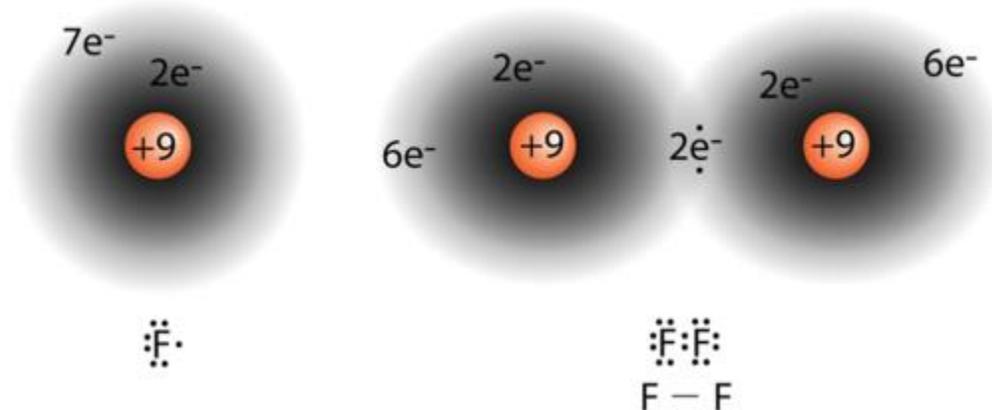


The shared electrons in the complete  $H_2$  molecule must have opposite spins, so they are also shown with opposite spins in the atomic 1s orbitals.

The halogens also form single covalent bonds to produce diatomic molecules. An atom of any halogen, such as fluorine, has seven valence electrons. Fluorine's unpaired electron is located in the 2p orbital.



Unpaired electrons in 2p orbitals from two adjacent fluorine atoms combine to form a covalent bond (**Figure** below).



On the left is a fluorine atom with seven valence electrons, and on the right is the  $F_2$  molecule. The shared electrons that form the single covalent bond are from the 2p sublevel.

The diatomic fluorine molecule ( $F_2$ ) contains a single shared pair of electrons. Each F atom also has three pairs of electrons that are not shared with the other atom. A **lone pair** is a pair of electrons in a Lewis electron-dot structure that

is not shared between atoms. Each F atom has three lone pairs. When combined with the two electrons in the covalent bond, each F atom effectively has eight valence electrons, so both atoms follow the octet rule.

### Sample Problem 9.1: Lewis Electron Dot Structures

Draw the Lewis electron dot structure for water.

*Step 1: List the known quantities and plan the problem.*

#### Known

- molecular formula of water =  $\text{H}_2\text{O}$
- 1 O atom = 6 valence electrons
- 2 H atoms =  $2 \times 1 = 2$  valence electrons
- total number of valence electrons = 8

Use the periodic table to determine the number of valence electrons for each atom and the total number of valence electrons in the entire molecule. Arrange the atoms and distribute the electrons so that each atom follows the octet rule. The oxygen atom will have 8 electrons, while the hydrogen atoms will each have 2.

*Step 2: Solve.*

The electron dot diagram for each atom is:



Each hydrogen atom will use its single electron to form a covalent bond with one of the unpaired electrons on the oxygen atom. The resulting Lewis electron dot structure is:



*Step 3: Think about your result.*

The oxygen atom follows the octet rule with two pairs of bonding electrons and two lone pairs. Each hydrogen atom follows the octet rule with one bonding pair of electrons.

#### **Practice Problems**

1. Draw the Lewis electron dot structure for each atom.
  - a.  $\text{NH}_3$
  - b.  $\text{CH}_4$
  - c.  $\text{CH}_2\text{Cl}_2$

## Multiple Covalent Bonds

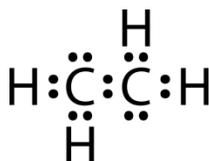
Some molecules are not able to satisfy the octet rule by making only single covalent bonds between the atoms. Consider the compound ethene, which has a molecular formula of  $C_2H_4$ . The carbon atoms are bonded together, and each carbon is also bonded to two hydrogen atoms.

two C atoms =  $2 \times 4 = 8$  valence electrons

four H atoms =  $4 \times 1 = 4$  valence electrons

total of 12 valence electrons in the molecule

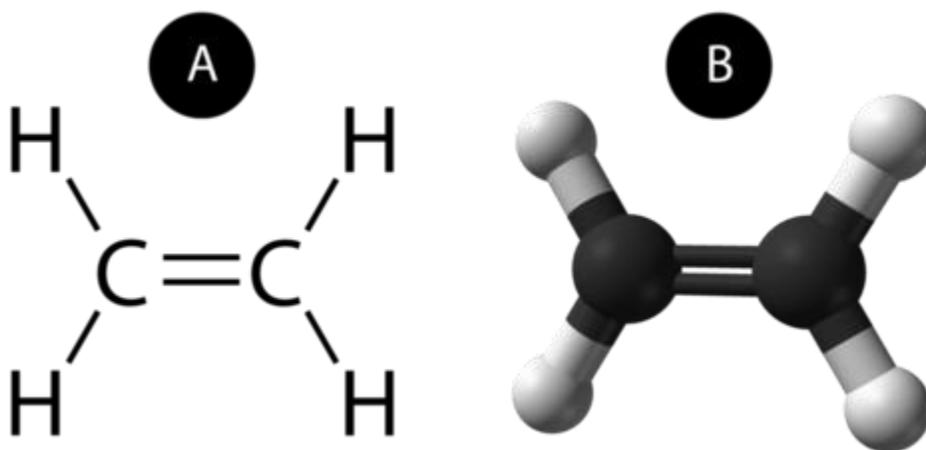
If the Lewis electron dot structure were drawn with a single bond between the carbon atoms and lone pairs were then added until all atoms satisfied the octet rule, it would look like this:



However, this Lewis structure is incorrect because it contains 14 valence electrons, and the atoms in this molecule only have a total of 12 valence electrons available. The Lewis structure can be corrected by eliminating one lone pair and moving another lone pair to a bonding position. Now, the two carbon atoms share two pairs of electrons instead of just one.



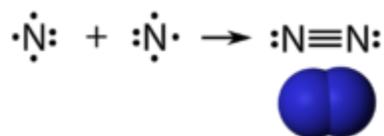
A **double covalent bond** is a covalent bond formed by atoms that share two pairs of electrons. The double covalent bond that occurs between the two carbon atoms in ethene can also be represented by a structural formula or a molecular model, as pictured below (**Figure** below).



(A) The structural model for  $C_2H_4$  consists of a double covalent bond between the two carbon atoms and single bonds to each of the hydrogen atoms. (B) Molecular model of  $C_2H_4$ .

Similarly, a **triple covalent bond** is a covalent bond formed by atoms that share three pairs of electrons. In its pure form, the element nitrogen exists as a diatomic gas. The majority of Earth's atmosphere is made up of  $N_2$  molecules (**Figure** below). A nitrogen atom has five valence electrons, which can be shown as one pair and three unpaired

electrons. When combining with another nitrogen atom to form a diatomic molecule, the three single electrons on each atom combine to form three shared pairs of electrons.



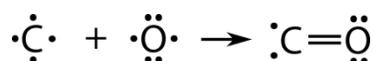
Each nitrogen atom has one lone pair of electrons and six electrons that are shared with the other atom, so each atom obeys the octet rule.

### Practice Problems

2. Draw Lewis electron dot structures for the molecules below, each of which contains one or more multiple covalent bonds.
  - a.  $\text{CO}_2$
  - b.  $\text{C}_2\text{H}_2$

### Coordinate Covalent Bonds

For all of the covalent bonds that we have looked at so far, each of the atoms involved in the bond has contributed one electron to each shared pair. However, there is an alternate type of covalent bond in which one of the atoms provides both of the electrons in a shared pair. Carbon monoxide,  $\text{CO}$ , is a toxic gas that is released as a by-product during the burning of fossil fuels. The bonding between the C atom and the O atom can be thought of as follows:



At this point, a double bond has formed between the two atoms, with each atom providing one of the electrons to each bond. The oxygen atom now has a stable octet of electrons, but the carbon atom only has six electrons and is unstable. This situation is resolved if the oxygen atom contributes one of its lone pairs in order to make a third bond with the carbon atom.

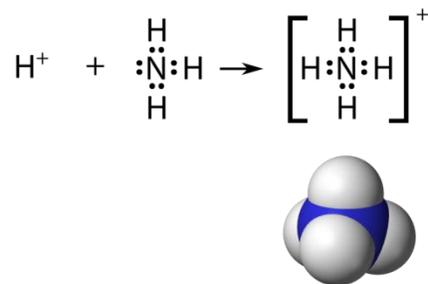


The carbon monoxide molecule is correctly represented by a triple covalent bond between the carbon and oxygen atoms. One of the bonds is considered a **coordinate covalent bond**, which is a covalent bond in which one of the atoms contributes both of the electrons in the shared pair.

Once formed, a coordinate covalent bond is the same as any other covalent bond. The two "conventional" bonds in the  $\text{CO}$  molecule are not stronger or different in any other way from the coordinate covalent bond.

### Polyatomic Ions

Recall that a polyatomic ion is a group of covalently bonded atoms that carries an overall electrical charge. For example, the ammonium ion ( $\text{NH}_4^+$ ) is formed when a hydrogen ion ( $\text{H}^+$ ) attaches to the lone pair of an ammonia ( $\text{NH}_3$ ) molecule via a coordinate covalent bond.



When drawing the Lewis structure of a polyatomic ion, the charge of the ion is reflected in the total number of valence electrons in the structure. In the case of the ammonium ion:

1 N atom = 5 valence electrons

4 H atoms =  $4 \times 1 = 4$  valence electrons

subtract 1 electron to give the ion an overall charge of 1+

total of 8 valence electrons in the ion

It is customary to put the Lewis structure of a polyatomic ion into a large set of brackets, with the charge of the ion as a superscript outside the brackets.

### Sample Problem 9.2: Lewis Electron Dot Structure of a Polyatomic Ion

Draw the Lewis electron dot structure for the sulfate ion.

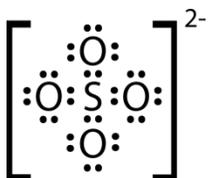
*Step 1: List the known quantities and plan the problem.*

#### Known

- molecular formula of the sulfate ion =  $\text{SO}_4^{2-}$
- 1 S atom = 6 valence electrons
- 4 O atoms =  $4 \times 6 = 24$  valence electrons
- add 2 electrons to give the ion an overall charge of 2-
- total of 32 valence electrons

The less electronegative sulfur atom is the central atom in the structure. Place the oxygen atoms around the sulfur atom, each connected to the central atom by a single covalent bond. Distribute lone pairs to each oxygen atom in order to satisfy the octet rule. Count the total number of electrons. If there are too many electrons in the structure, make multiple bonds between the S and O.

*Step 2: Solve.*



Step 3: Think about your result.

The Lewis structure for the sulfate ion consists of a central sulfur atom with four single bonds to oxygen atoms. This yields the expected total of 32 electrons. Since the sulfur atom started with six valence electrons, two of the S-O bonds are coordinate covalent.

### Practice Problems

3. Draw the Lewis structure for the chlorate ion,  $\text{ClO}_3^-$ . Chlorine is the central atom.

### Resonance

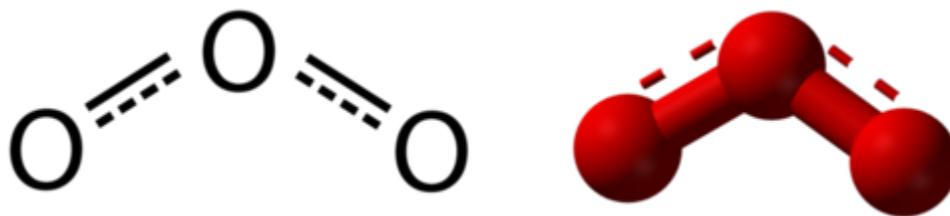
There are some cases in which more than one viable Lewis structure can be drawn for a molecule. An example is the ozone ( $\text{O}_3$ ) molecule. By distributing a total of 18 valence electrons in a way that allows each atom to satisfy the octet rule, both of the following structures can be drawn.



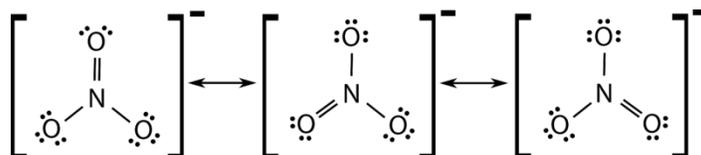
The structure on the left can be converted to the structure on the right by shifting electrons without altering the positions of the atoms.

It was once thought that the structure of a molecule, such as  $\text{O}_3$ , consisted of one single bond and one double bond that shifted rapidly back and forth, as shown above. However, further studies showed that the two bonds are identical. Additionally, the properties of each bond are in between those expected for a single bond and a double bond between two oxygen atoms. For example, a double covalent bond between two given atoms is typically stronger and shorter than a single covalent bond between those two atoms. Studies have shown that the two identical bonds in  $\text{O}_3$  are stronger and shorter than a typical O-O single bond but longer and weaker than an O-O double bond.

**Resonance** is the use of two or more Lewis structures to represent the covalent bonding in a molecule. Each of the valid structures is referred to as a resonance structure. It is now understood that the true structure of a molecule that displays resonance is an average or a hybrid of all the resonance structures. In the case of the  $\text{O}_3$  molecule, each of the covalent bonds between O atoms is best thought of as being “one and a half” bonds, as opposed to either a pure single bond or a pure double bond. This “half-bond” (**Figure** below) can be shown as a dotted line in both the Lewis structure and the molecular model.



Many polyatomic ions also display resonance. In some cases, the true structure may be an average of three valid resonance structures, as in the case of the nitrate ion,  $\text{NO}_3^-$ .



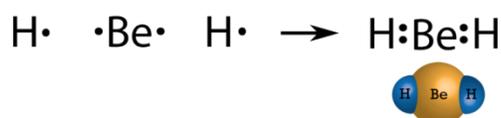
The bond lengths between the central N atom and each O atom are identical, and each bond can be approximated as a "one and one-third" bond.

### Exceptions to the Octet Rule

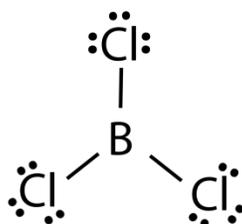
It is said that all rules are made to be broken, and this saying certainly applies to the octet rule. Exceptions to the octet rule generally fall into one of three categories: (1) an incomplete octet, (2) odd-electron molecules, and (3) an expanded octet.

#### Incomplete Octet

In some compounds, the number of electrons surrounding the central atom in a stable molecule is fewer than eight. Beryllium is an alkaline earth metal, so you might expect it to form ionic bonds. However, due to its small size and relatively high ionization energy (compared to other metals), beryllium forms primarily molecular compounds when combined with many other elements. Since beryllium only has two valence electrons, it does not typically attain a full octet by sharing electrons. The Lewis structure of gaseous beryllium hydride ( $\text{BeH}_2$ ) consists of two single covalent bonds between Be and two H atoms.

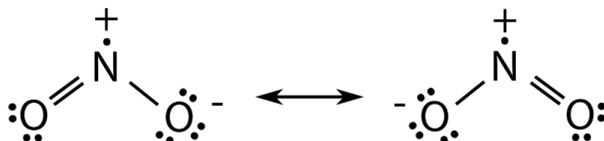


Boron and aluminum, with three valence electrons, also tend to have an incomplete octet when they form covalent compounds. The central boron atom in boron trichloride ( $\text{BCl}_3$ ) has six valence electrons as shown below.



#### Odd-Electron Molecules

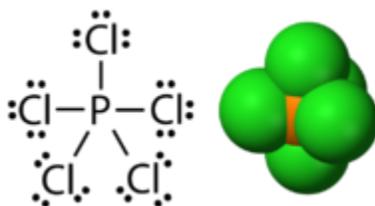
There are a number of molecules whose total number of valence electrons is an odd number. It is not possible for all of the atoms in such a molecule to satisfy the octet rule. An example is nitrogen dioxide ( $\text{NO}_2$ ). Each oxygen atom contributes six valence electrons and the nitrogen atom contributes five, for a total of 17. Possible Lewis structures for  $\text{NO}_2$  are:



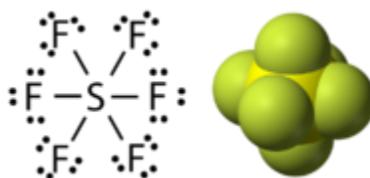
#### Expanded Octets

Atoms of elements in the second period cannot have more than eight valence electrons around the central atom. However, elements of the third period and beyond are capable of exceeding the octet rule. Starting with the third period, the  $d$  sublevel becomes available, so it is possible to use these orbitals in bonding, resulting in more than eight electrons around the central atom.

Phosphorus and sulfur are two elements that react with halogens to make stable compounds in which the central atom has an expanded octet. In phosphorus pentachloride (**Figure** below), the central phosphorus atom makes five single bonds to chlorine atoms, so it is surrounded by a total of 10 valence electrons. In sulfur hexafluoride (**Figure** below), the central sulfur atom has 12 electrons from its six bonds to the fluorine atoms.



Phosphorus pentachloride.



Sulfur hexafluoride.

### Bond Energy

As you saw in the first section of this lesson, the formation of a chemical bond results in a decrease in potential energy. Consequently, breaking a chemical bond requires an input of energy. **Bond energy** is the energy required to break a covalent bond between two atoms. A high bond energy means that a bond is strong, and a molecule containing such a bond is likely to be more stable and less reactive than similar molecules that contain weaker bonds. Reactive compounds often contain at least one bond that has a low bond energy. Some bond energies are listed below (**Table** below).

Bond	Bond Energy (kJ/mol)
H-H	436
C-H	414
C-C	347
C=C	620
C≡C	812
F-F	157
Cl-Cl	243
Br-Br	193
I-I	151

Bond	Bond Energy (kJ/mol)
N≡N	941

The halogen elements all exist naturally as diatomic molecules ( $F_2$ ,  $Cl_2$ ,  $Br_2$ , and  $I_2$ ). However, relatively small amounts of energy are required to break these bonds, which makes them very reactive.

Comparing the bond energies for various carbon-carbon bonds, you can see that double bonds are substantially stronger than single bonds, and triple bonds are even stronger. The triple bond that exists between the nitrogen atoms in nitrogen gas ( $N_2$ ) makes it very unreactive. All plants and animals require the element nitrogen, but the direct absorption of nitrogen gas from the atmosphere does not provide the element in a readily usable form, due to its strong, unreactive triple bond. However, some species of bacteria have the ability to convert nitrogen gas into other compounds, such as ammonium and nitrate ions, which are then absorbed by plants from the soil. By eating those plants, animals can obtain nitrogen in a form that can be used by the body to manufacture other more complex molecules.

## Molecular Shapes and Bond Angles

### VSEPR Theory

The **valence shell** is the outermost occupied shell of electrons in an atom. This shell holds the valence electrons, which are the electrons that are involved in bonding and shown in a Lewis structure. The **valence-shell electron pair repulsion model**, or VSEPR model, states that *a molecule will adjust its shape so that the valence electron pairs stay as far apart from each other as possible*. This makes sense, based on the fact that negatively charged electrons repel one another. We will systematically classify molecules according to the number of bonding pairs of electrons and the number of nonbonding or lone pairs around the central atom. For the purposes of the VSEPR model, a double or triple bond is no different in terms of repulsion than a single bond. We will begin by examining molecules in which the central atom does not have any lone pairs.

### Central Atom with No Lone Pairs

In order to easily understand the types of molecules possible, we will use a simple system to identify the parts of any molecule.

A = central atom in a molecule

B = atoms surrounding the central atom

Subscripts after the B will denote the number of B atoms that are bonded to the central A atom. For example,  $AB_4$  is a molecule with a central atom surrounded by four covalently bonded atoms. Again, it does not matter if those bonds are single, double, or triple bonds.

### $AB_2$ : Beryllium Hydride ( $BeH_2$ )

Beryllium hydride consists of a central beryllium atom with two single bonds to hydrogen atoms. Recall that it violates the octet rule.

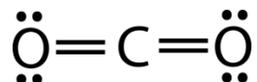


According to the requirement that electron pairs maximize their distance from one another, the two bonding pairs in the  $\text{BeH}_2$  molecules will arrange themselves on directly opposite sides of the central Be atom. The resulting geometry is a *linear* molecule, shown in a “ball and stick” model below (**Figure** below).

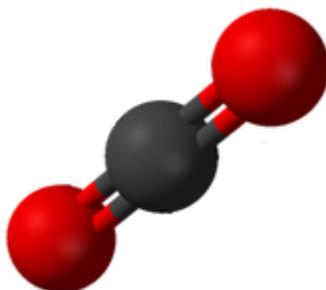


The H-Be-H bond angle is  $180^\circ$  because of its linear geometry.

Carbon dioxide is another example of a molecule which falls under the  $\text{AB}_2$  category. Its Lewis structure consists of double bonds between the central carbon atom and each oxygen atom.

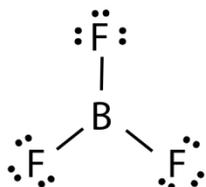


The repulsion between the two groups of four electrons (two pairs) is no different than the repulsion between the two groups of two electrons (one pair) in the  $\text{BeH}_2$  molecule. Carbon dioxide is also linear.

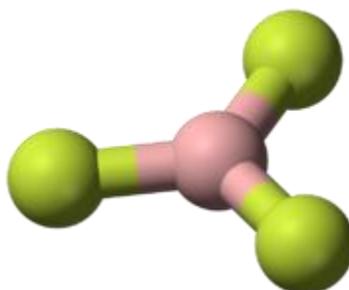


### **$\text{AB}_3$ : Boron Trifluoride ( $\text{BF}_3$ )**

Boron trifluoride consists of a central boron atom with three single bonds to fluorine atoms. The boron atom also has an incomplete octet.

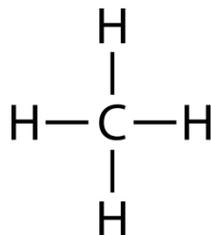


The geometry of the  $\text{BF}_3$  molecule is called *trigonal planar*. The fluorine atoms are positioned at the vertices of an equilateral triangle. The F-B-F angle is  $120^\circ$ , and all four atoms lie in the same plane.

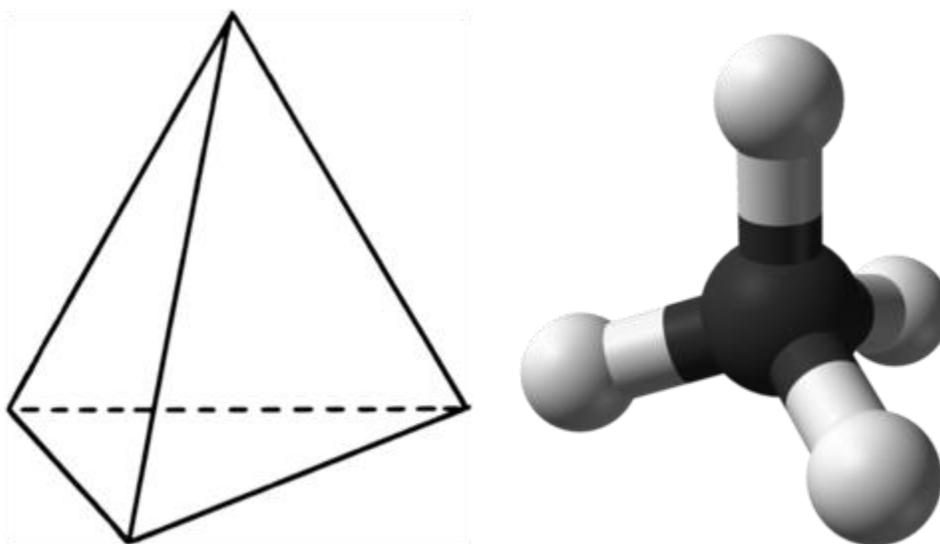


#### AB<sub>4</sub>: Methane (CH<sub>4</sub>)

Methane is an organic compound that is the primary component of natural gas. Its structure consists of a central carbon atom with four single bonds to hydrogen atoms.

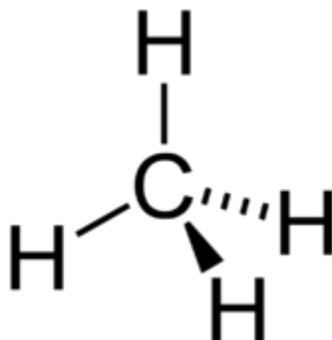


In order to maximize their distance from one another, the four groups of bonding electrons do not lie in the same plane. Instead, each of the hydrogen atoms lies at the corners of a geometrical shape called a tetrahedron. The carbon atom is at the center of the tetrahedron. Each face of a tetrahedron is an equilateral triangle.



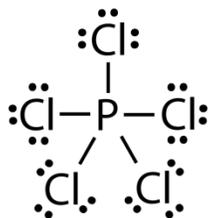
(left) Tetrahedron. (right) Ball and stick model of methane.

The molecular geometry of the methane molecule is referred to as *tetrahedral* (**Figure** above). The H-C-H bond angles are 109.5°, which is larger than the 90° that they would be if the molecule was planar. When drawing a structural formula for a molecule such as methane, it is advantageous to be able to indicate the three-dimensional character of its shape. The structural formula below (**Figure** below) is called a *perspective drawing*. The dotted line bond should be visualized as receding into the page, while the solid triangle bond should be visualized as coming out of the page.

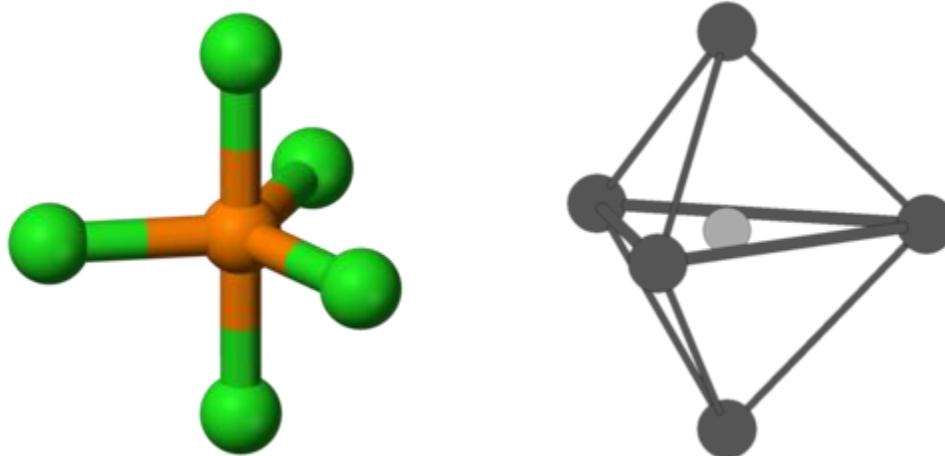


### AB<sub>5</sub>: Phosphorus Pentachloride (PCl<sub>5</sub>)

The central phosphorus atom in a molecule of phosphorus pentachloride has ten electrons surrounding it, exceeding the octet rule.



Unlike the other basic shapes, the five chlorine atoms in this arrangement are not equivalent with respect to their geometric relationship to the phosphorus atom. Three of the chlorine atoms lie in a plane, with Cl-P-Cl bond angles of 120°. This portion of the molecule is essentially the same as a trigonal planar arrangement. These chlorine atoms are referred to as the *equatorial* atoms because they are arranged around the center of the molecule. The other two chlorine atoms are oriented exactly perpendicular to the plane formed by the phosphorus atom and the equatorial chlorine atoms. These are called the *axial* chlorine atoms.

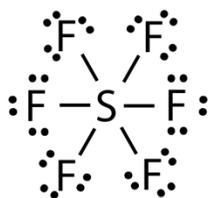


(left) Trigonal bipyramidal. (right) Ball and stick model of phosphorus pentachloride.

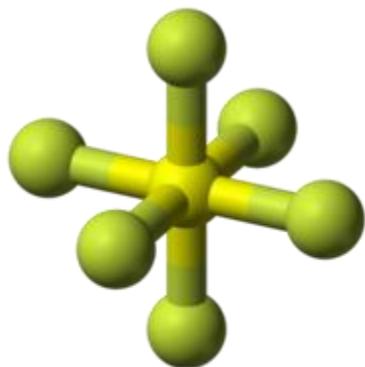
In the figure above (**Figure** above), the axial chlorine atoms form a vertical axis with the central phosphorus atom. There is a 90° angle between P-Cl<sub>axial</sub> bonds and P-Cl<sub>equatorial</sub> bonds. The molecular geometry of PCl<sub>5</sub> is called *trigonal bipyramidal*. A surface covering the molecule would take the shape of two three-sided pyramids pointing in opposite directions.

### AB<sub>6</sub>: Sulfur Hexafluoride (SF<sub>6</sub>)

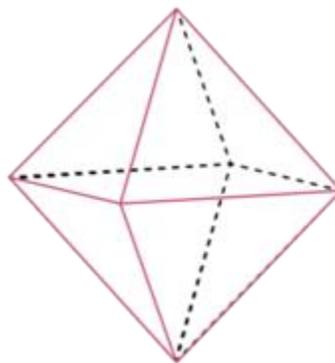
The sulfur atom in sulfur hexafluoride also exceeds the octet rule.



Unlike the trigonal bipyramidal structure, all of the fluorine atoms in SF<sub>6</sub> are equivalent. The molecular geometry is called *octahedral* (**Figure** below) because a surface covering the molecule would have eight sides. All of the F-S-F angles are 90° in an octahedral molecule, with the exception of the fluorine atoms that are directly opposite one another.



Sulfur Hexafluoride, SF<sub>6</sub>



Octahedron

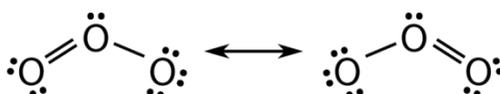
### Central Atom with One or More Lone Pairs

The molecular geometries of molecules change when the central atom has one or more lone pairs of electrons. *The total number of electron pairs, both bonding pairs and lone pairs, leads to what is called the **electron domain geometry**.*

Electron domain geometries are one of the five learned so far: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral. However, when one or more of the bonding pairs of electrons is replaced with a lone pair, the molecular geometry, or actual shape of the molecule, is altered. In keeping with the A and B symbols established in the previous section, we will use E to represent a lone pair on the central atom (A). A subscript will be used when there is more than one lone pair. Lone pairs on the surrounding atoms (B) do not affect the geometry.

### AB<sub>2</sub>E: Ozone (O<sub>3</sub>)

The Lewis structure for ozone consists of a central oxygen atom that has a double bond to one of the outer oxygen atoms and a single bond to the other.



This leaves one lone pair on the central atom, and the molecule displays resonance. Since VSEPR does not distinguish between double and single bonds, the resonance does not affect the geometry. Molecules with three electron pairs have a domain geometry that is trigonal planar. Here, the lone pair on the central atom repels the electrons in the two bonds, causing the atom to adopt a *bent* molecular geometry.



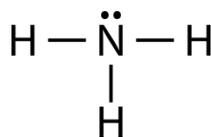
Ozone, O<sub>3</sub>.

One might expect the O-O-O bond angle to be 120°, as in a trigonal planar molecule. However, within the context of the VSEPR model, lone pairs of electrons can be considered to be slightly more repulsive than bonding pairs of electrons,

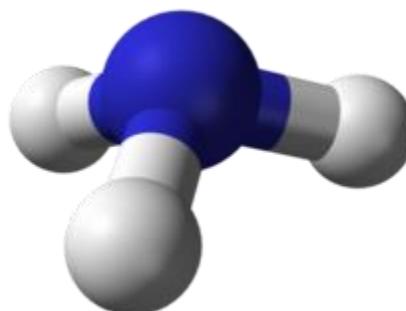
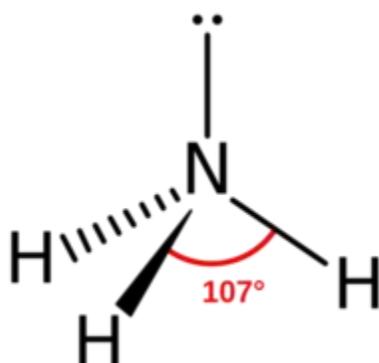
due to their closer proximity to the central atom. In other words, lone pairs take up more space. Therefore the O-O-O angle is slightly less than  $120^\circ$ .

### AB<sub>3</sub>E: Ammonia (NH<sub>3</sub>)

The ammonia molecule contains three single bonds and one lone pair on the central nitrogen atom.



The domain geometry for a molecule with four electron pairs is tetrahedral, as was seen with CH<sub>4</sub>. In the ammonia molecule, one of the electron pairs is a lone pair rather than a bonding pair. The molecular geometry of NH<sub>3</sub> is called *trigonal pyramidal* (Figure below).



Ammonia, NH<sub>3</sub>.

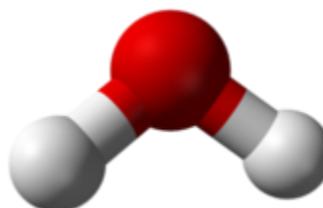
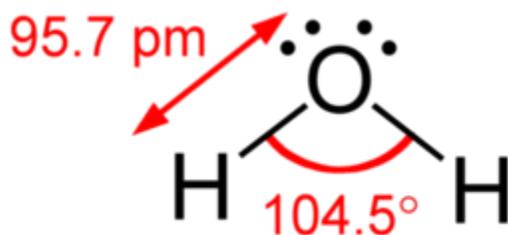
Recall that the bond angles in the tetrahedral CH<sub>4</sub> molecule are all equal to  $109.5^\circ$ . Again, the replacement of one of the bonded electron pairs with a lone pair compresses these angles slightly. The H-N-H angle is approximately  $107^\circ$ .

### AB<sub>2</sub>E<sub>2</sub>: Water (H<sub>2</sub>O)

A water molecule consists of two bonding pairs and two lone pairs.



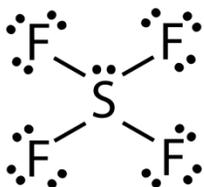
As for methane and ammonia, the domain geometry for a molecule with four electron pairs is tetrahedral. In the water molecule, two of the electron pairs are lone pairs rather than bonding pairs. The molecular geometry of the water molecule is referred to as *bent* (Figure below). The H-O-H bond angle is  $104.5^\circ$ , which is smaller than the bond angle in NH<sub>3</sub>.



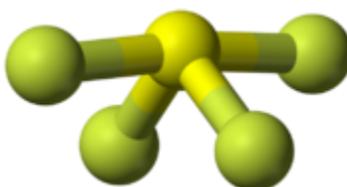
Water, H<sub>2</sub>O.

#### AB<sub>4</sub>E: Sulfur Tetrafluoride (SF<sub>4</sub>)

The Lewis structure for SF<sub>4</sub> contains four single bonds and a lone pair on the sulfur atom.



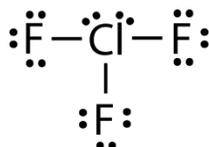
The sulfur atom (**Figure** below) has five electron groups around it, which corresponds to the trigonal bipyramidal domain geometry, as in PCl<sub>5</sub>. Recall that the trigonal bipyramidal geometry has three equatorial atoms and two axial atoms attached to the central atom. Because of the greater repulsion of a lone pair, it is one of the equatorial atoms that is replaced by a lone pair. The geometry of the molecule is called a *distorted tetrahedron* or *seesaw*.



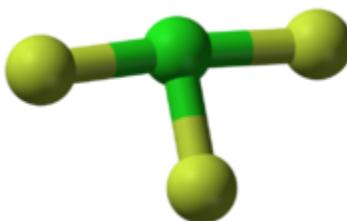
Sulfur tetrafluoride, SF<sub>4</sub>.

#### AB<sub>3</sub>E<sub>2</sub>: Chlorine Trifluoride (ClF<sub>3</sub>)

The Lewis structure of ClF<sub>3</sub> consists of three Cl-F single bonds and two lone pairs on the central chlorine atom.

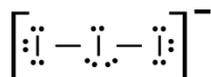


As in the case of SF<sub>4</sub>, the central atom has five electron groups and a trigonal bipyramidal domain geometry. In ClF<sub>3</sub>, both of the bonded pairs that have been replaced with lone pairs are equatorial. The resulting molecular geometry is called *T-shaped*.



#### AB<sub>2</sub>E<sub>3</sub>: Triiodide Ion (I<sub>3</sub><sup>-</sup>)

The triiodide ion (**Figure** below) consists of three iodine atoms linked together by covalent bonds. Its overall charge of 1- gives this structure 22 total valence electrons, resulting in a Lewis structure with three lone pairs on the central iodine atom.



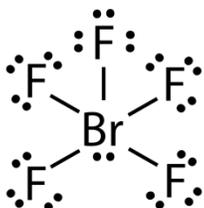
The five electron groups around the central atom give it a trigonal bipyramidal domain geometry, and all three equatorial atoms have been replaced by lone pairs. The result is a linear ion—the central atom and the two axial atoms.



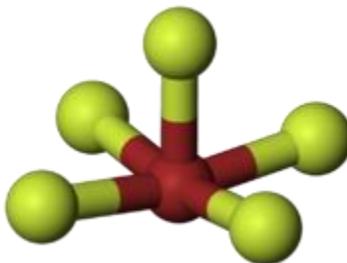
Triiodide ion,  $\text{I}_3^-$ .

#### **AB<sub>5</sub>E: Bromine Pentafluoride (BrF<sub>5</sub>)**

The bromine pentafluoride molecule (**Figure** below) has a central bromine atom, five single bonds to fluorine atoms, and one lone pair.



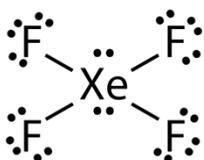
The six groups of electrons around the central atom give it an octahedral domain geometry. Since all of the peripheral atoms in an octahedral molecule are equivalent, any one of them could equally be replaced by the lone pair. The resulting geometry is called *square pyramidal*. A surface covering a square pyramidal molecule is a four sided pyramid on a flat base.



Bromine pentafluoride,  $\text{BrF}_5$ .

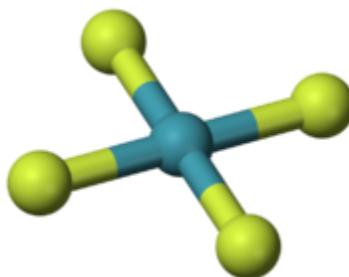
#### **AB<sub>4</sub>E<sub>2</sub>: Xenon Tetrafluoride (XeF<sub>4</sub>)**

Xenon tetrafluoride (**Figure** below) has a Lewis structure consisting of four single bonds and two lone pairs on the central xenon atom.



The six groups of electrons give it an octahedral domain geometry, but two of the atoms are replaced by two lone pairs. In order to maximize the space available to each of the lone pairs, they occupy positions that are directly opposite each

other. As a result, the four remaining fluorine atoms are in the same plane as the xenon atom, and all F-Xe-F angles are equal to  $90^\circ$ . This molecular geometry is called *square planar*.



Xenon tetrafluoride,  $\text{XeF}_4$ .

**Table** below summarizes the different molecular geometries.

Summary of Molecular Geometry			
Valence Shell Electron Pairs Total	Valence Shell Electron Pairs Shared	Valence Shell Electron Pairs Unshared	Molecular Geometry
1	1	0	Linear
2	2	0	Linear
2	1	1	Linear
3	3	0	Trigonal Planar
3	2	1	Angular
3	1	2	Linear
4	4	0	Tetrahedral
4	3	1	Trigonal Pyramidal
4	2	2	Angular
4	1	3	Linear
5	5	0	Trigonal Bipyramidal
5	4	1	Distorted Tetrahedron

Summary of Molecular Geometry			
Valence Shell Electron Pairs Total	Valence Shell Electron Pairs Shared	Valence Shell Electron Pairs Unshared	Molecular Geometry
5	3	2	T-shaped
5	2	3	Linear
5	1	4	Linear
6	6	0	Octahedral
6	5	1	Square Pyramidal
6	4	2	Square Planar
6	3	3	T-shaped
6	2	4	Linear
6	1	5	Linear

## Electronegativity and Polar Bonds

In an ionic bond, one or more electrons are transferred from one atom to another. In a covalent bond, one or more pairs of electrons are shared between atoms. However, bonding between atoms of different elements is rarely purely ionic or purely covalent. The true nature of a chemical bond often falls somewhere in between these two extremes.

### Bond Polarity

Recall from the earlier chapter, *The Periodic Table*, that electronegativity is defined as the relative ability of an atom to attract electrons when present in a compound. The electronegativities of most elements are shown below (**Figure** below).

**PAULING ELECTRONEGATIVITY VALUES**

1 <b>H</b> 2.20																	5 <b>B</b> 2.04	6 <b>C</b> 2.55	7 <b>N</b> 3.04	8 <b>O</b> 3.44	9 <b>F</b> 3.98													
3 <b>Li</b> 0.98	4 <b>Be</b> 1.57																	13 <b>Al</b> 1.61	14 <b>Si</b> 1.90	15 <b>P</b> 2.19	16 <b>S</b> 2.58	17 <b>Cl</b> 3.16												
11 <b>Na</b> 0.93	12 <b>Mg</b> 1.31																	19 <b>K</b> 0.82	20 <b>Ca</b> 1.00	21 <b>Sc</b> 1.36	22 <b>Ti</b> 1.54	23 <b>V</b> 1.63	24 <b>Cr</b> 1.66	25 <b>Mn</b> 1.55	26 <b>Fe</b> 1.83	27 <b>Co</b> 1.88	28 <b>Ni</b> 1.91	29 <b>Cu</b> 1.90	30 <b>Zn</b> 1.65	31 <b>Ga</b> 1.81	32 <b>Ge</b> 2.01	33 <b>As</b> 2.18	34 <b>Se</b> 2.55	35 <b>Br</b> 2.96
37 <b>Rb</b> 0.82	38 <b>Sr</b> 0.95	39 <b>Y</b> 1.22	40 <b>Zr</b> 1.33	41 <b>Nb</b> 1.6	42 <b>Mo</b> 2.16	43 <b>Tc</b> 1.9	44 <b>Ru</b> 2.2	45 <b>Rh</b> 2.28	46 <b>Pd</b> 2.20	47 <b>Ag</b> 1.93	48 <b>Cd</b> 1.69	49 <b>In</b> 1.78	50 <b>Sn</b> 1.96	51 <b>Sb</b> 2.05	52 <b>Te</b> 2.1	53 <b>I</b> 2.66																		
55 <b>Cs</b> 0.79	56 <b>Ba</b> 0.89	57 <b>La</b> 1.1	72 <b>Hf</b> 1.3	73 <b>Ta</b> 1.5	74 <b>W</b> 2.36	75 <b>Re</b> 1.9	76 <b>Os</b> 2.2	77 <b>Ir</b> 2.20	78 <b>Pt</b> 2.28	79 <b>Au</b> 2.54	80 <b>Hg</b> 2.00	81 <b>Tl</b> 1.62	82 <b>Pb</b> 2.33	83 <b>Bi</b> 2.02	84 <b>Po</b> 2.0	85 <b>At</b> 2.2																		
87 <b>Fr</b> 0.7	88 <b>Ra</b> 0.9																																	

Electronegativities of the elements.

The degree to which a given bond is ionic or covalent is determined by calculating the difference in electronegativity between the two atoms involved in the bond.

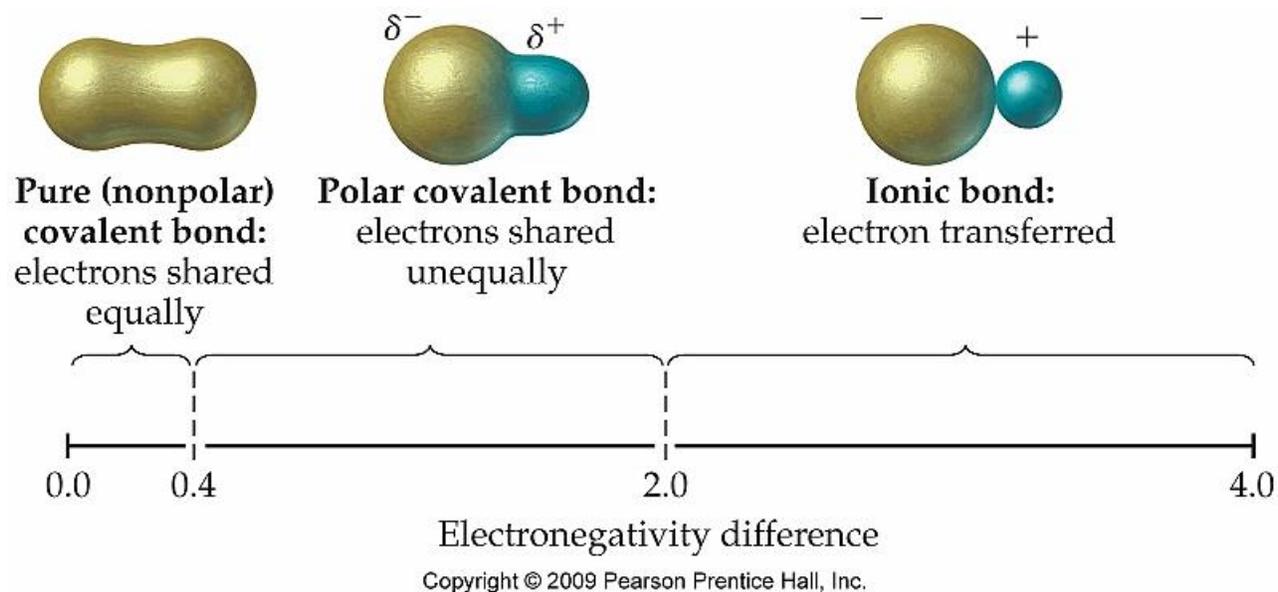
As an example, consider the bond that occurs between an atom of potassium and an atom of fluorine. Using the table, the difference in electronegativity is  $4.0 - 0.8 = 3.2$ . Because the difference in electronegativity is relatively large, the bond between the two atoms is primarily ionic. Since the fluorine atom has a much larger attraction for electrons than the potassium atom does, the valence electron from the potassium atom is considered to have completely transferred to the fluorine atom. The figure below (**Figure** below) shows how the difference in electronegativity relates to the ionic or covalent character of a chemical bond.

The difference in electronegativity between the two elements involved in a chemical bond is predictive of the type of bond made by those two atoms. A small difference ( $<0.4$ ) results in a nonpolar covalent bond, an intermediate difference ( $0.4-1.7$ ) results in a polar covalent bond, and a large difference ( $>1.7$ ) results in an ionic bond.

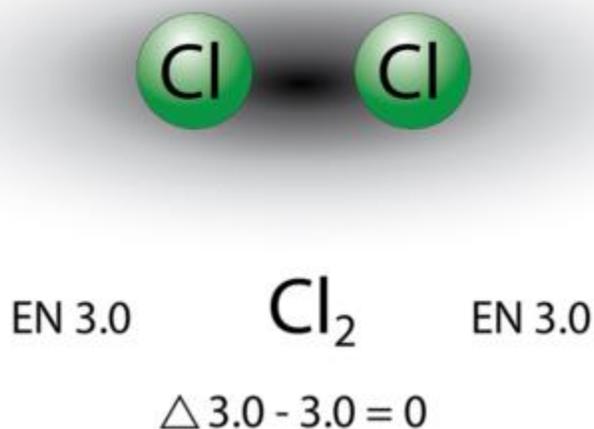
According to the figure above (**Figure** above), a difference in electronegativity ( $\Delta EN$ ) greater than 1.7 results in a bond that is mostly ionic in character.

### Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.7 is considered to be mostly covalent in character. However, a distinction is often made between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms (**Figure** below).



### Nonpolar Covalent Bonding



A nonpolar covalent bond is one in which the shared electrons are distributed equally between the two atoms.

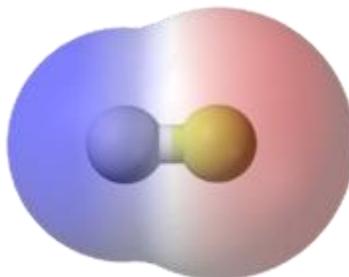
The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the  $\text{Cl}_2$  molecule is symmetrical. Any diatomic molecule in which the two atoms are the same element must be joined by a nonpolar covalent bond.

There are seven **diatomic elements**, which are *elements whose natural form is of a diatomic molecule*. They are hydrogen ( $\text{H}_2$ ), nitrogen ( $\text{N}_2$ ), oxygen ( $\text{O}_2$ ), fluorine ( $\text{F}_2$ ), chlorine ( $\text{Cl}_2$ ), bromine ( $\text{Br}_2$ ), and iodine ( $\text{I}_2$ ). By forming a diatomic molecule, both atoms in each of these molecules satisfy the octet rule, resulting in a structure that is much more stable than the isolated atoms.

Notice from the figure above (**Figure** above) that molecules in which the electronegativity difference is very small ( $< 0.4$ ) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ( $\Delta\text{EN} = 3.16 - 2.96 = 0.20$ ).

## Polar Covalent Bonds

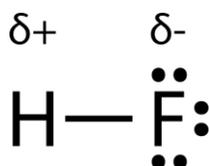
A bond in which the electronegativity difference between the atoms is between 0.4 and 1.7 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons, so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of shared electrons within the molecule is no longer symmetrical (**Figure** below).



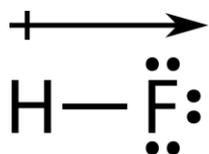
In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

The hydrogen fluoride molecule has an electronegativity difference of 1.9, which places it in the category of being slightly ionic. However, the hydrogen ion ( $\text{H}^+$ ) is so very small that it is not capable of adopting the crystal lattice structure of an ionic compound. Hydrogen fluoride is a highly polar molecule. Because of its greater electronegativity, the electron density around the fluorine atom is much higher than the electron density around the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter, delta ( $\delta$ ) along with a positive or negative sign to indicate that an atom has a partial positive or negative charge.



The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.



### Sample Problem 9.3: Identifying Bond Types

Which type of bond will form between each of the following pairs of atoms?

- C and O
- Na and N
- B and H

*Step 1: List the known quantities and plan the problem.*

## Known

Using the electronegativity chart:

- a. C = 2.5, O = 3.5
- b. Na = 0.9, N = 3.0
- c. B = 2.0, H = 2.1

*Step 2: Solve.*

Calculate the difference and use the diagram above (**Figure** above) to identify the bond type.

- a.  $3.5 - 2.5 = 1.0 \rightarrow$  C-O bond is polar covalent
- b.  $3.0 - 0.9 = 2.1 \rightarrow$  Na-N bond is ionic
- c.  $2.1 - 2.0 = 0.1 \rightarrow$  B-H bond is nonpolar covalent

*Step 3: Think about your result.*

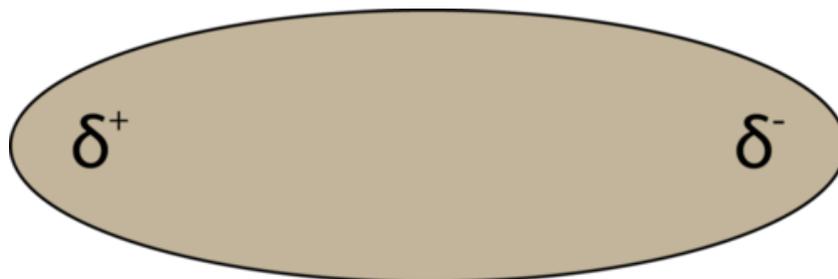
Bonds between nonmetal atoms are generally covalent in nature (A and C), while bonds between a metal atom and a nonmetal atom are generally ionic.

## **Practice Problems**

1. Place the following bonds in order from least polar to most polar.
  - a. Fe-N
  - b. H-Cl
  - c. Ca-O
  - d. C-S

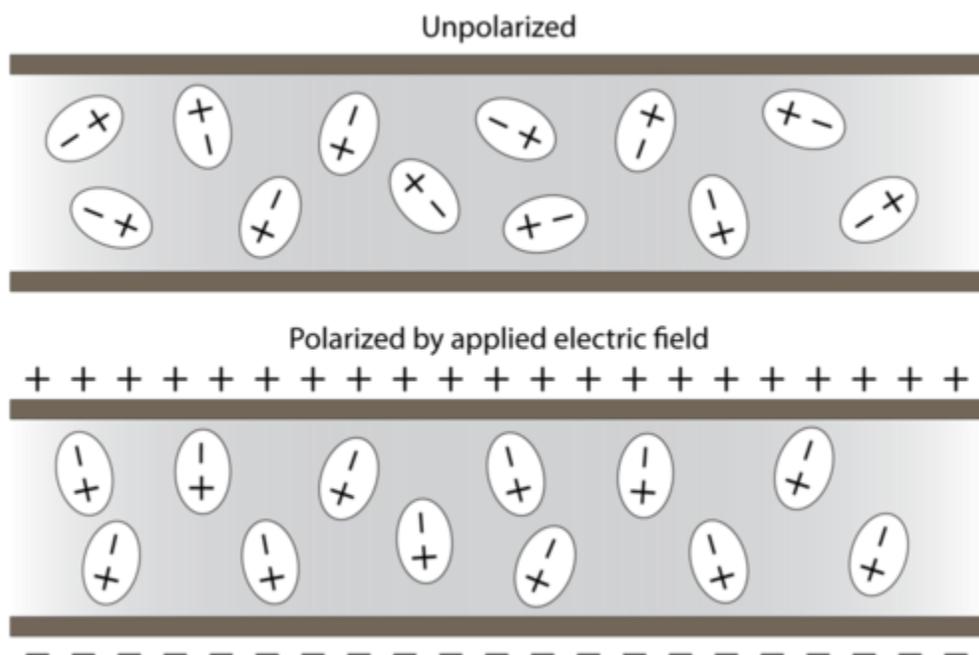
## **Molecular Polarity**

A **polar molecule** is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. A diatomic molecule that consists of a polar covalent bond, such as HF, is a polar molecule. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. A molecule with two poles is called a **dipole**. Hydrogen fluoride is a dipole. A simplified way to depict polar molecules is pictured below (**Figure** below).



A molecular dipole results from the unequal distribution of electron density throughout a molecule.

When placed between oppositely charged plates, polar molecules orient themselves so that their positive ends are closer to the negative plate and their negative ends are closer to the positive plate (**Figure** below).

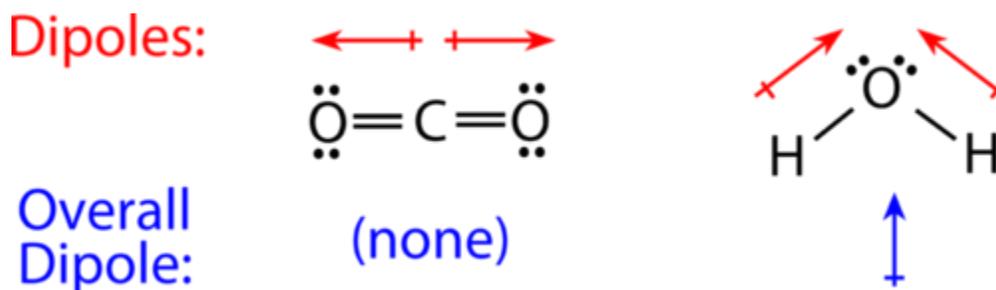


Polar molecules are randomly oriented in the absence of an applied electric field (*top*). In an electric field, the molecules orient themselves to maximize the attraction between opposite charges (*bottom*).

Experimental techniques involving electric fields can be used to determine if a certain substance is composed of polar molecules and to measure the degree of polarity.

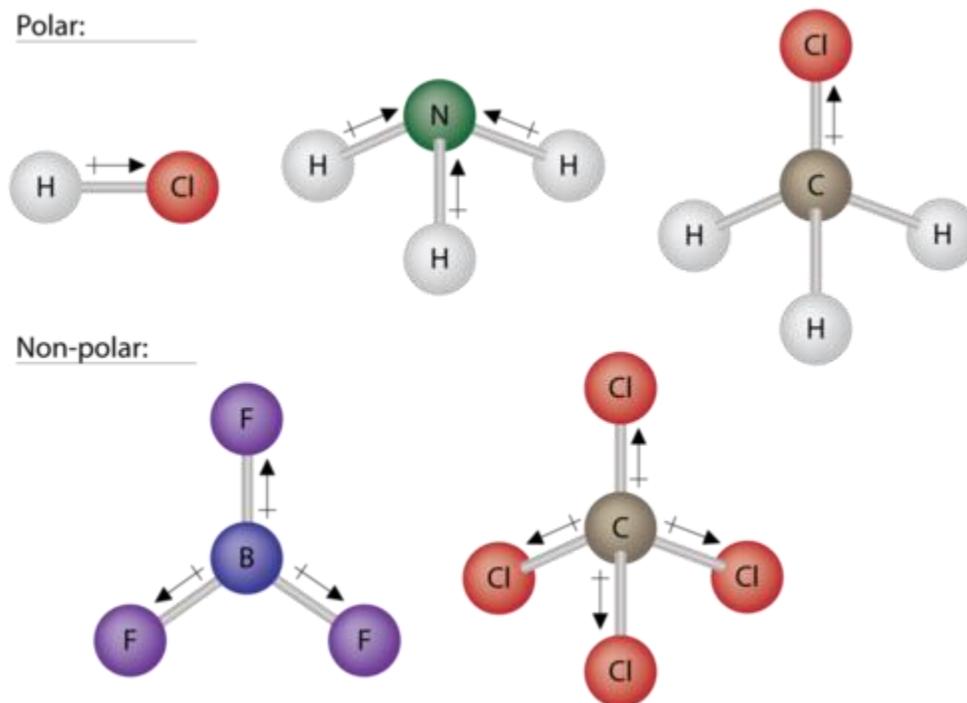
For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. Pictured below (**Figure** below) is a comparison between carbon dioxide and water. Carbon dioxide ( $\text{CO}_2$ ) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented in this way, they cancel each other out, and the overall molecular polarity of  $\text{CO}_2$  is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the H atoms toward the O atom. Because of the shape, the dipoles do not cancel each other out, and the water molecule is polar. In the figure, the net dipole is shown in blue and points upward.



The molecular geometry of a molecule affects its polarity. In  $\text{CO}_2$ , the two polar bonds cancel each other out, and the result is a nonpolar molecule. Water is polar because its bent shape means that the two polar bonds do not cancel.

Some other molecules are shown below (**Figure** below). Notice that a tetrahedral molecule such as  $\text{CH}_4$  is nonpolar. However, if one of the peripheral H atoms is replaced by another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule ( $\text{BF}_3$ ) may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule ( $\text{NH}_3$ ) is polar.



Some examples of polar and nonpolar molecules with various molecular geometries.

### Intermolecular Forces

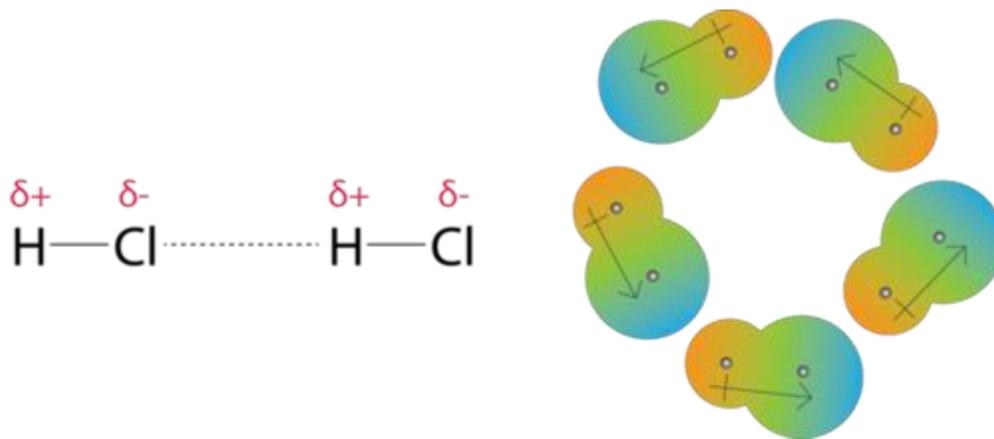
Covalent and ionic bonds can be called intramolecular forces: forces that act within a molecule or crystal. Molecules also attract other molecules. **Intermolecular forces** are attractions that occur between molecules. Intermolecular forces are weaker than either ionic or covalent bonds. However, the varying strengths of different types of intermolecular forces are responsible for physical properties of molecular compounds such as melting and boiling points.

### Van der Waals Forces

The first type of intermolecular force we will consider are called van der Waals forces, after Dutch chemist, Johannes van der Waals (1837-1923). **Van der Waals forces** are the weakest intermolecular force and consist of dipole-dipole forces and dispersion forces.

### Dipole-Dipole Forces

**Dipole-dipole forces** are the attractive forces that occur between polar molecules (**Figure** below). A molecule of hydrogen chloride has a partially positive hydrogen atom and a partially negative chlorine atom. A collection of many hydrogen chloride molecules will align themselves so that the oppositely charged regions of neighboring molecules are near each other.

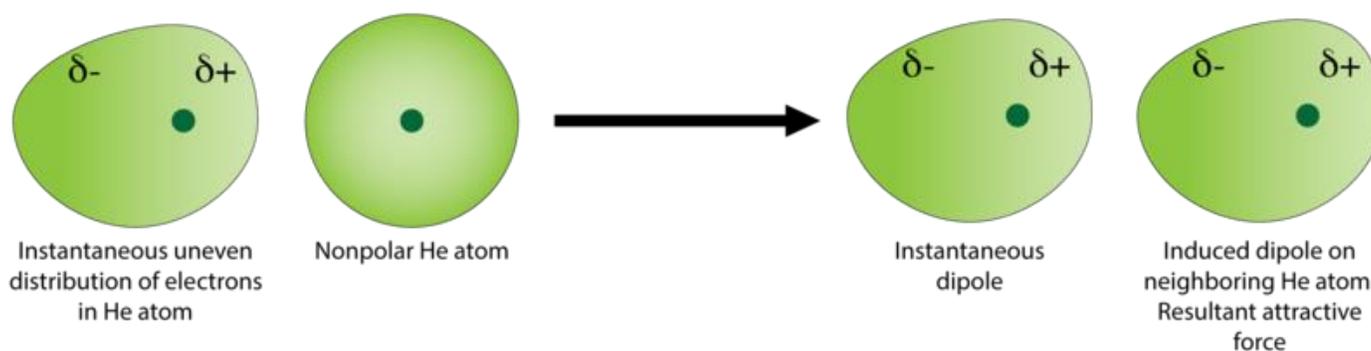


Dipole-dipole forces result from the attraction between the positive end of one dipole and the negative end of a neighboring dipole. Dipole-dipole forces are similar to ionic bonds, but because they involve only partial charges, they are much weaker.

### London Dispersion Forces

Dispersion forces are also considered a type of van der Waals force and are the weakest of all intermolecular forces. They are often called London forces after Fritz London (1900-1954), who first proposed their existence in 1930. **London dispersion forces** are *intermolecular forces that occur between all atoms and molecules due to the random motion of electrons*.

For example, the electron cloud of a helium atom contains two electrons, and, when averaged over time, these electrons will distribute themselves evenly around the nucleus. However, at any given moment, the electron distribution may be uneven, resulting in an *instantaneous dipole*. This weak and temporary dipole can subsequently influence neighboring helium atoms through electrostatic attraction and repulsion. The formation of an induced dipole is illustrated below (**Figure** below).



Random fluctuations in the electron density within the electron cloud of a helium atom results in a short-lived ("instantaneous") dipole. The attractive force between instantaneous dipoles and the resulting induced dipoles in neighboring molecules is called the London dispersion force.

The instantaneous and induced dipoles are weakly attracted to one another. The strength of dispersion forces increases as the total number of electrons in the atoms or nonpolar molecules increases.

The halogen group consists of four elements that all take the form of nonpolar diatomic molecules. Listed below (**Table** below) is a comparison of the melting and boiling points for each.

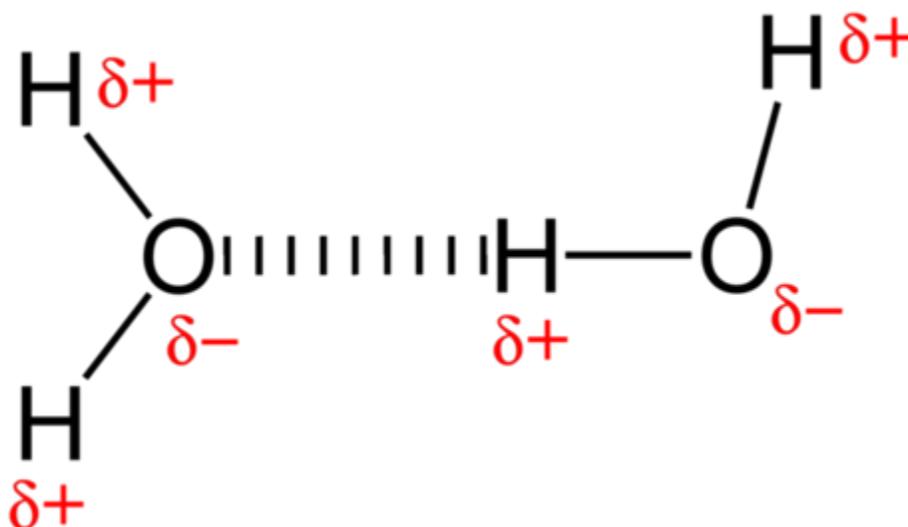
### Melting and Boiling Points of Halogens

Molecule	Total Number of Electrons	Melting Point (°C)	Boiling Point (°C)	Physical State at Room Temperature
F <sub>2</sub>	18	-220	-188	gas
Cl <sub>2</sub>	34	-102	-34	gas
Br <sub>2</sub>	70	-7	59	liquid
I <sub>2</sub>	106	114	184	solid

The dispersion forces are strongest for iodine molecules because they have the greatest number of electrons. The relatively stronger forces result in melting and boiling points which are the highest of the halogen group. These forces are strong enough to hold iodine molecules close together in the solid state at room temperature. The dispersion forces are progressively weaker for bromine, chlorine, and fluorine, as illustrated by their steadily lower melting and boiling points. Bromine is a liquid at room temperature, while chlorine and fluorine are gases. Because gaseous molecules are so far apart from one another, intermolecular forces are nearly nonexistent in the gas state, and so the dispersion forces in chlorine and fluorine only become measurable as the temperature decreases and they condense into the liquid state.

### Hydrogen Bonding

The attractive force between water molecules is an unusually strong type of dipole-dipole interaction. Water contains hydrogen atoms that are bound to a highly electronegative oxygen atom, making for very polar bonds. The partially positive hydrogen atom of one molecule is then attracted to the oxygen atom of a nearby water molecule (Figure below).

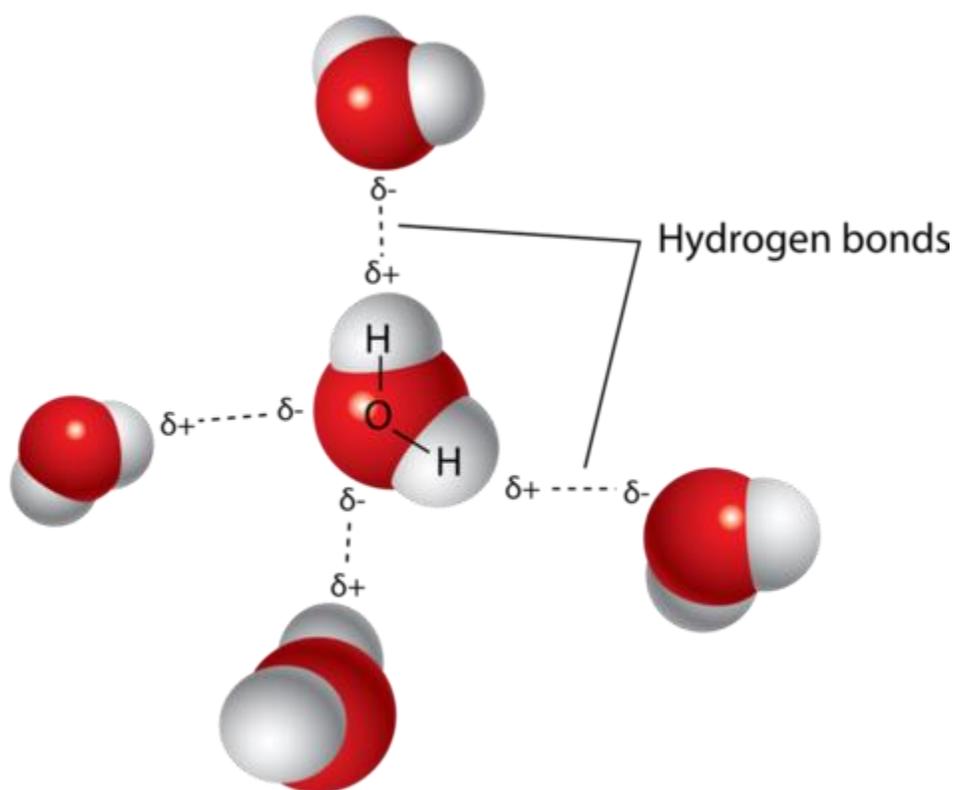


A hydrogen bond in water occurs between the hydrogen atom of one water molecule and the lone pair of electrons on the oxygen atom of a neighboring water molecule.

A **hydrogen bond** is an intermolecular attractive force in which a hydrogen atom, that is covalently bonded to a small, highly electronegative atom, is attracted to a lone pair of electrons on an atom in a neighboring molecule. Hydrogen bonds are very strong compared to other dipole-dipole interactions. A typical hydrogen bond is about 5% as strong as a covalent bond.

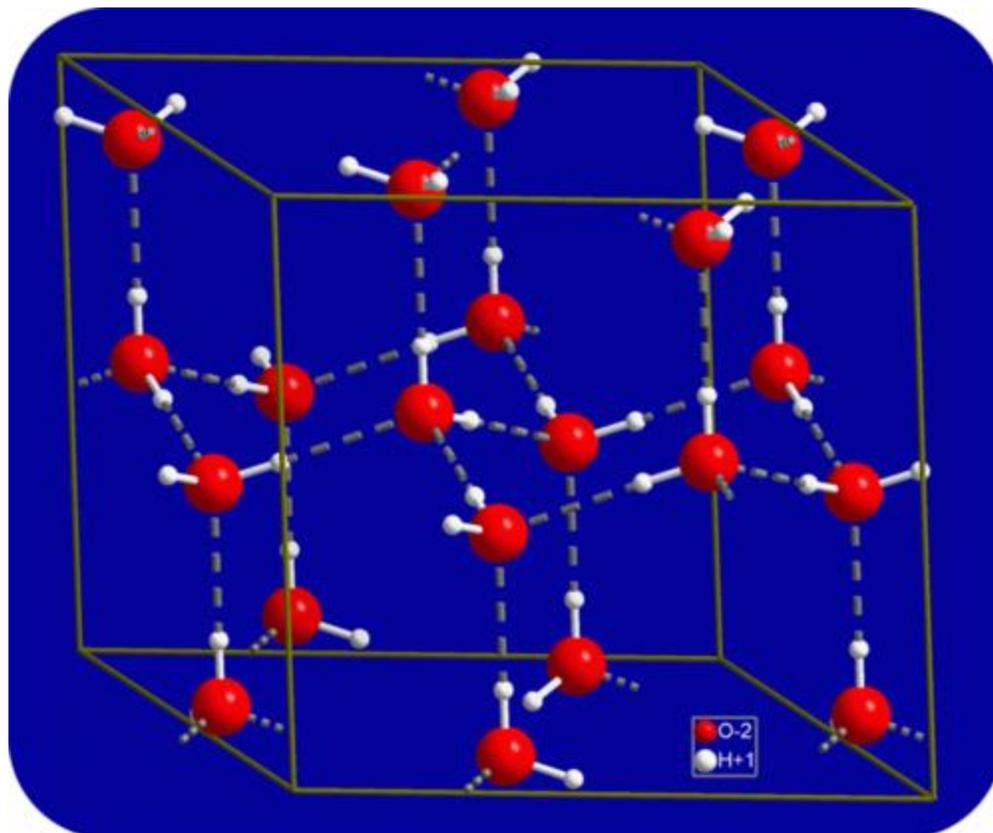
Hydrogen bonding occurs only in molecules where hydrogen is covalently bonded to one of three elements: fluorine, oxygen, or nitrogen. These three elements are so electronegative that they withdraw the majority of the electron density from the covalent bond with hydrogen, leaving the H atom very electron-deficient. Because the hydrogen atom does not have any electrons other than the ones in the covalent bond, its positively charged nucleus is almost completely exposed, allowing strong attractions to other nearby lone pairs.

The hydrogen bonding that occurs in water leads to some unusual, but very important properties. Most molecular compounds that have a mass similar to water are gases at room temperature. However, because of the strong hydrogen bonds, water molecules are able to stay condensed in the liquid state. The figure below (**Figure** below) shows how its bent shape and the presence of two hydrogen atoms per molecule allows each water molecule to hydrogen bond with several other molecules.



Multiple hydrogen bonds occur simultaneously in water because of its bent shape and the presence of two hydrogen atoms per molecule.

In the liquid state, the hydrogen bonds of water can break and reform as the molecules flow from one place to another. When water is cooled, the molecules begin to slow down. Eventually, when water is frozen to ice, the hydrogen bonds become more rigid and form a well-defined network (**Figure** below).



When water freezes to ice, the hydrogen bonding network becomes fixed until the ice melts. Each oxygen atom has an approximately tetrahedral geometry that includes two covalent bonds and two hydrogen bonds.

The bent shape of the molecules leads to gaps in the hydrogen bonding network of ice. Ice has the very unusual property that its solid state is less dense than its liquid state. As a result, ice floats in liquid water. Virtually all other substances are denser in the solid state than in the liquid state. Hydrogen bonds also play a very important biological role in the physical structures of proteins and nucleic acids.

### Boiling Points and Bonding Types

In order for a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction. However, when the mass of a nonpolar molecule is sufficiently large, its dispersion forces can be stronger than the dipole-dipole forces in a lighter polar molecule. Thus, nonpolar  $\text{Cl}_2$  has a higher boiling point than polar  $\text{HCl}$ .

Intermolecular Forces and Boiling Points		
Substance	Strongest Intermolecular Force	Boiling Point ( $^{\circ}\text{C}$ )
$\text{H}_2$	dispersion	-253
Ne	dispersion	-246

### Intermolecular Forces and Boiling Points

Substance	Strongest Intermolecular Force	Boiling Point (°C)
O <sub>2</sub>	dispersion	-183
Cl <sub>2</sub>	dispersion	-34
HCl	dipole-dipole	-85
HBr	dipole-dipole	-66
H <sub>2</sub> S	dipole-dipole	-61
NH <sub>3</sub>	hydrogen bonding	-33
HF	hydrogen bonding	20
H <sub>2</sub> O	hydrogen bonding	100

### Molecular and Ionic Compounds

The physical state and properties of a particular compound depend largely on the type of chemical bonding it displays. Molecular compounds, sometimes called covalent compounds, display a wide range of physical properties due to the different types of intermolecular attractions discussed in this lesson. The melting and boiling points of molecular compounds are generally quite low compared to those of ionic compounds. This is because the energy required to disrupt the intermolecular forces between molecules is far less than the energy required to break the ionic bonds in a crystalline ionic compound. Since molecular compounds are composed of neutral molecules, their electrical conductivity is generally quite poor, whether in the solid or liquid state. Ionic compounds do not conduct electricity well in the solid state because of their rigid structures, but they conduct well when they are molten (in the liquid state) or dissolved in water. The water solubility of molecular compounds is variable and depends primarily on the type of intermolecular forces involved. Substances that exhibit hydrogen bonding or dipole-dipole forces are generally water soluble, whereas those that exhibit only London dispersion forces are generally insoluble. Most, but not all, ionic compounds are quite soluble in water. The table below (**Table** below) summarizes some of the differences between ionic and molecular compounds.

### Comparison of Ionic and Molecular Compounds

Property	Ionic Compounds	Molecular Compounds
Type of elements	metal and nonmetal	nonmetals only
Bonding	ionic – transfer of electron(s) between atoms	covalent – sharing of pair(s) of electrons between atoms

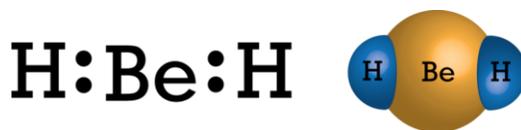
### Comparison of Ionic and Molecular Compounds

Property	Ionic Compounds	Molecular Compounds
Representative unit	formula unit	molecule
Physical state at room temperature	solid	gas, liquid, or solid
Water solubility	usually high	variable
Melting and boiling temperature	generally high	generally low
Electrical conductivity	good when molten or in solution	poor

One type of covalent substance behaves quite differently than the molecular substances already described. A covalent network solid is a compound in which all of the atoms are connected to one another by covalent bonds. For example, diamond is composed entirely of carbon atoms, each of which is bonded to four other carbon atoms in a tetrahedral geometry. Because this type of solid is not composed of discrete molecules, melting a covalent network solid cannot be accomplished by overcoming relatively weak intermolecular forces. Instead, covalent bonds must be broken, a process which requires extremely high temperatures. In fact, diamond does not melt at all. Instead, it vaporizes to a gas at temperatures above 3500°C.

### Electron Promotion

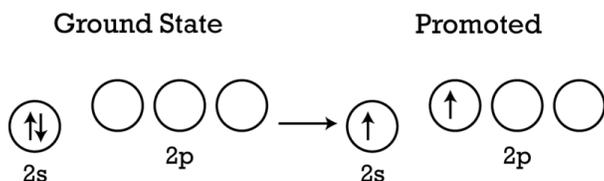
Consider the molecule formed by the combination of beryllium and hydrogen, beryllium hydride ( $\text{BeH}_2$ ). The electronegativity difference between these two atoms is only 0.6, with beryllium being slightly more electropositive. Therefore, the bonds in  $\text{BeH}_2$  are polar covalent bonds. The Lewis structure for the molecule is:



The first thing we might notice about the  $\text{BeH}_2$  molecule is that it does not obey the octet rule. Beryllium has two valence electrons and each hydrogen has one, so there are not enough valence electrons to produce an octet around the beryllium atom.

There is also another unusual thing about  $\text{BeH}_2$ . The orbital representation for the electron configuration of beryllium shows the  $2s$  orbital is full. Earlier in this chapter, we said that the atoms involved in covalent bonding must each have a half-filled orbital. How can beryllium form two bonds when it does not have any half-filled orbitals? The explanation to this question involves the concept of **electron promotion**. As illustrated below, by promoting an electron from the  $2s$  orbital to one of the  $2p$  orbitals, beryllium theoretically acquires two half-filled orbitals. These half-filled orbitals are therefore able to form two covalent bonds. The amount of necessary to promote an electron from a  $2s$  orbital to

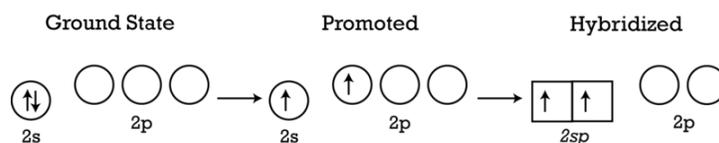
a  $2p$  orbital is small compared to the amount of energy released when beryllium forms two covalent bonds. As a result, in exchange for a small input of energy, a large quantity of energy is released.



### Orbital Hybridization

We have not, however, completed the explanation as to why  $\text{BeH}_2$  does not follow the octet rule. Bonds formed by overlapping  $s$  orbitals are, in general, shorter, stronger, and more flexible than bonds formed by overlapping  $p$  orbitals from the same shell. Therefore, when considering the two bonds in  $\text{BeH}_2$ , it would be reasonable to assume that we could determine which bond was formed by hydrogen overlapping with beryllium's half-filled  $2s$  orbital and which was formed by hydrogen overlapping beryllium's half-filled  $2p$  orbital. Examination of the two bonds, however, shows them to be identical in length, strength, and flexibility. The values for the length, strength, and flexibility also fall in between the values expected for overlapping  $s$  and  $p$  orbitals. The concept used to explain these observations is called **orbital hybridization**.

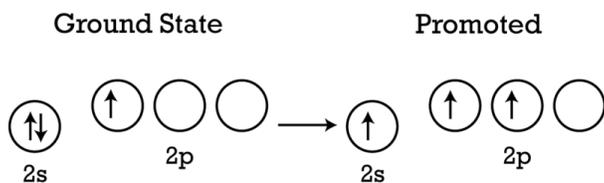
In orbital hybridization, all the orbitals involved in bonding are hybridized and form a set of identical orbitals that have properties intermediate to the properties of the orbitals from which they were created.



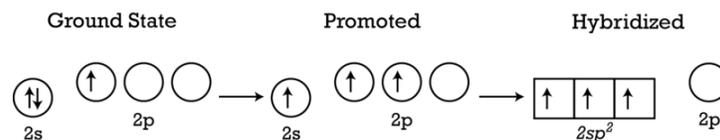
As seen in the image above, the half-filled  $2s$  and  $2p$  orbitals hybridize to form two completely new orbitals named  $sp$  hybridized orbitals. These two new orbitals are identical to each other, and both have characteristics somewhere between the characteristics of  $2s$  and  $2p$  orbitals. When these half-filled  $sp$  hybridized orbitals overlap with the hydrogen atoms, two identical bonds are produced.

### Covalent Bonds of Group 3A

The only member of Group 3A that forms a significant number of covalent compounds is boron. Numerous boron compounds exist, with boron forming three bonds in many of the compounds. Since the ground state electron configuration of boron,  $1s^2 2s^2 2p^1$ , has a filled  $2s$  orbital and one half-filled  $2p$  orbital, the concept of electron promotion is needed to explain boron's formation of three bonds.



One of the electrons in the  $2s$  orbital is promoted to an empty  $2p$  orbital, producing three half-filled orbitals that allows boron to form three covalent bonds (illustrated in the figure above). The three bonds in boron compounds such as  $\text{BH}_3$  are found to be identical in length, strength, and flexibility. The  $2s$  orbital and two  $2p$  orbitals hybridize to form three identical  $sp^2$  hybridized orbitals.

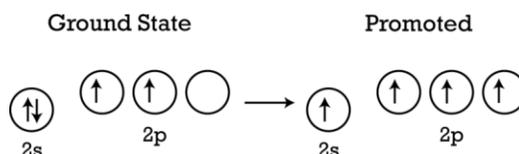


The three hybridized orbitals can now overlap with other atoms and form three identical bonds, making compounds such as  $\text{BH}_3$  and  $\text{BCl}_3$ . In these boron compounds, the central atom is surrounded by only six electrons, and therefore this is another exception to the octet rule.

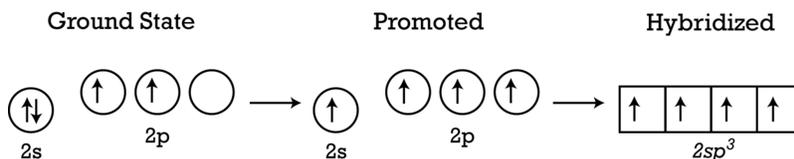
It should be recognized that the  $sp^2$  hybridized orbitals are not the same as  $sp$  hybridized orbitals. If you mix one bucket of blue paint with one bucket of yellow paint, you get green paint. If you mix two buckets of blue with one bucket of yellow, you will also get green paint, but it will not be the same shade of green as before. Hybridizing one  $s$  and one  $p$  orbital does not produce the same orbitals as hybridizing one  $s$  and two  $p$  orbitals.

### Covalent Bonds of Group 4A

The members of Group 4A that form covalent bonds are carbon and silicon. Their electron configurations are  $1s^2 2s^2 2p^2$  and  $1s^2 2s^2 2p^6 3s^2 3p^2$ , respectively. In the outer energy level of both atoms, the  $s$  orbital is filled, two of the  $p$  orbitals are half-filled, and the third  $p$  orbital is empty. In the majority of the covalent compounds containing carbon and silicon, these atoms are found to have four bonds. As a result, electron promotion must also occur in these atoms. If one of the electrons in the  $s$  orbital is promoted to the empty  $p$  orbital, four half-filled orbitals are produced, as shown in the image below.



With four half-filled orbitals, carbon and silicon can form the four covalent bonds necessary to create  $\text{CH}_4$ ,  $\text{CCl}_4$ , and so on. As you may have already suspected, the four bonds in carbon and silicon compounds are all identical. Therefore, orbital hybridization also occurs in this family. The four hybridized orbitals, as shown below, are called  $sp^3$  hybridized orbitals.

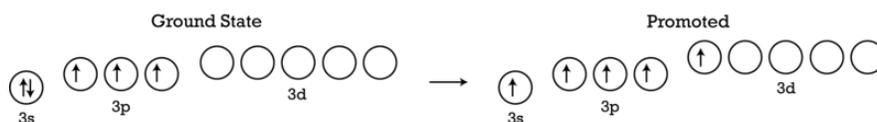


Since the  $sp^3$  hybridized orbitals are a mix of one  $s$  and three  $p$  orbitals, their characteristics are not the same as  $sp^2$  hybridized orbitals or  $sp$  hybridized orbitals. These four identical orbitals can be overlapped by four hydrogen atoms and form four identical bonds. Consequently, the covalent compounds in Group 4A do obey the octet rule.

### Covalent Bonds of Group 5A

In Group 5A, the electron configuration of the outermost energy level is  $s^2 p^3$ . These atoms have three half-filled  $p$  orbitals available for bonding and would appear to form three covalent bonds with no need for either electron promotion or hybridization. The first member of the family, nitrogen, commonly forms three bonds in compounds such as  $\text{NH}_3$ ,  $\text{NCl}_3$ , and  $\text{N}_2\text{O}_3$ . The second member of the family, phosphorus, also forms similar compounds, like  $\text{PH}_3$

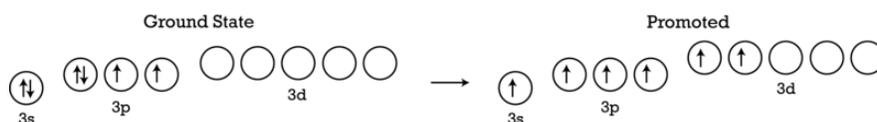
and  $\text{PCl}_3$ . Phosphorus, however, can also form compounds with five covalent bonds, such as  $\text{PCl}_5$ . In order to explain five identical bonds for the phosphorus atom, we will need to use the concepts of electron promotion and orbital hybridization.



As shown in the figure above, phosphorus promotes one of its  $3s$  electrons into an orbital in the  $3d$  sub-level. This gives phosphorus five half-filled orbitals and allows it to form the five bonds in  $\text{PCl}_5$  and other phosphorus compounds with five covalent bonds. It also makes it clear why nitrogen does not form compounds with five bonds, because nitrogen does not have a  $d$  sub-energy level available. The five bonds in these compounds are identical, which means that one  $s$  orbital, three  $p$  orbitals, and one  $d$  orbital hybridize. These hybridized orbitals will be called  $sp^3d$  or  $dsp^3$  hybridized orbitals. Molecules like  $\text{PCl}_5$  and  $\text{PF}_5$  will have the central atom surrounded by 10 electrons, so this electron promotion produces another group of molecules that do not obey the octet rule.

### Covalent Bonds of Group 6A

The outermost energy level of the members of Group 6A has the electron configuration  $s^2p^4$ . This outer energy level has a filled  $s$  orbital, one filled  $p$  orbital, and two half-filled  $p$  orbitals. With two half-filled orbitals available for overlap, all of the members of this family can and do form two covalent bonds. There are, however, some compounds that form more than two covalent bonds. Oxygen has no  $d$  orbitals, so promotion into the  $d$  sub-energy level is not possible. Sulfur and larger members of the family, however, do have  $d$  orbitals that allow for electron promotion.



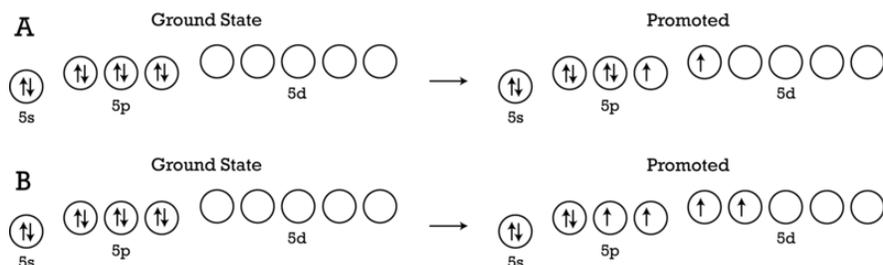
As you can see in the image above, sulfur can promote two electrons into the  $d$  orbitals and produce six half-filled orbitals available for overlap. The six orbitals are hybridized and form  $d^2sp^3$  or  $sp^3d^2$  hybridized orbitals. Such orbitals are necessary for the formation of compounds such as  $\text{SF}_6$ .

### Covalent Bonds of Group 7A

All of the members of Group 7A have outermost energy level electron configurations  $s^2p^5$ . This configuration has one half-filled  $p$  orbital, which allows the members of this family to form one covalent bond. The majority of compounds formed by this family contain one bond. Fluorine has no  $d$  orbitals and can only form one bond. Unlike fluorine, chlorine and the larger members of the family have empty  $d$  orbitals that allow them to undergo electron promotion. Chlorine can promote one  $p$  electron to a  $d$  orbital to produce three half-filled orbitals, which allow compounds like  $\text{ClF}_3$  to form. Chlorine can also promote two electrons to form five half-filled orbitals, which results in compounds like  $\text{ClF}_5$ .

## Covalent Bonds of Group 8A

Even members of the noble gases, under extreme conditions, can form some covalent compounds. Since the ground state electron configuration for these atoms has completely filled outer energy levels, the only way that they can form bonds is by electron promotion and orbital hybridization.



In the diagram above, figure A shows xenon promoting one electron from a  $p$  to a  $d$  orbital. This allows xenon to form compounds like  $\text{XeF}_2$  that contain two covalent bonds. In figure B, xenon is promoting two electrons from  $p$  to  $d$  orbitals, producing four orbitals available for bonding and forming compounds like  $\text{XeF}_4$ . In both Groups 7A and 8A, when electrons are promoted and orbitals are hybridized, even though some of the orbitals are filled and some are half-filled, hybridization is considered to involve *all* the outer energy level orbitals that contain electrons. Therefore, in figure A, the orbital hybridization would be  $sp^3d$ , and in figure B, the hybridization would be  $sp^3d^2$ .

**Table** below summarizes the different types of hybridized orbitals discussed in this section.

Summary of Hybridized Orbitals		
Orbitals Hybridized	Hybridized Orbital Names	Number of Orbitals
$s + p$	$sp$	2
$s + p + p$	$sp^2$	3
$s + p + p + p$	$sp^3$	4
$s + p + p + p + d$	$sp^3d$	5
$s + p + p + p + d + d$	$sp^3d^2$	6

This material adapted from