

Calculations In Chemistry

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Module 25 – Bonding

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Module 25 — Bonding

Prerequisites: For this topic, you will need a set of molecular models. These can be purchased at college bookstores or online. In some courses, models are provided in your “lab drawer.” As an alternative, patterns for cardboard models are provided in Lesson 25B, but commercial models are recommended.

Pretests: If you believe that you know the material in a lesson, try two problems at the end of the lesson. If you can do those, you can skip the lesson.

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Introduction

Bonds are forces that hold atoms together. The nature of the chemical bond is a question at the heart of chemistry, but the answer is not completely understood. An explanation of bonding must take into account protons and electron pairs, wave equations and orbitals, electrical attraction and repulsion, neutral molecules, and polyatomic ions. A theory that successfully unites all those factors does not yet exist.

However, a variety of models predict bond behavior. We will begin with two simple models, Lewis diagrams and VSEPR, that allow us to predict the composition and shape of a significant percentage of the molecules within and around us.

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Lesson 25A: Lewis (Electron Dot) Diagrams

Ionic Versus Covalent Bonds

In *ionic* bonding, charged particles (ions) are held together by electrical attraction. Ions that are monatomic usually have the valence electron configuration of the nearest noble gas.

Covalent bonding is often described as electron sharing. As in ionic bonding, each atom is often found surrounded by valence electrons in a noble gas configuration, but in covalent bonding, a pair of electrons between two atoms can play the role of valence electrons for *both* atoms. These shared electrons are the covalent bond that holds the two atoms together.

In reality, bonds are not “either ionic or covalent.” All ionic bonds have some covalent character that is evident under certain conditions. Covalent bonds often have some ionic character. Whether a molecule should be considered as primarily ionic or covalent is best determined by its behavior.

Atoms that are bonded covalently in a molecule or a polyatomic ion do not easily separate when melted or dissolved. The forces holding atoms together inside a covalent molecule are strong compared to the forces between the molecules. Compared to the ions in ionic compounds, covalently bonded molecules are more easily pulled apart from each other when heated, so covalent molecules typically melt and boil at temperatures much below that of ionic compounds.

Lewis (Dot) Diagrams

Lewis diagrams (also called **Lewis formulas or structures**, or **electron dot diagrams**) can be drawn to represent covalent bonds in covalent molecules and polyatomic ions.

Example: The Lewis diagram of H₂ is **H • H**

Lewis diagrams are useful for predicting the bonding, shape, and solubility of substances. To draw the Lewis (dot) diagrams for molecules, we begin by drawing the dot diagrams for atoms.

Rules for Drawing Lewis Diagrams for Neutral Atoms



1. Write the symbol for the atom.
2. Determine the number of *valence* electrons for the atom.

Recall that the number of valence electrons for an atom is equal to the number for the main group (the *tall* columns) of the periodic table in which the atom is located.

Examples:

- First column neutral atoms have *one* valence electron.
- Neutral atoms in the carbon family have *four* valence electrons.
- Noble gases have 8 valence electrons (except *helium* which has 2).

3. Assume that each atom symbol has *four* sides. On each side can go at most two electrons. Using dots to represent the valence electrons, draw the valence electrons around the atom symbol. Put *one* electron on each of the four sides of the symbol *before* you start to *pair* electrons. The four sides are *equivalent*: you may place the paired and unpaired electrons on any side.

Examples: Boron, with 3 valence e⁻, is  Nitrogen (5 valence e⁻) is 

The dot diagram for a neutral boron atom has three **unpaired** electrons. Nitrogen has three unpaired electrons and one **pair** of electrons.

The Octet Rule

To draw dot diagrams for molecules and ions, apply the **octet rule**: in achieve maximum stability, an atom needs to be surrounded by *eight valence* electrons. (Hydrogen, however, needs only *two*.)

The octet rule is related to the orbital energy level diagram for atoms: filled clusters in the diagram have high stability, and (except for row 1 atoms), filled clusters have 8 valence (s and p) electrons.

Combinations of atoms that result in all atoms being surrounded by eight valence electrons (two for H atoms) tend to be *stable* combinations: those that are likely to be found in nature and formed in chemical reactions. A species that does not have a *satisfied octet* may exist, but it is likely to be unstable: it will tend to be a very *reactive* species.

Using Dot Diagrams To Predict Bonding

To predict the bonding in stable molecules, depending on the type of problem, there are two methods for drawing dot diagrams.

Method 1:

This method *predicts* the molecular formula that combine one or two kinds of atoms, if the formula is *not* supplied but the compound has all *single* bonds (*one pair* of electrons per bond).

Let's learn Method 1 with an example.

- Q.** Draw the Lewis diagram for a stable molecule that contains only chlorine atoms with single bonds.

Complete the following steps, then check your answer below.

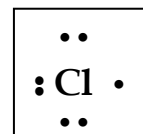
Method 1 Steps. If you do not know the molecular formula, but you know which atoms are combining and that the molecule has single bonds:

1. Draw the dot diagram for each neutral atom.
2. *Combine* the diagrams of the atoms so that the *unpaired* electrons *pair* and are *shared* between two atoms. Combine the atom diagrams until each symbol is surrounded by *eight* valence electrons (except H which needs two).

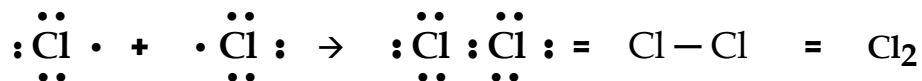
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Answer

A neutral chlorine *atom* has seven valence electrons. Place one on each of the four sides of the symbol, then start to pair electrons. This results in 3 *pairs* and one *unpaired* dots representing the valence electrons around chlorine. The chlorine has seven valence electrons and it needs *eight* to be stable.



To make a stable molecule, slide two chlorines together so that their unpaired electrons pair. *Each* chlorine is now surrounded by *eight* valence electrons. The *octet rule* is satisfied. The two shared electrons are a *bond* between the two chlorines. Each chlorine atom has 3 **lone pairs**: pairs around the atom that are not part of a bond.



Two atom dot diagrams ↑ *molecule* dot diagram ↑ structural ↑ and molecular ↑ formulas

In a particle with more than one atom, the *lone* pairs may also be termed **unshared pairs** or **non-bonding pairs**.

Method 1 is over-simplified, but it does predict the bonding in cases when the molecular formula (and therefore the total number of valence electrons) is not known.

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Practice A: Use a periodic table. If needed, check your answers after each part. The atoms in covalent compounds will most often be the non-metals found toward the top right of the periodic table, plus hydrogen.

- How many valence electrons are in these neutral atoms?
 - Silicon
 - Phosphorous
 - Bromine
 - Sulfur
 - Draw the Lewis diagram for each atom in #1.
 - Si
 - P
 - Br
 - S
 - Using Method 1, draw a Lewis diagram for the predicted stable molecules formed by combinations of
 - Fluorine atoms
 - Hydrogen and chlorine atoms
 - For each of the molecules in Problem 3, list the number of covalent *bonds* and the total number of *lone pairs* of electrons.
 Bonds: 3a. _____ 3b. _____ Lone Pairs: 3a. _____ 3b. _____
-

Method 2:

If the formula for a molecule or polyatomic ion is *supplied*, a model that better predicts the nature of bonds in both simple and more complex molecules is to combine the valence electrons without regard to which atom contributes the electrons.

In simple molecules with more than two atoms, the central atom is usually the atom with the *most unpaired electrons* in its atom dot diagram. This means that the central atom in a formula is usually the atom closest to Group 4A (the carbon family) in the periodic table. Carbon family atoms have 4 unpaired electrons.

Let's try a simple example using Method 2. Use the following steps.

- Q.** Draw the Lewis diagram for a water molecule (H_2O).

Method 2. When you know the molecular formula:

- Count the *total* number of valence electrons in the neutral atoms of the molecule.
- Arrange the valence electrons around the atoms to satisfy the octet/duet rule: For maximum stability, each symbol needs to be surrounded by *eight* valence electrons (H needs two). Do not worry about which atom contributes which electrons.

* * * * *

Answer

- Each neutral hydrogen has one valence electron (and wants 2). The one neutral oxygen has six valence electrons (and wants 8). The total for the molecule is 8 valence electrons.

In predicting typical formulas for covalent molecules, it is helpful to remember that “carbon bonds 4 times, nitrogen 3 times, oxygen twice, and hydrogen and halogens once.”

Practice B: Use a periodic table.

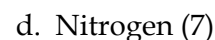
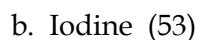
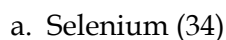
1. Using Method 2, draw a Lewis diagram and then a structural formula for these.



2. For each of the molecules in Problem 1, list the number of covalent *bonds* and the total number of *lone pairs* of electrons.

Bonds: 1a. _____ 1b. _____ Lone Pairs: 1a. _____ 1b. _____

3. Predict how many bonds will typically be found around these neutral atoms.



ANSWERS

Practice A

1. Valence electrons: a. Silicon 4 b. Phosphorus 5 c. Bromine 7 d. Sulfur 6

2. Dot diagrams: a. $\cdot \overset{\cdot\cdot}{\text{Si}} \cdot$ b. $\cdot \overset{\cdot\cdot}{\text{P}} \cdot$ c. $:\overset{\cdot\cdot}{\text{Br}}:$ d. $:\overset{\cdot\cdot}{\text{S}}:$

It does not matter which of the four sides have the paired or unpaired electrons.

3a. $:\overset{\cdot\cdot}{\text{F}}:\overset{\cdot\cdot}{\text{F}}:$ = F—F 3b. $\text{H}:\overset{\cdot\cdot}{\text{Cl}}:$ = H—Cl

4. Bonds: 3a. 1 3b. 1 Lone Pairs: 3a. 6 3b. 3

Practice B

1a. $\begin{array}{c} \text{H} \\ \cdot\cdot \\ \text{H}:\text{C}:\text{H} \\ \cdot\cdot \\ \text{H} \end{array} = \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H} \\ | \\ \text{H} \end{array}$ 1b. $:\overset{\cdot\cdot}{\text{Cl}}:\overset{\cdot\cdot}{\text{P}}:\overset{\cdot\cdot}{\text{Cl}}:\overset{\cdot\cdot}{\text{Cl}}:$ = $\begin{array}{c} \text{Cl}-\text{P}-\text{Cl} \\ | \\ \text{Cl} \end{array}$

2. Bonds: 1a. 4 1b. 3 Lone Pairs: 1a. 0 1b. 10

3. a. Selenium 2 (main group 6) b. Iodine 1 c. Silicon 4 d. Nitrogen 3

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Lesson 25B: Molecular Shapes and Bond Angles

VSEPR

A key factor that determines the behavior of molecules is their shape: how the atoms and electrons are arranged in three-dimensional space.

The shapes and bond angles of most molecules can be predicted with reasonable accuracy using Lewis diagrams. This technique is called **valence shell electron-pair repulsion** theory (VSEPR). The term simply means that all electron pairs, whether they are lone pairs or bonds, will repel each other, and they will separate by the maximum possible angle around the nucleus of an atom.

Below, we will learn to predict how atoms and electrons are arranged based on the columns of the periodic table. A chart at the end will summarize these rules.

To Predict the Shape of a Covalent Molecule

1. Draw the Lewis diagram for the molecule.
2. The general *shape* of a molecule is named based on the number of *directions* in which the electron pairs are found around the central atom. For the *general* shape, it will not matter whether electrons are in bonds or lone pairs, or single, double, or triple bonds.

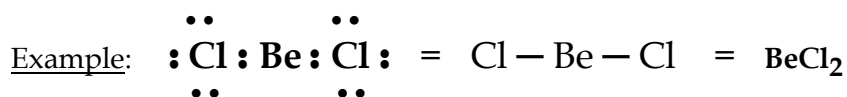
All of the electron pairs must be considered to determine the shape and bond angles, but the shape is *named* based only on the positions of the atoms. The lone pairs help to *determine* the shape, but they are ignored in *naming* the shape, of a covalent molecule.

- a. **One pair:** If a bonded atom is surrounded by only **one** electron pair, it has one bond to a second atom. The shape around this atom is said to be **linear**. Since it takes three points to determine an angle, and two atoms are two points, an atom with only one bond has **no** bond angles.



Each H has one bond. The molecule has a *linear* shape with *no* bond angles.

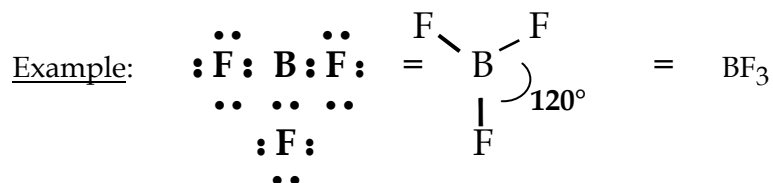
- b. **Two pairs:** If an atom in a molecule is surrounded by **two** electron pairs, both will be bonds. The two electron pairs will separate as much as possible by assuming a **linear** shape around the central atom. This shape results in three atoms in a line. With three points to determine an angle, the **bond angle** around the central atom is **180°**.



The **Be** in BeCl_2 is surrounded by two electron pairs, and both are bonds. The arrangement of the bonds around the central atom, and the shape of the molecule, is **linear** with **180°** bond angles.

Note that BeCl_2 is *electron deficient*: it violates the octet rule. BeCl_2 does form, but as an electron-deficient molecule it has some unusual properties.

- c. **Three pairs:** If a central atom is surrounded by electron pairs in **three** directions, the shape that allows the electron pairs to get as far apart as possible is termed **trigonal planar**. The three bonds are in a plane (flat) with **120°** bond angles.



The shape of the BF_3 molecule is **trigonal planar**. All bond angles are **120°**.

Like BeCl_2 , a BF_3 Lewis diagram can be drawn using single bonds, but it violates the octet rule. BF_3 does form, but as you might predict with its electron deficient structure, it has some unusual properties.

- d. **Four pairs:** Due to the octet rule, *most* stable atoms are surrounded by *four* electron pairs. The three-dimensional **tetrahedral** shape allows those four pairs to get as far apart as possible. In a **tetrahedron**, *all* of the angles are **109.47°**.

You will need a tetrahedral molecular model for the sections below. If you have not purchased models, build the cardboard model on the next page, then return here.

Building A Cutout Tetrahedral Model

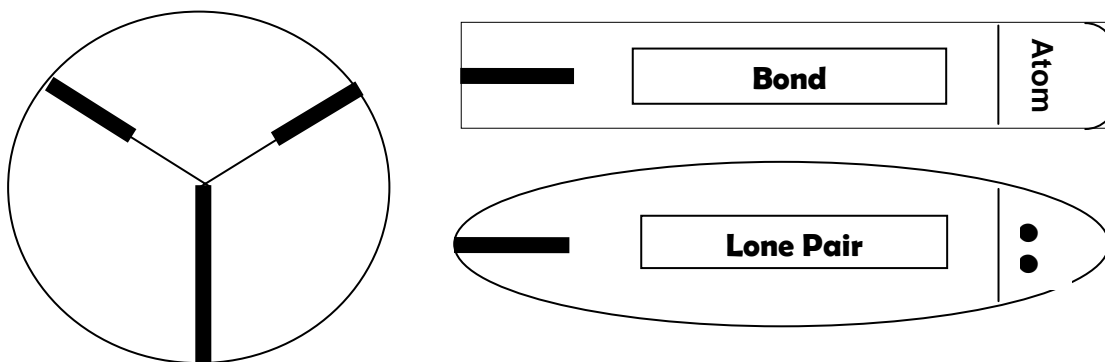
If you do not have access to a commercial molecular model kit, a tetrahedral model can be constructed from the patterns below.

Steps:

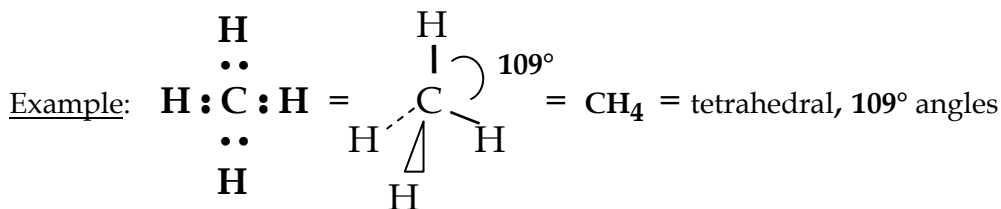
1. Obtain a sheet of foamboard or thick or corrugated cardboard at least one-half the size of this sheet of paper.
2. Either copy this page, or cover this page with thin paper and trace onto the paper, the three shapes below. Cut out the three paper patterns.
3. Using the patterns and blunt scissors, carefully cut the foamboard or cardboard to make **2** circles, **4** rectangles, and **3** ovals.
4. Cut slots in the 9 pieces at the thick lines. The slots should be to the *depth* shown by the thick lines. Cut the slots to a *width* that matches the thickness of the cardboard, so that the pieces slide together in the slots tightly, but with minimal binding.
5. On the four *bonds*, round off the corners of the *atom* ends just a bit.
6. Push together the two circles using the deep slot in each. Arrange them so that they are at right angles, simulating a spherical shape.
7. Add two bonds to each circle to give four bonds total. Push the slots on the bonds into the shallow slots on each circle. Try to get the bonds to be perpendicular to the circle to which they are attached.

With four *bonds*, the model represents central atoms in the *carbon* family. The four *electron pairs* around the central atom are in a tetrahedral shape. Since all of the electron pairs are bonds to atoms, the *atoms* around the central atom are in a tetrahedral shape. Since the position of the atoms decides the shape of the molecule, the molecule is tetrahedral, and the angle between any two bonds is 109° .

Models for other families will be made by substituting lone pairs for bonds.



- a. For a single-bonded central atom in the *carbon* family (main group 4), all four electron pairs around a central atom are *bonds*, and the arrangement of the *bonds* is said to be *tetrahedral*, with $\sim 109^\circ$ angles between all of the bonds.



A three-dimensional tetrahedron is difficult to represent on two-dimensional paper. In the diagram above, the - - - line represents a bond going behind the plane of the paper, and the Δ represents a bond coming out of the paper. A 3-D model will assist in working with this important shape.

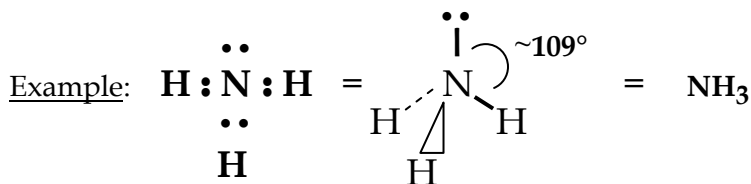
Build a CH_4 molecule from your molecular model pieces. Place the assembled model on a flat surface, then flip it so that it rests on three different points. Flip it again. Note the high symmetry of a three-dimensional tetrahedron: the shape of the molecule should be the same no matter which three atoms the model sits upon.

- b. A single-bonded central atom in the *nitrogen* family (main group 5) most often is surrounded by *three bonds* and *one lone pair*.

There are four electron pairs around the central atom, and the pairs assume a tetrahedral shape to get as far apart as possible. Because this electronic geometry is tetrahedral, the angles between all of the electron pairs, bonds, and the atoms are tetrahedral ($\sim 109^\circ$).

However, the lone pairs, though they count in determining the shape around a central atom, are not considered when *naming* the shape. The shape is named based on the position of only bonds and atoms.

For this case of one lone pair and three bonds around a central atom, the four atoms are in the shape of a low pyramid. The central atom is above the plane of the three atoms to which it bonds. Since the pyramid rests on 3 points, the shape of the atoms is called a **trigonal pyramid**, and the *molecular* geometry is termed **trigonal pyramidal**.

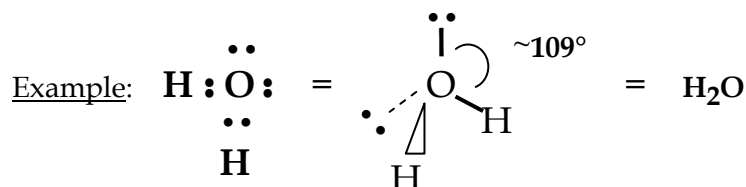


Build this NH_3 molecule from your kit. Starting from CH_4 , replace one bond with a lone pair. The four electron pairs are still in a tetrahedral shape. Then take off the lone pair to look at just the shape and angles of the *bonds* and *atoms*. With the central nitrogen atom on top, check that the atoms form a low *pyramid* with tetrahedral ($\sim 109^\circ$) angles.

The shape of NH_3 is **trigonal pyramidal** with $\sim 109^\circ$ bond angles.

- c. A single-bonded neutral atom in the *oxygen* family (main group 6) is most often surrounded by *two bonds* and *two lone pairs*. These four electron pairs repel to assume a tetrahedral shape with $\sim 109^\circ$ angles around the central atom.

As always, the lone pairs count in deciding the shape, but do not count when naming the shape of the bonds around the central atom or the molecule. The two bonds and the three atoms are said to be in a *bent* shape, with $\sim 109^\circ$ angles.



Build this water molecule. Place two bonds and two lone pairs around the central atom. This puts the four electron pairs into a tetrahedral shape.

Switch the position of one bond and one lone pair. Does this create a new molecule?

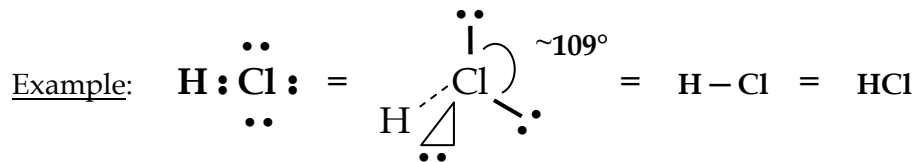
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No. Due to the symmetry of a tetrahedron, all four electron pairs around the central atom are in equivalent positions. The *same molecule* results no matter where the two bonds and two lone pairs are attached.

In Lewis diagrams, we treat four sides around an atom symbol as equivalent because four electron pairs repel into a tetrahedral shape, and the four sides of a tetrahedron are equivalent.

Now remove the two lone pairs. The geometric shape of the bonds and atoms, and of the H_2O molecule, is **bent**. Its one bond angle is $\sim 109^\circ$.

- d. If four electron pairs surround a central atom, but only one is a bond, the electronic geometry is tetrahedral. However, since there are only two atoms, and the atoms determine the name of the shape, the shape of the molecule is *linear*. Since there is only one bond, there is no bond angle.



The shape around the chlorine, and of the HCl molecule, is **linear** with *no* bond angles.

3. **FINE TUNING:** We can increase the accuracy of VSEPR bond-angle predictions with the following rule:

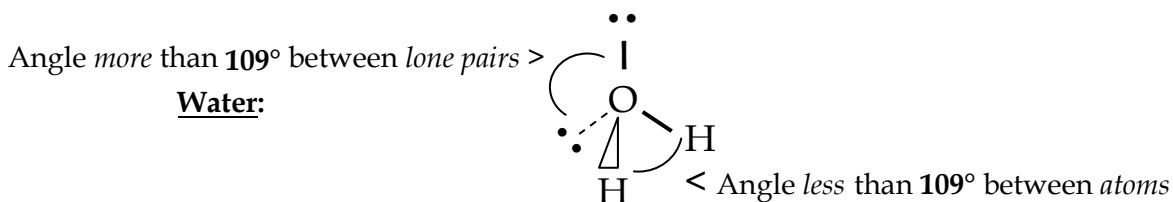
Lone pairs repel slightly more than bonds. The lone pairs need more room.

If one or two lone pairs are present in a tetrahedral shape, the angles around the lone pairs will be slightly larger than 109° . This will push the angles between *bonds* to be slightly *less than* 109° .

Lone pairs tend to occupy slightly more space than bonds, because *bonding* pairs are more localized along the axis between the atomic nuclei. This means that the lone pairs repel other pairs slightly more than bonds. The angle between the lone pairs is therefore slightly larger than the angle between bonds.

For example, the general model predicts that in a water molecule, the shape is bent with bond angles of $\sim 109^\circ$. However, because water has two lone pairs, they repel each other and the bonds slightly more than the bonds repel each other. This “lone pair scrunch” forces the bonds into an angle slightly *smaller* than 109° .

In water, the shape is bent as predicted, but the actual measured bond angle is 104.5° , slightly less than the tetrahedral angle that the general rules predict. The angle in water is a typical value for central atoms surrounded by two lone pairs and two bonds.



In what cases for single-bonded compounds will bond angles be *less* than 109° ? Only cases with *one* lone pair and three bonds, or *two* lone pairs and two bonds: those with central atoms in the *nitrogen* or *oxygen* family, which are those in the 5th or 6th tall column of the periodic table.

For single-bonded *carbon* family neutral atoms, the bond angles are 109° rather than *less* than 109° . When there are no lone pairs around the central atom, there is no lone pair effect on the angles.

We will call this the “lone pair scrunch” rule:

In neutral molecules containing only single bonds, around central atoms in the nitrogen family (column 5) or oxygen family (column 6), the bond angles are usually 103° to 109° : slightly less than 109° .

Summary

For the second row of the periodic table, and with frequent exceptions for rows below the second row, central atoms in neutral compounds will generally have the characteristics listed in the table below. Learn this table so that given the terms in the first column you can fill in the blanks, based on the rules for the behavior of electron pairs.

For neutral, single-bonded atoms:

Second Row Symbol	Li	Be		B	C	N	O	F	Ne
Main Group Number	1	2		3	4	5	6	7	8
Valence Electrons	1	2		3	4	5	6	7	8
Bonds	Ionic Bonds			3	4	3	2	1	0
Lone Pairs	-	-		0	0	1	2	3	4
Shape	Linear	Linear		Trigonal Planar	Tetrahedral	Trigonal Pyramidal	Bent	Linear	No Bonds
Bond Angles	None	180°		120°	109°	<109°	<109°	None	

Practice: Use a periodic table, plus models if needed. Check answers after each part.

- For a molecule in which the central atom is surrounded by two bonds and two lone pairs,
 - What is the shape of the electron pairs?
 - What is the shape of the atoms?
 - What is the bond angle?
- From memory, list the predicted shapes of the bonds around central atoms for the atoms in the second row of the periodic table, in order.
- From memory, under each shape in Problem 2, write the predicted bond angles.

4. Complete this table based on VSEPR predictions for neutral, single-bonded atoms.

Molecule	NF ₃	SiH ₄	AlCl ₃	SI ₂
Lewis (Dot) Diagram				
Shape of Electron Pairs				
Shape of Molecule and Bonds				
Bond Angles				

5. Which molecule in Problem 4 would likely be the least stable and most reactive? Why?

ANSWERS

1. The four electron pairs repel to into a tetrahedral shape. The three atoms are bent, with a bond angle of slightly *less* than 109°.

2. Linear, Linear, Trigonal Planar, Tetrahedral, Pyramidal, Bent, Linear, No Bonds

3. None 180° 120° ~109° <109° <109° None

4.

Molecule	NF ₃	SiH ₄	AlCl ₃	SI ₂
Dot Diagram	<pre> :F:N:F: :F: .. </pre>	<pre> H .. H:Si:H .. H </pre>	<pre> :Cl:Al:Cl: :Cl: .. </pre>	<pre> :I:S:I: </pre> <p>(also could be drawn at 90°)</p>
e ⁻ Pairs	Tetrahedral	Tetrahedral	Trigonal Planar	Tetrahedral
Molecule and Bonds	Trigonal Pyramidal	Tetrahedral	Trigonal Planar	Bent
Bond Angles	<109°	109°	120°	<109°

5. AlCl₃ would be predicted to be the least stable and most reactive because Al has an unsatisfied octet.

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Lesson 25C: Electronegativity

The Electronegativity Scale

What decides if a particular bond will be ionic or covalent? Our previous “rule of thumb” has been that if a bond is between a metal and a non-metal atom, it will likely be ionic, but if it is between two non-metals, it will be covalent. A more precise view is that bonds have a mixture of ionic and covalent character. This latter model for bonding will allow more accurate predictions of the properties and behavior of bonds and substances.

Atoms have differing attractions for electrons. **Electronegativity** (a model developed by the American chemist Linus Pauling) predicts how strongly each atom attracts the electrons in a bond.

The electronegativity scale assigns each atom a value between 0.7 and 4.0. Fluorine (EN = 4.0) is the strongest electron attractor of all the atoms. Cesium and francium (EN = 0.7) are the weakest electron attractors.

The following table lists the electronegativity values of the atoms. (These numbers are termed the *Pauling values*. Other models may use slightly different EN values.)

The electronegativity values (EN) for the *second* row atoms should be memorized. This is easy, since the 2nd row numbers start at 1.0 and increase by 0.5 for each atom to the right. The frequently used values for hydrogen (2.1) and chlorine (3.0) should also be memorized.

It will speed your work if the electronegativity values (EN) for the *second* row atoms are memorized. This is easy, since the 2nd row numbers start at 1.0 and increase by 0.5 for each atom to the right. The values for hydrogen (2.1) and chlorine (3.0) are also encountered frequently and should be committed to memory.

Electronegativity Values

Row 1	2.1								
Row 2	1.0	1.5		2.0	2.5	3.0	3.5	4.0	
Row 3	0.9	1.2		1.5	1.8	2.1	2.5	3.0	
Row 4	0.8	1.0	1.3-1.9	1.6	1.8	2.0	2.4	2.8	
Row 5	0.8	1.0	1.2-2.2	1.7	1.8	1.9	2.1	2.5	
Row 6	0.7	0.9	1.0-2.4	1.8	1.9	1.9	2.0	2.2	
Row 7	0.7	0.9							

In the table, note that

- hydrogen’s value of 2.1 is in the middle range of values.
- Only four atoms have EN values of 3.0 and above: N, O, F, and Cl.
- Values generally (but not always) increase toward the top right corner of the periodic table: to the right across a row and up a column.

To predict bond behavior, the electronegativity model divides bonds into three types: Ionic, polar covalent, and non-polar covalent.

Ionic Bonds

In general, if the *difference* between the electronegativities of two bonded atoms

- is *greater* than 1.7, the bond will generally have *ionic* character;
- is 1.7 or *less*, the bond is likely to have *covalent* character.

(Different texts may use different cutoff values, but 1.7 is a typical choice.)

An ionic bond can be thought of as a bond in which the difference in electron attraction is so strong that the more electronegative atom removes valence electrons from the other atom to form two charged particles.

Polar Versus Non-Polar Covalent Bonds

Covalent bonds are divided into two types: **polar** and **non-polar**.

For a covalent bond between two atoms that have the same or very similar electronegativity values, the electrons on average will be found at an equal distance between the two nuclei.



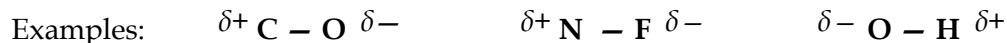
A covalent bond in which the electrons are *equally shared* is said to be *non-polar*.

Whether bonds are single, double, or triple bonds (as in $C \equiv C$ above) does not affect the electronegativity difference.

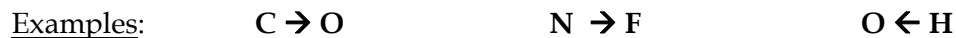
As the difference in the electronegativity of two bonded atoms increases, the bond becomes more *polar*. The electrons are still shared, but they tend to be found closer to the more electron-attracting atom.

This uneven electron sharing creates a **dipole**: an uneven distribution of electric charge. The more electronegative atom takes on a *partial* negative charge, while the weaker electron attractor takes on a *partial* positive charge.

In chemistry, dipoles are generally represented using two types of notation. In math and science, a δ (a lower-case Greek *delta*) is often used as a symbol meaning *partial*. In this notation, a polar bond is labeled with two deltas: The atom that is the stronger electron attractor, with the higher electronegativity value, has its partial negative charge labeled δ^- (pronounced *delta minus*), and the weaker electron attractor is labeled δ^+ (*delta plus*).



An alternate way to represent the dipole in a bond is to use an arrow in place of the bond. The arrow points toward the end of the bond with the stronger electron attractor; toward the side where on average the electrons are more likely to be found.



As the difference in electronegativity in bonds rises, from zero to as high as 3.3, the character of the bond changes *gradually* from non-polar to polar to ionic. However, in general, if the difference in electronegativity between two atoms is

- from **0 to 0.4**, the bond is considered to be covalent and *non-polar*;
- from **0.5 to 1.7**, the bond is considered to be covalent but *polar*;
- **above 1.7**, the bond is considered to be *ionic*.

The choice of the breakpoints at 0.4 and 1.7 is arbitrary. Some textbooks use values such as 0.3 or 0.7 and 2.0. In any case, the electronegativity differences are best understood as gradually shifting as they increase: from non-polar, to polar, to ionic character.

Practice: Memorize the electronegativity values for H and Cl. Note the pattern for the values for the second row atoms. Then use a periodic table that does not include electronegativity values on the problems below. Check your answers after each part.

- For each of the bonds below,
 - write the electronegativity value above each atom from memory.
 - Below the bond, label each atom as δ^+ or δ^- .
 - On the next line down, calculate the electronegativity difference.
 - On the next line down, label the bond as non-polar, polar, or ionic.
 - On the next line down, re-write the bond using an arrow in place of the bond to show the direction of the dipole.



ANSWERS

1a.	2.5 2.1	3.0 3.0	2.5 4.0	3.5 2.0
	C – H	N – Cl	C – F	O – B
1b.	$\delta^- \delta^+$	no δ	$\delta^+ \delta^-$	$\delta^- \delta^+$
1c.	0.4	0	1.5	1.5
1d.	non-polar or slightly polar	non-polar	polar	polar
1e.	C \leftarrow H	N – Cl (no dipole)	C \rightarrow F	O \leftarrow B

* * * * *

Lesson 25D: Predicting Polarity

Polar versus Non-Polar Substances

- Why do salad oil and water-based vinegar, after being shaken, separate into two layers, yet most alcohols and water dissolve into each other without forming two layers?
- Why do soaps and detergents dissolve in water, but also dissolve oils from food and skin that normally do not dissolve in water?
- Why do salts and sugars dissolve in water, but most rocks do not?
- Can we predict formulas for pharmaceuticals that will relieve pain and cure disease?

The answers to these practical and important questions are often found in the shapes and polarities of bonds and of substances.

In the previous lesson, electronegativity was used to classify *bonds* as ionic, polar and non-polar. *Molecules* can also be classified as having *ionic*, *polar*, and *non-polar* character.

In classifying the polarity of combinations of atoms, the rules are:

1. A compound with just *one* ionic bond will generally (but not always) have ionic behavior, even if it also has many non-polar bonds.
2. A *molecule* with all covalent bonds will be *polar* if
 - it has polar bonds *and*
 - the dipoles do *not* cancel due to molecular symmetry.
3. A *molecule* will be *non-polar* if
 - it has *all* non-polar bonds, *or*
 - it has polar bonds, but the dipoles cancel due to symmetry.

Flow Chart: Predicting the Polarity of Molecules

Knowing the chemical formula for a substance, we can often make *general* predictions about whether its whether molecules will have ionic, polar, or non-polar behavior. The rules below comprise a simplified model, but they provide reasonably good predictions for the polarity of *most* substances.

Compounds that are combinations of metals and non-metals usually (but not always) display ionic behavior. Formulas that you recognize as ionic solids will also be ionic.

In other cases, to predict whether a substance will have ionic, non-polar, or polar behavior, apply the rules in the following *flow chart* in order.

1. Write the formula for the substance. If the substance includes a metal and a non-metal, the *substance* is *ionic*. In addition, if any *one* bond is ionic, the *substance* is *ionic*.
2. If rule 1 does not apply, list each type of *bond* in the substance, then
 - a. add electronegativity (EN) values to each atom.
 - b. Based on the EN *differences*, label the *bonds* as ionic, non-polar, or polar.

- c. If *all* of the bonds are *non-polar*, the *substance* is *non-polar*.
3. If rules 1 and 2 do not apply to the particle, one or more of the bonds must be polar.
- Draw the Lewis diagram and sketch the shape of the molecule.
 - On the sketch, replace the bonds with arrows representing the dipoles. Use geometry and symmetry to see if the dipoles cancel. If needed, make a 3-D model.
 - If the dipoles *cancel*, the molecule is *non-polar*. If the dipoles do *not* cancel, there is a net dipole, and the molecule is *polar*.

Dipole Cancellation

You may have had practice *adding vectors* in math or physics classes. Dipoles are one of the types of quantities that add in two or three dimensions using vector addition. Even if you have not practiced vector addition, dipole addition can often be simplified by this rule:

Equal but opposite dipoles *cancel*.

Let's learn the method by example. Based on the flow chart rules above, apply the steps above to the following cases, and then check your answers below.

Q. Label these substances as *ionic*, *polar*, or *non-polar*. Use a periodic table without EN values (all of these atoms have values you should know). Because these particles are *two-dimensional*, you should not need models to evaluate symmetry.

1. Cl₂

2. LiCl

3. O=C=O (linear)

4. HCl

* * * * *

Answers

1. In Cl₂, the shape must be **Cl—Cl**. Both have the same electronegativity value, so the difference in EN values between the two atoms is *zero*. When the EN difference is 0 to 0.4, the bond is non-polar, and the *molecule* is covalent **non-polar**.

When the electronegativity difference between two atoms is zero, there is *equal* sharing of the electrons in the bond between the two atoms. On average, the two electrons in the bond will be found half-way between each atom, so there is no bond dipole.

* * * * *

2. Li has a 1.0 EN and Cl has a 3.0 EN. The difference is 2.0, which is above 1.7, so the bond is likely to have *ionic* behavior. If one bond (or more) in a compound is ionic, the compound is **ionic**. The more electronegative atom will tend to take the two electrons in the bond. The result is an Li⁺ ion and a Cl[−] ion.

* * * * *

3. CO₂ is a linear molecule with two double bonds. In calculating an EN difference, it does not matter whether the bond is single, double, or triple. The carbon EN is 2.5, oxygen's EN is 3.5, the EN difference is 1.0, so both *bonds* are *polar*.

When bonds are polar, the symmetry test must be applied to see if the dipoles cancel. Add the dipoles to the molecular shape: O←C→O. When dipoles are *equal* but in *opposite directions*, they *cancel* due to symmetry. That is true in this case. O←C→O has polar *bonds* but is a **non-polar** molecule because the dipoles cancel.

* * * * *

4. H has a 2.1 EN and Cl a 3.0 EN. The difference is 0.9, which is in the range of 0.5 to 1.7, so the bond is polar. The shape for this molecule must be **H–Cl**. Because Cl is more electronegative than H, the dipole points toward Cl: $\text{H} \rightarrow \text{Cl}$. Since this bond is polar and there are no other bonds to cancel its dipole, the *molecule* has a dipole and is **polar**.

Practice A: Use a periodic table that does not include electronegativity values (you should know these from their table position). If needed, check answers after each part.

Based on VSEPR and electronegativity, predict whether these compounds will be *ionic*, *covalent polar*, or *covalent non-polar*.

1. BeH_2 2. LiF 3. $\begin{array}{c} \text{H} \\ \backslash \\ \text{C}=\text{O} \text{ (flat shape)} \\ / \\ \text{H} \end{array}$ 4. BCl_3

Polarity In 3-D Molecules

In the section above, we considered two-dimensional molecules. For compounds that are three-dimensional, it helps to make a model to judge the dipoles and symmetry. For three-dimensional molecules with tetrahedral pairs, the following are general rules.

1. If a central atom in the *carbon* family has single bonds to four atoms that are the *same* kind of atom, even if the bonds are polar, the dipoles will cancel due to symmetry. The *molecule* will be *non-polar*.

Examples: CH_4 and SiF_4 are non-polar molecules.

2. For a single-bonded central atom that obeys the octet rule in the nitrogen or oxygen family, the molecular shape is *trigonal pyramidal* or *bent*. If *any* of the three bonds are polar, *and if all* of the dipoles point to, or all point away from, the central atom, the *molecule* is *polar* because the dipoles cannot cancel.

Examples: NH_3 , OF_2 are polar molecules.

3. In more complex cases, a model should be made and the dipoles analyzed.

Some examples will help with these rules. Do the parts below one at a time, checking your answers after each part.

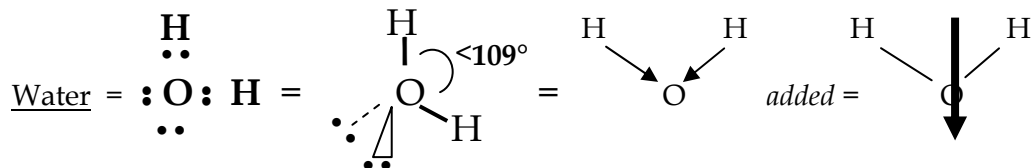
Q. Using the flow chart and symmetry rules, label these compounds as *ionic*, *polar*, or *non-polar*. Use a periodic table without electronegativity values. Make molecular models if needed.

1. H_2O 2. CCl_4 3. NH_3 4. CHF_3

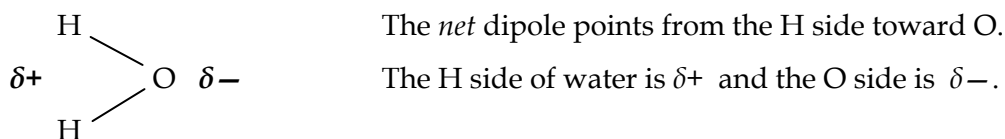
* * * * *

To evaluate molecular polarity, use the flow chart. First evaluate bond polarity. *If* the bonds are *polar*, evaluate symmetry to see if the dipoles cancel.

1. H_2O : H has an EN of 2.1, O has an EN of 3.5. The difference of 1.4 makes the bond polar. When the bond is polar, evaluate the symmetry.



H_2O has tetrahedral 3-D electron pairs but 2-D bonds and atoms. In this model, assume that bonds, not lone pairs, contain the dipoles. The bonds in water have a bent shape with $<109^\circ$ angles. Both of the dipoles point toward oxygen, so they do *not* cancel. The bonds are polar *and* the water *molecule* is **polar**. The dipole in water can be represented by an arrow (above) or using $\delta+$ notation below.



Even with its polar bonds, if water were H-O-H linear in shape, it would not have a net dipole. However, the bonds in water are *bent* rather than linear. This means that

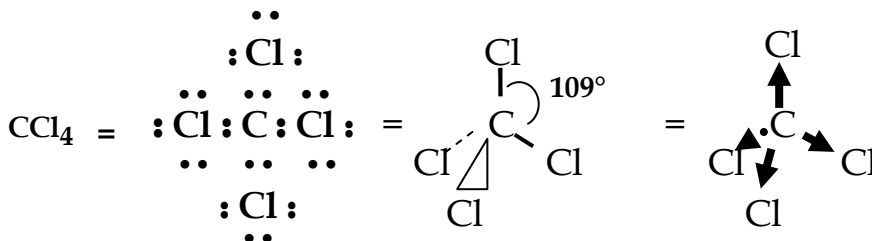
Water is *polar*.

The polarity of water is an important factor in many reactions in chemistry and biology.

★ ★ ★ ★ ★

2. CCl_4 : C is EN 2.5 and Cl is EN 3.0, so the C–Cl bond weakly polar, and the dipoles point toward Cl.

CCl_4 is *tetrahedral* with 4 *equal* bond dipoles. Turning the model so that two bonds are up and two down, the top and the bottom two dipoles cancel side to side. The resultants are two dipoles, one pointing up and the other down. These two resultant dipoles also cancel, because they are equal but in opposite directions.

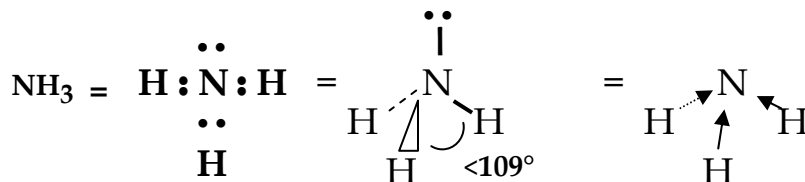


When a central atom is surrounded by four tetrahedral bonds to the same atom, the molecule is always *non-polar* due to symmetry.

★ ★ ★ ★ ★

3. **NH₃**: First evaluate *bond* polarity. The EN of N is 3.0, and of H is 2.1. The difference of 0.9 means that the bonds are polar, with the dipoles pointing toward N.

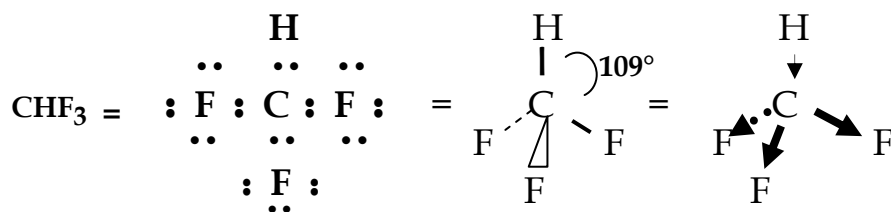
Polar bonds can mean polar *or* non-polar molecules, depending on whether the dipoles cancel. To check for dipole cancellation, draw the Lewis diagram: NH₃ has tetrahedral electron pairs with one lone pair and 3 bonds. Make the tetrahedral model, then take off the lone pair, to focus on the bonds that determine the polarity. If the model is placed so that the central N is up, all of the dipoles point upward from the H's toward N. The dipoles are equal but not *opposite*: they do not cancel. NH₃ is **polar**.



In pyramidal molecules, three dipoles in the same direction, pointing either to or from a central atom, always result in polar molecules.

* * * * *

4. **CHF₃**: The bonds between C (2.5) and F (4.0) are strongly polar toward F, with an EN difference of 1.5. The C–H bond is only slightly polar. The molecule may be non-polar if the C–F dipoles cancel. To check for dipole cancellation, draw the Lewis diagram. CHF₃ has tetrahedral electron pairs with 4 bonds. Then assemble the tetrahedral model. If the model is held so that the H atom is up, all of the dipoles point down. The dipoles are *not* equal and opposite: they do not cancel. By VSEPR and electronegativity rules, CHF₃ is predicted to be a **polar** molecule.



Exceptions

The above rules classify substances as non-polar, polar, and ionic. In reality, polarity is not that simple.

- The polarity of substances can be measured numerically, and those measurements show a *continuum* of values from totally non-polar to highly ionic.
- There are factors that affect polarity in addition to the electronegativity and atom geometry considered in our model above.
- Our rules classify as non-polar molecules that are slightly polar.

That said, our simplified model is a starting point for evaluating polarity. It does provide predictions of properties based on polarity, such as whether or not the substance will be soluble in water, that hold true for a wide variety of substances.

Practice B: On these, use a periodic table *and* a table of electronegativity values. Be prepared to build tetrahedral models. If needed, check your answers after each part.

Based on VSEPR and electronegativity, predict whether these compounds will be *ionic*, *polar*, or *non-polar*.

1. SF₂ 2. PCl₃ 3. SiH₄ 4. SiH₃Cl

ANSWERS

Practice A

All of the molecules in Practice A are *two* dimensional: their shapes can be drawn on paper.

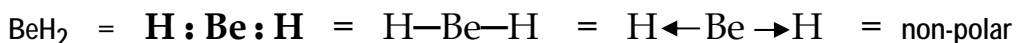
1. BeH₂ First assign EN values to categorize the bonds. $2.1 \text{ H} - 1.5 \text{ Be} = 0.6 > 0.4 = \text{polar bonds}$.

//bonds are polar, draw the Lewis diagram and shape to see if the dipoles cancel.

The central atom Be has a linear shape for its bonds and 180° bond angles.

Add the dipoles by vector addition. Because they are equal and in opposite directions: they cancel. The VSEPR prediction is that the molecule is **non-polar**.

$$\text{EN: } 2.1 \quad 1.5 \quad 2.1$$



2. LiF First assign EN values to categorize the bonds. $4.0 \text{ F} - 1.0 \text{ Li} = 3.0 > 1.7 = \text{ionic bonds}$.

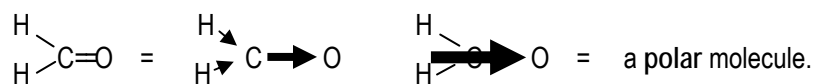
If one bond is ionic, the compound is **ionic**.

3. H₂C=O Assign EN values to categorize the bonds.

$2.1 \text{ H} - 2.5 \text{ C} = 0.4 = \text{slightly polar bond toward C}$. $3.5 \text{ O} - 2.5 \text{ C} = 1.0 = \text{a polar bond toward O}$.

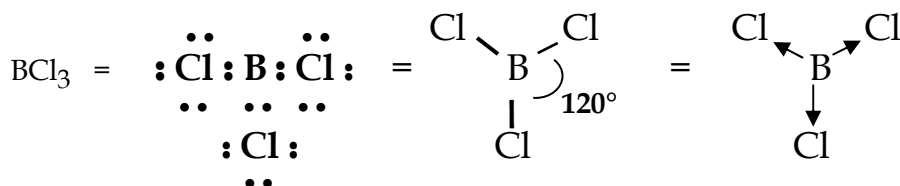
Electronegativity differences apply in the same way to single and double bonds.

If one or more bonds are polar, draw the Lewis diagram, sketch the shape, add the dipoles, and see if the dipoles cancel. Since this molecule is flat, it can be analyzed on paper.



4. BCl₃ Assign EN values to categorize the bonds. $3.0 \text{ Cl} - 2.0 \text{ B} = 1.0 > 0.4 = \text{polar bonds}$.

If bonds are polar, draw the Lewis diagram and shape to see if the dipoles cancel.



The central atom B is predicted by VSEPR to have a trigonal planar shape for its bonds and 120° bond angles. Adding the dipoles by vector addition, they are equal and in opposite directions: they cancel. The VSEPR prediction is that the molecule is **non-polar**.

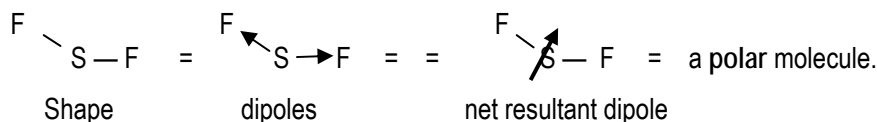
Practice B

1. SF_2 : Assign EN values to categorize the bonds. $4.0 \text{ F} - 2.5 \text{ S} = 1.5 > 0.4 = \text{polar bonds}$.

If bonds are polar, *either* draw the Lewis diagram and shape, add the vectors and see if they cancel.

Since sulfur is in the oxygen family, it generally bonds twice. Fluorine, a halogen, generally bonds once. Sulfur, with more bonds, is therefore the central atom. Central atoms in the oxygen family form neutral covalent molecules that are bent, with slightly less than 109° bond angles. *Bent* molecules are two dimensional; their polarity can be evaluated on paper.

Since the two dipoles are 109° apart and not 180° , they are equal but not opposite. Adding the two dipoles by vector addition gives a net, resultant dipole. The molecule is predicted to be polar.

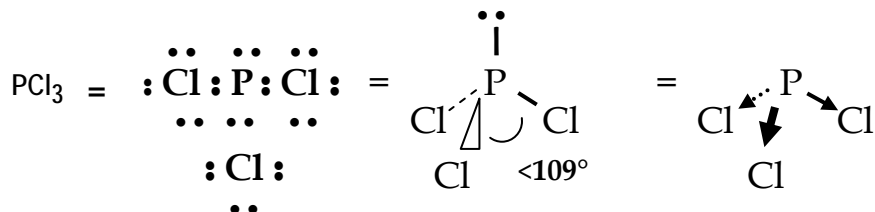


Or use the rule that *bent* molecules with two or *trigonal pyramidal* molecules with three of the same polar bonds are always polar molecules.

2. PCl_3 : First label the bonds. $3.0 \text{ Cl} - 2.1 \text{ P} = 0.9 = \text{polar bonds}$.

If any of the bonds are polar, draw the Lewis diagram and shape, then add the dipole vectors to see if they cancel.

Since phosphorus is in the nitrogen family, it typically bonds 3 times. Chlorine, a halogen, usually bonds once. Phosphorus, bonding more, is therefore the central atom. Single bonded central atoms in the nitrogen family form neutral covalent molecules that are *trigonal pyramids* with slightly less than 109° bond angles.



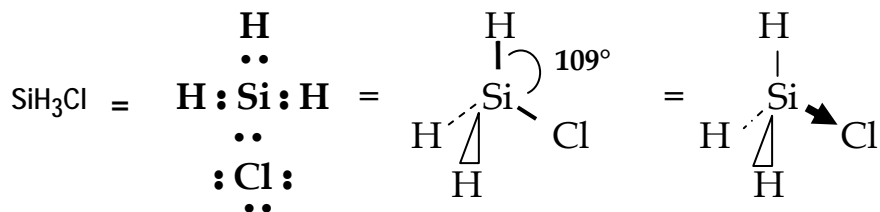
Lone pairs are not bonds and do not have dipoles. The three bond dipoles are equal but *not* in opposite directions, so they do not cancel. The molecule is **polar**.

Bent and *trigonal pyramidal* molecules with the same polar bonds are always polar molecules.

3. SiH_4 : For a central atom in the carbon family, whenever four of the same atoms are attached, any dipoles will cancel due to tetrahedral symmetry. SiH_4 is a **non-polar** molecule.
4. SiH_3Cl Assign EN values to categorize the bonds.

$2.1 \text{ H} - 1.8 \text{ Si} = 0.3 = \text{non-polar Si—H bonds}$. $3.0 \text{ Cl} - 1.8 \text{ Si} = 1.2 = \text{a polar Si—Cl bond with the dipole toward Cl}$. If any bonds are polar, draw the Lewis diagram and shape, add the vectors and see if they cancel.

Since silicon is in the carbon family, it bonds four times. Chlorine and hydrogen bond once. Silicon, bonding more, is the central atom. For neutral covalent compounds with their central atoms in the carbon family, molecules are *tetrahedral* with 109° bond angles. Make a model to investigate the symmetry.



SiH_3Cl has one polar bond un-cancelled by others. The molecule is predicted to be polar.

* * * * *

Lesson 25E: Solubility

How much of a substance will dissolve in a given liquid is complex: it depends on the size, geometry, electronic properties, temperature, and relative amounts of the particles of the substance and the liquid. However, some useful general rules can predict solubility for a large number of substances and solvents.

If a liquid composed of *non*-polar molecules (such as a salad oil) is shaken with a liquid composed of *polar* molecules (such as vinegar, which is primarily water), when the shaking stops, the two liquids will slowly separate into two layers.

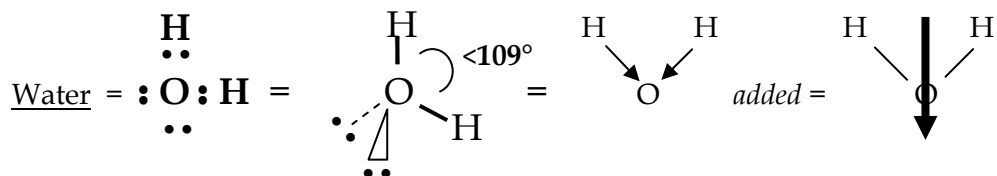
When two liquids composed of polar molecules, such as water and alcohols, are mixed, the liquids dissolve in each other. One solution without layers is the result.

Why the difference?

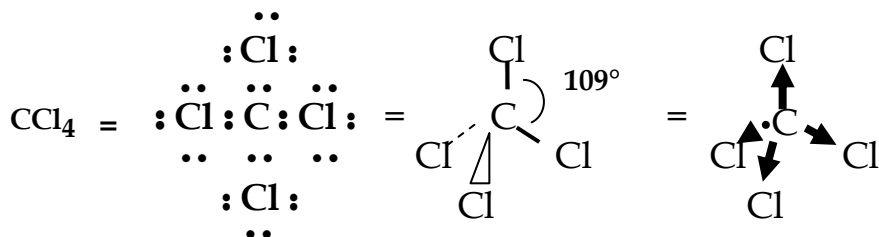
For solubility, the general rule is: *like dissolves like*.

- Polar liquids tend to dissolve *polar* or *ionic* particles.
- Non-polar liquids tend to dissolve *non-polar* molecules.
- Polar and non-polar substances tend not to dissolve in each other.

The most common *polar* solvent is water.



An example of a *non*-polar liquid is carbon tetrachloride, in which the four equal and opposite dipoles cancel to give a non-polar molecule.



If H_2O and CCl_4 are shaken together, after the shaking stops, the two liquids separate into two layers, just as with oil and vinegar dressing. In oil and vinegar, the salad oil will rise above the denser water. If water is mixed with CCl_4 , the denser CCl_4 will be the bottom layer, with the water on top.

When mixed liquids separate into layers, they are said to be **immiscible** (pronounced em-MISS-ible). When liquids dissolve in each other, as in the case of water and ethanol, they are termed **miscible** (MISS-ible).

Choosing a Solvent

A solvent can be any liquid that dissolves other materials, but different liquids dissolve different substances. By analyzing the polarity of substances and solvents, we can generally predict whether a solvent will dissolve a substance.

Because water is polar, it tends to dissolve ionic solids, polar sugars, and polar alcohols. Carbon tetrachloride at one time was used as a “dry cleaning fluid.” It dissolves non-polar oils from clothing without the use of the water that could damage some fabrics. (Modern dry cleaning liquids are also non-polar but are less hazardous than CCl_4 .)

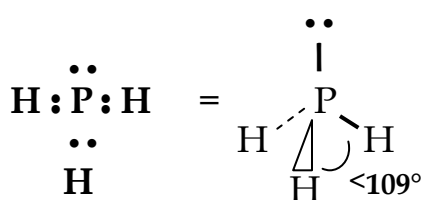
Compounds that are classified as oils do not dissolve well in water. For this reason, water is a poor solvent for the oils produced by skin that can soil clothing. **Soaps** and **detergents** are generally long-chain molecules that have a polar group on one end of a long non-polar chain. The polar group on one end allows soaps and detergents to dissolve in water, while the non-polar segment of the molecules can attract the skin oils coating fabrics. This “both polar and non-polar” structure allows soaps to dissolve in water and dissolve oils at the same time.

To choose a solvent to dissolve a substance, we begin by analyzing whether its particles are ionic, polar, or non-polar, then apply the solubility rule: “like dissolves like.”

Let’s try a few examples. Below, complete the PH_3 column first, check your answers on the next page, and then complete the remaining columns.

Molecule	PH ₃	H ₂	HBr
Lewis Diagram			
Shape of Electron Pairs			
Shape of Molecule			
Bond Angles			
Bond Polarity			
Molecule Polarity			
Dissolves in Oil or Water?			

* * * * *

AnswersPH₃ :

PH₃ is predicted to have tetrahedral electron pairs, a trigonal pyramidal shape, and bond angles of $< 109^\circ$.

For the bond polarity: EN of P = 2.1, EN of H = 2.1 . The P–H bond is non-polar. Because all of the bonds are non-polar, the molecule is predicted to be non-polar. Non-polar molecules dissolve in non-polar solvents, such as **oils**, gasoline, or CCl₄. They tend not to dissolve in water.

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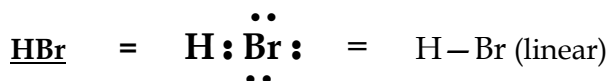


Two atoms in a molecule always have a linear shape with no bond angles.

For bond polarity: The EN difference is zero, so the *bond* is **non-polar**. If the only bond is non-polar, then the particle must be non-polar.

Non-polar compounds tend to dissolve in *polar* solvents like *oils* more than in water. You would predict that hydrogen gas is *not* very soluble in water.

* * * * *



HBr has tetrahedral electron pairs around bromine, a linear shape, and no bond angles.

For the bond polarity: The EN of H = 2.1, the EN of Br = 2.8.

The difference is 0.7, in the range of 0.5 to 1.7, so the *bond* is **polar**.

Adding the dipole to the linear shape gives $\text{H} \rightarrow \text{Br}$. The molecule is **polar**.

Polar compounds tend to dissolve in *polar* solvents like **water**, but not in non-polar oils. For solubility, like dissolves like.

* * * * *

The Reliability of VSEPR and Solubility Predictions

“Like dissolved like” is a simplified solubility rule, and there are many exceptions. Factors other than bond polarity and geometry, including molecular size, affect solubility. Most molecules are soluble to at least a slight extent in all solvents. Bond and molecular polarities are better described as a continuum than as a simple case of “polar versus nonpolar.” The VSEPR and electronegativity models are useful in predicting shape and solubility, but there are many exceptions.

For example, in PH₃ above, the VSEPR bond angles would be predicted to be about 107° as in NH₃, but actual bond angles are about 94°. For some substances, more sophisticated models will be needed to explain experimental results. That said, the rules for VSEPR, electronegativity, and “like dissolves like” will generally predict the shape, polarity, and solubility of *most* substances.

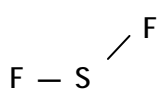
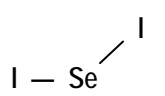
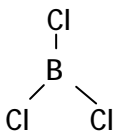
Practice. You may use a periodic table *and* a table of electronegativity values. Be prepared to build models. If needed, check your answers after each part.

Fill in the following chart for the substances shown. Based your predictions on the general rules for VSEPR, electronegativity, and solubility.

Molecule	SF ₂	SeI ₂	BCl ₃
Lewis Diagram			
Shape of Electron Pairs			
Shape of Molecule (Name and Sketch)			
Bond Angles			
Bond Polarity			
Molecule Polarity			
Dissolves in Oil or Water?			

ANSWERS

Molecule	SF ₂	SeI ₂	BCl ₃
Lewis Diagram	$\begin{array}{c} \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot\text{F} & : \text{S} & : \text{F}\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \end{array}$ <p>(also could be drawn at 90°)</p>	$\begin{array}{c} \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot\text{I} & : \text{Se} & : \text{I}\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \end{array}$ <p>(also could be drawn at 90°)</p>	$\begin{array}{c} \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot\text{Cl} & : \text{B} & : \text{Cl}\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \\ & \cdot\text{Cl}\cdot & \\ & \cdot\cdot & \end{array}$
Shape of Electron Pairs	Tetrahedral	Tetrahedral	Trigonal Planar

Shape of Molecule (Name and Sketch)	Bent 	Bent 	Trigonal Planar 
Bond Angles	$<109^\circ$	$<109^\circ$	120°
Bond Polarity	$4.0 - 2.5 = 1.5 = \text{polar}$	$2.6 - 2.4 = 0.2 = \text{nonpolar}$	$3.0 - 2.0 = 1.0 = \text{polar}$
Molecule Polarity	Polar (bent with polar bonds)	Non-Polar (non-polar bonds)	Non-Polar (the 3 dipoles cancel)
Dissolves in Oil or Water?	Water	Oil	Oil

* * * * *

Lesson 25F: Double and Triple Bonds

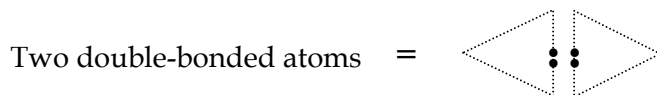
Double Bonds

Atoms in main groups 4 and above of the periodic table can satisfy the octet rule by forming **double bonds** that have *two* pairs of electrons between the atoms. In the Lewis diagram, the valence electrons for each double-bonded atom are placed on *three* sides of the atom symbol instead of the four sides used for single bonds.

Drawing Double Bonded Lewis Diagrams

If you know the molecular formula for a substance *and* you know that the molecule contains a double bond, draw the Lewis diagram using these steps.

- Count the total number valence electrons in the particle.
- Determine which atoms in the formula have the double bond between them. Because hydrogen bonds only once, it will not double bond. (The octet rule can be used for double-bonded halogens, but in most cases halogens will bond only once).
- Write the two double-bonded atoms next to each other so that there are *two pairs* of valence electrons (four electrons total) between them.



- Distribute the remaining valence electrons around each atom symbol. If the remaining bonds are single bonds, each bond will have two valence electrons. Double-bonded atoms may have lone pairs of electrons.

Satisfy the octet rule for the remaining atoms (but duet rule for H).

An example of a compound with one double bond is *ethene* (also called *ethylene*), C_2H_4 . Use the rules above to draw the Lewis diagram for ethene. Try steps one and two, and then check your answer below.

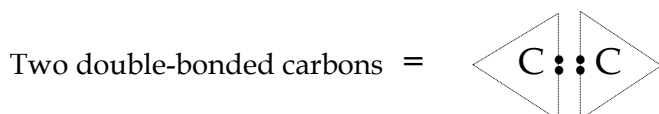
* * * * *

- C_2H_4 has 4 valence electrons from each carbon and one from each hydrogen, for a total of 12 valence electrons.
- Since hydrogen is in column one, it can bond only once and it can form only *single* covalent bonds. That leaves the two carbons to form the double bond.

Try step 3.

* * * * *

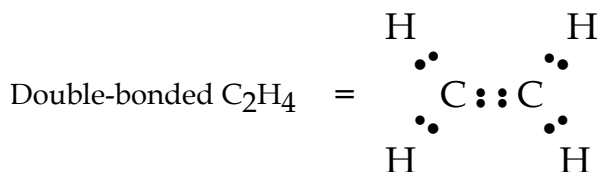
- Combine the two double-bonded atoms to form the double bond. It will have two pairs: four valence electrons. Note how the triangles faces meet in arranging the valence electrons around the double-bonded atoms.



Try step 4.

* * * * *

- Distribute the remaining 8 valence electrons and four atoms. Satisfy the octet for each carbon and the duet for each hydrogen.

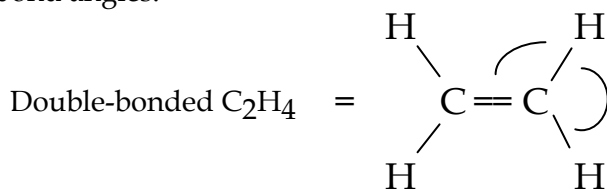


Double Bond Shape

The shape around a double-bonded atom can be predicted using the fundamental VSEPR rule: The directions with the electron pairs around each atom get as far apart as possible.

In determining shape, the pairs in a double bond have about the same repulsion as a single *lone pair*, only slightly more repulsion than a single bond. In determining shape, what matters primarily is the number of *directions* in which electron pairs are found around the central atom.

The shape that lets the electron pairs get as far apart as possible around each carbon is **trigonal planar**. The shape of the bonds around a double-bonded atom is *flat*, with $\sim 120^\circ$ bond angles.



The H-C-H angles are $< 120^\circ$.
All atoms are in the
plane of the paper.

Practice A: Use a periodic table. If needed, check your answers after each part. Do Problems 1 and 3, and 2 if you need more practice.

Draw Lewis diagrams, sketch the shape, and add the bond angles for each of these molecules.

1. H_2CO with one double bond.
 2. N_2H_2 with one double bond.
 3. Try CO_2 with two double bonds and C in the middle. Follow the octet rule.
-

Triple Bonds

Triple bonds most often occur for atoms in main groups 4 and 5 (the carbon and nitrogen families). In triple bonds, the valence electrons are put on *two* sides of the atom symbol, with three pairs of valence electrons between the two triple-bonded atoms.

To draw Lewis diagrams for triple-bonded atoms, use these steps.

1. Total the valence electrons for the neutral atoms in the molecule.
2. Determine the two atoms that triple bond.
3. Write symbols for the two triple-bonded atoms. Place the valence electrons on *two* sides, with *three* pairs of valence electrons between them.
4. Distribute the remaining atoms and valence electrons to satisfy the octet/duet rule.

An example of a triple-bonded compound is *ethyne* (also called *acetylene*), C_2H_2 , a gas that is used in torches that cut steel.

Try steps one and two above for C_2H_2 , and then check your answer below.

★ ★ ★ ★ ★

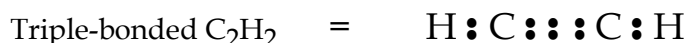
1. C_2H_2 has 4 valence electrons from each carbon and one from each hydrogen.
 $4+4+1+1=$ a total of 10 valence electrons.
2. H can only form *single* bonds, so the triple bond must be between the two C's.
3. Place three electron pairs between the two triple-bonded C atoms.



Try steps 4 and 5.

★ ★ ★ ★ ★

4. Match the unpaired electrons on the single-bonded atoms to the remaining unpaired electrons on the double bonded atoms. Satisfy the octets (and duet for H).



Check that each carbon is surrounded by 8, and each hydrogen by 2, valence electrons.

Triple Bond Shape

The shape that lets electron pairs in two directions around a central atom get as far apart as possible is *linear* with 180° bond angles.



Practice B: Try to do these without a periodic table. If needed, check your answers after each part.

Draw Lewis diagrams, sketch the shape, and add the bond angles for each of these molecules.

- HCN with a triple bond.
- N_2 with a triple bond.

Predicting Single, Double, or Triple Bonds From the Formula

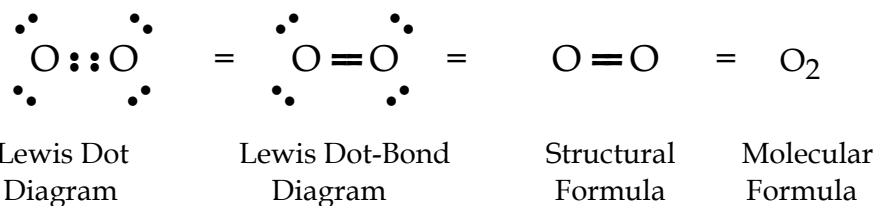
For many relatively simple molecules, if you know the formula, you can use the octet/duet rule to predict whether the molecule will have single, double, or triple bonds.

The steps are: count the valence electrons, and then draw Lewis diagrams that satisfy the octet/duet rule.

Q. Draw a Lewis diagram and then a structural formula for O_2 , and then check your answer below.

* * * * *

O_2 has 12 total valence electrons. Lewis diagrams that satisfy the octet rule are

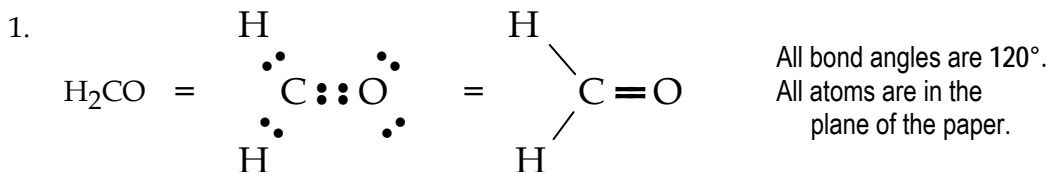


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Practice C: Try to do these without a periodic table. If needed, check your answers after each part.

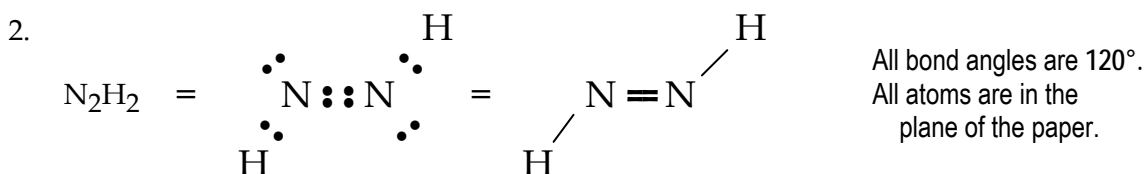
Draw a Lewis diagram and then a structural formula for

- C_2Cl_2
- O_3
- H_2S

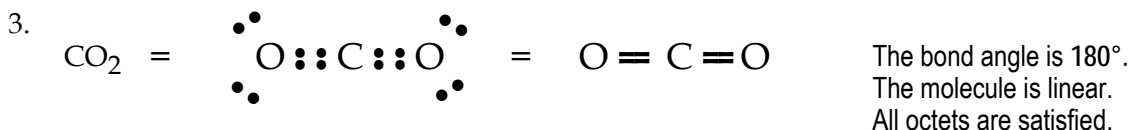
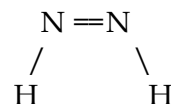
ANSWERS**Practice A**

The double bond must be between C and O, since H only bonds once.

The electron pairs in a double bond are placed on two triangle shapes ◀▶ around the atoms. The shape lets electron pairs on 3 sides of an atom get as far apart as possible is trigonal planar.



Note that octets and duets are satisfied. The shape can also be drawn as

**Practice B**

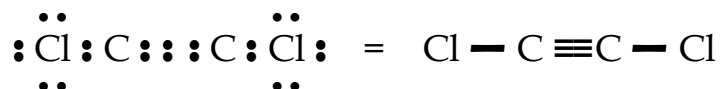
The molecule is linear with a 180° bond angle between the three atoms



Both N's have satisfied octets. The molecule is linear with no bond angle (it takes three atoms to have an angle in the molecule).

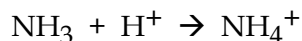
Practice C

1. C_2Cl_2 has $4+4+7+7 = 22$ total valence electrons. The chlorines generally bond only once because they are halogens. A Lewis diagram that satisfies the octet rule for all four atoms is

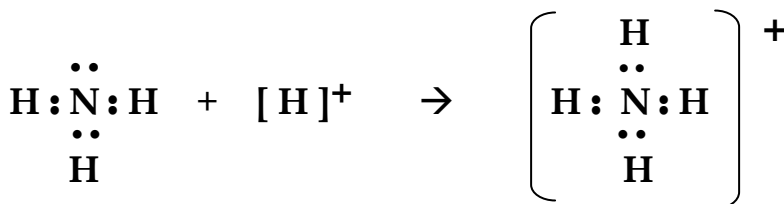


2. To make Lewis diagrams for *polyatomic ions*,
- Count the valence electrons as you would for a neutral particle, then add valence electrons to form a negative ion, and take away valence electrons to form a positive ion.
 - Construct the Lewis diagram as you would for a neutral particle, but use the corrected number of valence electrons.
 - Put the Lewis diagram in brackets, and add the charge as a superscript.

Let's try an example. Represent the following reaction by drawing Lewis diagrams for each particle.



* * * * *



Note that in NH_4^+ , the octet rule for N and the duet rule for H are satisfied.

- Using VSEPR, predict the shape and bond angles for NH_3 .
- Using VSEPR, predict the shape and bond angles for NH_4^+ .

* * * * *

For NH_3 , with one lone pair, the shape is a trigonal pyramid with bond angles of $<109^\circ$ (build the model if needed). The actual bond angles in NH_3 are $\sim 107^\circ$.

In NH_4^+ , the N is surrounded by *four* electron pairs. When four pairs surround a central atom, the electron pairs are tetrahedral. Since all four pairs are bonds, the molecular shape is also tetrahedral. Since there are no lone pairs, the bond angles are 109° , rather than $<109^\circ$.

Let's try a negative ion. Draw the Lewis diagram for the hydroxide ion, OH^- .

* * * * *

A neutral OH particle would be *unstable* due to its unsatisfied octet: $\text{H}:\ddot{\text{O}}:$

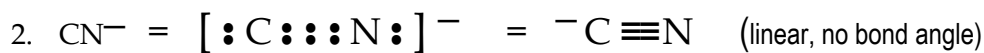
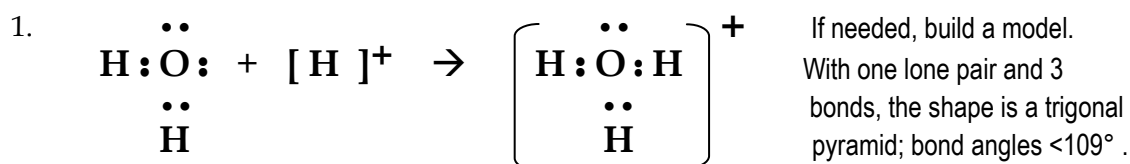
An OH^- is *stable*, with a satisfied octet and duet: $\left[\text{H}:\ddot{\text{O}}: \right]^-$

Practice: Try these without a periodic table. Check your answers after each part.

Draw Lewis diagrams, sketch the shape, and write the bond angles for these ions.

1. The hydronium ion, H_3O^+ , formed by the reaction $\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+$.
2. CN^- , the cyanide ion, with a triple bond.

ANSWERS



* * * * *

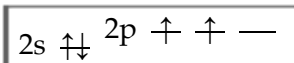
Lesson 25H: Orbital Models For Bonding

The Hybridized-Orbital Model For Bonding

The octet rule is easy to use, and it accurately predicts the formulas and shapes for most covalently bonded molecules. A bonding model that is a bit more complex, but explains many facets of bonding that the octet rule does not, is based on the *wave equation* model of the atom.

The orbital configuration for neutral atoms (Lesson 24A), based on the wave equation model for the atom, explains the electron configuration in single neutral atoms.

For example, according to the wave equation model, the configuration of the valence electron orbitals for carbon as a single neutral atom is :



This prediction, that carbon has *two* unpaired electrons, is consistent with measurements of single carbon atoms. However, in Lewis diagrams for *bonding*, a single-bonded carbon is assigned *four equivalent* unpaired electrons.



This configuration accurately predicts carbon's bonding behavior in millions of carbon compounds. How do we explain the apparent discrepancy between number of unpaired electrons predicted the wave equation model and the octet rule?

One mathematical solution to the wave equation does predict separate s and p orbitals. That solution accurately predicts much of the behavior of electrons in isolated single atoms. However, as with quadratic equations, wave equations can have more than one correct solution. An alternate but valid solution to the wave equation predicts that stable orbitals can form in molecules if the single s and the three p orbitals are **hybridized**.

Hybridization results in four equivalent orbitals termed sp^3 hybridized orbitals (pronounced "s p three"). The wave equation predicts that these four hybridized orbitals will have the same energy and will be equally spaced around the central atom, matching the behavior of carbon when it forms single bonds. For a series of orbitals at the same energy, the electrons go into the orbitals one at a time before they start to pair.

For a single-bonded carbon, the hybridized configuration is: $2sp^3 \uparrow \uparrow \uparrow \uparrow$

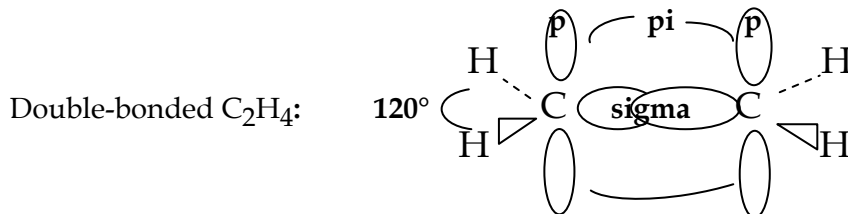
Lower potential energy is favored in physical and chemical systems. Hybridized orbitals are *not* the lowest energy arrangement for *single* carbon atoms, but bonded atoms have lower energy than the atoms by themselves. Hybridized orbitals allow more unpaired electrons and therefore more bonds. The bonds reduce the energy of the system. Because the hybridized orbitals allow more bonds, they are usually *favored* when atoms *bond*.

Hybrid Orbitals For Double Bonds

Other mathematical solutions to the wave equation explain double and triple bonds.

In molecules with one double-bond, the wave equation permits the hybridization of a single s and the two of the three p orbitals to form three sp^2 orbitals (pronounced "s p two"). This leaves one p valence orbital that does not hybridize.

In the case of a molecule with one double-bond, the bond has two parts. A single bond called a σ (sigma) bond is created by the overlap of an unpaired electron from an sp^2 orbital on each atom. A second bond between those atoms, called a π (pi) bond, is formed by the pairing of an unpaired electron from the p orbital of each atom. A single π bond has electron density both above and below the plane of the σ bonds.



Hybrid Orbitals For Triple Bonds

In each triple-bonded atom, the valence s and one of the three valence p orbitals are hybridized to form two sp hybrid orbitals. This leaves two p orbitals that are not hybridized.

Between two atoms that are triple-bonded are *one* σ bond, created by the overlap of unpaired electrons in an sp orbital, and *two* π bonds at right angles to each other around the

σ bond. The π bonds are formed by pairing the unpaired electrons in the two p orbitals of each atom.

Summary

The following table compares the terminology for multiple bonding for these two models of bonding.

If two atoms are attached by a	In the dot (Lewis) diagram model	In the hybridized-orbital model
Double bond	Two pairs of shared valence electrons between two atoms.	From each atom, overlap of one sp^2 orbital to form one σ bond, and one p orbital to form one π bond.
Triple bond	Three pairs of shared valence electrons between two atoms.	From each atom, overlap of one sp orbital to form one σ bond, and two p orbitals to form two π bonds.

The shapes and bond angles predicted by the hybridized orbital and Lewis diagram models are the same.

Exceptions to the Octet Rule and sp^x Hybridization

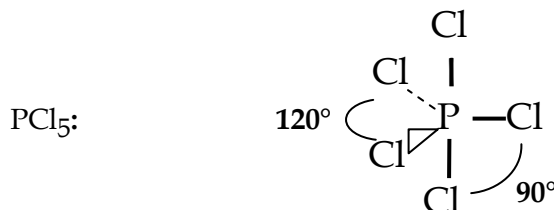
Both the octet rule and sp^x hybridization models successfully predict many of the characteristics of most covalent molecules, but there are molecules that are quite stable that these models do not explain.

Row 3 Exceptions

Frequently encountered exceptions to the octet rule occur for non-metal central atoms in rows 3 and above. For example,

- When combining with chlorine, phosphorus forms both PCl_3 , with the lone pair predicted by the octet rule, and PCl_5 , which violates the octet rule. In PCl_5 , all 5 of the phosphorus valence electrons are used for bonds.

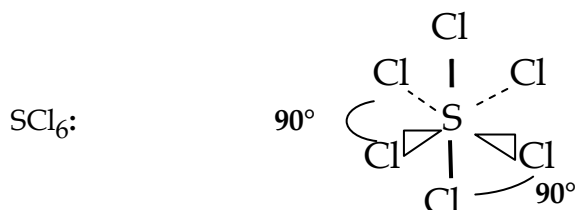
In PCl_5 , the shape predicted by VSEPR that allows the 5 electron pairs to get as far apart as possible is a **trigonal bipyramid** (which can be described as a Y in the plane of the paper with a pin stuck down through the middle).



PCl_5 is often labeled as having dsp^3 hybridization, suggesting that the empty $3d$ orbitals in phosphorus may participate in hybridization with the $3s$ and $3p$ to maximize the opportunity for bonding.

- Combining with chlorine, sulfur forms both SCl_2 , with the two lone pairs predicted by the octet rule, and SCl_6 , in which all 6 valence electrons are used for bonds.

In SCl_6 , the shape that allows the 6 electron pairs to get as far apart as possible is **octahedral**, which can be described as an X in the plane of the paper with a pin stuck down through the middle. All bond angles are 90° .



These single-bonded octahedral molecules are sometimes referred to as examples of d^2sp^3 hybridization, suggesting the bonding of six unpaired electrons using the empty $3d$ orbitals in sulfur.

Noble Gas Exceptions

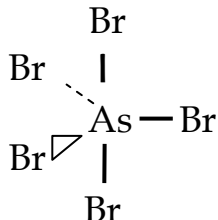
The octet rule predicts that a noble gas, which has a filled valence cluster, should be stable without bonding. This rule holds for the noble gases helium and neon, which form no stable compounds. However, noble gases in rows 3 and above form a few compounds. One is XeO_3 , a molecule which can be isolated (but tends to decompose explosively). XeO_3 has several possible single and double-bonded Lewis-diagrams that do not violate the octet rule.

Practice: Use a periodic table.

- Based on VSEPR, sketch the shape and name the shape you would predict for
 - Arsenic pentabromide
 - Selenium hexafluoride
- For molecules that contain at most one double or triple bond between two atoms, label the following types of bonds in those molecules as *single*, *double*, or *triple* bonds.
 - One σ bond and one π bond
 - One σ bond and two π bonds
 - σ bonds but no π bonds

ANSWERS

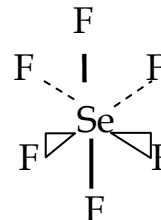
1a.

 AsBr_5 :Trigonal
Bipyramid

1b.

 SeF_6 :

Octahedral



2. a. One σ bond and one π bond -- a double bond
- b. One σ bond and two π bonds -- a triple bond
- c. σ bonds but no π bonds -- a single bond

* * * * *

Summary: Bonding

1. The Octet Rule: Most atoms want to be surrounded by 8 valence electrons (H and He want 2). The electrons can be shared, as in covalent bonds, or gained or lost from neutral atoms, as in ionic bonds.
2. In covalent molecules, atoms in the carbon family tend to bond 4 times, nitrogen family 3 times, oxygen family two times, and halogen family one time. A covalent hydrogen forms one bond.
3. In drawing dot diagrams, if the bonds around an atom include
 - All single bonds, place the valence electrons on 4 equivalent sides around the atom;
 - One double bond, place the electrons on 3 sides;
 - One triple bond, place the electrons on 2 sides.
4. The Valence Shell Electron Pair Repulsion (VSEPR) model for predicting shapes: Electron pairs tend to get as far apart as possible around an atom. Lone pairs and double bonds repel other pairs slightly more than single bonds.
5. When there are 4 electron pairs around an atom, the pairs tend to be in a tetrahedral shape, but the shape of the molecule is named based on where the atoms are.
6. Electronegative atoms have more attraction for electrons. Electronegativity tends to increase as you go toward the top right corner of the periodic table. Across row 2, the EN values increase by 0.5 per atom, from Li (1.0) to F (4.0).
7. A molecule will tend to be polar IF its bonds are polar, and if the dipoles do not cancel due to symmetry when added by vector addition.
8. The Solubility Rule: like dissolves like. Polar solvents such as water tend to dissolve polar and ionic compounds. Non-polar molecules tend to dissolve in non-polar solvents.

#