

# Calculations In Chemistry

Modules 19 and above have been re-numbered.

Module 24 on Bonding is now Module 25 in this packet

Module 25 on Kinetics is now Module 27

If you are looking for Kinetics topics, check Module 27

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## Module 25 — Bonding



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## **Module 25 — Bonding**

**Timing:** Begin this module when *Lewis (electron dot)* diagrams or molecular *shapes* are assigned.

**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.

\* \* \* \* \*

### **Introduction**

Bonds are forces that hold atoms together to form larger, independent particles. 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 bonding models predict most 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.

\* \* \* \* \*

## **Lesson 25A: Lewis (Electron Dot) Diagrams**

### **Ionic Versus Covalent Bonds**

In *ionic* bonding, charged particles (ions) are held together by electrical attraction. Monatomic ions 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 electrons in a noble gas configuration, but in covalent bonding, a pair of electrons can serve as valence electrons for *two* adjacent 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 is considered to be primarily ionic or covalent is best determined by its behavior.

Atoms bonded covalently in a molecule or a polyatomic ion do not easily separate when melted or dissolved. The forces holding bonds 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, so that they 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 H<sub>2</sub> is **H : H**



Lewis diagrams are useful for predicting the bonding, shape, and solubility of substances.

### Rules for Drawing Lewis Diagrams for Elements

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

An easy way to count the valence electrons is to note that the number the main groups (the *tall* columns) of the periodic table that the element is in, from one to eight, is the number of valence electrons for an element.

- All first column elements have *one* valence electron.
  - All elements in the carbon family have *four* valence electrons.
  - All noble gases have 8 valence electrons (*except* helium has 2).
3. Assume that each symbol has *four*-sided box around it. On each side can go at most two electrons. Using dots to represent the valence electrons, draw the valence electrons around the element symbol. Put *one* electron on each of the four sides of the symbol *before* you start to *pair* electrons.

Examples: Boron:  3 valence e<sup>-</sup>      Nitrogen:  5 valence e<sup>-</sup>

Boron has three **unpaired** electrons. Nitrogen has three unpaired electrons and one **lone pair** of electrons. In dot diagrams, the four sides are *equivalent*: you may place the paired and unpaired electrons on any side.

### Using Dot Diagrams To Predict Bonding Ratios

1. To draw dot diagrams for stable molecules and ions, the key principal is the **octet rule**: an element tends to be found surrounded by *eight valence* electrons. (Hydrogen, an exception, wants only *two*.)

Combinations that can 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.

2. To make stable molecules, depending on the type of problem, most textbooks use two methods for drawing dot diagrams.

Method 1: If a molecular formula is *not* known, a model that is helpful in predicting the molecular formula for simple single-bonded molecules is to *combine* the dot diagrams of its elements so that the *unpaired* electrons *pair* and are *shared* between two atoms, and all of the atoms are surrounded by 8 valence electrons (2 for hydrogen).

Method 2: If the formula and the central atom in a molecule or polyatomic ion is *known*, a better model that predicts bonding for both simple and more complex molecules is to

combine the valence electrons without regard to which atom contributes the valence electrons. This method, if you know the formula and the central atom in the molecule, will allow you to predict whether the bonds will be single, double, or triple bonds. This in turn will allow you to predict the shape of the molecule.

In simple molecules with more than two atoms, the central atom is usually the atom with the most unpaired electrons in its element dot diagram. In more complex molecules, it helps to know data about the arrangement of some of the atoms, or whether it includes double or triple bonds, in order to draw a proper dot diagram.

For simple molecules, both methods give the same answer. Method 2 is used most often, because in most problems we begin from a formula and central atom for the molecule. Method 2 also predicts the bonding in many more cases. However, most textbooks have examples of both methods.

Let's begin with an example of Method 1.

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

Do the following steps, and then check your answer below

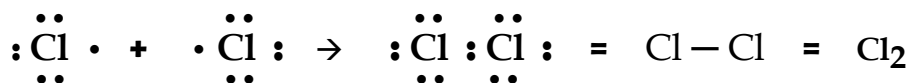
**Method 1.** If you do not know the molecular formula (the number and kind of atoms in the covalent molecule), but the molecule has single bonds:

1. Draw the Lewis diagram for the neutral elements using the rules for *element* diagrams above.
2. *Combine* the Lewis diagrams of the elements so that the *unpaired* electrons *pair* and are *shared* between two atoms. Combine the Lewis diagrams until each symbol is surrounded by *eight* valence electrons (H wants two).

\* \* \* \* \*

### 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 *lone pairs* and one *unpaired* valence electron around chlorine. A neutral chlorine has seven valence electrons and it *wants* eight.



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 also retains its 3 lone pairs.

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

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



\* \* \* \* \*

Many of the frequently encountered covalent molecules in first-year chemistry, as well as second-year organic chemistry, consist of hydrogen plus the second-row non-metals. In general, elements in the *second* row of the periodic table have the following characteristics when they bond covalently. These patterns apply, with many additions and exceptions, for elements below the second row. Learn this table so that given the terms in the first column you can fill in the blanks.

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 or 0
Bonds	1	2	3	4	<b>3</b>	<b>2</b>	<b>1</b>	<b>0</b>
Lone Pairs	0	0	0	0	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>

In predicting 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:** Use a periodic table. If needed, check your answers after each part. In covalent compounds, elements will most often be non-metals found at 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 element in #1.
  - Silicon
  - Phosphorous
  - Bromine
  - Sulfur
- Using Method 1, draw a Lewis diagram and then a structural formula for these.
  - F<sub>2</sub>
  - HCl
- Using Method 2, draw a Lewis diagram and then a structural formula for these.
  - CH<sub>4</sub>
  - PCl<sub>3</sub>
- 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. _____	4a. _____	4b. _____
Lone Pairs:	3a. _____	3b. _____	4a. _____	4b. _____
- Predict how many bonds will typically be found around these neutral atoms.
  - Selenium
  - Iodine
  - Silicon
  - Nitrogen

**ANSWERS**

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

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

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

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

4a.  $\begin{array}{c} \text{H} \\ \cdot\cdot \\ \text{H} : \text{C} : \text{H} \\ \cdot\cdot \\ \text{H} \end{array}$  =  $\begin{array}{c} \text{H} \\ | \\ \text{H} - \text{C} - \text{H} \\ | \\ \text{H} \end{array}$       4b.  $\overset{\cdot\cdot}{\text{Cl}} \overset{\cdot\cdot}{:} \overset{\cdot\cdot}{\text{P}} \overset{\cdot\cdot}{:} \overset{\cdot\cdot}{\text{Cl}} \overset{\cdot\cdot}{:}$  =  $\begin{array}{c} \text{Cl} - \text{P} - \text{Cl} \\ | \\ \text{Cl} \end{array}$

5. Bonds:      3a. 1      3b. 1      4a. 4      4b. 3

Lone Pairs:      3a. 6      3b. 3      4a. 0      4b. 10

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

\* \* \* \* \*

**Lesson 25B: Molecular Shapes and Bond Angles****VSEPR**

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 discuss in detail the shapes around atoms in the columns of the periodic table. A chart at the end will summarize these rules.

**Predicting the Shape of a Covalent Molecule**

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

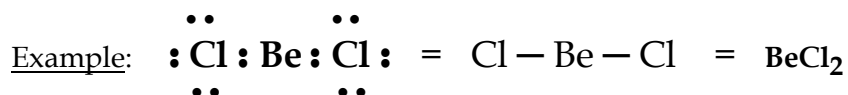
All of the electron pairs must be considered to determine the shape and bond angles, but the shape is *named* based only on the positions of the atoms. The lone pairs help to *determine* the shape, but they are ignored in *naming* the shape, of a covalent molecule.

- 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 atom has one *linear* bond and *no* bond angles.

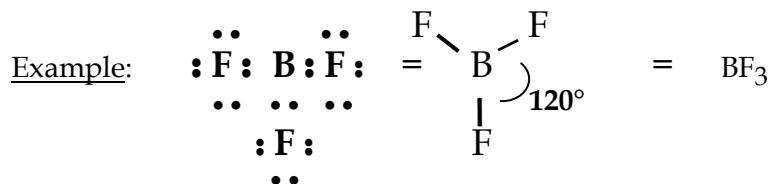
- b. **Two pairs:** If an atom in a molecule is surrounded by **two** electron pairs, both will be bonds. The two electron pairs will separate as much as possible by assuming a **linear** shape around the central atom. This shape will result in three atoms in a line, and with three points to determine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



The **Be** in  $\text{BeCl}_2$  has two linear bonds. The shape around the central atom, and the shape of the molecule, is **linear** with **180°** bond angles.

Note that  $\text{BeCl}_2$  is *electron deficient*: it violates the octet rule.  $\text{BeCl}_2$  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  $\text{BF}_3$  molecule is **trigonal planar**. All bond angles are **120°**.

Like  $\text{BeCl}_2$ , a  $\text{BF}_3$  Lewis diagram can be drawn using single bonds, but it violates the octet rule.  $\text{BF}_3$  does form and has three equivalent bonds, but as you might predict with its electron deficient structure, it has many 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

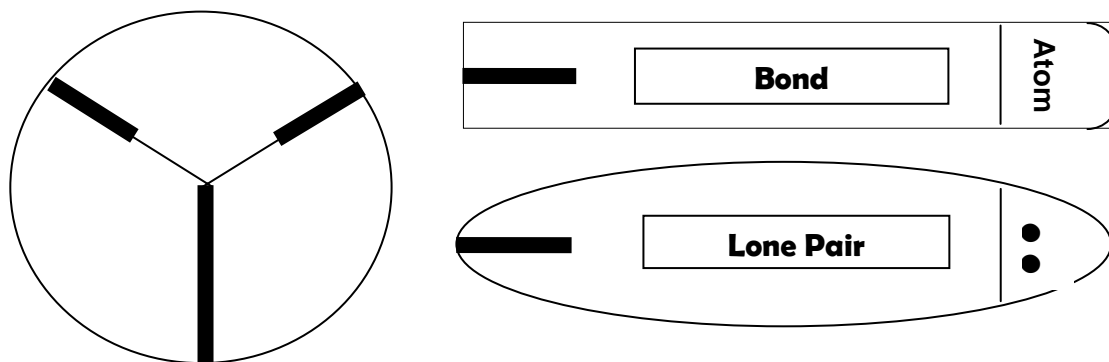
If you do not have access to a commercial molecular model kit, a tetrahedral model can be constructed from the patterns below.

#### Steps:

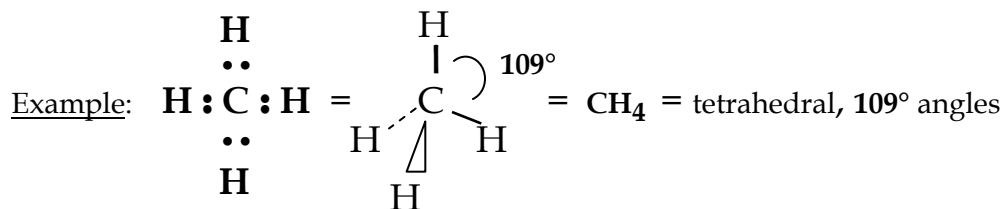
1. Obtain a sheet of foamboard or thick or corrugated cardboard at least one-half the size of this sheet of paper.
2. Either copy this page, or cover this page with thin paper and trace onto the paper, the three shapes below. Cut out the three paper patterns.
3. Using the patterns and blunt scissors, 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  $109^\circ$ .

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  $\triangle$  represents a bond coming out of the paper. A 3-D model will assist in working with this important shape.

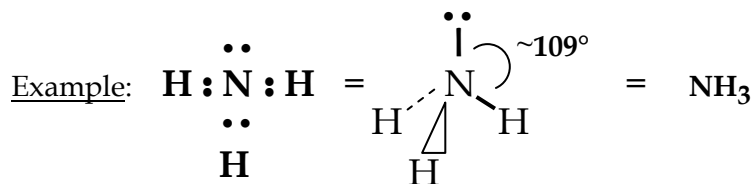
Build a  $\text{CH}_4$  molecule from your molecular model pieces. Place the assembled model on a flat surface, then flip it so that it rests on three different points. Flip it again. Note the high symmetry of a three-dimensional tetrahedron: the shape of the molecule should be the same no matter which 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**.

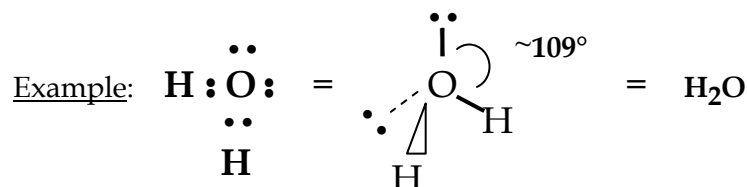


Build this  $\text{NH}_3$  molecule from your kit. Starting from  $\text{CH}_4$ , replace one bond with a lone pair. The four electron pairs are still in a tetrahedral shape. Then take off the lone pair to look at just the shape and angles of the *bonds* and *atoms*. With the central nitrogen atom on top, check that the atoms form a low *pyramid* with tetrahedral ( $\sim 109^\circ$ ) angles.

The shape of  $\text{NH}_3$  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?

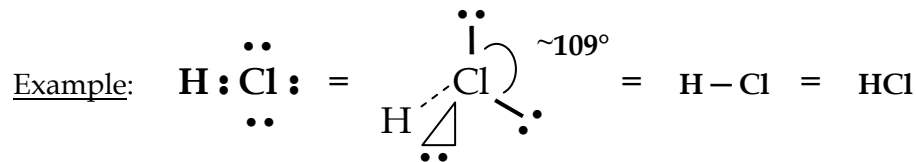
\* \* \* \* \*

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 element 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  $\text{H}_2\text{O}$  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  $\text{HCl}$  molecule, is **linear** with *no bond angles*.

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

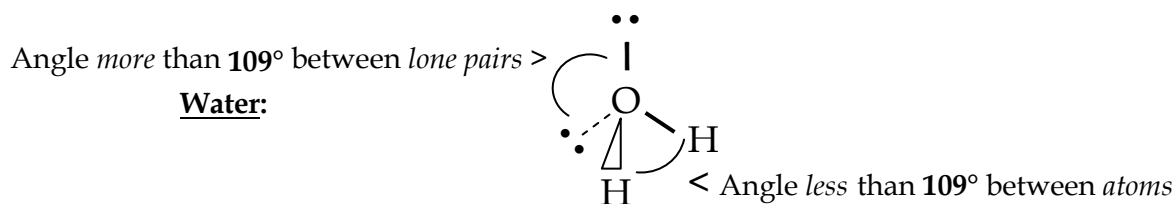
*Lone pairs repel slightly more than bonds. The lone pairs need more room.*

If lone pairs are present in a tetrahedral shape, the angles around the lone pairs will be slightly larger than  $109^\circ$ . This will push the angles between *bonds* to be slightly *less than*  $109^\circ$ .

Lone pairs tend to occupy slightly more space than bonds, because in bonds, the electron 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  $109^\circ$ .

In water, the shape is bent as predicted, but the actual, measured bond angle is  $104.5^\circ$ , 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  $109^\circ$ ? 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  $109^\circ$  rather than *less* than  $109^\circ$ . When there are no lone pairs around the central atom, there is no lone pair effect on the angles.

**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	1	2	3	4	<b>3</b>	<b>2</b>	<b>1</b>	<b>0</b>
Lone Pairs	0	0	0	0	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
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 elements 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 <sub>3</sub>	SiH <sub>4</sub>	AlCl <sub>3</sub>	SI <sub>2</sub>
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

- The four electron pairs repel to into a tetrahedral shape. The three atoms are bent, with a bond angle of slightly *less* than 109°.
- Linear, Linear, Trigonal Planar, Tetrahedral, Pyramidal, Bent, Linear, No Bonds
- None 180° 120° 109° <109° <109° None
- 

Molecule	NF <sub>3</sub>	SiH <sub>4</sub>	AlCl <sub>3</sub>	SI <sub>2</sub>
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 <sup>-</sup> Pairs	Tetrahedral	Tetrahedral	Trigonal Planar	Tetrahedral
Molecule and Bonds	Trigonal Pyramidal	Tetrahedral	Trigonal Planar	Bent
Bond Angles	<109°	109°	120°	<109°

5. AlCl<sub>3</sub> 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 Linus Pauling) predicts how strongly each atom attracts the electrons in a bond.

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

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

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

### **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	1.3-2.2	1.7	1.8	1.9	2.1	2.5	
Row 6	0.7	0.9	1.1-2.4	1.8	1.8	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 elements 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.

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.

<u>Examples:</u>	F — F	Cl — Cl	N — Cl
EN:	4.0 4.0	3.0 3.0	3.0 3.0

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

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  $\delta$  (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  $\delta^-$  (pronounced *delta minus*), and the weaker electron attractor is labeled  $\delta^+$  (*delta plus*).

<u>Examples:</u>	$\delta^+$ C — O $\delta^-$	$\delta^+$ N — F $\delta^-$	$\delta^-$ O — H $\delta^+$
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An alternate way to represent a dipole is to use an arrow over top of a 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.

<u>Examples:</u>	C $\rightarrow$ O	N $\rightarrow$ F	O $\leftarrow$ H
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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 should be seen as a gradual shifting from non-polar, to polar, to ionic character.

**Practice:** Memorize the electronegativity values for H, Cl, and the second row elements. Then use those values and a periodic table that does not include electronegativity values on the problems below. If needed, check your answers after each part.

1. For each of the bonds below,
  - a. write the electronegativity value above each atom from memory.
  - b. Below the bond, label each atom as  $\delta+$  or  $\delta-$ .
  - c. On the next line down, calculate the electronegativity difference.
  - d. On the next line down, label the bond as non-polar, polar, or ionic.
  - e. 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 $\delta$	$\delta+$ $\delta-$	$\delta-$ $\delta+$
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

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## **Lesson 25D: Molecular Polarity**

### **Polar versus Non-Polar Molecules**

- Why do salad oil and water-based vinegar, after being shaken, separate into two layers, yet 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 molecules.

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**

Compounds that are combinations of metals and non-metals strongly tend to be ionic. Formulas that you recognize as ionic solids will also be ionic.

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

1. Assign electronegativity (EN) values to each atom.
2. Based on the EN *differences*, label the *bonds* as ionic, non-polar, or polar.
3. If *one* bond is ionic, the *molecule* is *ionic*.
4. If *all* of the bonds are *non-polar*, the *molecule* is *non-polar*.
5. If steps 3 and 4 do not apply, one or more of the bonds must be polar.
  - a. Draw the Lewis diagram and sketch the shape of the molecule.
  - b. 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.
  - c. 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 compounds as *ionic*, *covalent polar*, or *covalent non-polar*. Use a periodic table without EN values (all of these atoms have values you should know). Because these molecules are *two-dimensional*, you should not need models to evaluate symmetry.

1. Cl<sub>2</sub>

2. LiCl

3. O=C=O (linear)

4. HCl

\* \* \* \* \*

1. In Cl<sub>2</sub>, both atoms have the same electronegativity value. 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**.

In Cl<sub>2</sub>, the shape for two atoms must be **Cl—Cl**. 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<sup>+</sup> ion and a Cl<sup>−</sup> ion.

\* \* \* \* \*

3. CO<sub>2</sub> 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: **H→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.  $\text{BeH}_2$                       2.  $\text{LiF}$                       3.  $\begin{array}{c} \text{H} \\ \backslash \\ \text{C}=\text{O} \text{ (flat shape)} \\ / \\ \text{H} \end{array}$                       4.  $\text{BCl}_3$

### 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 four single *bonds* to the *same* atom, even if the bonds are polar, the dipoles will cancel due to symmetry. The *molecule* will be *non-polar*.

Examples:  $\text{CH}_4$ ,  $\text{SiF}_4$  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:  $\text{NH}_3$ ,  $\text{OF}_2$  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.

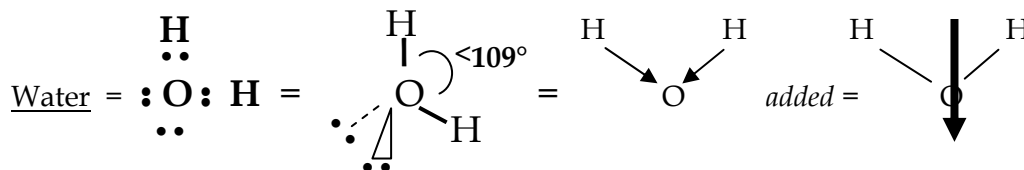
**Q.** Using the flow chart and symmetry rules, label these compounds as *ionic*, *covalent polar*, or *covalent non-polar*. Use a periodic table without electronegativity values. Make molecular models if needed.

1.  $\text{H}_2\text{O}$                       2.  $\text{CCl}_4$                       3.  $\text{NH}_3$                       4.  $\text{CHF}_3$

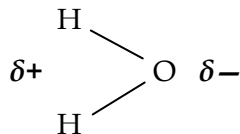
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To evaluate molecular polarity, use the flow chart. First evaluate bond polarity. *If* the bonds are *polar*, evaluate symmetry to see if the dipoles cancel.

1.  **$\text{H}_2\text{O}$ :** 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<sub>2</sub>O has tetrahedral 3-D electron pairs but 2-D bonds and atoms. Bonds, not lone pairs, contain the dipoles. The bonds in water have a bent shape with <109° 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. .



The *net* dipole points from the H side toward O.

The H side is  $\delta+$  and the O side is  $\delta-$ .

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

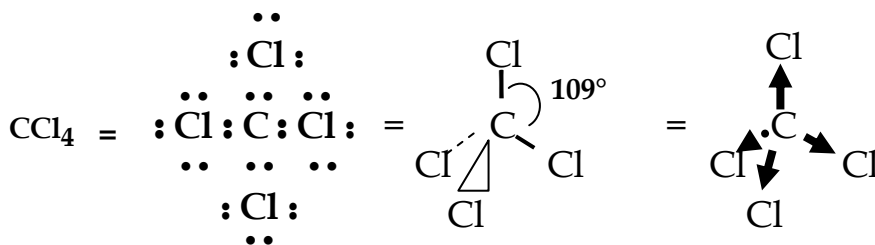
Water is *polar*.

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

\* \* \* \* \*

2. **CCl<sub>4</sub>**: 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<sub>4</sub> 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.

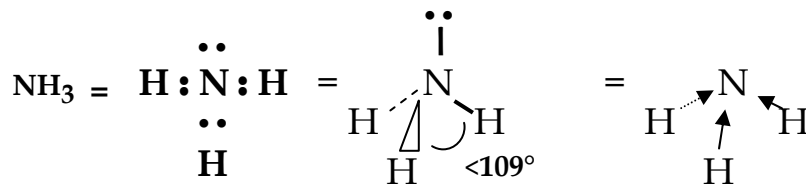


When a central atom is surrounded by four tetrahedral bonds to the same atom, the molecule is always *non-polar* due to symmetry.

\* \* \* \* \*

3. **NH<sub>3</sub>**: 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.

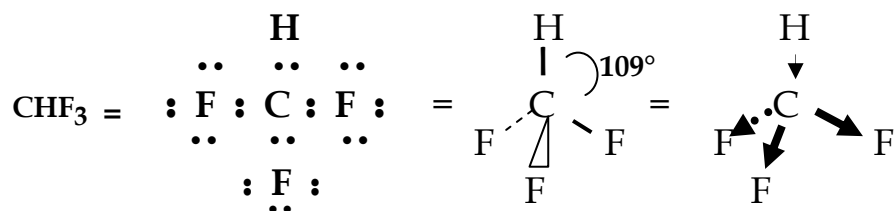
Polar bonds can mean polar *or* non-polar molecules, depending on whether the dipoles cancel. To check for dipole cancellation, draw the Lewis diagram: NH<sub>3</sub> has tetrahedral electron pairs with one lone pair and 3 bonds. Make the tetrahedral model, then take off the lone pair, to focus on the 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. NH<sub>3</sub> 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. **CHF<sub>3</sub>**: 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. CHF<sub>3</sub> 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, CHF<sub>3</sub> is predicted to be a **polar** molecule.



**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*, *covalent polar*, or *covalent non-polar*.

1. SF<sub>2</sub>                      2. PCl<sub>3</sub>                      3. SiH<sub>4</sub>                      4. SiH<sub>3</sub>Cl

## ANSWERS

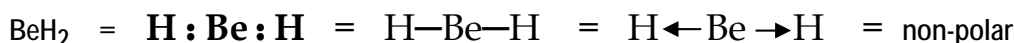
### Practice A

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

1. BeH<sub>2</sub> First assign EN values to categorize the bonds. 2.1 H – 1.5 Be = 0.6 > 0.4 = polar bonds.  
If 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.  $4.0 \text{ F} - 1.0 \text{ Li} = 3.0 > 1.7 =$  ionic bonds.

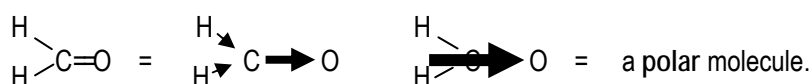
If one bond is ionic, the compound is ionic.

3.  $\text{H}_2\text{C=O}$  Assign EN values to categorize the bonds.

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

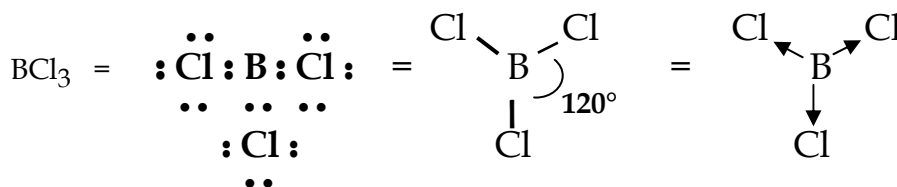
Electronegativity differences apply in the same way to single and double bonds.

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.  $\text{BCl}_3$  Assign EN values to categorize the bonds.  $3.0 \text{ Cl} - 2.0 \text{ B} = 1.0 > 0.4 =$  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  $120^\circ$  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**.

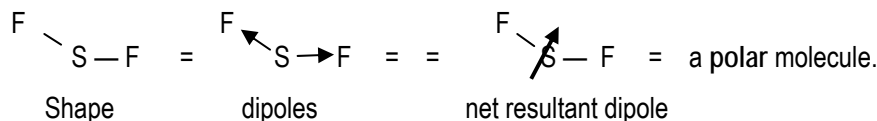
### Practice B

1.  $\text{SF}_2$ : Assign EN values to categorize the bonds.  $4.0 \text{ F} - 2.5 \text{ S} = 1.5 > 0.4 =$  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  $109^\circ$  bond angles. *Bent* molecules are two dimensional; their polarity can be evaluated on paper.

Since the two dipoles are  $109^\circ$  apart and not  $180^\circ$ , 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.



## 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.

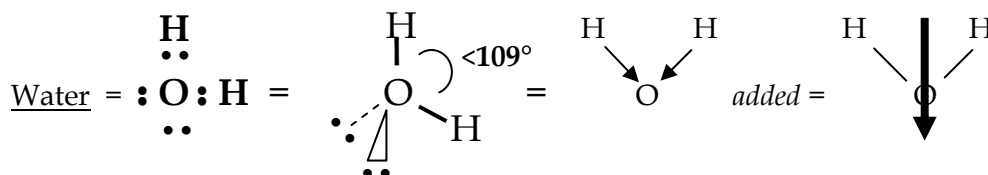
When two liquids composed of polar molecules, such as water and alcohols, are mixed, the liquids dissolve in each other. One solution without layers is the result.

Why the difference?

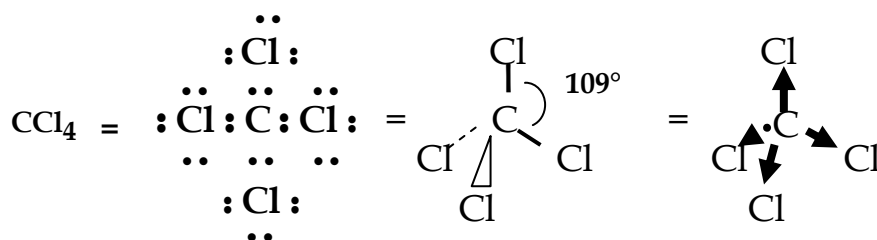
For solubility, the general rule is: *like dissolves like*.

- Polar liquids will dissolve *polar* or *ionic* particles.
- Non-polar liquids dissolve non-polar molecules.
- Polar and non-polar substances do not 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  $\text{H}_2\text{O}$  and  $\text{CCl}_4$  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  $\text{CCl}_4$ , the denser  $\text{CCl}_4$  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**.

### Choosing a Solvent

Water is a good solvent for many ionic solids, polar sugars, and polar alcohols. Those substances do not dissolve well in  $\text{CCl}_4$  and other non-polar solvents.

Carbon tetrachloride at one time was used as a “dry cleaning fluid.” It dissolved non-polar oils from clothing without the use of the water that could damage some fabrics. (More modern dry cleaning liquids are also non-polar, but not as hazardous as  $\text{CCl}_4$ .)

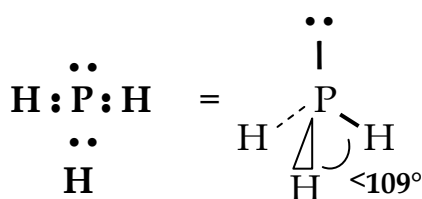
Oils do not dissolve well in water. **Soaps** and **detergents** are substances added to water to remove skin oils from fabrics. These long-chain molecules combine a polar group on one end to dissolve in polar water and non-polar groups on the other to dissolve oils. This structure allows soaps to dissolve oils and dissolve in water 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  $\text{PH}_3$  column first, check your answers on the next page, and then complete the remaining columns.

Molecule	$\text{PH}_3$	$\text{NaCl}$	$\text{HBr}$
Lewis Diagram			
Shape of Electron Pairs			
Shape of Molecule			
Bond Angles			
Bond Polarity			
Molecule Polarity			
Dissolves in Oil or Water?			

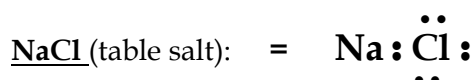
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AnswersPH<sub>3</sub> :

PH<sub>3</sub> 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 non-polar. Non-polar molecules dissolve in non-polar solvents, such as **oils**, gasoline, or CCl<sub>4</sub>. They tend not to dissolve in water.

\* \* \* \* \*



In a covalent molecule, NaCl would have tetrahedral electron pairs around chlorine. Two atoms in a molecule always have a linear shape with no bond angles.

For bond polarity: The EN of Na = 0.9, the EN of Cl = 3.0. The EN difference is 2.1, which is greater than 1.7, so the *bond* is **ionic**. Any ionic bonds in a compound means that the compound will have primarily **ionic** behavior.

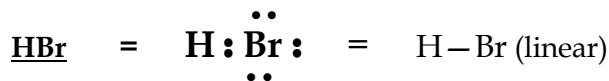
*Ionic* compounds tend to dissolve in *polar* solvents like water more than in oils.

A Lewis diagram can be drawn representing a covalently bonded NaCl, as above, but NaCl most often behaves as two separate ions rather than as a covalent compound with shared electrons.

Table salt dissolves readily in **water** because polar solvents dissolve ionic compounds.

If table salt is added to salad oil alone, the salt will fall to the bottom and remain undissolved, because non-polar solvents do not dissolve ionic compounds.

\* \* \* \* \*



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 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 dissolves 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  $\text{PH}_3$  above, the predicted VSEPR bond angles would be about  $107^\circ$ , but actual bond angles are about  $94^\circ$ . For some substances, more sophisticated models will be needed to explain experimental results. That said, the rules for VSEPR, electronegativity, and “like dissolves like” accurately 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 tetrahedral 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	$\text{SF}_2$	$\text{SeI}_2$	$\text{GaBr}_3$
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 <sub>2</sub>	SeI <sub>2</sub>	GaBr <sub>3</sub>
Lewis Diagram	<pre>       ..   ..   ..       : F : S : F :       ..   ..   ..           (also could be           drawn at 90°)           </pre>	<pre>       ..   ..   ..       : I : Se : I :       ..   ..   ..           (also could be           drawn at 90°)           </pre>	<pre>       ..   ..   ..       : Br : Ga : Br :       ..   ..   ..       : Br :       ..           </pre>
Shape of Electron Pairs	Tetrahedral	Tetrahedral	Trigonal Planar
Shape of Molecule (Name and Sketch)	Bent <pre>           F          / F — S           </pre>	Bent <pre>           I          / I — Se           </pre>	Trigonal Planar <pre>           Br                       Ga          / \         Br  Br           </pre>
Bond Angles	<109°	<109°	120°
Bond Polarity	4.0 – 2.5 = 1.5 = polar	2.6 – 2.4 = 0.2 = nonpolar	2.6 – 1.8 = 0.8 = 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**

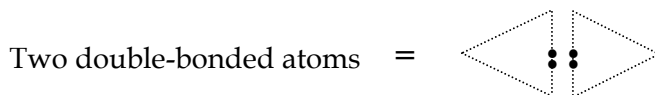
Atoms in main groups 4 and above of the periodic table can satisfy the octet rule by forming **double bonds** that have *two* pairs of electrons between the atoms. In the Lewis diagram, the valence electrons for each double-bonded atom are placed on *three* sides of the element symbol instead of the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

3. Write the two double-bonded atoms next to each other so that there are *two pairs* of valence electrons (four electrons total) between them.



4. 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.

\* \* \* \* \*

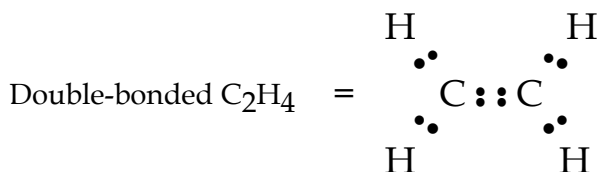
- Combine the two double-bonded atoms to form the double bond. It will have two pairs: four valence electrons. Note how the triangles faces meet in arranging the valence electrons around the double-bonded atoms.



Try step 4.

\* \* \* \* \*

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



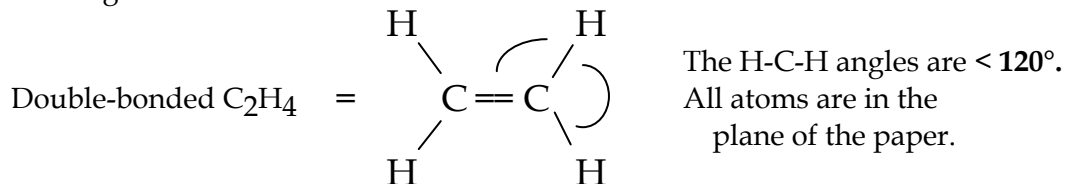
### Double Bond Shape

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.



**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 element 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 elements 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.

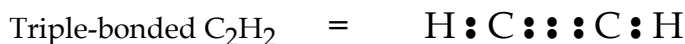
3. Place three electron pairs between the two triple-bonded C atoms.



Try steps 4 and 5.

\* \* \* \* \*

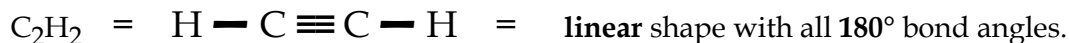
4. Match the unpaired electrons on the single-bonded atoms to the remaining unpaired electrons on the double bonded atoms. Satisfy the octets (and duet for H).



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  $180^\circ$  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.

1. HCN with a triple bond.                      2. N<sub>2</sub> with a triple bond.

### Predicting Single, Double, or Triple Bonds From the Formula

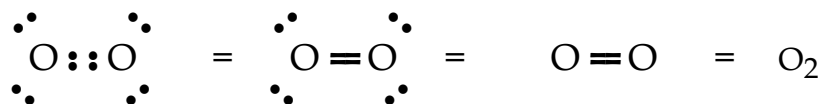
For many relatively simple molecules, if you know the formula, you can use the octet/duet rule to predict whether the molecule will have single, double, or triple bonds.

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<sub>2</sub>, and then check your answer below.

\* \* \* \* \*

O<sub>2</sub> has 12 total valence electrons. Lewis diagrams that satisfy the octet rule are



Lewis Dot  
Diagram

Lewis Dot-Bond  
Diagram

Structural  
Formula

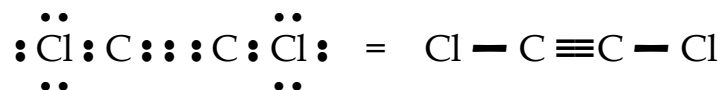
Molecular  
Formula

\* \* \* \* \*

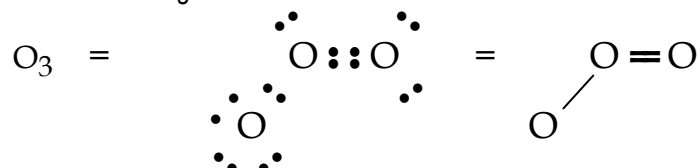


**Practice C**

1.  $\text{C}_2\text{Cl}_2$  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

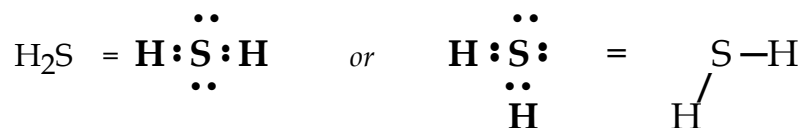


2.  $\text{O}_3$  has  $6+6+6 = 18$  total valence electrons. The chlorines must bond only once because they are halogens. One Lewis diagram that satisfies the octet rule for all four atoms is



An equally valid diagram (called a resonance structure) can be drawn with the single and double bonds switched in position. When resonance structures are possible for a particle, the properties of the particle will be a blend of the two resonance structures, and the particle will have special stability.

3.  $\text{H}_2\text{S}$  has  $1+1+6 = 8$  total valence electrons. A Lewis diagram that satisfies the octet rule for S and duet rule for H is



These two Lewis diagrams are *not* two different structures; they represent the same molecule. If four sides are shown around a central atom, the four sides are equivalent.  $\text{H}_2\text{S}$  will have tetrahedral electron pairs and a bent shape, with bond angles of slightly less than  $109^\circ$ .

\* \* \* \* \*

**Lesson 25G: Dot Diagrams For Ions****Ion Dot Diagrams**

Dot diagrams for ions are drawn by adding and subtracting electrons from the Lewis diagrams for neutral particles.

1. To make Lewis diagrams for *monatomic* ions,
  - a. draw the Lewis diagram for the neutral atom.
  - b. Take away electrons to form positive ions. Add electrons to form negative ions. Most often, a positive ion shows *no* valence electrons around the symbol, and a negative ion has 8 valence electrons (hydride ion,  $\text{H}^-$ , has 2 valence electrons).
  - c. Put brackets [ ] around the Lewis diagram, then add the charge as a superscript.

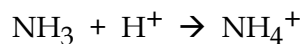
Examples: Neutral Na atom = Na • ; Na<sup>+</sup> ion = [ Na ]<sup>+</sup> ;

Neutral Al atom = • Al • ; Al<sup>3+</sup> ion = [ Al ]<sup>3+</sup> ,

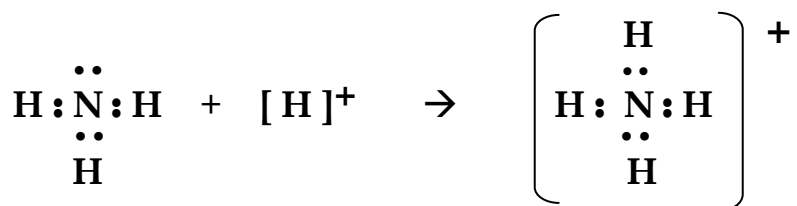
Neutral S atom = :S: ; S<sup>2-</sup> ion = [ :S: ]<sup>2-</sup>

2. To make Lewis diagrams for *polyatomic* ions,
  - a. 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.
  - b. Construct the Lewis diagram as you would for a neutral particle, but use the corrected number of valence electrons.
  - c. 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<sub>4</sub><sup>+</sup>, the octet rule for N and the duet rule for H are satisfied.

- Using VSEPR, predict the shape and bond angles for NH<sub>3</sub>.
- Using VSEPR, predict the shape and bond angles for NH<sub>4</sub><sup>+</sup>.

\* \* \* \* \*

For NH<sub>3</sub>, with one lone pair, the shape is a trigonal pyramid with bond angles of <109° (build the model if needed). The actual bond angles in NH<sub>3</sub> are ~107°.

In NH<sub>4</sub><sup>+</sup>, 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°.

Let's try a negative ion. Draw the Lewis diagram for the hydroxide ion, OH<sup>-</sup>.

\* \* \* \* \*

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

An OH<sup>-</sup> is *stable*, with a satisfied octet and duet:  $\left[ \text{H} : \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} : \right]^-$

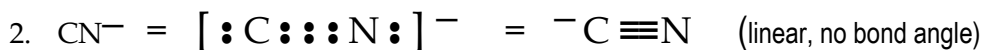
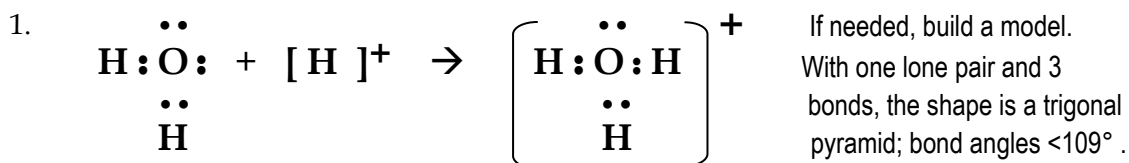
••

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

## ANSWERS



\* \* \* \* \*

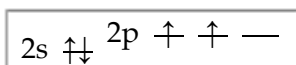
## Lesson 25H: Orbital Models For Bonding

### 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 elements (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 of elements. 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:  $2sp^3 \uparrow \uparrow \uparrow \uparrow$

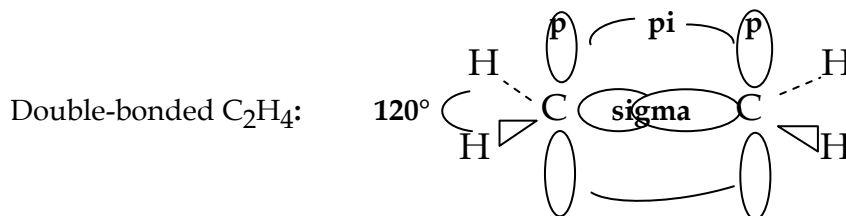
Lower potential energy is favored in physical and chemical systems. Hybridized orbitals are *not* the lowest energy arrangement for *single* carbon atoms, but bonded atoms have lower energy than the atoms by themselves. Hybridized orbitals allow more unpaired electrons and therefore more bonds. The bonds 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  $\sigma$  (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  $\pi$  (pi) bond, is formed by the pairing of an unpaired electron from the  $p$  orbital of each atom. A single  $\pi$  bond has electron density both above and below the plane of the  $\sigma$  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*  $\sigma$  bond, created by the overlap of unpaired electrons in an  $sp$  orbital, and *two*  $\pi$  bonds at right angles to each other around the

$\sigma$  bond. The  $\pi$  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
<b>Double</b> bond	<b>Two pairs</b> of shared valence electrons between two atoms.	From each atom, overlap of <b>one</b> $sp^2$ orbital to form <b>one</b> $\sigma$ bond, and <b>one</b> $p$ orbital to form <b>one</b> $\pi$ bond.
<b>Triple</b> bond	<b>Three pairs</b> of shared valence electrons between two atoms.	From each atom, overlap of <b>one</b> $sp$ orbital to form <b>one</b> $\sigma$ bond, and <b>two</b> $p$ orbitals to form <b>two</b> $\pi$ 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

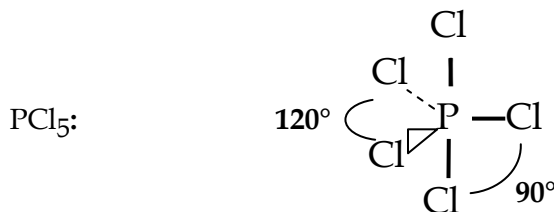
Both the octet rule and  $sp^x$  hybridization models successfully predict many of the characteristics of most covalent molecules, but there are molecules that are quite stable that these models do not explain.

#### 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, phosphorous 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 phosphorous valence electrons are used for bonds.

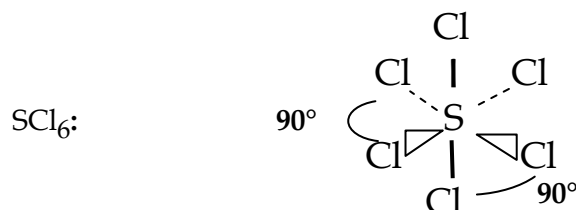
In  $PCl_5$ , the shape predicted by VSEPR that allows the 5 electron pairs to get as far apart as possible is a **trigonal bipyramid** (which can be described as a Y in the plane of the paper with a pin stuck down through the middle).



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

- Combining with chlorine, sulfur forms both  $\text{SCl}_2$ , with the two lone pairs predicted by the octet rule, and  $\text{SCl}_6$ , in which all 6 valence electrons are used for bonds.

In  $\text{SCl}_6$ , the shape that allows the 6 electron pairs to get as far apart as possible is **octahedral**, which can be described of as an X in the plane of the paper with a pin stuck down through the middle. All bond angles are  $90^\circ$ .



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

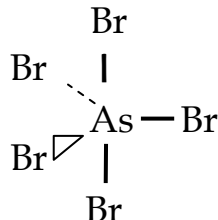
The octet rule predicts that a noble gas, which has a filled valence cluster, should be stable without bonding. This rule holds for the noble gases helium and neon, which form no stable compounds. However, noble gases in rows 3 and above form a few compounds. One is  $\text{XeO}_3$ , a molecule which can be isolated (but tends to decompose explosively).  $\text{XeO}_3$  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 would you 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  $\sigma$  bond and one  $\pi$  bond
  - One  $\sigma$  bond and two  $\pi$  bonds
  - $\sigma$  bonds but no  $\pi$  bonds

**ANSWERS**

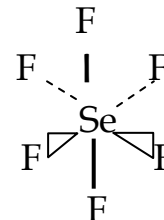
1a.

Trigonal  
Bipyramid

1b.



Octahedral



2. a. One  $\sigma$  bond and one  $\pi$  bond -- a double bond
- b. One  $\sigma$  bond and two  $\pi$  bonds -- a triple bond
- c.  $\sigma$  bonds but no  $\pi$  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 bonding pairs 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 (0.5) 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.

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