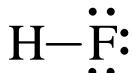


# Geometry of Covalent Compounds

## Introduction:

In order to utilize lab time and use the molecular model kits most effectively, we recommend completing as many of the Lewis Dot Structures as you can before coming to lab!

A **Lewis structure** (or **electron-dot formula**) is a two-dimensional structural formula showing the arrangement of electrons around atoms in covalently bonded molecules—i.e., molecules where nonmetal atoms are held together because they **share** one or more pairs of electrons. For example, the Lewis structure for the hydrogen fluoride (HF) molecule is shown below:



Note that the bonding pair of electrons is shown as a dash between the two atoms, each represented by its element symbol. The nonbonding electrons on the fluorine atom are shown as dots. In most cases, nonbonding electrons are paired, so they are also called **lone pairs of electrons**.

## Octet Rule:

This example also illustrates the **octet rule**, which states that atoms bond to attain eight valence electrons (an octet). The electrons shared in a covalent bond “count” towards the octet for both atoms they are between. One exception to the octet rule is H, which is such a small atom that it can only hold 2 electrons. For the HF molecule, H has the two electrons it needs from the bonded pair it shares with F, and F has an octet (6 nonbonding electrons + 2 electrons from the pair it shares with H). Exceptions to the octet rule will be discussed later.

In this lab, you will study covalently-bonded molecules. You will

- count all the valence electrons from atoms in a molecule or ion;
- draw Lewis electron-dot structures of simple molecules and polyatomic ions;
- build models for various molecules to determine their molecular geometry (or three-dimensional shape) and properties such as bond angles and atomic hybridization;
- use the polarity of each bond and the molecular geometry of the molecule to determine if the molecule is polar or nonpolar overall.

You will work in pairs and use a molecular model set to build models of all the molecules to be explored. Finally, you will use the **3D-Angles** program individually to master the determination of coordination number (i.e. the number of atoms bonded to a central atom), bond angle, and atomic hybridization given a rotating three-dimensional representation of simple molecules.

## Guidelines for Drawing Lewis Electron-Dot Structures:

1. Add up the total number of valence electrons for all the atoms in the molecule. Remember that the number of valence electrons is equal to the Group Number (from the Periodic Table) for all the Main (A) Group elements.
  - For **polyatomic ions**, also account for the electrons gained or lost due to its charge. For example, add 2 electrons for sulfate ion ( $\text{SO}_4^{2-}$ ) since the -2 charge indicates 2 electrons gained, but subtract 1 electron for ammonium ion ( $\text{NH}_4^+$ ) since the +1 charge indicates one electron was lost.
2. Divide the total number of valence electrons by 2 to get the number of electron pairs. *Note: The molecule can only have this number of electron pairs, and each atom in the molecule must obey the octet rule (unless specified otherwise).*
3. Write the element symbol for the central atom (usually the least electronegative and typically written first in a formula). Note that **H and F must always be outer atoms** since H only forms one bond, and F is so electronegative, it will also only form one bond.

- Write the element symbols for all the outer atoms around the central atom. Next, draw a straight line to connect each outer atom to the central atom. Subtract the number of bonds drawn from the total number of electron pairs in the structure.
- Distribute the remaining valence electrons in pairs, first around the outer atoms then around the central atom, so each atom has an octet.
  - If there are not enough electrons for each atom to have an octet, then move a nonbonding (lone) pair of electrons to be shared between 2 atoms, resulting in a double bond (2 pairs of electrons shared). If additional electrons are still required, move another pair of electrons to be shared, resulting in a triple bond (3 pairs of shared electrons). **Do not draw double or triple bonds if there are enough valence electrons for each atom to attain an octet using single bonds.**
  - In some cases, the central atom may get more than an octet. Molecules with an “expanded octet” are discussed below.
- For polyatomic ions, square brackets are drawn around the entire Lewis structure, and the polyatomic ion’s charge is placed in the upper right-hand corner outside the brackets to indicate the overall charge is spread out among all the atoms in the ion.

### **Exceptions to the Octet Rule:**

In some molecules or polyatomic ions, the central atom may have less than an octet or more than an octet. These **Exceptions to the Octet Rule** are described below:

#### **Molecules with Incomplete Octets**

Beryllium (Be) and boron (B) can form molecules in which Be only has 4 electrons and B only has 6 electrons. (These compounds are unstable and often react immediately with other atoms or compounds, so Be or B will ultimately get an octet, but these molecules do exist for a short time with less than an octet.)

#### **Molecules with an odd number of electrons:**

A few molecules will have an odd number of electrons. These compounds are called **free radicals** and are extremely unstable and reactive. They tend to react with other free radicals to pair up their unpaired electrons. **The molecules included in this experiment that are free radicals will always have nitrogen as the central atom**, and in these molecules, the nitrogen atom will only have **7 electrons**.

#### **Molecules with Expanded Octets**

Many molecules and polyatomic ions have more than eight valence electrons around the central atom. The central atom can have an *expanded octet only if it is from Period 3 or higher*, where empty d orbitals are available to hold these additional valence electrons. For example, sulfur can form molecules with an expanded octet because it is in the 3<sup>rd</sup> period, but oxygen cannot because it is in the 2<sup>nd</sup> period and is too small to hold more than an octet.

### **Examples:**

#### **Case 1: Draw the Lewis structure for CH<sub>3</sub>Cl.**

- Calculate the total number of valence electrons for all atoms in the compound:

$$\text{valence } e^- \text{ for C} + 3 \text{ (valence } e^- \text{ for H)} + \text{valence } e^- \text{ for Cl} = 4 + 3(1) + 7 = 14 \text{ } e^-$$

- Divide the total number of valence electrons by 2 for the number of electron pairs:  $\frac{14 \text{ } e^-}{2} = 7 \text{ electron pairs}$
- The central atom is usually the least electronegative. Although H is less electronegative than C, H must always be an outer atom. Thus, C is the central atom, and the Cl and H atoms are all outer atoms. (See Figure 1, Step 3 below.)

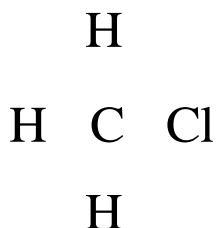
4. Next, we connect all the atoms with single bonds. (See Figure 1 Step 4 below.)

**7 electron pairs - 4 bonding pairs = 3 electron pairs left**

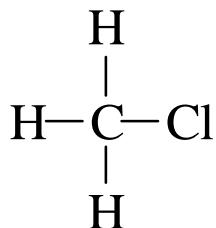
5. The C atom already has an octet, and each H atom has a pair of electrons, so they need no additional electrons. The last three pairs are put around the Cl, so it also has an octet. Now C and Cl each have an octet, and each H has the pair of electrons needed. Thus, the Lewis electron-dot structure for CH<sub>3</sub>Cl is shown below.
6. Finally, confirm that electrons were neither created nor destroyed – that there are in fact 14 electrons, no more or less, in the final Lewis structure.

**Figure 1. Drawing the Lewis structure for CH<sub>3</sub>Cl**

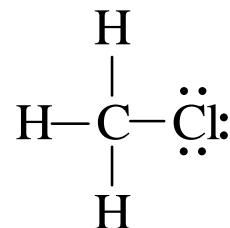
**Step 3**



**Step 4**



**Step 5**



### Case 2: Draw the Lewis electron-dot structure for nitrite ion, NO<sub>2</sub><sup>-</sup>.

1. Calculate the total number of valence electrons for all atoms in the compound:

$$\text{valence } e^- \text{ for N} + 2(\text{valence } e^- \text{ for O}) + e^- \text{ from charge} = 5 + 2(6) + 1 = 18 e^-$$

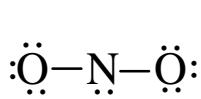
2. Divide the total number of valence electrons by 2 for the number of electron pairs:
- $$\frac{18 e^-}{2} = 9 \text{ electron pairs}$$
3. The central atom is usually the least electronegative, N is the central atom, and the O atoms are the outer atoms. Next, we connect all the atoms with single bonds.
4. Distribute the remaining 7 electron pairs around the outer atoms first then put the last pair on the N atom (see Figure 2, Step 4 below).



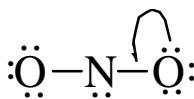
with single bonds.

**Figure 2: Drawing the Lewis structure for NO<sub>2</sub><sup>-</sup>**

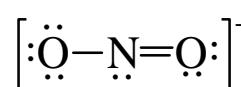
**Step 4**



**Step 5**



**Step 6**



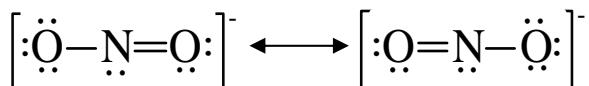
5. While the two O atoms have an octet, the N atom needs one more pair. Giving a lone pair of electrons from an O atom to the N atom would prevent the O atom from having an octet. For all the atoms to get an octet, one O atom must *share* a lone pair of electrons with the N atom to form a double bond (see Figure 2, Step 5 above).
6. To finish off a polyatomic ion, place square brackets around the Lewis structure, and show the charge in the upper right-hand corner outside the brackets. The complete Lewis structure for the nitrite ion, NO<sub>2</sub><sup>-</sup>, is shown in Figure 2 Step 6 on the previous page.
7. Finally, confirm that electrons were neither created nor destroyed – that there are in fact 14 electrons, no more or less, in the final Lewis structure.

## **Resonance Structures:**

Note that the double bond on the nitrite ion can be made with either oxygen atom, so two different Lewis structures can be drawn for the nitrite ion, as shown below:



However, experimental measurements on the nitrite ion indicate that the two N–O bonds are equal in length, so these Lewis structures cannot be correct since single bonds are longer than double bonds. Thus, the bonds in the nitrite ion must be between a single and a double bond, something like a “bond and a half.” Because we cannot draw a bond and a half, we need both Lewis structures, called **resonance structures** (or resonance forms), to portray nitrite ion as accurately as possible. Resonance structures apply to molecules and polyatomic ions that contain a combination of single and double bond or other combination of multiple bonds. When resonance structures are needed to correctly represent a molecule or polyatomic ion, all of the resonance structures are shown with double arrows between them, as shown below.



The double arrow indicates the actual structure is a combination of the resonance structures.

## **VALENCE-SHELL ELECTRON-PAIR REPULSION (VSEPR) MODEL:**

Lewis structures show the two-dimensional distribution of atoms and electrons. The molecular geometry, or three-dimensional shape of a molecule or polyatomic ion, can be determined using valence-shell electron-pair repulsion (abbreviated VSEPR and pronounced “VES-per”) theory, in which the basic principle is *valence electrons around a central atom stay as far apart as possible to minimize the repulsions*. The general rules for VSEPR theory are described below.

### **General Rules for the VSEPR Model**

- Consider double and triple bonds like single bonds. (This is an approximation as extra electrons occupy space, but this allows a simplified model to determine general shape.)
- If two or more resonance structures can be drawn for a molecule, VSEPR model can be applied to any one of them.

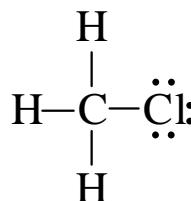
### **Guidelines for Applying the VSEPR Model**

1. Draw the Lewis electron-dot structure.
2. Count the number of outer atoms and lone pairs *around the central atom*.
  - Determine the general formula, and match it up with the molecular geometry, name and bond angle(s) using the VSEPR and Molecular Geometry Tables supplement.
  - Remember that lone pair electrons occupy more space than bonded pairs of electrons, so the bond angles are compressed (e.g. <120°, <109.5°, etc.) when the central atom has lone pairs.

### **Case 1: Determine the molecular geometry for CH<sub>3</sub>Cl.**

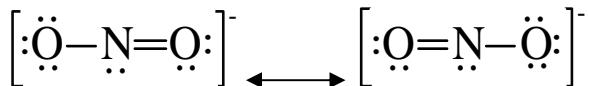
Using the Lewis structure drawn on p. 3 (shown at the right), we determine that there are four atoms and no lone pairs on the central atom, C, so CH<sub>3</sub>Cl's general formula is AB<sub>4</sub>.

Using the VSEPR and Molecular Geometry Tables supplement (p. 2), we find AB<sub>4</sub> corresponds to the molecular geometry *tetrahedral*, which has 109.5° bond angles. Thus, CH<sub>3</sub>Cl's molecular geometry is **tetrahedral**, and its **bond angles are 109.5°**.



## Case 2: Determine the molecular geometry for the nitrite ion, $\text{NO}_2^-$ .

Consider the resonance structure determined for nitrite ion below:



Both of these show two outer atoms and one lone pair on the central atom, so nitrite ion's general formula is  $\text{AB}_2\text{E}$ . Using the VSEPR and Molecular Geometry Tables supplement (p. 2), we find  $\text{AB}_2\text{E}$  corresponds to the molecular geometry *bent* with  $<120^\circ$  bond angles. Recall that lone pairs around the central atom repel the bonding pairs of electrons, so the bond angles become compressed. Thus, **nitrite ion's molecular geometry is actually bent**, not linear as it appears from the Lewis dot structure, and its **bond angles are  $<120^\circ$** .

## POLARITY OF MOLECULES:

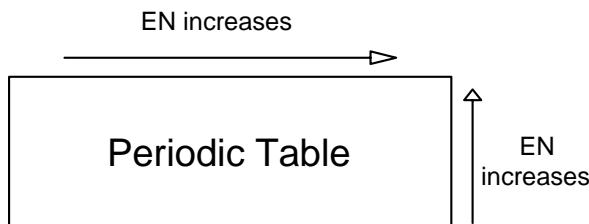
**Electronegativity** is the ability of an atom in a chemical bond to attract electrons to itself.

### Trends for Electronegativity (EN)

Fluorine (F) is the most electronegative element in the Periodic Table. In general, the closer an element is to fluorine, the more electronegative it is. The one exception is hydrogen (H) which has an electronegativity value between those of

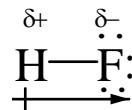
### Exception: H's EN is between B and C!

boron (B) and carbon (C). For example, to determine if C or Cl is more electronegative, note that Cl is closer to F in the Periodic Table, so Cl is more electronegative than C.



When two atoms share electrons in a covalent bond, they do not share equally if one atom is more electronegative than the other. The “tug of war” for the electrons shared results in the atom with the higher electronegativity pulling the electrons more strongly towards itself, and thus, forming a partly **negative (electron rich) end** of the bond. Since electrons spend less time around the other atom, that atom becomes the partly **positive (electron deficient) end** of the bond. Thus, one atom is partially negative and the other atom is partially positive, so the bond has two poles (like the positive and negative end of a magnet). This separation of charges is called a **dipole**, and bonds with a dipole are **polar covalent bonds**.

In the example at the right, the very electronegative F pulls the bonding electrons away from the less electronegative H. This is shown using **delta ( $\delta$ ) notation**, where the more electronegative atom gets the  $\delta^-$  and the less electronegative atom gets the  $\delta^+$ . Dipoles are also indicated using an arrow with a cross; the cross (+) is shown at the positive end and the arrow points from the positive end towards the negative end. In general, the greater the **difference** in electronegativities, the more polar the bond.



In some molecules, two atoms have equal electronegativities, so they share the bonding electrons equally in what is called a **nonpolar covalent bond**. For example, the electrons in the H–H bond in  $\text{H}_2$  are shared equally by the H atoms, so this is a nonpolar covalent bond.

To determine whether an entire molecule is polar or nonpolar, refer to the following:

**For diatomic molecules** (consisting of only two atoms):

- When the two atoms have **equal electronegativity values**, there is **no dipole**, so the **molecule is nonpolar**.
- When the two atoms have **different electronegativity values**, there is a **dipole**, so the **molecule is polar**.

### For molecules of three or more atoms:

The molecule's polarity depends on the sum of all the bonds' polarity and the geometry of atoms around the central atom. A molecule can actually have polar bonds but still be nonpolar overall if the polar bonds completely cancel out one another. The following guidelines will allow you to determine whether a molecule is polar or nonpolar:

### Guidelines for Determining the Polarity of a Molecule with Three or more Atoms

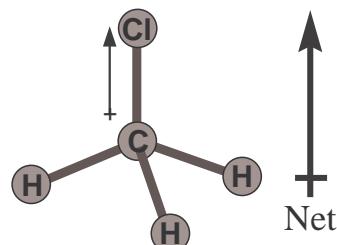
1. Sketch or build the *three-dimensional shape* of a molecule. (Note: The two-dimensional Lewis structure does not provide the three-dimensional arrangement of atoms, so it is not sufficient for determining whether a molecule is polar or nonpolar.)
2. Use the trend for electronegativity values (see p. 5 for details) to determine the more electronegative atom for each bond on the central atom, then a dipole arrow from the less electronegative atom to the more electronegative atom.
3. If the dipole arrows completely **cancel one another**, the molecule is **nonpolar**.  
If the dipole arrows add up to give an overall or **net dipole**, the molecule is **polar**.

Note: Since hydrogen's electronegativity value is between boron's and carbon's, the difference in electronegativity values for hydrogen and carbon is so small that the **carbon-hydrogen bond is considered nonpolar**.

### Case 1: Determine whether the CH<sub>3</sub>Cl molecule is polar or nonpolar

On page 12, we determined the shape of the CH<sub>3</sub>Cl molecule to be tetrahedral with 109.5° bond angles. A sketch of the molecule's three-dimensional shape is shown at the right. Comparing the electronegativity values of each pair of bonded atoms allows us to determine if each bond is polar or nonpolar. Since Cl is closer than C to F on the Periodic Table, Cl is more electronegative than C; thus, a dipole arrow is drawn from C to Cl. Since the H is between B and C in terms of electronegativity values, their difference in electronegativity values is so small, the C-H bond is considered nonpolar; thus, no dipole arrow is drawn for the C-H bonds.

Because the C-Cl bond is polar, the **CH<sub>3</sub>Cl has a net dipole, so CH<sub>3</sub>Cl is polar**.



### Valence Bond Theory

While Lewis electron-dot structures show the two-dimensional arrangement of electrons in a molecule or polyatomic ion, and the VSEPR model predicts the three-dimensional shape of the molecule or polyatomic ion, neither explains how the various shapes result from the atomic orbitals holding the bonding and nonbonding electrons. This is accomplished using **Valence Bond Theory**.

A covalent bond is formed by the overlap of two half-filled orbitals. One electron from one atom and one electron from a second atom can have overlapping orbitals form a covalent bond. For example, in H<sub>2</sub> the two hydrogen atoms share the two electrons forming the covalent bond between them. Thus, the electron configuration for each atom in H<sub>2</sub> has 2 electrons in the 1s orbital, and the hybrid orbital diagram for each H atom is shown below:

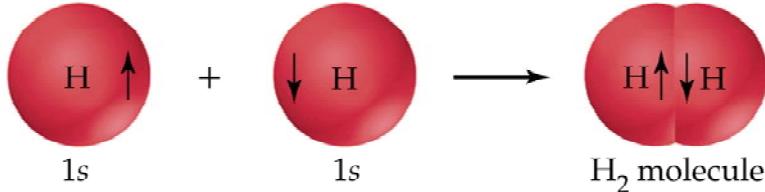
#### Electron Configuration

for each H in H<sub>2</sub>: 1s<sup>2</sup>

#### Hybrid Orbital Diagram

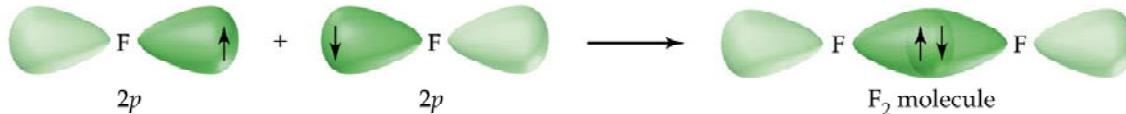


In three dimensions, the two hydrogen atoms come together and overlap with one another to form the H<sub>2</sub> molecule. Since s orbitals are spherical in shape, each H atom's 1s orbital can be shown as a sphere, so the formation of the H<sub>2</sub> molecule can be shown as follow:



Note the overlapping region between the two atoms. This is where the shared electrons are located. In general, for most covalent bonds, the shared electrons exist in the overlapping region between the two bonded atoms.

Similarly, two unstable F atoms come together to form the more stable F<sub>2</sub> molecule. Note the unpaired electron in one of the 2p orbitals in the atomic orbital diagram for the F atom above. However, the covalent bond between F atoms in F<sub>2</sub> forms between two 2p orbitals, which have a dumb-bell shape, as shown below:

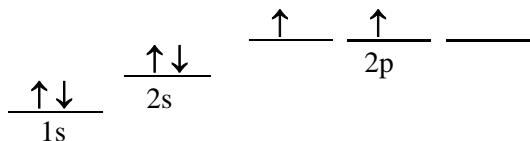


To form the CH<sub>4</sub> molecule, the carbon atom needs 4 unpaired electrons to form the single bonds with the H atoms. To get 4 unpaired electrons, one electron from the 2s orbital must be “promoted” to the unoccupied 2p orbital. Carbon’s ground state electron configuration and atomic orbital diagram are shown below:

**Electron Configuration**

$$\text{carbon: } 1s^2 2s^2 2p^2$$

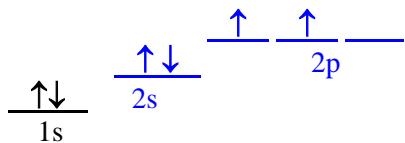
**Atomic Orbital Diagram**



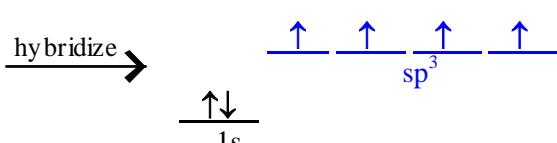
Given this atomic orbital diagram, the C-H bonds in CH<sub>4</sub> should be different since one forms from the overlap with the 2s orbital while three form with the 2p orbitals. Furthermore, since the 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> orbitals lie on the x-axis, y-axis, and z-axis, the bond angles for the atoms in CH<sub>4</sub> formed from these orbitals should be 90°. Yet, the VSEPR model predicts CH<sub>4</sub>’s molecular geometry is tetrahedral with 109.5° bond angles. Furthermore, experimental measurements indicate the four bond lengths, and thus, the four bonds, in CH<sub>4</sub> are identical. Thus, the four orbitals in carbon that form the single bonds to each H atom must be identical to form identical bonds.

The only way to get four identical orbitals is to “hybridize” or combine the 2s and three 2p orbitals to get four new “sp<sup>3</sup>” atomic hybrid orbitals, as shown on the next page.

**Atomic Orbital Diagram (Before)**



**Hybrid Orbital Diagram (After)**



Note that the new hybrid orbitals are called “sp<sup>3</sup>” since one s orbital and three p orbitals were hybridized to make the new orbitals. To maximize the distance between the electrons, the four sp<sup>3</sup> hybrid orbitals orient themselves as far away from each other to get the tetrahedral shape and 109.5° bond angles, matching the results from VSEPR.