# WS 4:Drawing Lewis Structures[i]

The Lewis structure of a molecule is 2-dimensionl representation of a molecule. It is flat and shows the relative placement of atoms and electrons, connections and attachments like lone pair electrons. The Lewis structure is the first step to visualizing what a molecule looks like.

We will follow the basic flow chart below to determine electron pair and molecular geometry. In future handouts we will continue this path to help us picture 3-D structures of molecules.


## Part 1: Lewis structures for molecules that obey the octet rule.

The first step in determining shapes of molecules is drawing a good Lewis structure from the molecular formula. Most atoms in molecules and polyatomic ions, except for hydrogen, tend to be surrounded by eight electrons. **This is the octet rule.** Electrons are distributed about the Lewis structure in such a way as to make this happen. However, there are exceptions to the octet rule. However, **drawing Lewis structures follow the same rules.** The elements that MUST obey the octet rule are in the second period [COFN]

Using the basic rules of Lewis theory to propose a plausible skeleton structure for a molecule and assign valence electrons to this structure. Too often students believe that they must start with the Lewis symbols for the elements to draw Lewis structures—in this way lies madness. The guidelines that follow avoid that difficulty and embrace sanity.

1. Count the total number of valence electrons (Group numbers!!!) in the species, remembering to add electrons for anions and subtract them for cations.
2. Decide which atom in the molecule goes in the center. It will be either the most electro-positive element in the formula, or the largest of the atoms in the formula, or both. The other atoms can be referred to as terminal atoms because they are on the outside of the central atom. There are exceptions; F and H are NEVER in the center of a molecule.
3. Arrange the remaining atoms so that they are geometrically distributed around the central atom in a plane.
4. Connect each of the outer atoms to the central atom with a line. This line represents a bond using 2 electrons per line from your Step 1 total (3 lines = 6 electrons).
5. The remaining electrons are used as lone pair electrons. They go on the outer electrons first (most electronegative) then the central atom.
6. Evaluate the structure based on the octet rule and formal charges to form multiply bonds and the best Lewis structure. The octet rule is a useful guideline when drawing Lewis structures. Multiple bonds are often formed with the following atoms: C, N, O, S, Cl, Br, and I. When the halogens are terminal atoms, they form single bonds. Try the following as a first guess: one bond: H, F, Cl, Br, I. Two bonds: O, S, Se, Te, Be. Three Bonds: N, P, As, Sb. Four bonds: C, Si, and Ge.[ii]

## Multiple bonds

The rules above are good guidelines for Lewis structures with single bonds. However, many compounds have the best Lewis structure with multiple bonds (rule 6). When atoms share two electron pairs, we say they form a double bond. When they share three electron pairs, we say they form a triple bond. This is often the only way that atoms in COFN can complete their octets.

How do you know if you have a multiple bond?

1. First, follow the rules for drawing a good Lewis structure.
2. After counting and distributing the electrons correctly, you will see that some of the atoms will not have a complete octet. Usually this is the central atom. This means you need a multiple bond between the atom that has lone pairs to share and the central atom.
3. Double and triple bonds reduce the number of lone pairs in the structure.

Draw the BEST Lewis structures for the molecules listed below. Some of these molecules form multiple bonds. FOR ANY PART OF THE HANDOUT THAT REQUIRES AN ANSWER, IF YOU DO NOT HAVE ENOUGH SPACE, PUT YOUR ANSWERS ON A SEPARATE SHEET OF PAPER.

| Lewis Structure | |
|---|---|
| $CH_4$ | $N_2$ |
| $CO_2$ | CO |
| HCN | $NH_3$ |
| HOBr | $NO_2Cl$ (N is the central atom) |
| $GeCl_4$ | $NF_3$ |

# PART 2: MOLECULES THAT VIOLATE THE OCTET RULE

In this part of the handout, we will look at molecules that violate the octet rule by having an extended valence shell. We will not be looking at odd-electron molecules, focusing only on Lewis structures that are based on electron pairs. Molecules that violate the octet rule with more than eight electrons around the central atom, usually have central atoms of n=3 or greater. The general explanation for this difference between COFN and other elements is often attributed to the number of orbitals in the valance shell of an atom. Elements in the second period have four valence orbitals [one 2s and three 2 p orbital], summing for a total of 8 electrons. Elements in the third period or higher periods have more orbitals. These orbitals are empty but low enough in energy that they can be used for bonding if needed. Some theorize that the ability to have more than 8 electrons is a consequence of the size of the atom as well as the way the orbitals "line up" to make the bonds

These atoms have empty **n**d orbitals that can be used to house extra electrons. For example, $SF_6$ has a central atom with the electron configuration of [Ne] $3s^2 3p^4$. The 3d shell is unoccupied. The energy levels are thought to be low enough that (using Valence Bond Theory, WS 8) we can expand the octet to take in extra electrons, and therefore, form extra bonds. Notice that the n=2 atoms cannot expand the octet because there is no 2d sub shell. These molecules can have more than 4 electron pairs (8-electrons) around the central atom. However, they don't violate their group number as a rule. Fill in the table below with the best Lewis structures.

| Lewis Structure | |
|---|---|
| $BF_3$ | $SF_4$ |
| $IF_5$ | $PCl_5$ |
| $XeF_4O$ | $XeF_2$ |
| $SF_6$ | $XeF_4$ |

## PART 3: LEWIS STRUCTURES FOR IONS

Follow the rules for general Lewis structures. For negatively charged ions, add one more electron for each charge to the total valance electrons; for positive ions, subtract one electron per charge value. For example, the carbonate, $CO_3^{2-}$, has a total of 4e– for C + 18e- for O + 2e- (for the charge) = 24e-.

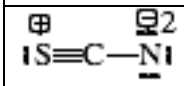
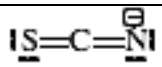
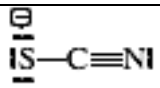
Fill in the table below with the best Lewis structures. For now, follow the octet rule as much as possible. Remember to use brackets around ions. Some of these ions will be repeated in the next section.

| Lewis Structure | |
|---|---|
| $SO_4^{2-}$ | $NO_3^{1-}$ |
| $NO_2^-$ | $ICl_2^{1-}$ |
| $[SiF_6]^{2-}$ | $BrF_4^-$ |
| $NO^+$ | $NO_2^+$ |
| $AlCl_4^-$ | $ClO_2^-$ |

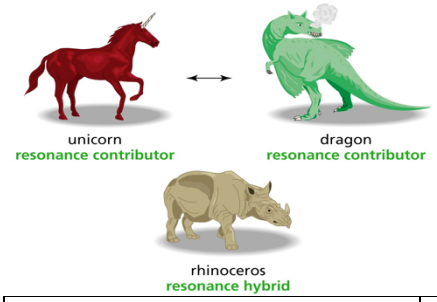
# PART 4: RESONANCE STRUCTURES AND FORMAL CHARGE.

Some compounds cannot be represented with a single Lewis structure. For these species, we write several equivalent structures, called resonance structures. Usually, these compounds have multiple bonds and a charge; the multiple bonds and charges may be written in several equivalent locations. The following features are true for all resonance structures:

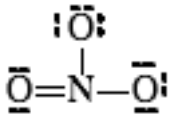
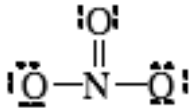
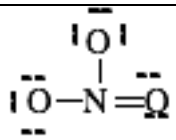
1. Often, the number of bonds of each type (single, double, triple) is the same in resonance structures. The emphasis is on the word "often". Look at the three structures for SCN⁻.
2. The molecular skeleton is the same in each structure. All that is involved in creating one resonance structure from another is shifting a few pairs of electrons.

| Structure 1 | Structure 2 | Structure 3 |
|---|---|---|
|  |  |  |

Many students have the mistaken impression that the resonance hybrid (the molecule) hops back and forth between its various resonance forms. This is no truer than believing a tangelo (a hybrid of a grapefruit or pomelo and a tangerine) is sometimes a grapefruit or other times a tangerine, or that a mule is sometimes a horse or sometimes a donkey. The difficulty in picturing hybrids is the Lewis theory itself. One structure is not enough to portray the structure since it implies set bond lengths in a molecule. The double bond in a hybrid is longer than a regular double bond but shorter than a signal bond. [1]




There are three possible Lewis structures for the nitrate ion; they are shown below. The three structures differ only in the position of the double bond and, therefore, correspond to the same energy. Experiments have shown that all three NO bonds are identical; the bonds have the same length and strength. Showing only one of these structures would not be correct since any one of them alone does not represent the BEST structure. The ion is taken to be a blend of all three Lewis structures.

| Structure 1 | Structure 2 | Structure 3 |
|---|---|---|
|  |  |  |

How can we then determine the best structure(s)? The answer lies in the formal charge. The formal charge is the charge assigned to atoms in molecules, by assuming the chemical bond is shared equally between the atoms. This is independent of the type of atom or the electro-negativity of those atoms. It is a way of looking at how the charge might be distributed in the molecule if the molecule was a 'potential map'. By minimizing the charges, we lower the energy of the map.

To determine the formal charge (FC) on an atom, use one of the formulas below. They give the same results.

1. FC = group number - number of unshared electrons - number of shared electrons/2
2. FC = group number -(sticks and dots), where sticks are bonds and dots are lone pair electrons

The most plausible structure is the one in which the formal charges are minimized, or the one in which the sum of the absolute values of the formal charges is the smallest. If formal charges remain in the species, the positive formula charges should be on the least electronegative atoms and the negative formal charges on the most electronegative atoms.

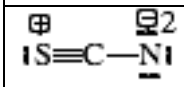
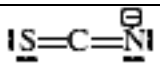
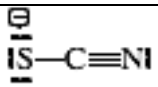
[1] Unicorns are real

Of course, there will always be some nonzero formal charges on atoms in the ion because it is an ion. However, even molecules can have atoms with formal charges.

Remember the sum of formal charges equals the charge on the ion (or zero for a molecules), and the formal charge is not the actual charge on the ion or atoms. For example, in the carbon monoxide ion, carbon has a formal charge of –1 and oxygen has a formal charge of +1. This does not mean that the bonds in CO are ionic (it is a molecule that has a charge, so it is covalent!), nor does it mean that each atom in the bond has the full charge indicated by the formal charge. Each atom does not equally share the electrons, in the bond. They spend more time around oxygen, the more electronegative of the two atoms. Based on ΔEN, there is a dipole in this molecule. The polarity of the dipole is as predicted by the formal charges.[2] However, the observed dipoles moment of CO is very small, 0.1 D.

## 3 basic rules for formal charge are:

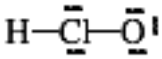
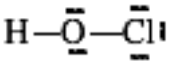
1. Lowest number of charges for the molecule. (This corresponds to the lowest sum of the absolute value of the formal charges.)
2. Lowest magnitude of charge for each atom
3. Positive charges go on more electropositive atoms; negative charges go on more electronegative atoms.

| Structure 1 | Structure 2 | Structure 3 |
|---|---|---|
|  |  |  |
| Structure 1 has the largest sum of the absolute value of the charges (3); it has the highest magnitude, and number of charges. | Structure 2 has the negative charge on the more electronegative atom. This is a better (best) structure than structure 1. | Structure 3 has the negative charge on the sulfur, which is more electropositive than nitrogen. This is a better structure than #1 but not as good as #2. The two structures that contribute the most are structures 1 & 3. |
| Notice that the Bonds move not the atoms | | |

Remember these are rules of thumb [👍], and should be applied so the best possible outcome is obtained. Many molecules and ions do not follow this rule. So, how will you know what to do? Before one applies the formal charge rule, check to make sure that the atom first is satisfied by the octet rule. If the ion or molecule can be drawn in such a way that it does satisfy the octet rule, then you don't have to worry about formal charge reductions (which is the case for most polyatomics with a central atom of n=3 or greater). For example, sulfate satisfies the octet rule, even though there are charges on each atom in the ion. So, one would not make multiple bonds for the sulfate ion to lower the formal charges. This is supported by molecular orbital calculations. It is less energetically favorable for the ion to form double bonds with 3d orbitals on sulfur and 2 p orbitals on oxygen.

Ions such as sulfate, bromate, perbromate, phosphate, are drawn with single bonds to oxygen. Contrast this with carbonate. The carbon needs to have the octet satisfied, and therefore, will double bond with one of the terminal oxygens.

Below is an example of how formal charge can be used to predict a better or more stable structure.

| | | |
|---|---|---|
| Lewis structure |  |  |
| FC = Group # - (sticks + dots) | H; 1 – 1 = 0<br>Cl; 7 – (2 + 4) = +1<br>O; 6 – (1 + 6) = –1 | H; 1 – 1 = 0<br>O; 6 – (2 + 4) = 0<br>Cl; 7 – (1 + 6) = 0 |

Notice that for the first structure the sum of the absolute values is 2, while on the other molecule, the sum is 0. The charge on the central atom is (+), while the terminal atom is (—). The charges on the second molecules are all zeros. Clearly based on our rules, the second structure is more stable.

[2] Bernice Segal page 499

These equations are based on two assumptions, the lone pairs are assumed to belong to the element on which they reside in the Lewis structure. One assumes that bond pairs are to be divided equally between bonded atoms. The sum of the formal charges on the atoms in a molecule or ion always equal the net-charge on the molecule or ion.

Going back to nitrate ion, we can apply the equation and find that the nitrogen has a +1 FC, while two of the oxygens are –1 FC and one of the oxygens is 0 FC. The sum of these charges is –1. Are these structures reasonable for Lewis structures? Yes. They satisfy the octet rule and formal charges are distributed as best as they can be. Is this a reasonable representation of the charge distribution for the nitrite ion? No! Nitrate has three resonance structures; the oxygens in the molecule must be the same, so the charges must be the same. We can resolve this problem if the formal charges are averaged to give each a charge of –2/3. However, we usually show the structure as the three resonance hybrids.[iii]

Fill in the table below with the best Lewis structure(s). Show how formal charge helped you make your choice. Show resonances when appropriate.

| Lewis, resonance, and formal charge | |
|---|---|
| $N_3^-$ | |
| $N_2O$ | There are two skeletons for this arrangement. Use formal charge to determine the best central atom. [try comparing the two structures that have the same bonding type. Might I suggest, 2 double bonds] The correct central atom isomer has three resonance structures, two of which are the most dominant. What are they? |
| $ICl_4^+$ | |
| $CO_3^{2-}$ | This ion has three resonance structures. Draw all three. |

| Lewis, resonance, and formal charge | |
|---|---|
| $CO_2$ | There are three possible structures for carbon dioxide, but only one makes sense. Draw the three structures with the formal charges and explain why the one you chose is the best. |
| $ClO_3^-$ | |
| ONCl | There are three structures that can be drawn for this molecular formula, each has a different central atom. Use formal charge to determine the best structure. Each structure has a double bond to satisfy the octet rule. [Hint: one structure has an NO double bond, one has an ON double bond, and one has a NCl double bond] no resonance here! |
| $ClO_2^+$ | Draw the two resonance structures for this ion |
| $Cl_2SO$ | (sulfur in the center, why? Draw a structure with O in the center, or Cl in the center to find out!) [SO double bond, vs OS double bond] |

| Lewis, resonance, and formal charge | |
|---|---|
| $HCO_2^-$ | This has two resonance structures |
| $FSO_3^-$ | |
| $ClF_2^-$ | |
| $ClF_3$ | |

[i] Brown and LeMay Chapter 8
[ii] Petrucci and Harwood
[iii] Bernice Segal