# Lewis Model of Electronic Structure

### *Why?*

The Lewis model of molecular electronic structure describes how atoms bond to each other to form molecules. It determines the number of bonds formed between pairs of atoms in a molecule and the number of electrons that exist as lone or nonbonding pairs. You need to know how to apply the Lewis model to obtain the bonding structure and geometry of molecules. Scientists who work with molecules often use the Lewis model and other simple models to interpret, predict, and understand molecular properties and chemical reactions.

### *Learning Objectives*

- Master the use of Lewis structures.
- Associate bond strengths with the Lewis structure.

### *Success Criteria*

- Ability to construct realistic Lewis structures.
- Correct identification of bond strengths from Lewis structures.

### *Resources*

Olmsted and Williams (*Chemistry 3/e*, Wiley, 2002) pp. 332-350.

### *Prerequisites*

valence electrons, electronegativity

### *New Concepts*

Lewis model, Lewis structure, duet rule, octet rule, bonding electron pairs, lone or nonbonding electron pairs, single bond, double bond, triple bond, resonance, formal charge

### *Information*

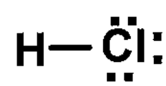
Lewis structures (or diagrams) are used to represent the electronic structure of molecules. In these diagrams, dots are used to represent electrons, A line between atoms represents a single bond formed by a pair of electrons, other dots represent nonbonding electrons, and charges reveal a formal distribution of charge. The bonds show how the atoms in a molecule are connected to each other. A Lewis structure does not show bond lengths, bond angles, arrangement in three-dimensional space, or the actual charges on atoms. Some molecules require more than one Lewis structure to describe them. These multiple structures are called *resonance structures.*

Some atoms (C, N, O, and S) form double bonds, which are represented by double lines. Some atoms (C and N) form triple bonds, which are represented by triple lines. Multiple bonds are stronger than single bonds.

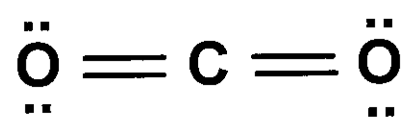
How does one determine and draw a Lewis structure? First determine whether the molecule is ionic or covalent. If it is ionic, draw each ion separately. For covalent molecules, follow the methodology given below.

***Model: Methodology for Constructing Lewis Structures***

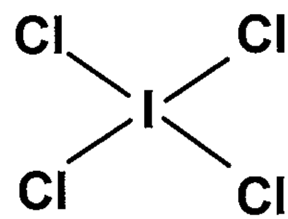
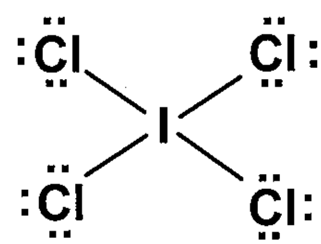
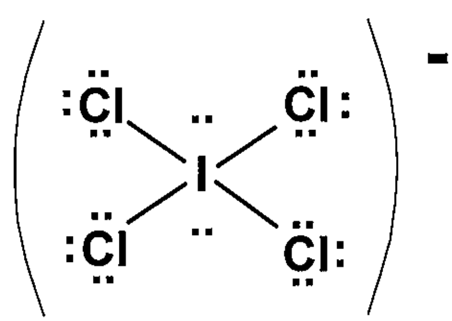
## HCl - A Simple Example

| Methodology | Example: Single Bond |
|---|---|
| **Step 1:** Count the number of valence electrons from all the atoms. Add electrons for negative ions, subtract electrons for positive ions. | For hydrochloric acid, H has 1 and Cl has 7 for a total of 8 valence electrons. |
| **Step 2:** Assemble the bonding framework. Decide which atoms are connected to each other and use a pair of electrons, represented by a line, to form a bond between each pair of atoms that are bonded together. | **H—Cl** |
| **Step 3:** Arrange the remaining electrons so each atom has 8 electrons around it (the octet rule), place additional pairs of electrons between the atoms to form additional bonds if necessary. |  |
| **Step 4:** Check for exceptions to the octet rule. For H only 2 electrons are needed (the duet rule). Be and B often are electron deficient and may only have 4 or 6 electrons. Atoms in the second period can not have more than 8 electrons. The third and higher period elements often have more than 8 electrons. | Cl satisfies the octet rule.<br>H satisfies the duet rule. |
| **Step 5:** Determine the formal charges (FC) on the atoms. FC = number of atomic valence electrons – number of lone pair electrons - 0.5(number of shared electrons). Evaluate whether the formal charges (FC) on the atoms are reasonable. | FC(H) = 1 - 1 = 0<br><br>FC(Cl) = 7 - 7 = 0<br><br>Reasonable because FC is zero or small. Negative charges need to reside on the most electronegative atoms |
| **Step 6:** Draw resonance structures. | none in this case |

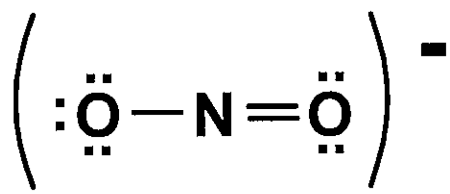
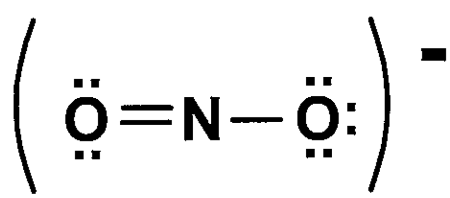
## $CO_2$ - Need for Double Bonds

| Methodology | Example: Multiple Bonds |
|---|---|
| **Step 1:** Count the number of valence electrons from all the atoms. | For carbon dioxide, C has 4 valence electrons and O has 6 valence electrons for a total of 16 valence electrons. |
| **Step 2:** Assemble the bonding framework. | O — C — O |
| **Step 3:** Arrange the remaining electrons so each atom has 8 electrons around it (the octet rule), placing additional pairs of electrons between the atoms to form additional bonds if necessary to satisfy the octet rule. |  |
| **Step 4:** Check for exceptions to the octet rule. | No exceptions present. |
| **Step 5:** Evaluate whether the formal charges on the atoms are reasonable. | FC(C) = 4 - 4 = 0<br>FC(O) = 6 - 6 = 0 |
| **Step 6:** Draw resonance structures. | none for this case |

## $ICl_4^-$ - Exception to the Octet Rule

| Methodology | Example: Third Period Element |
|---|---|
| **Step 1:** Count the number of valence electrons from all the atoms, add one because it is a –1 ion. | For $ICl_4^-$, there are 36 valence electrons (5 x 7 + 1). |
| **Step 2:** Assemble the bonding framework. |  |
| **Step 3:** Arrange the remaining electrons so each atom has 8 electrons around it. |  |
| **Step 4:** Check for exceptions to the octet rule. After satisfying the octet rule for each atom, there are 4 electrons remaining. These are placed as nonbonding electrons on the fifth period element, iodine. |  |
| **Step 5:** Evaluate whether the formal charges on the atoms are reasonable. | FC(I) = 7 - 8 = -1<br>FC(Cl) = 7 - 7 = 0 |
| **Step 6:** Draw resonance structures. | none for this case |

## $NO_2^-$ - The Need for Multiple Lewis Structures

| Methodology | Example: Resonance |
|---|---|
| **Step 1:** Count the number of valence electrons from all the atoms, add one because it is a –1 ion. | For $NO_2^-$, there are 18 valence electrons (5 + (2 x 6) + 1) |
| **Step 2:** Assemble the bonding framework. | O—N—O |
| **Step 3:** Arrange the remaining electrons so each atom has 8 electrons around it. |  |
| **Step 4:** Check for exceptions to the octet rule. | none |
| **Step 5:** Evaluate whether the formal charges on the atoms are reasonable. | FC(N) = 5 - 5 = 0<br>FC(O1) = 6 - 7 = -1<br>FC(O2) = 6 - 6 = 0 |
| **Step 6:** Draw the resonance structure because both oxygen atoms are equivalent. |  |

### *Key Questions*

1. What distinguishes each of the four examples in illustrating the methodology?

2. Why is it sometimes necessary to put double or even triple bonds between atoms in constructing Lewis structures?

3. How does the Lewis structure help you identify the strongest bonds in a molecule?

4. How is formal charge determined, and how is it used in identifying reasonable Lewis structures?

5. In the above examples illustrating the methodology, why is resonance present only in the case of $NO_2^-$ ?

6. List three observations or discoveries that your team has made about constructing Lewis structures by examining the model and responding to the key questions.

### *Information*

In assembling the bonding framework, you may find it difficult to identify which atoms are bonded to each other. Sometimes you simply need to know the molecular structure, it can not be deduced from first principles, but here are some guidelines that often are helpful. It is useful to think in terms of *inner atoms* and *outer atoms*. An *outer atom* bonds to only one other atom while an *inner atom* bonds to more than one other atom.

Hydrogen atoms are outer atoms because they can form just one bond.

Outer atoms other than hydrogen usually are the ones with the highest electronegativities.

The order in which the atoms are written in a molecular formula often indicates the bonding framework. For example in OCS, the carbon atom is the inner atom.

Parentheses often are used in a molecular formula to indicate the bonding framework. For example in $(CH_3)_2CO$, the hydrogen atoms are bonded to carbon to form two methyl radicals, and oxygen is an outer atom bonded to an inner carbon atom.

Multiple atoms of the same element usually are the outer atoms around a single atom of another element, e.g. in $PF_6$ phosphorous is the inner atom.

Sometimes a knowledge of the chemical properties is helpful. For example in $HNO_3$ the hydrogen atom could be bonded to the nitrogen or to oxygen. Knowing that nitric acid is an oxyacid locates the hydrogen as bonded to an oxygen atom.

Finally, the most likely structure is the one with the most reasonable formal charges on the atoms. By reasonable, we mean the formal charges should be small or zero, and the negative charges should be located on the most electronegative atoms.

### *Exercises*

1. Draw Lewis structures for the following molecules. A Lewis structure includes the formal charge on each atom if it differs from zero and any resonance structures that are significant.

$H_2O$ | $O_2$

$PF_5$ | $HNO_3$

$SeF_2$ | OCS

$I_3^-$ | $O_3$

2. Use Lewis structures to arrange the following compounds in order of increasing carbon-carbon bond strength. Explain.
   $C_2H_6$ $C_2H_4$ $C_2H_2$.

3.

### *Problems*

1. Use Lewis structures to identify which of the following compounds you would most likely be successful at synthesizing: $SiF_4$, $OF_4$, $SF_6$, or $OF_6$. Explain.

2. Two Lewis structures are needed to describe the bonding in formamide, $HCONH_2$. Write these two resonance structures. One should have no formal charges on the atoms, and the other will have a formal charge of +1 on N and -1 on O. Which structure do you expect to be the better (lower energy) structure?

3. For the two resonance structures of formamide in Problem 2, explain why each of the following statements is either correct or incorrect.

   (a) The molecule is oscillating back-and-forth between the two structures and each represents the molecule 50% of the time.

   (b) The expected CO bond length is in between that for a normal CO double bond and that for a normal CO single bond.

   (e) The nitrogen in the molecule has a lower electron density associated with it than is found for the free nitrogen atom.

   (f) Both resonance structures have the same energy.