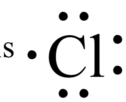
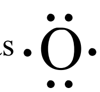
Lewis Structures

In the later part of the nineteenth century, chemists recognized a pattern in the formation of simple ions. Elements tended to form simple ions (one atom with some type of either positive or negative charge) that had a total number of electrons equal to one of the noble gases. In fact this electron total is sometimes referred to a "noble gas configuration". The elements, sodium, magnesium, nitrogen, oxygen, and fluorine all form their respective ions, Na^{+}, Mg^{+2}, N^{-3}, O^{-2}, and F^{-} which have the same total number of electrons as the element Ne. While the elements the elements K, Ca, P, S, and Cl, all form their respective ions, K^{+}, Ca^{+2}, P^{-3}, S^{-2}, and Cl^{-} which have the same total number of electrons as the element Ar. However, there was much confusion concerning the formation of molecules.

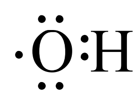
In 1916 the American chemist, G. N. Lewis, published his first paper, "The Atom and the Molecule" describing chemical bonding in molecules. In it he represented atoms in terms of their atomic symbol and a number of dots to represent the valence electrons. Over the years his original drawing evolved in what later became known as "Lewis Symbols".

For example, the Lewis symbol for a sodium atom is  and a chlorine atom is 

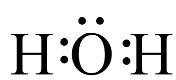
while an oxygen atom can be symbolized as  and a hydrogen atom as 

Lewis's idea was that in molecules, the atoms "share" electrons rather than transferring them as in the formation of ions, but the goal was the same - to achieve the number of electrons equal to the nearest noble gas.

This process can be visualized by connecting Lewis symbols like "Legos" until the atoms involved reach the noble gas configuration. When Lewis symbols are connected the resulting collection is called a "Lewis structure".

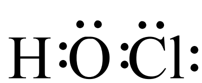
Let's begin by snapping together one H and one O. The result is. 

In this structure, the H has hold of two valence electrons which is the same number as the noble gas helium, He. However, the oxygen has hold of only seven valence electrons which is the same as the element fluorine and NOT the noble gas neon. Thus, we conclude this is NOT a stable structure. How, can this problem be "fixed"? Well, let's try a couple of things.

First, let's add a second H. This would generate the structure  .

This of course is water and as one can easily see both H's have hold of two valence electrons like He. Now, however, the O has hold of eight valence electron like Ne. Thus, in this structure all atoms have achieved the "noble gas configuration" and no additional H's can be added.

Can other atoms be added to the previous OH fragment? Yes, let's add a Cl atom.

This produces,  .

Once again, all atoms have achieved the noble gas configuration.
This molecule exists and is called hypochlorous acid.

Is it possible to simply join two OH fragments to achieve a stable arrangement? Yes!!

$$H:\underset{\cdot\cdot}{\ddot{O}}:\underset{\cdot\cdot}{\ddot{O}}:H$$

This is called hydrogen peroxide (the bathroom antiseptic).

Clearly, Lewis structure help us to visually explain why certain formula work and others do not.

Finally, let's combine the OH fragment with a sodium atom.

$Na:\underset{\cdot\cdot}{\ddot{O}}:H$ This doesn't seem to work.

Here Na only gains access to one additional valence electron or the equivalent of Mg and not Ne. Recall, however, that Na is a metal and thus doesn't form covalent bonds to non-metal. Instead, metals transfer electron to the non-metal atoms to create ions which are then ionically bonded together due to their opposing charges. If Na donates its sole valence electron to the oxygen in the OH fragment then an OH^- ion and an Na^+ ion are produced with NO sharing involved. How can we indicate this fact in our Lewis structure?

This is done as follows $[Na]^+[:\underset{\cdot\cdot}{\ddot{O}}:H]^-$

The [ ] are used to indicate that the electron shown between the Na and the O are NOT shared but belong only to the O (that is that Na donated the electron to the O to form ions). Recall, that a sodium atom has 11 electron of its own and after losing one to form Na^+ only ten remain. This Na^+ ion now has 10 total electrons - the same as neon! Thus, in the IONIC compound NaOH all three atoms have achieved noble gas configurations. The brackets, [ ], are used to surround **each ion** WHENEVER Lewis structures are drawn even if only a single ion is under discussion. For example, the hydroxide ion is drawn as

$$[:\underset{\cdot\cdot}{\ddot{O}}:H]^-$$

Sometimes it is necessary for more than two electrons to be shared between atoms. For example, nitrogen exist as N_2 but a nitrogen atom has seven total electrons and only five valence electrons.

That is, the Lewis symbol for nitrogen is $\cdot\underset{\cdot\cdot}{\dot{N}}\cdot$

How can a noble gas configuration be achieved? Easily!! $:N:::N:$

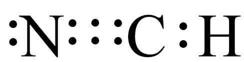
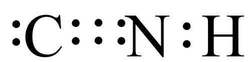
In this structure, each N now has hold of eight valence electrons. For obvious reasons, this type of bond is referred to as a "triple bond". Thus, single bonds, double bonds and triple bonds can be drawn into Lewis structures as needed, for the atoms to achieve the required eight valence electrons (with the exception of hydrogen which only acquires two valence electrons).

Finer points of Lewis structures

Now that we understand the basic of drawing Lewis structures we can move onto the subtler aspects. Consider the combination of these three atoms, C, H, and N.

The respective Lewis symbols are 

With these symbols it is possible to connect them together in two ways.

A)  and B) 

Notice that in each structure, every atom has achieved a noble gas configuration. However, a search of every chemical catalog the world over will turn up one a single compound (and not two) made up of the three atoms. Which one? Can we predict which one reliably without searching the catalogs?

Clearly, we need some help! We need a "tool" which we can use to find the correct answer. This tool is called "the formal charge concept". The formal charge concept is a good **idea**, but like other good ideas such as the "Tooth Fairy" and the "Easter Bunny", it exists only in our minds. These charges only exist in the context of Lewis structures.

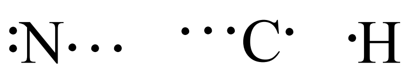
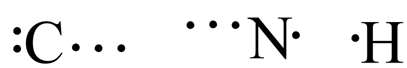
How do we calculate formal charges and how do we use them?

There are two steps to calculating FC's (formal charges).

#1) Divide all bonds in the Lewis structure in half. This will produce a set of "fragments" of the former molecule.

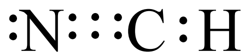
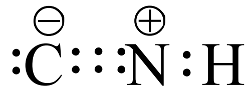
#2) Calculate the FC for each fragment by comparing the number of electrons in each fragment to the original number of valence electrons in the Lewis symbol.

Applying step one to each structure produces these fragments.

A)  B) 

Looking at the fragments from structure A, we see that the nitrogen fragment has 5 electron, the carbon fragment has 4 electrons and the hydrogen fragment has one electron. Applying step two to these fragments give zero charge on each fragment as the original Lewis symbol for each atom has the same number of electrons as the corresponding fragment. In other words the atoms have neither gained or lost any electrons and thus no charge is produced in the fragments.

Looking at the fragments from structure B, we see that the nitrogen fragment has 4 electron, the carbon fragment has 5 electrons and the hydrogen fragment has one electron. The original Lewis symbol for nitrogen had five electrons and thus the nitrogen in the fragment has lost one electron. The loss of one electron results in a positive charge and thus applying step two to the nitrogen fragment produces a formal charge of +1 on N. The carbon fragment has gained one electron and thus there is a -1 formal charge on carbon in this structure. The H fragment has zero FC as the fragment hasn't gained or lost electrons. (When actually writing out FC's a circle is drawn around any non-zero charge, e.g., ⊕ or ⊖. This is to distinguish FC's from any **real** existing charges).

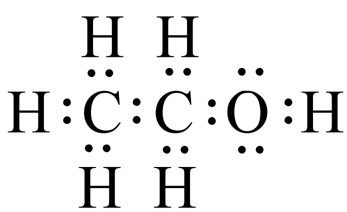
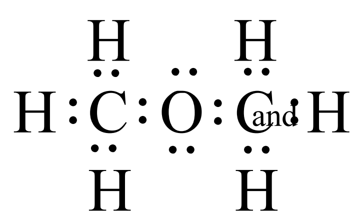
A)  and B) 

Now, we can see that there is a difference in the electron arrangements. Which structure is better? We know that energy must be added to separate positive and negative charges. We conclude, therefore, that structure B must be higher in energy than structure A (energy was added to structure B to pull the + and – charges apart as they are on two **separate** atoms). On the basis of FC we predict that structure A is the one found in all of the chemical catalogs. This is in agreement with chemical reality, only HCN exists (this gas is called hydrogen cyanide).

To summerize the use of FC, a structure in which there is no FC is more plausible than one where FC exists. In choosing among structure where FC exists the structure with less FC is more plausible than one with more FC. Finally, a structure where the ⊖ FC is on the more electronegative atom is more plausible than one where the ⊖ resides on an atom of lower electronegativity.

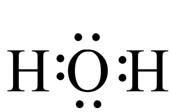
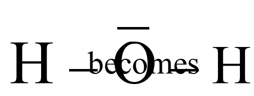
Consider the formula, C_2H_6O, where there are two (·C·), six (H), and one (·O·) fragments.

The 6 H's must be on the outside and thus the other 3 atoms are inside. After some trial and error period we will see that there are only two ways to assemble these 9 atoms.

A)  and  B)

After calculating the formal charges for all atoms in each structure we find that all are zeros! Which one is the "correct" answer? Both!! This is an example of a curious phenomenon in chemistry called isomers. Isomer are different substances that happen to have the exact same chemical formula. In isomers the atoms are in physically different positions relative to the other atoms. Unfortunately, there is no way to determine ahead of time whether or not a particular formula exists as isomers. One finds isomers only by trying to assemble the atoms in **every possible** manner and rejecting the unstable and less stable structures.

Some Lewis structures contain a very large number of electrons (more than 50!). These structures begin to look cluttered so at this point we will introduce a simplifying technique. Since electron are usually paired up it is easier to represent two electron at a time. To do this merely replace ":" with "—".

Thus,  becomes  .

Generalizations about Lewis Structures

1. **All** the valence electrons of the atoms in a Lewis structure must be accounted for.

2. **Usually**, each atom in a Lewis structure acquires an electron configuration with an outer-shell octet. (Hydrogen is limited to an outer-shell duet.)

3. **Usually**, all the electrons in a Lewis structure are paired.

4. **Often**, both atoms in a bonded pair contribute equal numbers of electrons to the covalent bond, but **sometimes**, both electrons in a bonded pair are derived from one atom. (Such a bond is referred to as a coordinate covalent bond.)

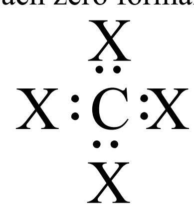
5. **Sometimes**, it is necessary to use double or triple bonds in a Lewis structure.

6. **Sometimes**, it is possible to draw more than one plausible structure (for a given formula) where the constituent atoms are in physically different locations with respect to one another. These different entities are called isomers.

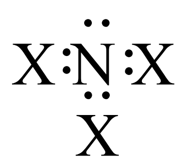
Alternate Strategy for Drawing Lewis Structures

With a little forethought, an alternate to the "Lego" approach for drawing Lewis structures can be created. This method is very useful when structure with many atoms are involved. Let's begin by recalling that in most stable structures the atoms end up with zero formal charge. How many bonds and lone pairs are required for different atoms to reach zero formal charge?

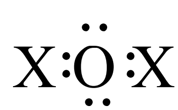
Carbon: four bonds and no lone pairs are needed.



Nitrogen: three bonds and one lone pair are needed.



Oxygen: two bonds and two lone pairs are needed.



Fluorine: one bond and three lone pair are needed.

Steps in drawing Lewis structure.

1. Start with a plausible skeleton structure. This is a representation of the order in which the atoms are bonded. The skeleton consists of one or more central atoms with other atoms (called terminal atoms) bonded to the central atom(s). **Usually, the atom of lowest electronegativity is the central atom.** When assembling a skeleton keep in mind the above formal charge requirements for each element.

2. Add up the total number of valence electrons for all atoms in the structure then add or subtract any electrons as indicated by the charge on the species. This is the number of electrons that **must** appear in the finished Lewis structure.

3. Starting with the **terminal** atoms, place the remaining electron pairs around the atoms to complete the valence shells of all atoms. If this is not possible with the number of electrons available **then** shift lone-pair electrons **from** terminal atoms to form multiple bonds to the central atoms in order to complete the valences of all atoms.

4. **If necessary**, use the **formal charge concept** to choose the best structure from among the possible Lewis structures.

FINAL NOTES ON DRAWING LEWIS STRUCTURES

When drawing Lewis structures one must keep in mind these **three factors**:

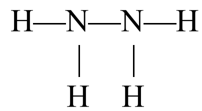
1) **minimizing formal charges** on all atoms.
2) **maximizing the number of bonds**. (Since it requires energy to break bonds then it follows that making bonds must release energy and is therefore a favorable factor)
3) **possession of a noble gas configuration**.

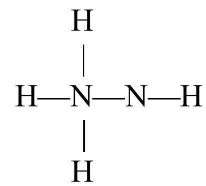
Examples of Drawing Lewis Structures

1. Draw the Lewis structure for N_2H_4.

   Start with a plausible skeleton.

   a) H—H—N—N—H—H

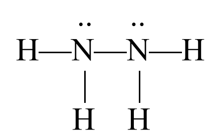
   b) 

   c) 

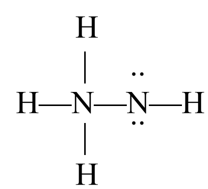
   Structure a) is not a plausible skeleton since two of the hydrogen atoms are shown with two other atoms attached to them. Hydrogen can only share two valance electrons and not four as shown in structure a). It is possible for nitrogen atoms to share more than two electrons. Thus structures b) and c) are more plausible skeletons. However, structure c) has problem. As mentioned above, N should have 3 bonds and one lone pair (which we haven't added yet) to achieve zero FC. The left N atom has 4 bonds and thus a +1 FC which can't be removed by adding electrons. Unless structure b) ends up with **higher** FC than +1, structure c) will be rejected.

   Next, count up the valance electron for all of the atoms in the formula. This totals 14 electrons in the example. These 14 electrons must appear somewhere in the final structure. In the skeletons b) and c) above have only 10 electrons depicted. Thus an additional four electrons are needed. Normally these "extra" electrons are placed on the terminal atoms but as mentioned previously, H atoms can only share two electron each and in our skeleton the H atoms already have two shared electrons. Therefore the electron must be placed around the N atoms to complete the structures.

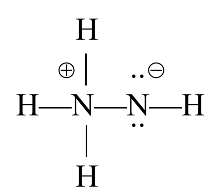
   In b) the N atoms can achieve the same configuration as the noble gas, Ne, if one lone pair is added to each N atom. The H atoms already possess the He configuration.

   b) 

   In c) the N atoms can achieve the same configuration as the noble gas, Ne, if two lone pairs are added to the N atom on the right. The H atoms already possess the He configuration.

   c) 

   Sure enough, formal charge assignment reveals than in structure b) all atoms have zero formal charge while in structure c), the left N atom has a +1 FC and the right N atom has a -1 FC.

   c) 

   As expected, structure b) is the correct structure for hydrazine, N_2H_4.

   b)