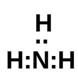
FORMAL CHARGE AND POLARITY

In your previous chemistry courses you probably relied heavily on Lewis dot structures to model simple molecules, since it is very easy to see where the electrons are. But, as you know, Lewis structures are tedious to write, and are subject to copying errors because fly specks look like electrons in these models; moreover, they make it impossible to show the shape of the molecule. As a result, chemists abbreviate bonding pairs with a line and often do not explicitly show unbonded pairs. Keeping track of the electrons then becomes a little more difficult. The simplest way to keep track is to identify any atoms that do not have their normal number, i.e. the number free neutral atoms have, their valence electrons. The method for keeping track is called *formal charge*.

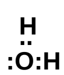
To illustrate the method for calculating formal charge, we will examine a simple reaction one reagent at a time: $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

First we make an approximation of bonding with a Lewis dot structure, once we know the connectivity of the atoms in the molecule (look up the connectivity if you don't remember). In the Lewis structure, each atom with its valence electrons will pair up electrons with other atoms; don't forget that ions have electrons removed or added to the collection to generate the charge. Remember that the maximum total number of electrons around each atom is 8, 2 for hydrogen. To calculate the *formal charge*, we look at what each atom sees around it and compare it to what the free neutral atom would have. To do that, we assume that each atom in the molecule has half of the shared electrons all to itself, no matter what atom they came from originally; any unshared pairs of electrons belong entirely to the atom they are on. We then compare the number of electrons it has now in the molecule with what it has when it is free and neutral: the formal charge is positive if it has fewer electrons in the molecule than in the neutral atom and negative if it has more.

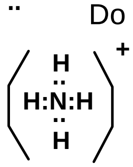
An example calculation of the formal charge for each atom in each molecule and ion for the reaction of ammonia with water follows. Remember that a neutral N has 5 valence electrons, oxygen has 6 and H has 1 (non-valence electrons are ignored).



1. The total number of electrons is 5 from N plus 3 from H, 8 total
2. The H's each have half a bonding pair or one electron: formal charge zero for all.
3. The N has the other electron from each of the bonds with H, or three electrons, plus a pair of unshared electrons, giving a total of 5 electrons: formal charge zero.
4. The sum of the formal charges on all the atoms should be the charge on the molecule; it is also zero.



Do this one yourself: all atoms have a formal charge of zero here too.



1. The total number of electrons is 4 from H, plus 5 from N less 1 from the + charge.
2. Each of the hydrogens has half a bonding pair, or one electron: formal charge zero.
3. The nitrogen now has half of 4 bonding pairs and no unshared pairs, or 4 electrons to itself, one less electron than a neutral N: formal charge plus one.
4. The total *formal charge* on the molecule is 4*(0) + 1*(+1) = +1, the observed charge on the molecule.

:O:H -

1. The total number of electrons is 1 from H plus 6 from O plus 1 from the - charge.
2. The hydrogen has half of one bonding pair or one electron: formal charge zero.
3. The oxygen has half of one bonding pair plus three unshared pairs, or 7 electrons, one more than a neutral oxygen: formal charge minus one.
4. The total *formal charge* on the molecule is 1*(0) + 1*(-1) = -1, the observed charge on the molecule.

The equation would be more correctly written: $NH_3 + H_2O \rightarrow H_4N^+ + HO^-$, to illustrate that the N is +1 and the O is -1. *Always show formal charges* when you write line structures and formulas of molecular ions as it can be extremely important (e.g. to distinguish SO_3 and $SO_3^{=}$).

After you calculate a few formal charges, you will no doubt notice that a nitrogen with 4 bonds is +, and an O with 1 bond is -, and you won't have to calculate it each time. We will usually work with elements for which the octet rule applies, but even the polarity and reactivity of compounds of elements like sulfur can be nicely understood using formal charge. The ability to determine formal charge is a fundamental skill which you will need to understand both organic chemistry and inorganic chemistry because it makes it possible to keep track of electrons that are not shown.

The mathematically inclined will have noticed that you can generate a formula to calculate formal charge. Sometimes memorizing formulas hides the physical basis of what you are calculating, but here it is for those who like formulas: For atom *i,* with valence V_I, B_i bonds and P_i non-bonding electrons, $FC_i = V_i - B_i/2 - P_i$.

The formal charge is a good *first approximation* to the charge distribution in the molecule or ion; it ignores a lot of subtleties but gives absolutely consistent numbers which result in a correct accounting for all the electrons. Moreover, it accounts qualitatively for the polarity of bonds and quantitatively for the overall charge of the ion or molecule. *Electronegativity* effects are much smaller and are most noticeable when the formal charges are all zero. Usually, we store the information about electronegativity in our heads for use as needed; sometimes we display the fine details of polarity resulting from electronegativity differences by using the symbols $\delta+$ and $\delta-$. We try not to use the + and - of formal charge and the electronegativity / polarity symbols $\delta+$ and $\delta-$ in the same picture to avoid confusion.

Try to determine the formal charge on each of the atoms in the examples below. If more than one Lewis structure is possible, this may mean that the compound is resonance-stabilized; the formal charge will depend on which Lewis structure you choose. You will use formal charge intensively when you study the reactions of resonance-stabilized molecules like benzene. Be sure you have correctly identified what is bonded to what before you attempt to write a Lewis dot structure. Look up the connectivity / bonding patterns if you need to, but don't be surprised if the text makes it sound as if you should be able to figure this out (if you could, most chemists would be unemployed). All of these compounds *can* be described with octet structures, even though some of the atoms (N, P and S) form compounds where the octet rule is not followed.

carbon dioxide	carbonic acid	carbonate ion
nitric acid	nitrous oxide	
sulfur dioxide	sulfur trioxide	
sulfurous acid	sulfuric acid	
phosphoric acid		
acetic acid	acetate ion	