Formal Charge and Bond Order

The concept of formal charge is useful because it can help us to distinguish between competing Lewis structures. Formal charge can be used to decide which Lewis (electron dot) structure is preferred from several.

Formal charge is an accounting procedure, it is a fictitious charge assigned to each atom in a Lewis structure. It allows chemists to determine the location of charge in a molecule as well as compare how good a Lewis structure might be.

Formal charge of an atom in a Lewis structure is *the charge an atom would have if* ***all*** *bonding electrons were shared equally between the bonded atoms*, i.e. formal charge is the calculated charge if we completely ignore the effects of electronegativity.

The Lewis (electron dot) structure with the atoms having the formal charge values closest to zero is preferred.

Smaller formal charge on individual atoms is better than larger ones on the most electronegative atom. Because energy is required to separate + and – charges, the structure without the formal charges is probably lower in energy than the structure with formal charges.
It takes energy to get a separation of charge in the molecule (as indicated by the formal charge) so the structure with the least formal charge should be lower in energy and thereby be the better Lewis structure.

Negative formal charge should reside on the most electronegative atom in a Lewis structure.

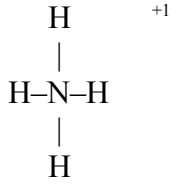
If the atom in a molecule has more electrons than the isolated atom, it has a negative formal charge, if it has less electrons, it has a positive formal charge

The sum of the formal charges in molecules or ions must equal the overall charge of the molecule or the ion. This means for neutral atoms, the sum of the formal charges must be zero, and for an ion, the sum of formal charges must be the charge on the ion.

The formula for calculating formal charge is shown below:

Formal charge = (# valence electrons in free atom) – ½ (# bonding electrons) – (# non-bonding electrons)

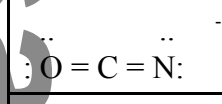
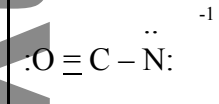
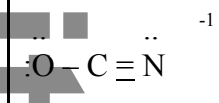
Consider the ammonium molecule, NH_4^{+1} :



Formal charge for each of the hydrogen's = 1– ½ (2) – 0 = 0
Formal charge for nitrogen = 5 – ½ (8) – 0 = + 1
The sum of the formal charges on all the atoms = + 1

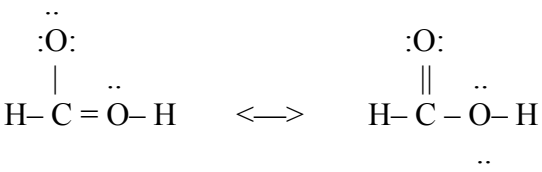
Formal charge is most useful in its application to the resonance structures.
When more than one structure is possible, usually one of the structures drawn may be better than the others.
The resonance hybrid is usually weighted more strongly towards the better structure.

Let us consider the cyanate ion, OCN^{-1}, there are three possible resonance structures:

Lewis structure	**Formal charge on:**			**Sum of formal charges**
	O	**C**	**N**	
	0	0	– 1	– 1
	+1	0	–2	– 1
	– 1	0	0	– 1

In the resonance structure 1 above, the formal charge is not on the most electronegative atom, the oxygen atom, thus is not the "better" structure.
In the resonance structure 2 above, the formal charge on the most electronegative atom, the oxygen atom is +1, indicating that the oxygen has less electrons, and thus is not the "better" structure.
The resonance structure 3 above is the "best fit" resonance structure.

Consider the methanoic acid molecule H_2CO_2 :
There are two possible Lewis structures for this molecule.



The two possible Lewis structures for the molecule H_2CO_2 are shown above. Each has the same number of bonds. They are connected by a double headed arrow to show that they are possible resonance structures.

The two structures differ only in the arrangement of the valence electrons in the molecule.
No atoms have been moved. These are called **resonance structures**.

We can determine which is better by determining which has the least formal charge. It takes energy to get a separation of charge in the molecule (as indicated by the formal charge) so the structure with the least formal charge should be lower in energy and thereby be the better Lewis structure.

VSEPR Theory is one method that chemists use to predict the shapes of molecules. This theory predicts that electron domains, whether involved in bonds or as non-bonding domains, will adopt a geometry in which they maximize the distance from one another in order to minimize repulsions. This will result in a geometry with the lowest possible energy.

The better Lewis structure or resonance structure is that which has the **least amount of formal charge.**

Calculate the formal charges on each of the atoms for the molecule H_2CO_2 above:

Calculate the sum of formal charges formal charges for the molecule H_2CO_2 above:

Thus, in the above case for the methanoic acid molecule H_2CO_2, the "better" structure is:

The bond order is equal to the number of electrons involved in bonds between two atoms.
Bond order for single bonds = 1
Bond order for single bonds = 2
Bond order for single bonds = 3

Resonance hybrids have fractional values of bond order.

Bond order may be calculated using the following formula:

$$\text{Bond order} = \frac{\text{total \# bonds between the atoms}}{\text{\# resonance structures}}$$

The bond length is the distance between those two atoms. The greater the number of electrons between two atoms, the closer the atoms can be brought towards one another, and the shorter the bond.

The Bond order is an indication of the bond length, the greater the bond order, the shorter the bond.

Assignment

1. Draw the three resonance Lewis structures for the nitrate ion, NO_3^{-1} , determine the formal charge on each atom and determine the best structure.

2. Draw the three resonance Lewis structures for N_2O , determine the formal charge on each atom and determine the best structure. [N=N=O, N≡N–O, N–N≡O]

3. Calculate the bond order for:
a. SO_2 b. O_3 c. CH_3COO^{-1} d. CO_3^{-2}