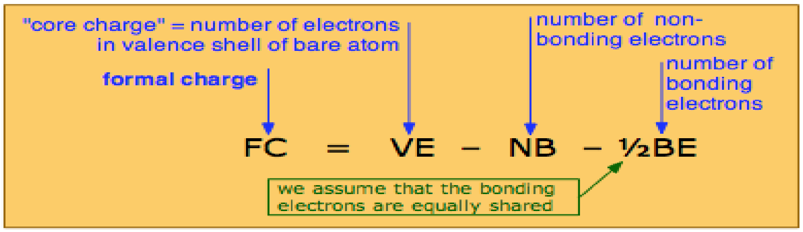
FORMAL CHARGE AND OXIDATION NUMBER

Although the total number of valence electrons in a molecule is easily calculated, there is not aways a simple and unambiguous way of determining how many reside in a particular bond or as non-bonding pairs on a particular atom. For example, one can write valid Lewis octet structures for carbon monoxide showing either a double or triple bond between the two atoms, depending on how many nonbonding pairs are placed on each: **C::O:::** and **:C:::O:** (see Problem Example 3 below). The choice between structures such as these is usually easy to make on the principle that the more electronegative atom tends to surround itself with the greater number of electrons. In cases where the distinction between competing structures is not all that clear, an arbitrarily-calculated quantity known as the **formal charge** can often serve as a guide.

The formal charge on an atom is the electric charge it would have if all bonding electrons were shared equally with its bonded neighbors.

<u>**How to calculate the formal charge on an atom in a molecule**</u>

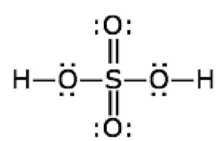
The formal charge on an atom is calculated by the following formula:



In which the core charge is the electric charge the atom would have if all its valence electrons were removed. In simple cases, the formal charge can be worked out visually directly from the Lewis structure, as is illustrated farther on.

Problem Example 1

Find the formal charges of all the atoms in the sulfuric acid structure shown here.



Solution: The atoms here are hydrogen, sulfur, and double- and single-bonded oxygens. Remember that a double bond is made up of two electron-pairs.

hydrogen: FC = 1 – 0 – 1 = 0

sulfur: FC = 6 – 0 – 6 = 0

hydroxyl oxygen: FC = 6 – 4 – 2 = 0

double-bonded oxygen: FC = 6 – 4 – 2 = 0

Using formal charge to select the best Lewis structure

The general rule for choosing between alternative structures is that the one involving the smallest formal charges is most favored, although the following example shows that this is not always the case.

Problem Example 2

Write out some structures for carbon monoxide CO, both those that do and do not obey the octet rule, and select the "best" on the basis of the formal charges.

Solution:

Structure that obeys the octet rule:

a) For :C:::O: Carbon: 4 – 2 – 3 = –1; Oxygen: 6 – 2 – 3 = +1

Structures that do not obey the octet rule (for carbon):

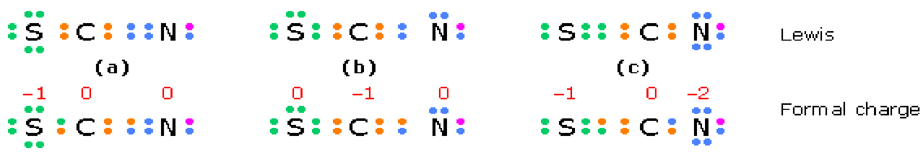
b) For :C:O::: Carbon: 4 – 2 – 1 = +1; Oxygen: 6 – 6 – 1 = –1

c) For :C::O:: Carbon: 4 – 2 –2 = 0; Oxygen: 6 – 4 – 2 = 0

Comment: All three structures are acceptable (because the formal charges add up to zero for this neutral molecule) and contribute to the overall structure of carbon monoxide, although not equally. Both experiment and more advanced models show that the triple-bonded form (a) predominates.

Formal charge, which is no more than a bookkeeping scheme for electrons, is by itself unable to predict this fact.

In a species such as the thiocyanate ion SCN— (below) in which two structures having the same minimal formal charges can be written, we would expect the one in which the negative charge is on the more electronegative atom to predominate.



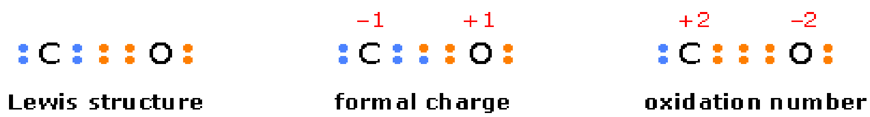
The electrons in the structures of the top row are the valence electrons for each atom; an additional electron (purple) completes the nitrogen octet in this negative ion. The electrons in the bottom row are divided equally between the bonded atoms; the difference between these numbers and those above gives the formal charges.

Formal charge can also help answer the question "where is the charge located?" that is frequently asked about polyatomic ions. Thus by writing out the Lewis structure for the ammonium ion NH4+, you should be able to convince yourself that the nitrogen atom has a formal charge of +1 and each of the hydrogens has 0, so we can say that the positive charge is localized on the central atom.

Oxidation number

This is another arbitrary way of characterizing atoms in molecules. In contrast to formal charge, in which the electrons in a bond are assumed to be shared equally, oxidation number is the electric charge an atom would have if the bonding electrons were assigned exclusively to the more electronegative atom. Oxidation number serves mainly as a tool for keeping track of electrons in reactions in which they are exchanged between reactants, and for characterizing the "combining power" of an atom in a molecule or ion.

The following diagram compares the way electrons are assigned to atoms in calculating formal charge and oxidation number in carbon monoxide.



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