Formal Charges

Discussion: Ions bear a positive or negative charge. If the ion is polyatomic (is constructed of more than on atom), we might ask which atom(s) of the ion carry the charge? Knowledge of charge distribution (identification of atoms that are electron rich or electron poor) can be useful to interpret many facets of organic chemistry, including how and why reactions occur (mechanisms) or how molecules interact with each other, a feature which strongly influences physical and biological properties.

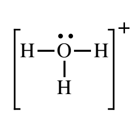
Valence electrons do not "belong" to any one atom in a molecule or ion. Quantum mechanics tells us that electrons are shared by a few neighboring atoms, or even by the whole molecule. Because atoms differ in electronegativity and hybridization, it is inaccurate to assume that these electrons are shared equally. (The rare exception is a pure covalent bond between two identical atoms such as in molecular chlorine, Cl–Cl.) Because of this uneven sharing atoms have fractional, rather than integer, charges. Calculations to determine exact electron distribution and atomic charges require complex computer programs and often many hours of computer time. Chemists need a way to rapidly estimate the electron rich and electron poor sites of a molecule or ion to allow a rough estimate of chemical and physical properties.

Chemists have developed a very simple bookkeeping method to determine if an atom within a molecule or ion is neutral, or bears a positive or negative charge. The method provides integer charges only. Because this method provides some indication of charge distribution, it is an excellent starting point for determining electron distribution within a molecule or ion, and hence give us a starting point to predict chemical and physical properties. These assigned integer charges are called formal charges. A formal charge is a comparison of electrons "owned" by an atom in a Lewis structure versus the number of electrons possessed by the same atom in its unbound, free atomic state.

Procedure: The procedure to determine formal charges on the atoms of an ion or molecule has three steps. The process is illustrated using hydronium ion (H_3O^+); an ion very frequently encountered in organic and biochemical reaction mechanisms.

Step 1: Draw the best Lewis structure for the molecule, including all unpaired electrons. Be sure to show all nonbonded electrons, as these influence formal charges.

The best Lewis structure for the hydronium ion is shown below. The brackets indicate the positive charge belongs to the entire molecule.

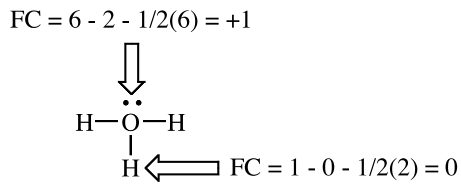


Step 2. Assign the formal charge to each atom. Formal charge is calculated using this formula:

$$FC = GN - UE - 1/2\ BE$$

Where:
FC = formal charge
GN = periodic table group number (number of valence electrons in free, nonbonded atom)
UE = number of unshared electrons
BE = number of electrons shared in covalent bonds.

Thus for hydronium ion:



The formal charge on hydrogen is calculated as follows. Hydrogen has one valence electron (GN = 1), no unshared electrons (UE = 0) and two shared electrons in the oxygen-hydrogen covalent bond (BE = 2). Thus the calculated formal charge on hydrogen is zero. Because each hydrogen atom in this molecule is identical, each hydrogen atom has the same formal charge of zero. *Any hydrogen bearing one covalent bond always has a formal charge of zero.*

The formal charge on oxygen is calculated as follows. Oxygen has six valence electrons (GN = 6), two unshared electrons in one lone pair (UE = 2), and six shared electrons in three oxygen-hydrogen covalent bonds (BE = 6). Thus the calculated formal charge on oxygen is +1. This indicates the oxygen atom bears the majority of the positive charge of this ion.

Step 3. Check your work. The sum of the formal charges of all atoms must equal the overall charge on the structure. For hydronium ion, the sum of the formal charges on the hydrogen atoms (3 x zero) plus one for the oxygen gives a total charge of +1, which agrees with the overall charge.

After you practice this procedure with a few structures, you will begin to notice patterns in formal charge distribution. Becoming familiar with these patterns will help you avoid having the tedious task of calculating formal charge for every atom of every structure you encounter.

Formal Charge Patterns

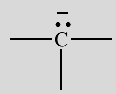
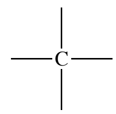
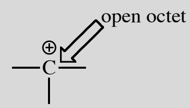
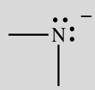
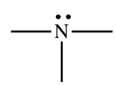
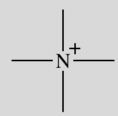
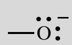
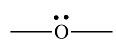
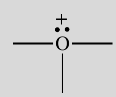
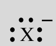
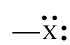
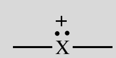
1. The best Lewis structure or resonance contributing structure has the least number of atoms with formal charge.

2. Equivalent atoms have the same formal charge. For example, all the hydrogen atoms of methane (CH_4) are equivalent and therefore have the same formal charge. All six hydrogens of ethane (H_3C-CH_3) have the same formal charge, as do the two carbon atoms.

3. Formal charges other than +1, 0 or -1 are uncommon except for metals.

4. The vast majority of organic structures are made up of a small set of atoms with a limited number of bonding possibilities. Recognizing these cases will allow you to avoid formal charge calculations most of the time, and speed your understanding of how charge influences reactions and properties of molecules. These patterns are summarized in the table below.

Formal Charge Patterns

Element	**FC = -1**		**FC = 0**	**FC = +1**	
Hydrogen	$H:^-$	Hydride ion	—H	H^+	Naked proton ***Never ever!***
Carbon		Carbanion			Carbocation
Nitrogen		Nitranion			Ammonium
Oxygen		Oxyanion			Oxonium
Halogen (X = F, Cl, Br, I)		Halide ion			Halonium

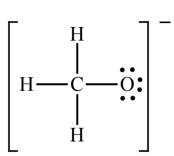
Frequently Asked Questions

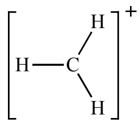
Question: What is the relationship between having full valence shells and formal charges? Do full valence shells always result in a formal charge of zero?

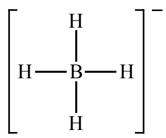
Answer: Valence shell occupancy alone does not determine formal charge. The element involved also matters. For example the full valence shell for carbon in methane (CH_4) results in a formal charge of zero for carbon, whereas the full valence shell for nitrogen in the ammonium cation (NH_4^+) results in a +1 formal charge for nitrogen.

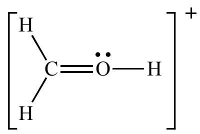
Exercises

Calculate the formal charge on each atom in the following Lewis structures.

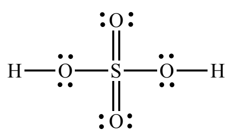
1.  Methoxide ion

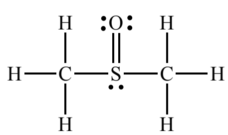
2.  Methyl carbocation

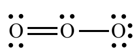
3.  Tetrahydridoborate ion

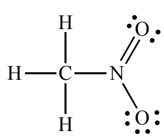
4.  An oxonium ion

5.  Carbon monoxide

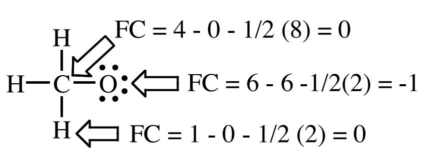
6.  Sulfuric acid

7.  Dimethyl sulfoxide

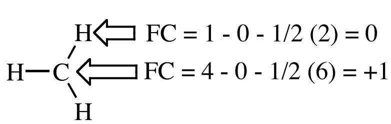
8.  Ozone

9.  Nitromethane

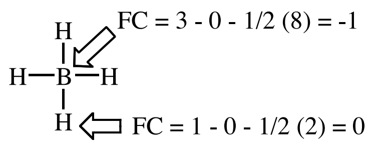
Exercise Solutions

1. 

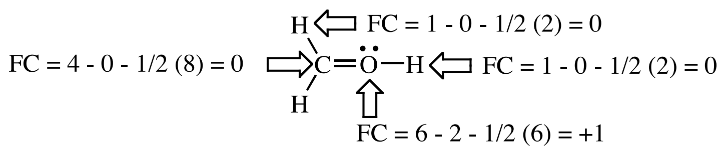
All three hydrogen atoms are equivalent and therefore have the same charge (neutral). The oxygen atom bears the bulk of the ion's negative charge. The sum of the atomic charges = (3 x 0) + 0 + (-1) = -1 = charge on the ion.

2. 

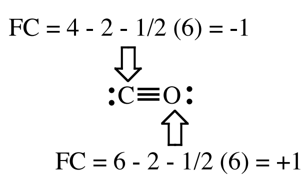
All three hydrogen atoms are equivalent and therefore have the same charge (neutral). The carbon atom bears the bulk of the ion's positive charge. The sum of the atomic charges = (3 x 0) + (+1) = +1 = charge on the ion.

3. 

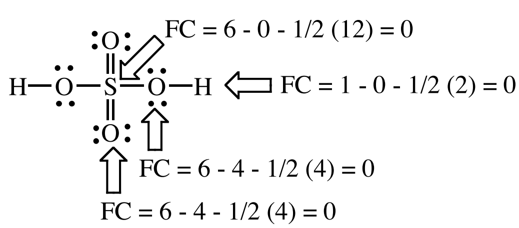
All four hydrogen atoms are equivalent and therefore have the same charge (neutral). The boron atom bears the bulk of the ion's negative charge. The sum of the atomic charges = (4 x 0) + (-1) = -1 = charge on the ion.

4. 

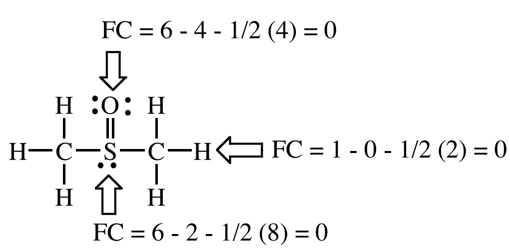
The two hydrogens attached to carbon are equivalent and therefore have the same charge (neutral). The oxygen atom bears the bulk of the oxonium ion's positive charge. The sum of the atomic charges = (2 x 0; C-H) + 0 (O-H) + 0 (C) + (+1; O) = +1 = charge on the ion.

5. 

Although the formal charge of the entire molecule is neutral, the carbon bears a negative charge and the oxygen bears a positive charge. The sum of the atomic charges = (-1) + (+1) = 0 = charge on carbon monoxide.

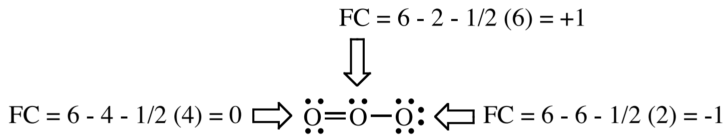
6. 

All atoms have formal charges of zero, equal to the molecular charge of zero.

7. 

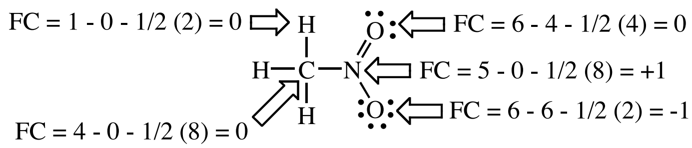
The six hydrogen atoms are all equivalent, so they all have the same formal charge of zero. All atoms have a zero formal charge, in agreement with the molecular charge of zero.

8.



The three oxygen atoms in this resonance structure for ozone are not equivalent, because they have different numbers of oxygen-oxygen bonds and different formal charges. The sum of the atomic charges = 0 + (+1) + (-1) = 0 = molecular charge.

9.



The three hydrogen atoms are equivalent and thus have the same neutral charge. The oxygen atoms do not have the same bond order with the nitrogen, so these oxygen atoms are not equivalent. The sum of the atomic charges = 3 x 0 (for the hydrogens) + 0 (for the carbon) + (+1 for the nitrogen) + (0 for the double bonded oxygen) + (-1 for the single bonded oxygen) = 0 = molecular charge. Although the molecule is neutral, the nitrogen and one of the oxygens carry charge.