■ Formal charge

Sometimes the recipe results in alternative structures. Formal charge is a counting method that is useful in deciding which is structures are more likely than others. Likely structures are those in which the formal charge on the atoms is as close to zero as possible.

Here is a way to assign formal charge to an atom in a Lewis structure.

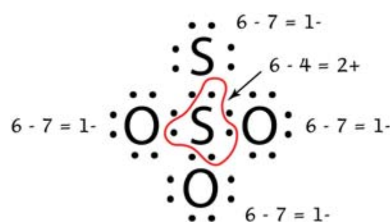
1. Assign electron to each atom as follows: An atom is assigned all of its unshared electrons and half of its bonding electrons (electrons connecting the atom to other atoms).
2. Then on an atom the $\text{formal charge} = \text{number valence} - \text{number assigned}$, where number valence is the number of valence electrons the isolated, non-bonded atom has.

For example, in H_2O the O atom has two lone-pairs (four electrons) and is single bonded to the two H atoms (four electrons, of which half—two—are assigned to the O atom); a total of six electrons are thus assigned to the O atom. The isolated, non-bonded O atom has six valence electrons. Therefore, we compute that the formal charge on the oxygen is $6 - 6 = 0$.

Here is a visual method to determine formal charge. Draw a corral around each atom that encloses all of the lone pairs assigned to the atom but just half of the bonding electrons. The forma charge of an atom is the number of electron enclosed by its corral minus the group number of the atom,

$$\text{formal charge} = \text{electrons in corral} - \text{group number}.$$

Here is a graphic illustrating this method, for thiosulfate ion, $S_2O_3^{2-}$.



Lewis structure and formal charges for thiosulfate ion, $S_2O_3^{2-}$.

The total formal charge is always the total charge, in this case $2-$.

It is important to keep in mind that formal charge is a useful device for deciding between Lewis structures. It does not correspond to a real net charge on the atom. We will learn that formal charge is also an important indicator of how molecules react with one another.

■ Odd-number of electrons

Whenever there are an odd number of electrons, it will not be possible to have octets around all atoms. Perhaps the most important example is NO. Two possibilities are for the N to have seven electrons or for the O to have seven electrons. On the basis of formal charge, we would choose the structure with eight electrons around the O.

■ Octet-deficient structures

Sometimes there will not be enough electrons to surround the central atom with an octet. BH3 and AlCl3 are good examples; the B and Al are each surrounded by only six electrons. Such structures are called octet-deficient.

■ Valence-shell expansion

Sometimes there will be too many electrons, so that more than eight electrons must be assigned to an atom. This is called valence-shell expansion., It always involves atoms with configurations only a few electrons away form having to fill a d shell. In such atoms the d shell is close by in energy terms and so the extra electrons can be accommodated there. SF_6 and XeF_4 are good examples. Elements in the second row of the periodic table (Li to Ne) are too far away from filling the d shell and so never have more than an octet of electrons.

> For thiosulfate ion, discussed above, there is an alternate structure in which S undergoes octet expansion: two of the O atoms each share two pairs of electrons with the sulfur atom. Use the visual method to show that the formal charge on these two O atoms changes from 1 − to 0, and the formal charge on the sulfur changes from 1 − to 0.

When such alternative Lewis structures are possible, it is found experimentally that the Lewis structure for which the formal charges are closest to 0 is the most stable one.