Chapter 27   THE POLYATOMIC UNIT, Part 2

All of the Lewis structures so far have involved electrons shared between two atoms only. Now we turn to cases of sharing between three or more atoms.

27.1 Delocalization

We start with a bit of terminology. "Localization" and "delocalization" are general terms referring to whether electrons are contained within one particular region or whether they can extend over a more extensive region or regions. As used here, when bond electrons are shared between only two atoms A and B, then we say that those shared electrons are "localized" between A and B. We also call the bond itself a localized bond. When bond electrons are shared between three or more atoms, we say that those electrons are "delocalized" or we say that the bond is delocalized. For example, if two electrons are shared between the three atoms A, B and C, then we say that those two electrons are delocalized among A, B and C. In essence, a localized bond involves one connection between two atoms; a delocalized bond is spread over two or more connections and involves three or more atoms. The noun for the process is "delocalization".

Delocalization can also involve lone pair electrons. I mentioned this possibility in Chapter 25.

   ❝ Most cases of lone pairs are associated with one (lone) atom; on the other hand, some are associated with more than one atom. ❞

A lone pair which is associated with only one atom is localized on that atom. If a lone pair is associated with two or more atoms, then it is delocalized. Typically, the delocalization of LPs is not nearly as important as the delocalization of bond pairs, so we don't do much with them.

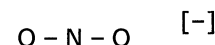How do you know when electrons are localized or when they are delocalized?

It's in the Lewis structure. Let's do a simple example. We'll work out the Lewis structure for nitrite.

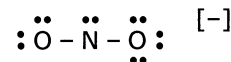▸ Step 1. NO_2^-. The N is central and the O's are terminal.

$$O \quad N \quad O \qquad [-]$$
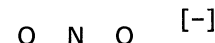
▸ Step 2. Find the total number of valence electrons: it's 18. Check this yourself.

▸ Step 3. Draw the single bonds.

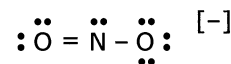$$O-N-O \qquad [-]$$

▸ Step 4. Enter lone pairs on terminal atoms, then on the central atom.

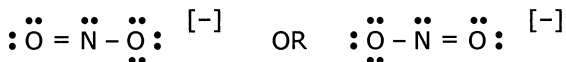$$:\overset{..}{O}-\overset{..}{N}-\overset{..}{\underset{..}{O}}: \qquad [-]$$

▸ Step 5. The central nitrogen is short of octet, so we need to fix that. We need Step 6.

▸ Step 6. Bring in a lone pair from a terminal O and share it. Which terminal O? Good question. Does it matter? We'll see. Do the O on the left for now.

$$:\overset{..}{O}=\overset{..}{N}-\overset{..}{\underset{..}{O}}: \qquad [-]$$

That completes the Basic Steps, but it's not the final answer for nitrite. In Step 6, you can bring in a lone pair from the left O or you can bring in a lone pair from the right O. These are two equal options, as pictured on the left. For both cases, we can write the exact same summary as follows: there is one NO single bond and there is one NO double bond; the central N atom has one LP; one terminal O has three LPs; and, the other terminal O has two LPs. Given that the summary is the exact same for both options, we say the two structures are "equivalent". Some compounds can have two or more "inequivalent" Lewis structures; we'll see this later in the Chapter.

$$:\overset{..}{O}=\overset{..}{N}-\overset{..}{\underset{..}{O}}: \quad [-] \qquad OR \qquad :\overset{..}{\underset{..}{O}}-\overset{..}{N}=\overset{..}{O}: \quad [-]$$

Whenever you can draw different Lewis structures for the same polyatomic unit, this indicates that one or more bonds (and, perhaps, lone pairs) is delocalized. For nitrite, there is a total of three bond pairs in the ion. Two of these bond pairs are localized and these are the ones covered in Step 3. The third bond pair is delocalized over both NO connections.

Delocalization is very important, so I need to go over some terminology here and bring in some other aspects about this. I'll continue with nitrite for now.

In Lewis terminology, this type of delocalization is called "resonance". The two equivalent Lewis structures above are called "resonance structures". A single resonance structure by itself does not completely describe the polyatomic unit; one must consider all resonance structures taken together. When the resonance structures are equivalent, then the actual, real polyatomic unit is represented by the simple average of the separate resonance structures.

Frequently, you'll see resonance structures with a two-headed arrow between them. This is shown at right for the two nitrite resonance structures. There is no new meaning with the arrow; it's just a common practice. Some people do it and some don't.

$$:\overset{\bullet\bullet}{O} = \overset{\bullet\bullet}{N} - \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}: \quad {}^{[-]} \qquad \leftrightarrow \qquad :\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} - \overset{\bullet\bullet}{N} = \overset{\bullet\bullet}{O}: \quad {}^{[-]}$$

Delocalization can result in fractional bond orders. In nitrite, there are three bond pairs among two connections, so this gives an average of 3/2 bond pairs for each connection. This means that each NO bond order is 3/2 or 1.5. There's another way you can look at this: focus on one bond at a time in the resonance structures and then find the average bond order. For example, let's focus only on the left NO bond in the two resonance structures. I've redrawn this much on the left. In one case, the NO bond is a double bond and in the other case it's a single bond; if you take the average, you get 3/2. If you repeat this for the other NO connection, you again get 3/2. When resonance structures are equivalent, you just take a simple average for bond order.

$$:\overset{\bullet\bullet}{O} = N \quad O \quad {}^{[-]} \qquad\qquad :\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} - N \quad O \quad {}^{[-]}$$
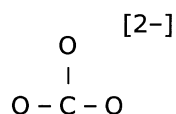
There's something you need to be careful about when dealing with delocalization. If you're asked a question about a compound with delocalization, then you need to be clear as to whether the question refers to the unit as a whole or to one resonance structure in particular. For example, you can be asked, "What are the bond orders in nitrite?", or you can be asked, "What are the bond orders in one resonance structure of nitrite?". These aren't the same question. The bond orders in nitrite, taken as a whole, are 3/2 each. The bond orders in one resonance structure are one single bond and one double bond. The questions are different and the answers are different. Be careful on this.
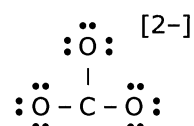
If you peel open your eyeballs and look at the two resonance structures for nitrite, you might notice that the number of lone pairs changes on the terminal O's. One lone pair is actually delocalized while the others are not. In the resonance structures as drawn on the right above with the two-headed arrow ↔, the LP on the bottom is delocalized over the two terminal oxygens. Regardless, as I said upstairs, the important thing about delocalization has to do with bonds and that's what we'll be primarily concerned with.

Let's do another example. Carbonate is a real common example for delocalization, so let's do that. I'll go quickly through the Lewis Steps. Be sure you can go through them by yourself. Step 1, the atoms are arranged by the usual formula format. Step 2, there are 24 valence electrons total.
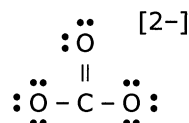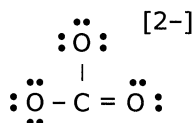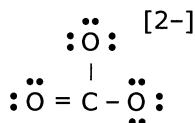
▸ Step 3.
$$\begin{array}{c} O \\ | \\ O-C-O \end{array} \quad {}^{[2-]}$$

▸ Step 4.
$$\begin{array}{c} :\overset{\bullet\bullet}{O}: \\ | \\ :\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-C-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}: \end{array} \quad {}^{[2-]}$$

▸ Step 5 will tell you that you need Step 6.

▸ Step 6 will leave you with three options for forming one double bond. The three options are the following.

$$\begin{array}{c} :\overset{\bullet\bullet}{O}: \\ | \\ :\overset{\bullet\bullet}{O}=C-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}: \end{array} {}^{[2-]} \qquad \begin{array}{c} :\overset{\bullet\bullet}{O}: \\ | \\ :\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-C=\overset{\bullet\bullet}{O}: \end{array} {}^{[2-]} \qquad \begin{array}{c} :\overset{\bullet\bullet}{O} \\ \| \\ :\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}-C-\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}: \end{array} {}^{[2-]}$$

For each of the three resonance structure, we can write the exact same summary: there are two CO single bonds and those O's have three lone pairs each; there is one CO double bond and that O has two LPs. Since all three resonance structures have the same summary, then all three are equivalent. There are a total of four bond pairs: three are localized and one is delocalized. Taken as a whole, the four bond pairs over three equivalent CO connections mean that each CO bond order in carbonate is 4/3 or 1.33.

By the way, the localized bonds were done in Step 3 again. In general, the bonds identified in Step 3 will be localized. For compounds with delocalization, this will first be evident in Step 6 if two or more

options for Lewis structures are available. If only one Lewis structure is possible, then all bonds are localized.

This concludes the current discussion on resonance. As a matter of fact, it concludes our Basic level for doing Lewis structures. We'll do the Refinement later in this Chapter. For now, we touch on three aspects which are related to Lewis. Two are old; the third is new and it is needed in order to do the Refinement.

27.2 More food for thought

I want to return to the notion of bond energies from Chapter 25, specifically with respect to covalent bond energies. In that Chapter, we touched on the primary factors which influence those energies, namely the type of atoms in the bond and the bond order. The Lewis structure tells us both of these things. This allows us to make a major, new connection within the Grand Puzzle. It is now appropriate to restate how important bond energies are, especially on the big scale of your world. Bond energies are a major chunk of the enthalpies of reactions. I first said this in Chapter 18.

> ❝ Notice that I threw in the bit about the energies of the molecules themselves. This energy primarily arises from the fact that different molecules have different bonds with different energies. During a reaction, some bonds are broken and new ones are made. That's a big part of the total energy of a chemical reaction, although other factors can also contribute. We'll see more about these bond energies in Chapter 25 and in Chapter 27. ❞

As we move along at this point in the text, we think about one molecule at a time; as such, it is easy to lose sight of the impact of these things on the normal scale. Typically, most of the chemical energy of a reaction ties into bond energies and this is the important point for now. For example, at that time in Chapter 18, we were talking about combustion.

$$2 \text{ H}_2(g) \ + \ \text{O}_2(g) \ \rightarrow \ 2 \text{ H}_2\text{O}(g) \qquad \Delta H° \ = \ -483.66 \text{ kJ}$$

Where does that reaction energy come from? Most of that −483.66 kJ comes from the bonds which are involved. Using Lewis structures and the bond energies from Chapter 25, we can see the contribution of bond energies to the overall process. Let's take a look at this.

We consider the Lewis structures of each reagent.

$$2 \text{ H}-\text{H} \qquad + \qquad \overset{\bullet\bullet}{\underset{}{:}}\text{O} = \text{O}\overset{\bullet\bullet}{:} \qquad \rightarrow \qquad 2 \text{ H}-\overset{\bullet\bullet}{\underset{\bullet\bullet}{\text{O}}}-\text{H}$$

We then tally all bonds lost and all bonds made during the reaction. Lone pairs are not involved in this analysis, so we don't worry about them. When this reaction occurs in the amounts as written, there is some cost to break the two moles of H–H bonds and there is some cost to break the one mole of O=O bonds, but there is a large payback in forming two moles of water molecules with two O–H bonds each. The average bond energies (which you flagged as BEs in Chapter 25) for these types of bonds are 436 kJ/mol for H–H, 498 kJ/mol for O=O, and 463 kJ/mol for O–H. Using these values, we can estimate the kJ's involved for the reaction as follows.

H–H bond energy: 436 kJ/mol	
To break two moles of these will cost 872 kJ.	+ 872 kJ
O=O bond energy: 498 kJ/mol	
To break one mole of these will cost 498 kJ.	+ 498 kJ
O–H bond energy: 463 kJ/mol	
To form four moles of these will release 1,852 kJ.	<u>−1,852 kJ</u>
The entire process sums to	− 482 kJ

Remember that the use of average bond energies is only an estimate, so the value of −482 kJ is an estimate for this reaction. Even as an estimate, we can see that these bond energies constitute the majority of the total reaction enthalpy of −483.66 kJ.

Do this for methane combustion.

. . . .

Example. Using bond energy values, estimate $\Delta H°$ for the combustion of $CH_4(g)$ to form $CO_2(g)$ and $H_2O(g)$.

. . . .

First, you need a balanced equation.

Then, draw out the Lewis structure for each reactant and each product. (Lewis structures for O_2 and H_2O are shown above.)

Now, start the tally. Get your bond energies from Chapter 25.

How many CH bonds of what order are lost in the reaction?   _____

What is the energy of each?   _____

What is the total energy for breaking these bonds?   (+) _____

How many OO bonds of what order are lost in the reaction?   _____

What is the energy of each?   _____

What is the total energy for breaking these bonds?   (+) _____

How many CO bonds of what order are formed in the reaction?   _____

What is the energy of each?   _____

What is the total energy for forming these bonds?   (−) _____

How many OH bonds of what order are formed in the reaction?   _____

What is the energy of each?   _____

What is the total energy for forming these bonds?   (−) _____

Add everything up.   _____

You can calculate the actual ΔH°_{comb} using values for ΔH°_f from Appendix A. You will see that your estimate above is close to that actual ΔH°_{comb}.

You can do this method for any ΔH° for any reaction, not just combustion. This can be helpful when we do not have sufficient values for ΔH°_f to allow for a direct calculation of ΔH°_{rxn}. Overall, this method commonly gives a decent estimate although it is subject to a few limitations. For example, it can only be done for reactants and products in the gas phase; if a reactant or product is in another phase, then additional steps are needed. Also, the method does not work well in cases of resonance since the BEs of Chapter 25 are for single, double or triple bonds and resonance can change bond order and bond energy. Except for these limitations, however, this method does provide a reasonable estimate.

The point for emphasis now is the restatement of the importance of bond energies and their contribution to enthalpies of reaction. Bond energies are incredibly important to you and to your world, both in the natural sense and in the sense of modern human society. The greatest example of the latter is the massive combustion of fuels on a daily basis worldwide. By far, most cars, most cities, most lifestyles are powered primarily by chemical bond energies. Nuclear, solar, wind, and other environmental sources make small contributions when compared to fuel combustion. Even you yourself, in the natural sense, are powered primarily by chemical bond energies. Most of the food molecules which you eat contain C–H, C–C and C–O single bonds; the O_2 which you breathe contains an O=O double bond. From these reactants, you produce H_2O and CO_2, which have O–H single bonds and C=O double bonds. When you account for all the bond energies of the product molecules and the bond energies of the reactant molecules, you account for a large part of the energy of your life. Bond energies, and the factors which influence them, are all a part of your world.

Keep the big picture in mind.

27.3 Return to oxnos

Oxidation numbers. Remember? In Chapter 13 we first introduced oxidation numbers and their applications in working with redox. At that time I could only give some guidelines for doing oxnos.

> ❝ We will see in Section 27.3 how oxidation numbers derive from the counting system which is used in these applications, but we won't need that connection here. We don't need that here because there are general trends for assigning oxidation numbers. These trends give rise to a set of guidelines which, although not perfect, are good enough for a number of applications including our current interest in interpreting redox processes. ❞

Here we are in Section 27.3 and we've covered a lot of material since then. We are now ready to do the actual counting method which is behind oxidation numbers. For this, we needed two things in particular: electronegativities and Lewis structures. The only thing different here is that we are redefining the method of assignment in order to be applicable to more things. The uses for oxnos are the same; none of that changes here.

Here's how the technically correct method works: start with a Lewis structure, and then assign oxidation numbers (ON) for each atom according to the following formula.

> ON = number of (original) valence electrons – number of electrons counted for the atom

The number of original valence electrons is what the atom would have by its lonesome self; this is just the number of valence electrons as first defined in Chapter 23.

Now we address how to count electrons for an atom based on the Lewis structure. All lone pairs on an atom count for that atom. Bond pairs, however, only count for the more electronegative atom of the bond. This is the tricky part.

Let's start with a simple example, hydrogen chloride. You'll need the Lewis. $H - \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} :$
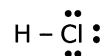
Now count the electrons per atom according to oxnos counting rules. Cl has three lone pairs, so those six electrons count for Cl. What about the bond pair? Bond pairs count for the more electronegative atom which, in this case, is Cl. Thus, the two bond electrons count toward the Cl. Count up the electrons, as shown at left: the count is zero for H and eight for Cl. Plug these into the ON equation from above.
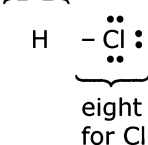
> ON = number of valence electrons – number of electrons counted for the atom

This gives you the oxidation numbers for each atom.

oxnos for H: ON = 1 – 0 = +1

oxnos for Cl: ON = 7 – 8 = –1

That's all there is to it.

Let's do another example: carbon dioxide. Start with Lewis, on the right. $: \overset{\cdot\cdot}{O} = C = \overset{\cdot\cdot}{O} :$
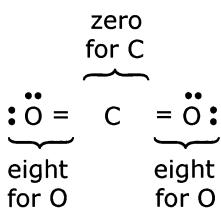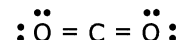
Apply the oxnos counting rules. Each O is assigned its own lone pair electrons. Each O also lays claim to the bond pairs since O is more electronegative than C. The count is then zero for C and eight for each O. Plug these into the ON equation to get the oxnos for each atom.

oxnos for C: ON = 4 – 0 = +4

oxnos for each O: ON = 6 – 8 = –2

By the way, in all cases, the algebraic sum rule from Chapter 13 applies. For CO_2:

2(oxnos of O) + 1(oxnos of C) = 0

2(–2) + 1(4) = 0

Don't forget the algebraic sum rule. It's still true.

Hopefully, this will seem straightforward but there's one detail which I must add. This applies whenever there's a bond between identical atoms. Since identical, the atoms have the same EN, so we

H – Ö – Ö – H

can't count the bond electrons for just one atom. Instead, the bond electrons are evenly split between the two atoms. Here's an example: hydrogen peroxide, H_2O_2. The Lewis structure is on the left. The two electrons in each OH bond count toward the O, due to electronegativity. The count for H is then zero. For the two electrons in the OO bond, we split them evenly and count one toward each O. This gives a total count of seven for each O as shown at right. Plug these into the ON equation.

zero   seven
for H   for O

H – Ö • • Ö – H

seven   zero
for O   for H

oxnos for each H: ON = 1 – 0 = +1

oxnos for each O: ON = 6 – 7 = –1

Each H has the same oxnos and each O has the same oxnos, so I didn't have to do them separately.
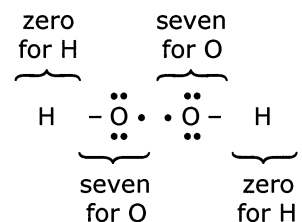
Compared to the methods in Chapter 13, the method of assigning oxidation numbers here is more general and includes many more things than we could do by Chapter 13 methods. Ironically, those older Chapter 13 methods can be faster in many simple cases, so you may want to keep them in mind even if they aren't perfect. Like I've said before, different methods are different tools; use whichever works best for you for the situation at hand.

Since Chapter 13, we have seen various uses for oxnos although we certainly haven't seen them all. There remain other applications but that is not where we need to go right now. We're going to do something a bit different although somewhat similar.

27.4 Formal charge

Formal charge is a (usually) hypothetical charge on an atom in a compound, based on assuming an even share of bond electrons. It is an assigned value, much like an oxidation number, but its method of assignment is different. Also like ON, it will correspond to a true charge for monatomic atoms or ions. For compounds, however, it is typically not a true charge. Although it is usually hypothetical, it still conveys useful information and that is why we use it. Formal charge is often abbreviated as FC.

Like ONs, FCs are assigned to each atom in a chemical unit depending on that atom's electronic arrangement within the unit. There is a key difference, however, in how the two values are assigned. First, let me note that lone pairs are counted the same in the two systems: LPs always count for the atom on which they are located. Bond pairs, however, are counted differently. For ON, we count the bond electrons toward the more electronegative atom. For FC, we count all bond electrons as evenly divided between the bonded atoms. Here's the equation for assigning formal charges.

FC = number of (original) valence electrons – number of electrons counted for the atom

Compare this to the initial equation from above for assigning oxnos.

ON = number of (original) valence electrons – number of electrons counted for the atom

They're the same! What's different is the manner of counting the electrons for the atoms. THE MANNER OF COUNTING IS KEY.

To do formal charge, you still start with the Lewis structure. You count the electrons per atom and plug that number into the equation. I'm going to do FC for all the examples which were done above for ON. Watch how formal charge differs from oxidation number.

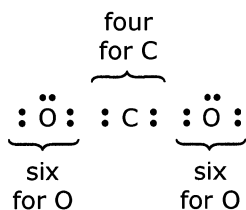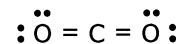I'll start with HCl, the easiest. Here's our Lewis structure again.

H – Cl:
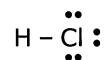
Count the electrons according to formal charge counting rules. The bond pair is considered evenly split between H and Cl: of the two bond electrons, one counts for H and one counts for Cl. Cl also has three LPs, so these six are added to the count for Cl. The grand totals are: one electron counts for H and seven electrons count for Cl. Plug these counts into the FC equation.

one
for H

H • • Cl :

seven
for Cl

FC = number of valence electrons – number of electrons counted for the atom

formal charge for H: FC = 1 – 1 = 0

formal charge for Cl: FC = 7 – 7 = 0

Both atoms end with formal charges of zero. This differs from the oxnos values of +1 and –1 as shown upstairs.

Next, carbon dioxide. Lewis is on the right. $: \overset{\cdot\cdot}{O} = C = \overset{\cdot\cdot}{O} :$

$\underset{\text{for C}}{\overset{\text{four}}{\overbrace{}}}$

$: \underset{\underset{\text{for O}}{\text{six}}}{\underbrace{\overset{\cdot\cdot}{O}}} : \ : C : \ : \underset{\underset{\text{for O}}{\text{six}}}{\underbrace{\overset{\cdot\cdot}{O}}} :$

For formal charge, each O is assigned its lone pair electrons. Bond pairs are evenly split between C and the O's. This gives C a total count of four; each O has a total count of six. Plug these into the FC equation.

formal charge for C: FC = 4 – 4 = 0

formal charge for each O: FC = 6 – 6 = 0

We see that all the atoms have formal charges of zero. This differs from the oxnos which were 4 (for C) and –2 (for each O).

Note! The algebraic sum rule also applies for FC. Always! For CO_2, it would be

2(formal charge of O) + 1(formal charge of C) = 0

2(0) + 1(0) = 0

Don't ever violate algebraic sum rule for formal charge or for oxidation number.

Final example, H_2O_2. You do it. Both H's have the same value and both O's have the same value. Fill in the Lewis structure first and then answer the questions.

What is the total count for each H?   _____   H   O   O   H

What is the total count for each O?   _____

formal charge for each H: FC = _____ – _____ = _____

formal charge for each O: FC = _____ – _____ = _____

Do your answers obey algebraic sum rule?

Having now seen how to determine the formal charge, it would be a good thing to ask, "So what good is formal charge?" I'll show you in a moment. First, this would be a good time to summarize oxidation numbers and formal charges, or at least to summarize their differences. It will also be useful to point out some underlying notions to the two systems.

➡ The system of counting electrons for oxidation numbers involves the notion of pretending that all bonds are ionic bonds. This will only be true for ionic compounds of monatomic ions. When covalent bonds are involved, however, ON represents a charge which would exist on the atoms if all bonds were ionic instead of covalent. If HCl were ionic, then the ion charges would be H^+ and Cl^-. If CO_2 were ionic, the ion charges would be C^{4+} and O^{2-}. If H_2O_2 were ionic, the ion charges would be H^+ and O^-. Of course, these are not ionic bonds and these are not real charges. Instead, they are oxidation numbers.

➡ The system of counting electrons for formal charge involves the notion of pretending that all bonds in the polyatomic unit are nonpolar covalent bonds, meaning all electrons are shared 50/50. FC represents the charge which would exist on the atoms if all covalent bonds were nonpolar instead of polar. If the bond in HCl was nonpolar, the atoms would have zero partial charges and there would be no bond polarity. If the bonds in CO_2 were nonpolar, there would be zero partial charges and there would be no bond polarity. If the bonds in H_2O_2 were nonpolar, there would be zero partial charges and there would be no bond polarity. Of course, most covalent bonds are polar covalent and so these are not true charges. Instead, they are formal charges.

In essence, ON and FC represent the two extremes of bonding which we've covered so far: oxidation numbers are based on ionic bonding and formal charges are based on nonpolar covalent bonding. The reality is, however, that most bonds in most polyatomic units are polar covalent and their atoms carry partial charges. Commonly, the actual partial charges on atoms in many chemical units will lie somewhere between their values of ON and FC. Even this much represents an important use for both oxidation numbers and formal charge.

Given the importance of ON and of FC, and given their connection with the Lewis structure, let's now modify the schematic which we began at the end of the last Chapter. I show this at right. There will still be more to go, so we're not done yet. We'll call this Stage 2 for now.

lone pairs

↖

bond pairs ← Lewis
(order) → structure

↙

ON, FC
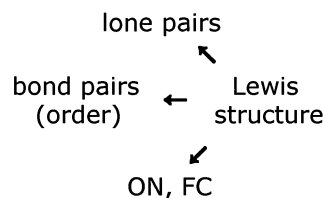
27.5 A formal application

In all the formal charge examples above, all atoms have zero FC. Lewis structures which have zero formal charges on all atoms commonly represent the most favorable arrangement of electrons in a polyatomic unit, although this will be subject to constraints. For example, polyatomic ions must have at least one atom with a nonzero FC. There will even be some neutral molecules which cannot have zero formal charges on every atom, in which close-to-zero is preferred. There will also be expanded valence cases in which the FC preference is over-ridden by other factors. We'll look at some of these aspects in this Section.

Despite the limitations, formal charge considerations can be important when it is possible to draw inequivalent Lewis structures for a given chemical unit. We summarize these as two Guidelines. The tendency toward zero or close-to-zero FCs is referred to as the "minimization of formal charge", here presented as FC Guideline 1.
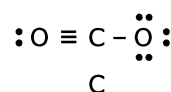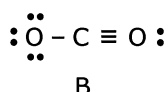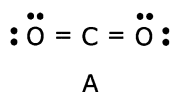
• FC Guideline 1: Given two or more inequivalent choices for Lewis structures of a given polyatomic unit, then the Lewis structure with minimum formal charges is the preferred arrangement.

We can take this further by noting which atoms carry a nonzero FC, if any. For this we invoke a second Guideline.

• FC Guideline 2: Among inequivalent Lewis structures, if there are atoms with nonzero formal charges, then that Lewis structure is favored which has the more negative FC on the more electronegative atom.
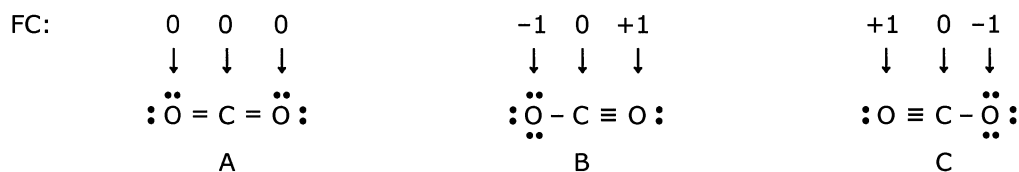
Of the two Guidelines, number 1 is more important than number 2. Number 1 is the <u>minimization</u> of formal charges, but both together give the <u>optimum</u> formal charges. These Guidelines can be used to assess inequivalent resonance structures in terms of which one best represents the various properties of a given molecule or ion. There's one catch, however: FC Guideline 1 is very good for octet or less cases but not for expanded valence, and I'll come back to this point later below. FC Guideline 2 works for all cases. Let's look at several different scenarios.

We start with octet cases. For the first example, let's return to CO_2. Earlier, I gave the Lewis structure of CO_2 but it's not the only Lewis structure which can be drawn; there are two others. Here are all three of them, labeled A - C.

$$:\overset{\bullet\bullet}{O} = C = \overset{\bullet\bullet}{O}: \qquad :\overset{\bullet\bullet}{\underset{\bullet\bullet}{O}} - C \equiv O: \qquad :O \equiv C - \overset{\bullet\bullet}{\underset{\bullet\bullet}{O}}:$$

A B C

All of these have all atoms with octet. Structure A is the same one as before; it has two CO double bonds and each O has two LPs. Structures B and C have one CO single bond and one CO triple bond; one O has three LPs and one O has one LP. Structures B and C are equivalent to each other, but they are inequivalent to A. Which one is right? Or are they all equally right?

When dealing with inequivalent Lewis structures, it's not always a question of a singular "right" answer. It is often a question of which is the preferred Lewis structure based on various criteria which we use, which include formal charge. For comparison, refer back to the prior examples of nitrite and of carbonate. For each of those, we drew resonance structures which were equivalent. When Lewis structures are equivalent, then each resonance structure is equally important to describing the properties of the chemical unit as a whole. Now for CO_2, however, the Lewis structures are not all equivalent and we need to judge which one is preferred. Let's look at formal charges for everybody in the three structures.
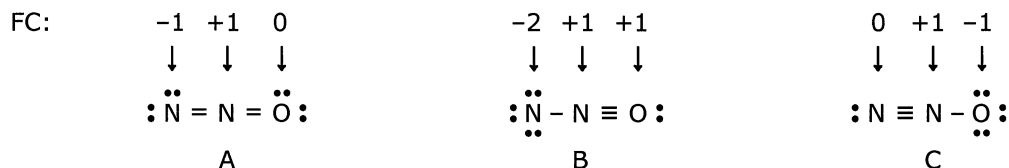
FC: 0   0   0   −1   0   +1   +1   0   −1
                 ↓   ↓   ↓   ↓   ↓   ↓   ↓   ↓   ↓
             $\ddot{\text{O}}$ = C = $\ddot{\text{O}}$ $\ddot{\text{O}}$ − C ≡ O   O ≡ C − $\ddot{\text{O}}$

                    A   B   C

Structure A has all formal charges of zero; B and C have −1/+1 formal charges on oxygen atoms. We judge Structure A to be preferred on the basis of the minimization of formal charge (FC Guideline 1). Does that mean Structures B and C are totally out of the picture? Well, we can't assess that at this level of coverage. Our job in these cases is to assess the preferred or favored Lewis structure, which means Structure A is the answer here.

This example is fairly simple since the minimization of formal charge is the only factor involved; as such, we only needed FC Guideline 1 in order to determine the preferred resonance structure. Now let's get a little more involved.

Let's do N_2O. I mentioned this in the last Chapter as a molecule which does not follow formula format; its atom connections are N N O. Given that arrangement, and if you follow the six Basic Steps for doing Lewis, it's possible to derive three resonance structures, shown as A - C below.

             $\ddot{\text{N}}$ = N = $\ddot{\text{O}}$ $\ddot{\text{N}}$ − N ≡ O   N ≡ N − $\ddot{\text{O}}$

                    A   B   C
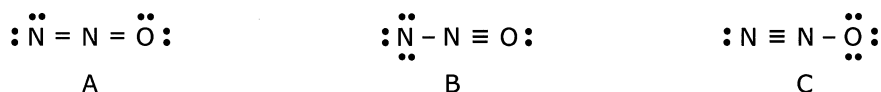
Everybody has octet. Interestingly, these three resonance structures are identical to the ones for CO_2 above. Now, however, we are dealing with different atoms; thus, we have different formal charges and a different outcome compared to the CO_2 case above. The FCs are shown below.

FC: −1 +1   0   −2 +1 +1   0 +1 −1
                 ↓   ↓   ↓   ↓   ↓   ↓   ↓   ↓   ↓
             $\ddot{\text{N}}$ = N = $\ddot{\text{O}}$ $\ddot{\text{N}}$ − N ≡ O   N ≡ N − $\ddot{\text{O}}$

                    A   B   C

All three structures are inequivalent; let's now judge them on the basis of the FC Guidelines. FC Guideline 1 prefers minimum formal charges overall: none of the three Structures A - C has every atom with zero, but Structures A and C have smaller (closer-to-zero) formal charges than Structure B. Based on this, we drop Structure B from further consideration. Structures A and C are not equivalent, but we cannot tell using Guideline 1 which is better. Let's bring in FC Guideline 2. Structure C places the −1 formal charge on oxygen, while Structure A places the −1 formal charge on nitrogen; the relative electronegativities (O > N) favor oxygen to have the −1 FC, so Structure C is favored by Guideline 2. Overall, Structure C has the optimum formal charges, so we judge this to be the preferred Lewis structure. If your instructor asks for a ranking of all possibilities, then Structure A is second and Structure B is third in importance.
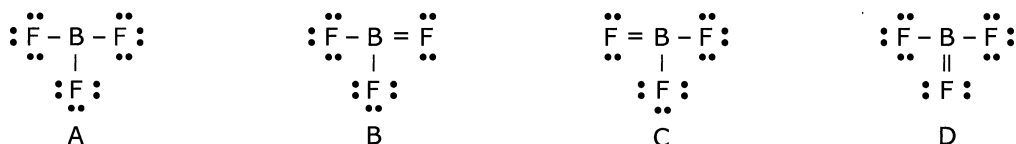
So what's with all of these? What do they really tell us?

When inequivalent resonance structures are involved, then we cannot take a simple average of properties as we did for bond order with the nitrite and carbonate examples earlier. There are methods for going further but those are not within our coverage here. Nevertheless, we can still refer to one resonance structure at a time. For example, we can say there is an NN triple bond and an NO single bond in the preferred Lewis structure for N_2O. As always, be clear on what your instructor is asking.

These CO_2 and N_2O cases nicely illustrate the minimization and optimization of formal charge for octet cases. Notice how we derived the various Lewis resonance structures: we moved bond pairs and lone pairs around in order to get the various options, even if some options got downgraded in the end. This brings us to the Refinement to the six Basic Steps for doing Lewis structures, as promised since the last Chapter.

● **Refinement Step.** Exchange electrons between adjacent atoms as needed for optimization of formal charges.

Let's bring in an electron deficient case. We'll look at BF_3 since we dealt with it a bit in Chapter 26. Let me present four Lewis structures which can be drawn for BF_3.

$$\ddot{:}\overset{\bullet\bullet}{\ddot{F}}-B-\overset{\bullet\bullet}{\ddot{F}}\ddot{:} \qquad :\overset{\bullet\bullet}{\ddot{F}}-B=\overset{\bullet\bullet}{\ddot{F}} \qquad \overset{\bullet\bullet}{F}=B-\overset{\bullet\bullet}{\ddot{F}}\ddot{:} \qquad :\overset{\bullet\bullet}{\ddot{F}}-B-\overset{\bullet\bullet}{\ddot{F}}\ddot{:}$$

A	B	C	D

Structure A is the one which we worked out in Chapter 26 by using our Basic Steps. Structure B is the one which I briefly mentioned early in Chapter 26 but I said we would forget about it until later. Later is now. Structures B - D are equivalent to each other, but inequivalent to Structure A; they can be derived if we ignore Part b of Step 5. Structure A has boron short of octet, while Structures B - D have octets on all atoms.

The formal charges in Structure A are all zero. The formal charges in Structures B, C and D don't work out as well: two fluorines have zero formal charges, but boron has –1 and the third F has +1. (Prove this to yourself; derive the formal charges for Structures A versus B.) This presents an interesting dilemma: formal charge Guideline 1 favors Structure A since it has minimum formal charges, but Structures B - D are favored by octet rule. Where does that put us?

We are back again to that magical word from Chapter 1: balance. Here, we have two opposing factors, the tendency to achieve octet and the tendency to minimize FC. The real answer lies in the balance. We can't decide the answer just from this information, but we can determine the answer from experimental measurements and calculations. The answer is that Structure A is the primary form. Formal charge wins over octet, at least in this case. Based only on Structure A, we can say that the BF bond will be a single bond.
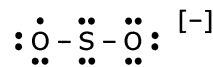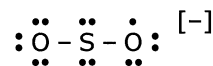
It turns out that boron and other elements of Group 13 will often forego octet in order to minimize (optimize) formal charge. This is also true for some cases of Group 14 compounds and also for some cases of beryllium compounds. All together, this is the reason for allowing Be/13/14 cases to be short of octet as provided by Part b of Step 5 of the Basic Steps. This is a simple compromise which works well for many electron deficient cases. If you follow Step 5, Part b, then this FC minimization business will be taken care of. Thus, there is nothing new here to worry about.

Now let's consider an odd-electron case.

Odd-electron compounds are actually straightforward using the Refinement and the FC Guidelines. We did not need them for the NF_2 example in Chapter 26 but there are many cases where you may need them. (If you go back and look at the Lewis structure for NF_2 you will see all atoms had zero FCs.) To illustrate, consider the ion SO_2^-. This is not a stable ion of its own accord; it does pop up in certain kinds of reactions but it just reacts right away. If you follow the Basic Steps for this ion, you end up with the Lewis structure at right. But is this the preferred Lewis structure? Consider the formal charges: each O has FC of –1, while the FC of S is +1. Somebody has to be –1 due to the ion charge, but all atoms carry some formal charge here.

$$:\overset{\bullet\bullet}{\ddot{O}}-\overset{\bullet}{\underset{\bullet\bullet}{S}}-\overset{\bullet\bullet}{\ddot{O}}: \quad [-]$$
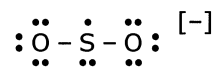
Let's swap an electron between one O and the S, to get the Lewis structure at right. Now do the FCs: the left O has FC of –1, the S and the right O have FCs of zero. These are your minimum formal charges. But this now opens up the possibility of resonance, since we can obtain an equivalent Lewis structure by moving the odd electron to the left O. These last two resonance structures are now the preferred Lewis structures based on formal charges.

$$:\overset{\bullet\bullet}{\ddot{O}}-\overset{\bullet\bullet}{\underset{\bullet\bullet}{S}}-\overset{\bullet}{\ddot{O}}: \quad [-]$$

$$:\overset{\bullet}{\ddot{O}}-\overset{\bullet\bullet}{\underset{\bullet\bullet}{S}}-\overset{\bullet\bullet}{\ddot{O}}: \quad [-]$$

From the examples so far, the FC Guidelines work quite well for octet cases, for electron deficient cases and for odd-electron compounds. Unfortunately, FC Guideline 1 does not work as well for expanded valance. Let's take a look.

Back in Chapter 26 when I introduced expanded valence for Lewis structures, I said,

❝ For the most part, cases with only single bond orders (and lone pairs, if applicable) will be accepted as such. The possibility of multiple bond cases, however, will be explained a bit at the end of Chapter 27. ❞

Here we are. I will begin the discussion using chlorate for illustration purposes.

If you follow Basic Steps from Chapter 26, you get the Lewis structure for ClO_3^- as shown on the right. We'll label it Structure A. All atoms have octet, which is good, but formal charges are considerable: the FC for Cl is +2 and the FCs are −1 for each O.
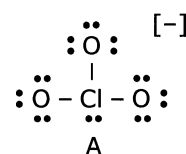
We can draw Lewis structures with better FCs overall by sharing more electrons between the chlorine and the oxygens to give multiple bonds. Let's share one LP from one O and form a double bond. There are three equal possibilities for this, so this results in three equivalent Structures B - D.
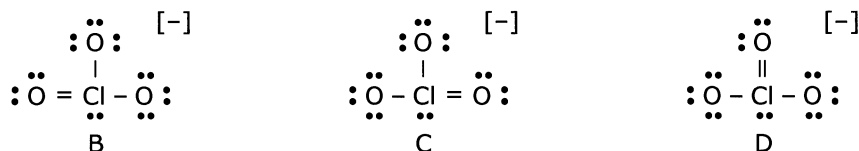
In each of these, Cl has a formal charge of +1. The doubly-bonded oxygen has FC of zero, although the other two O's still have FC of −1. (Go ahead and write them in for clarity if you want.) Overall, by forming one double bond, we have decreased the formal charges somewhat. In order to do this, however, chlorine has expanded its valence to ten electrons and now we get into some of the issues mentioned at the end of Section 26.1. So are we really better off with Lewis structures with expanded valence in order to minimize FC?

Let's go even further. You can minimize formal charges even moreso by forming another double bond, as shown by Structures E - G.
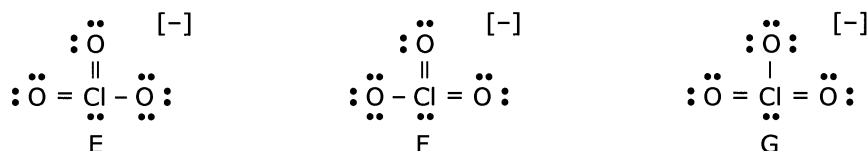
In each of these, only one O still carries a formal charge of −1 but everybody else is down to zero. Since this is an anion, somebody has to carry a formal charge of at least −1, so we can't hit zero for everybody. We are now at minimum FC but now we've expanded the valence for chlorine to 12 electrons.

So what's the answer here? That's a good question.

Historically, the emphasis on minimizing formal charges was applied to all compounds and all Lewis structures, and that contributed to our understanding of bonding and other properties of those polyatomic units. Expanded valence cases, however, are trickier by nature due to the complexities of their bonding. As bonding studies developed over the years for expanded valence cases, it has become clear that FC minimization does not reliably give a clear, preferred answer for a Lewis structure, and other factors can be more important. FC minimization continues to work well with octet-or-less cases and with odd-electron cases; it just does not work well as a general approach for expanded valence.

So where does that leave us?

The various factors which can get involved have engendered considerable debate over the years but we will go to a bottom line approach. For where we are now and where we are heading, we do not need to expand valence in order to minimize formal charge and we do not need to get into the resonance aspects as shown above for ClO_3^-. In the next Chapter we start into shape, and resonance usually does not matter for shape. Beginning in Chapter 30, we start into the orbital description of bonding but, as I said back in Section 26.1, we will not cover bonding for expanded valence due to the many complexities involved. Thus, we have sufficient tools for where we are going without getting into all of the complications.

So here's the bottom line approach: we will not expand valence if the purpose is simply to minimize formal charge. Thus, we consider Structure A to be preferred for chlorate, in which the central atom stops at octet. On the other hand, some instructors may choose to keep resonance in focus at this stage of the game. For example, expanding valence by one step in order to minimize formal charge may remain their choice, so heed if there's need. This would bring Structures B - D into the picture as resonance structures, with or without Structure A. There is no reason to go further, however, and Structures E - G are not applicable. As always, the really important part is for you to be aware of how your instructor is handling these points. You need to be clear on her/his expectations.

A result of our compromise approach is that we will not show multiple bonds on atoms with expanded valence. We can still do single bonds with expanded valence, such as was illustrated for PF_5 and PF_6^- in Section 26.1. We're not changing that (although even those cases have issues). We can also do lone pairs with expanded valence. This will be the extent of coverage for our purposes.

By the way, remember that Second Period elements cannot expand valence because they are too small. Thus, this business about expanding valence doesn't even apply to Second Period elements. Expanding valence becomes available for elements in the Third Period and the Periods lower in the Periodic Table.

Problems

1. Draw the resonance structures for each of the following. What are the (average) orders in these ions for the NO and CO bonds?

    a. NO_3^- b. HCO_2^-

2. Consider the following reaction.

    $$2 H_2(g) + CO(g) \rightarrow CH_3OH(g)$$
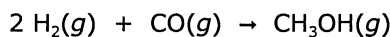
    (In CH_3OH, the C and O are central atoms.) Using average bond energies, estimate the $\Delta H°$ for the reaction. Using $\Delta H_f°$, calculate the actual $\Delta H°$ for the reaction. How important are bond energies to the actual $\Delta H°$ for the reaction?

3. What are the oxidation numbers and the formal charges for each atom in the following?

    a. CO   b. H_3O^+ c. BH_4^- d. BrF_4^- e. NO_4^{3-}

4. Draw the preferred Lewis structure for each of the following.

    a. S_2O (SSO)   b. $SeCN^-$ c. ClO