

Chapter 27

THE POLYATOMIC UNIT,
Part 2

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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 a bond connects two atoms or whether the bond connects three or more atoms. For bond electrons shared between only two atoms, then we say that those shared electrons are "localized" between those atoms. We also call the bond itself a localized bond. For bond electrons shared between three or more atoms, we say that those electrons are "delocalized" over those atoms. We can also say that the bond is delocalized. 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.

Localization and 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. ”

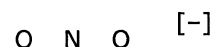
A lone pair which is associated with only one atom is localized on that atom. If a lone pair is associated with two or more atoms, then it is delocalized. Typically, the delocalization of LPs is not nearly as important as the delocalization of bond pairs, so these don't get as much attention.

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

It's in the Lewis structure.

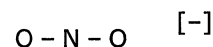
Let's do a simple example. We'll work out the Lewis structure for nitrite.

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

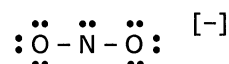


► Step 2. Find the total number of valence electrons: it's 18. Check this yourself.

► Step 3. Draw the single bonds.

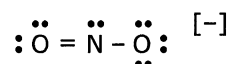


► Step 4. Enter lone pairs on terminal atoms, then on the central atom.

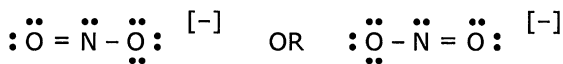


► Step 5. The central nitrogen is short of octet, so we need to fix that. We need Step 6.

► 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.



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; the O with a single bond has three LPs; and, the O with a double bond 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.



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. Each of the possible Lewis structures is called a resonance structure. A single resonance structure by itself does not describe the true polyatomic unit; one must consider all resonance structures taken together. When the resonance structures are equivalent, then the actual, real polyatomic unit is best 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.

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 average the bond orders. For example, let's focus only on the left NO bond in the two resonance structures. I've redrawn this much here on the left. In one case, the NO bond is a double bond and in the other case it's single; if you take the average, you get 1.5. If you repeat this for the other NO connection, you again get 1.5. When resonance structures are equivalent, you just take a simple average for bond order.

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 \leftrightarrow , the LP on the bottom is delocalized over the two terminal oxygens.

So what does all this mean?

In cases of delocalization, you cannot draw one single Lewis structure which adequately conveys the chemical information which may be of interest. Nitrite does not have one single and one double bond; it has two bonds, each of order 1.5. In nitrite, each O has two lone pairs of their own, but one more lone pair is distributed over both O atoms. There are yet other properties which can be cited (and another will be seen in Section 27.4). Although we cannot draw a single Lewis structure to convey all of this information, we can draw two equivalent resonance structures and average them together (mentally or computationally) to get a better understanding.

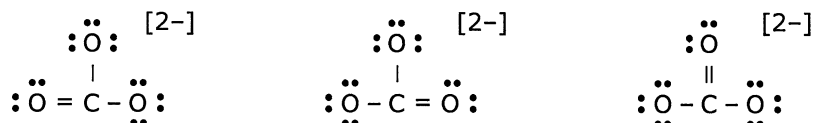
There's something you need to be aware of dealing with delocalization. If you're asked a question about a compound with delocalization, then you need to be clear as to whether the question refers to the unit as a whole or to one resonance structure in particular. For example, you can be asked, "What 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 1.5 each. The bond orders in one resonance structure are one single and one double. The questions are different and the answers are different. Be careful on this.

Let's do another example. Carbonate is a very 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 5 will tell you that you need Step 6. (We exclude carbon from the electron deficient category.)

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



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.

Note that 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.

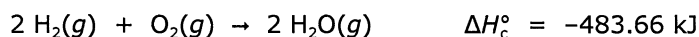
This concludes the current discussion on delocalization and resonance. As a matter of fact, it concludes our Basic Level for doing Lewis structures. We'll do the Refinement Step later in this Chapter. For now, we touch on three aspects which are related to Lewis. Two are old; the third is new and it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

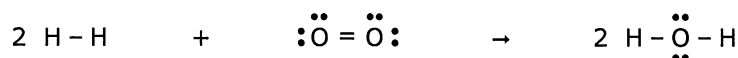
“ Notice that I threw in the bit about the energies of the molecules themselves. This energy primarily arises from the fact that different molecules have different bonds with different energies. During a reaction, some bonds are broken and new ones are made. That's a big part of the total energy of a 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. Commonly, much 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.



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 change in enthalpy. Let's take a look at this.

We consider the Lewis structures of each reagent.



We then tally all bonds broken and all bonds made during the reaction. Breaking bonds requires energy, so these amounts enter as a positive component to the overall change in enthalpy. Making bonds releases energy, so these enter as a negative component. Lone pairs are not involved in this analysis, so we don't worry about them. For the given reaction in the amounts as written, two moles of H-H bonds and one mole of O=O bonds are broken; two moles of water molecules are formed 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 $1,852 \text{ kJ}$.	<u>$-1,852 \text{ kJ}$</u>
The entire process sums to	<u>-482 kJ</u>

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.

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Example. Using bond energy values, estimate ΔH_c° for the combustion of $\text{CH}_4(g)$ to form $\text{CO}_2(g)$ and $\text{H}_2\text{O}(g)$.

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 moles of C–H bonds are broken in the reaction?	_____	
What is the energy (in kJ) of each?	_____	
What is the total energy (in kJ) for breaking these bonds?		(+) _____
How many moles of O=O bonds are broken in the reaction?	_____	
What is the energy (in kJ) of each?	_____	
What is the total energy (in kJ) for breaking these bonds?		(+) _____
How many moles of C=O bonds are formed in the reaction?	_____	
What is the energy (in kJ) of each?	_____	
What is the total energy (in kJ) for forming these bonds?		(-) _____
How many moles of O–H bonds are formed in the reaction?	_____	
What is the energy (in kJ) of each?	_____	
What is the total energy (in kJ) for forming these bonds?		(-) _____

Add everything up.

You can calculate the actual ΔH_c° using values for ΔH_f° from Appendix A. You will see that your estimate above is close to that actual ΔH_c° .

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° . 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 therefore the 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 all the bond energies of the reactant molecules, you account for a large part of the energy which you will expend in 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 the technical counting system for assigning oxidation numbers in Section 27.3 after we get into electronic arrangements, but we can't go there yet. For now, we work with a set of Guidelines for assigning oxidation numbers. These Guidelines are not perfect, but they are good enough for where we are now, including for 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 substances. The uses for oxnos are the same; none of that changes here.

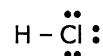
Here's how the technically correct method works: start with a Lewis structure, and then assign oxidation numbers (ON) for each atom according to the following formula.

$$\text{ON} = \text{number of (original) valence electrons} - \text{number of electrons counted for the atom}$$

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.

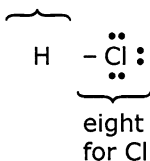
Now we address how to count electrons for an atom based on the Lewis structure. All lone pairs on an atom count for that atom. Bond pairs, however, only count for the more electronegative atom of the bond. This is the tricky part.

Let's start with a simple example, hydrogen chloride. You'll need the Lewis.



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

zero
for H



$$\text{ON} = \text{number of valence electrons} - \text{number of electrons counted for the atom}$$

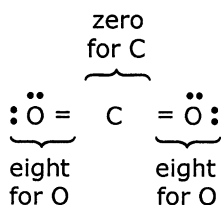
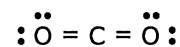
This gives you the oxidation numbers for each atom.

$$\text{oxnos for H: ON} = 1 - 0 = +1$$

$$\text{oxnos for Cl: ON} = 7 - 8 = -1$$

That's all there is to it.

Let's do another example: carbon dioxide. Start with Lewis, on the right.



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.

$$\text{oxnos for C: ON} = 4 - 0 = +4$$

$$\text{oxnos for each O: ON} = 6 - 8 = -2$$

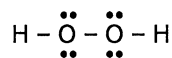
By the way, in all cases, the sum rule from Chapter 13 applies. For CO_2 :

$$2(\text{oxnos of O}) + 1(\text{oxnos of C}) = 0$$

$$2(-2) + 1(4) = 0$$

Don't forget the 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 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.

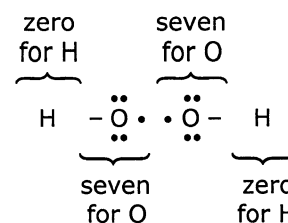


The Lewis structure is on the left. The two electrons in each OH bond count toward the O, due to electronegativity. The count for H is then zero. For the two electrons in the OO bond, we split them evenly and count one toward each O. This gives a total count of seven for each O as shown at right. Plug these into the ON equation.

$$\text{oxnos for each H: ON} = 1 - 0 = +1$$

$$\text{oxnos for each O: ON} = 6 - 7 = -1$$

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 molecule or polyatomic ion, 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 polyatomics, however, it is typically not a true charge, although it can help to inform us of the location of charges in a polyatomic unit. Although the numerical value is usually hypothetical, it still conveys useful information and that is why we use it. Formal charge is often abbreviated as FC.

Both formal charge and bond polarity give us clues as to the distribution of charges within a polyatomic unit, but they are determined differently. Both can be useful.

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 both 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.

$$\text{FC} = \text{number of (original) valence electrons} - \text{number of electrons counted for the atom}$$

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

$$\text{ON} = \text{number of (original) valence electrons} - \text{number of electrons counted for the atom}$$

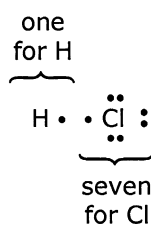
They're the same! What's different is the manner of counting the electrons for the atoms. THE MANNER OF COUNTING IS KEY.

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.

HCl: here's our Lewis structure again.



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.



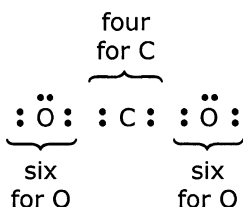
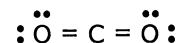
FC = number of valence electrons - number of electrons counted for the atom

$$\text{formal charge for H: FC} = 1 - 1 = 0$$

$$\text{formal charge for Cl: FC} = 7 - 7 = 0$$

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.



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.

$$\text{formal charge for C: FC} = 4 - 4 = 0$$

$$\text{formal charge for each O: FC} = 6 - 6 = 0$$

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

$$2(\text{formal charge of O}) + 1(\text{formal charge of C}) = 0$$

$$2(0) + 1(0) = 0$$

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

Next: 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? _____



What is the total count for each O? _____

$$\text{formal charge for each H: FC} = \underline{\hspace{1cm}} - \underline{\hspace{1cm}} = \underline{\hspace{1cm}}$$

$$\text{formal charge for each O: FC} = \underline{\hspace{1cm}} - \underline{\hspace{1cm}} = \underline{\hspace{1cm}}$$

Do your answers obey the sum rule?

Having now seen how to determine formal charges, 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.

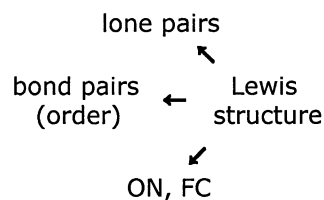
➤ The system of counting electrons for oxidation numbers involves the notion of pretending that all bonds are ionic bonds. This will only be true for ionic compounds of monatomic ions. When covalent bonds are involved, however, ON represents a charge which would exist on the atoms if all bonds were ionic 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 charges 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 real 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. Often, 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.

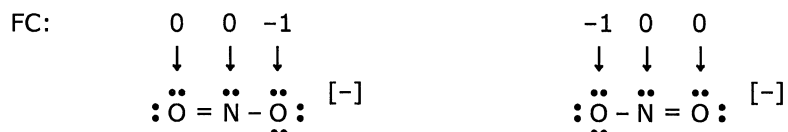
Given the importance of ON and of FC, and given their connection with the Lewis structure, let's now modify the schematic which we began at the end of the last Chapter. I show this at right. There will still be more to go, so we're not done yet. We'll call this Stage 2 for now.



27.5 Formal applications

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; for these, close-to-zero is preferred. There will also be expanded valence cases in which the preference for zero FCs is over-ridden.

When it comes to delocalization, the formal charges in the resonance structures may be the same or they may differ for the various atoms. For equivalent resonance structures, the formal charges will be equivalent. To illustrate, let's bring back the nitrite ion, and assign formal charges to each atom in each separate resonance structure.



Note that, since this is an ion, then at least one atom must have a nonzero FC; note that the sum rule is obeyed. You can also see that the formal charges are equivalent: both resonance structures have zero FC on N and on the doubly-bonded O; and, both resonance structures have an FC of -1 on the singly-bonded O. Since equivalent in all aspects, neither resonance structure is "better", and both contribute equally to the picture of the actual ion. We can also say that each contributes 50% to the true picture. The NO bond order is 1.5. One LP is delocalized over both oxygens. The formal charge is spread over both oxygens, so that each O would average -0.5 FC.

If resonance structures are not equivalent, then they do not contribute equally to the actual picture. The contributions from each can range widely. For example, if there are two inequivalent resonance structures, then one might contribute 70% and the other might contribute 30%. Or, for three inequivalent resonance structures, then the contributions might be 60%, 35% and 15%. Percents can be determined by various levels of computation, but we're not looking for numbers here. We seek a qualitative means to assess which resonance structure is "best", "dominant", "favored", "preferred", or whatever; in other words, we seek the resonance structure which most closely represents the actual properties of the polyatomic unit.

Our six Basic Steps have some of this built in, but we now bring in formal charge as another tool. We summarize this 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 resonance structures of a given polyatomic unit, then the Lewis structure with minimum formal charges is the preferred arrangement.

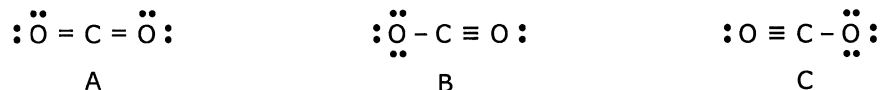
We can take this further by noting which atoms carry a nonzero FC, if any. For this we invoke a second Guideline.

- 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 minimization of formal charges, but both together give the optimum formal charges. There's a catch, however, to be

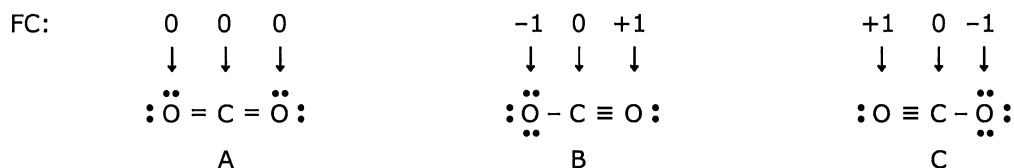
aware of: FC Guideline 1 is very good for octet or less cases but not for expanded valence. I'll come back to this point later. FC Guideline 2 works for all cases.

Let's start in on several different scenarios, beginning 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 following the six Basic Steps; there are two others. Here are all three of them, labeled A - C.



Each of these has all atoms with octets. 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. So, is Structure A the "best" to represent the molecule or are B and C, taken together, the "best"?

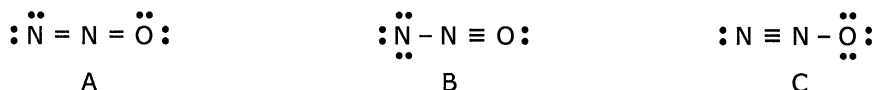
For this assessment, we need to assign the FCs in each atom of each resonance structure.



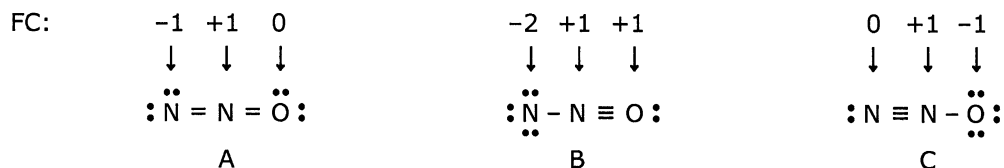
Structure A has all formal charges of zero; structures B and C have $-1/+1$ formal charges on oxygen atoms. We judge Structure A to be "best" on the basis of the minimization of formal charge (FC Guideline 1). Structures B and C may still contribute but we cannot assess how much; we can only say they are not dominant.

This example is fairly simple since the minimization of formal charge is the only factor involved; as such, we only needed FC Guideline 1. 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.



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. Here are the FCs.



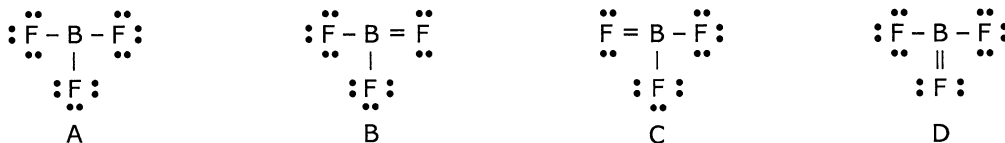
All three structures are inequivalent; let's now judge them on the basis of the FC Guidelines. FC Guideline 1 prefers minimum formal charges overall: none of the three Structures has every atom with zero, but Structures A and C have smaller (closer-to-zero) FCs than Structure B. Based on this, we drop Structure B from further consideration. Structures A and C are not equivalent, but we cannot tell using Guideline 1 which is better, so we 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 ($\text{O} > \text{N}$) 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 "best" Lewis structure to represent the actual molecule.

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 Step to add to the six Basic Steps, as promised since the last Chapter.

- **Refinement Step.** Except for expanded valence cases, exchange electrons between adjacent atoms as needed for optimization of formal charges.

I'll come back to the expanded valence cases momentarily, but we'll look at electron deficient and odd-electron before that.

For an electron deficient case, we'll bring back BF_3 which was worked out in Example 4 in Chapter 26. That gave us Structure A below.



Structure B is the one which I briefly mentioned early in Chapter 26 but I said we would forget about it until Chapter 27. Well, here it is. For illustration purposes, let's say we skipped Step 5 of the Basic Steps and went right into Step 6. That would lead us to Structures B - D. Structures B - D are equivalent to each other, but inequivalent to Structure A. 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 FC and the third F has $+1$ FC. (Prove this to yourself; derive and compare 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?

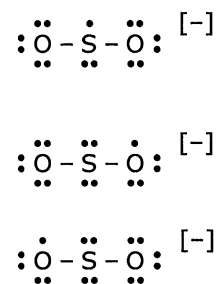
We are back again to that magical word from Chapter 1: balance. Here, we have two opposing factors, the tendency to achieve octet and the tendency to minimize FC. The real answer lies in the balance. We can't decide the answer just from this information, but we can determine the answer from experimental measurements and computations. 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 is 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 assumption 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 Step and the FC Guidelines. We did not need them for the NF_2 example in Chapter 26 because that Lewis structure for NF_2 already has all atoms with zero FCs. For a different example, 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 then 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 "best" Lewis structure? Consider the formal charges: each O has a 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.

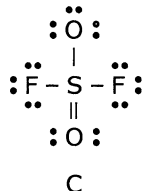
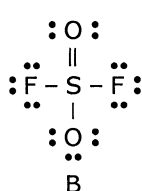
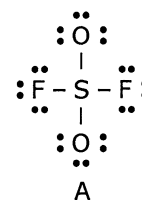
Let's move an electron from one O to the S, to get the Lewis structure at right. Now do the FCs: the left O has FC of -1 , and both the S and the right O have FCs of zero. These are your minimum formal charges. But this now opens up the possibility of additional resonance, since we can obtain an equivalent Lewis structure by moving the odd electron to the left O. These last two resonance structures are now the "best" Lewis structures based on formal charges.



From the examples so far, the FC Guidelines work quite well for octet cases, for electron deficient cases and for odd-electron compounds. Unfortunately, the Guidelines do not work well for expanded valence.

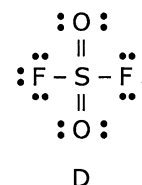
Let's take a look at some of the aspects involved, using F_2SO_2 .

If you follow the Basic Steps from Chapter 26, you end at Step 5a with the Lewis structure for F_2SO_2 as shown on the right, labeled Structure A. The FCs are zero for each F, -1 for each O, and $+2$ for S. Those are a bit high for FCs. On the other hand, all atoms have octet.



If we truly wanted to minimize FCs, we could take a LP from an oxygen and share it with the S to give a double bond. There are two options, as given by Structures B and C. The FCs are still zero for each F, still -1 for the singly bonded O, but now zero for the doubly bonded O and $+1$ for S. In addition, sulfur has expanded its valence to ten electrons.

We could take this one step further and take a LP from the other oxygen and share that one also with the S to give another double bond. This is shown at right as Structure D. The FCs are now zero for all atoms. But sulfur has expanded its valence to twelve electrons.



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

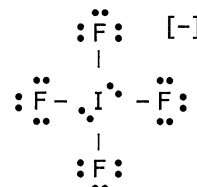
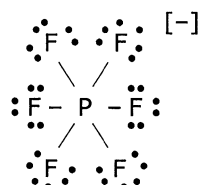
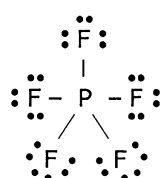
Historically, the emphasis on minimizing formal charges was applied to all compounds and all Lewis structures, and that contributed to our understanding of bonding and other properties of those polyatomic units. Expanded valence cases, however, are trickier by nature due to the complexities of their 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, in general, for a Lewis structure, and other factors can be involved. FC minimization continues to work well with octet-or-less cases and with odd-electron cases; it just does not work well as a reason for expanding 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, compromise 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 F_2SO_2 . 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. Basic Step 5a will take us to where we need to go. Thus, we consider Structure A to be preferred for F_2SO_2 , with the central atom having octet. This will have a notable consequence: our Lewis structures will not have any multiple bonds on any atom with expanded valence.

On the other hand, we can still do single bonds and lone pairs with expanded valence, such as those which were illustrated for the cases of PF_5 , PF_6^- and IF_4^- in Chapter 26.



Interestingly, these already have minimum formal charges: all atoms have zero FC except the P in PF_6^- and the I in IF_4^- , both of which have a formal charge of -1 . Since these two are anions, then at least one atom in each case must have a negative FC. Despite having minimum formal charges, even these cases have issues in the more modern interpretations. But we won't get into those, and we need to draw a line

somewhere. Thus, our extent of coverage for expanded valence is limited to central atoms with single bond orders. (Lone pairs are optional.) And, 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.

OK?


Well, there's a lot here in this Section. And in this Chapter overall. And in the prior Chapter. Time for a wrap up.


27.6 Wrap up


Here's how we started this in Chapter 26.

“ Before we proceed, you should understand that there are varying levels of complexity to the Lewis system and all the details are not covered in a typical first-year course. The level of coverage can vary with different instructors, based on their experience with their students and with the needs for their courses and program. I will first present to you a Basic Level of approach for doing Lewis. Later, in Chapter 27, I will add another level which provides a Refinement Step to the Basic approach, and we will also look at some of the other complexities which can arise. The Basic Level and the Refinement will cover many cases of polyatomics, but they won't be perfect for everything. That's OK. It is not my intention nor my desire to cover everything. Your instructor may also present different steps in order to present her/his slant on the method. That's OK, too. ”

As promised, we have indeed looked at some of the complexities, but I want you to understand that the six Basic Steps for doing Lewis structures as given in Chapter 26 are designed to avoid much of the issues which have been described. As such, be careful to follow those Steps closely. Here are some pointers.


 Step 5a is a dead-stop condition. If that condition is met, do not go any further. And do not do the Refinement Step.

 Step 5b is also a dead-stop condition. If that condition is met, do not go any further. And do not do the Refinement Step.

 Step 6 is where the possibility of resonance structures is encountered.

If there are resonance structures and they are all equivalent, stop with those; do not go any further.

If there are resonance structures and they are not all equivalent, then assess them by the FC Guidelines.

 Note B must be followed for odd-electron cases. One atom ends with seven electrons, and resonance structures may be possible.

If there are resonance structures and they are all equivalent, stop with those; do not go any further.

If there are resonance structures and they are not all equivalent, then assess them by the FC Guidelines.

The six Basic Steps and these pointers will serve our purpose well in our coverage.

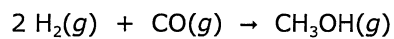
There is more to come! What lie ahead are two follow-ups to Lewis: determining the shapes of polyatomic units (starting in the next Chapter) and assessing the manner of bonding within polyatomic units (starting in Chapter 30). We will be able to do shapes for all Lewis structures covered here. For bonding, however, we will limit to octet or less cases. We will not do bonding for any Lewis structure which displays expanded valence; the newer bonding descriptions for these cases have become a bit more complicated and we will leave them out of coverage.

Besides, we have plenty to work with.

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.



(In CH_3OH , the C and O are central atoms.) Using average bond energies, estimate the ΔH° for the reaction. Using ΔH_f° , calculate the actual ΔH° for the reaction. How important are bond energies to the actual ΔH° 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. XeF_4 e. NO_4^{3-} f. PCl_4^+

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

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