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**CATHERINE DRENNAN:** So now we go on to the breakdown of the octet rule. So we've established the octet rule and now we're going to shake it all up and see its flaws. So case 1, we're going to consider what happens-- and this again is today's handout-- consider what happens when you have an odd number of valence electrons.

Case 1, all right, so for molecules with an odd number of electrons, odd number of valence electrons, it's not possible for every atom to have a complete octet. That involves pairing, that involves even numbers of electrons.

So let's look at an example of a place where we have an odd number of valence electrons. And this is our friend, CH<sub>3</sub>, our methyl group that we saw a few minutes ago. So we can also write it like this. And we can come up with a Lewis structure for our methyl group.

So hydrogen, remember, it only brings one valence electron to the table. There are three hydrogens. Carbon brings four valence electrons. So in sum, we have seven, an odd number of electrons.

To complete our octets-- remember, hydrogen is an exception, it only needs two, it just has that 1s orbital-- so we need two electrons for it for it to be happy. There are three hydrogens. That's six. Carbon needs eight. So total you need 14 to make carbon and hydrogens happy.

So if you consider then how many bonding electrons you have, that's the number of electrons needed for your octet, minus the number of valence electrons you have, so we get seven bonding electrons. How do you have seven bonding electrons? A bond has two electrons in it.

So let's look at that, what do we do. Well, we can put six-- six is good-- assign two electrons for the bond between this carbon and this hydrogen, two between this carbon and this hydrogen, two between this carbon and this hydrogen, six is good. But now what do we do with the extra one? We have seven. So we're just going to stick that right there on the carbon.

So what is this molecule, then? Well, what this molecule is is a radical species. So a radical

species is a molecule with an unpaired electron. And usually radical species are very reactive. Bonding electrons don't want to be unpaired, they want to be in bonds. So they're highly reactive, they're sort of searching out to either get rid of their electron, to get another electron. They're very, very reactive species.

So radicals turn out to be very important in human health. And free radicals in biology are both good and bad. So in the bad category, we have the fact that free radicals damage DNA, that leads to mutations in cancer and death. Not good.

And there are a lot of radical species, many of which involve oxygen, oxygen radical species that can be byproducts of metabolism, common cigarette smoke. So there are natural causes and also man-made causes of radical species. And this is very harmful.

But radical species can also be really good. So they're also essential for life. They're signaling agents in the body. Radicals are short-lived, they're highly reactive, so they're not around very long. That's a great signaling agent. You want the signal to turn itself off, so you want to have something short-lived.

They're also essential for enzyme reactions. We have no cell division, no growth, no multicellular organisms if it weren't for radical enzymes. And we use radicals in our body when we're fighting off illness. We generate radical species, or the white blood cells do, to kill invading microbes. So we're using radical defense in our bodies to fight off illness. So radicals are both good and bad.

So we talked about oxygen radicals a little bit. One other radical species is nitric oxide. And now why don't you identify for me which of these molecules is nitric oxide, knowing that it's a radical? All right, just 10 more seconds.

OK, so some of you might have just known that that molecule is nitric oxide. But if you had done the calculation, you would have realized that NO is the only one where you get an odd number of bonding electrons. For these other molecules, you have an even number and they can't be radical species with an even number. You need an odd number of bonding electrons to have a radical species.

So this is nitric oxide, NO. And what does NO do? So NO is an important signaling molecule in the body. So it activates something called guanylyl cyclase, which is an enzyme, which then starts a second signaling system that involves GTP forming another signaling agent, cyclic

GMP. And this causes vasodilation.

So scientists were very interested in this pathway, and they noted that cyclic GMP can be degraded by an enzyme turning off this signal. And they thought, if we inhibit this enzyme, then we can have a more continued effect of vasodilation. This could be good for people who are suffering from heart disease, they need to get more oxygen to their lungs, they might have emphysema. This could be a very good thing for these people.

So they designed an inhibitor for this, but it turned out it didn't work exactly as they expected. It did increase vasodilation, but only in one part of the body and only for one gender of individual. So this led to the bestselling pharmaceutical molecule of all time. So a good example of how science sometimes doesn't take you exactly where you wanted to go but nonetheless was highly profitable.

All right, so nitric oxide-- and I could tell you that actually a lot of the early work on nitric oxide was done at MIT. And for people who came from MIT, there's a whole just-say-no club here at MIT. And if you see this just-say-no, it's about nitric oxide. So just be aware of that.

OK, so now let's do a Lewis structure for this and see this radical species. So again, we need an odd number of valence electrons, if it's going to be a radical, and that's what we get. So nitrogen has five valence electrons and oxygen has six. So overall, we have 11.

To have complete octets, nitrogen needs eight, oxygen needs eight, so we need 16, which gives us five bonding electrons, 16 minus 11. That makes it a radical species. And now we have six remaining and we can put everything on.

So we can put four bonding electrons in between. We have five, we can only put four because you can't have a bond with just one electron. So the fifth one is why it's a radical species. But we have also six remaining valence electrons. And we can distribute those around one, two, three, four, five, six. And that would be our molecule. All right, so this is a highly reactive radical species.

Yeah.

**AUDIENCE:** How do you know that the radical one goes on the end instead of [INAUDIBLE]?

**CATHERINE DRENNAN:** Yeah, I actually was going to calculate whether we could use this, but that is in fact where that one is going. So that can be a clicker question maybe for next time. I didn't actually get to try it.

I was thinking, we should calculate the formal charges and think about where things are going to go, but I didn't do that. But that's a good question.

All right, so let's just look at another example. Let's look at molecular oxygen for a minute and do this one. So we're getting lots of practice with Lewis structures today.

So we need to think about valence electrons. So we have six for oxygen plus six, so we have 12 valence electrons. And we need eight plus eight, we need 16. Then we need to figure out how many bonding electrons. That's going to be 16 minus 12, or four.

And now we can assign. And so we'll put first two, and we have two more. So we're going to assign them. We have two more, and we'll put those in. So we have a double bond.

And then we can think about whether we have any left. And we had 12 valence electrons. Now we've used four, so we have eight more that we can distribute. So we're going to make some lone pairs here. So we can put two up here, a lone pair up here, a lone pair down here. One, two, three, four-- our eight extra electrons.

And that looks lovely. Everything is happy. That seems like a great structure, except for the fact that it's wrong. Lewis structures have failed us. So it turns out that it's a biradical.

And this is really why we live life as we know it. Oxygen-- there was a time before oxygen, life was very different. Oxygen came around, changed life as we know it, partly because it's a biradical. It has amazing properties, it can do amazing chemistry. It allows us to break down sugars and make energy.

And so in reality, oxygen is a biradical. We know that it is not a double bond, as drawn there. This is the structure. We have one bond, not a double bond, lone pairs. But then we have a single dot over here, a single dot over here. That makes it a biradical. One radical on this oxygen, one radical on that oxygen.

And we can't explain this with Lewis structures. We need molecular orbital theory. But you're in luck because that's what we're going to talk about on Monday. So Monday, I'll explain to you why this is a biradical, but you're going to have to wait for then.

Because we have more problems to address first, we have octet deficient molecules. Some of these atoms, they're just messing everything up for us. OK, but the good news is, octet deficient molecules-- incomplete octet. There's only two of them you need to know-- boron,

aluminum. There they are, just those two.

So let's look at boron. So we have boron and three fluorines. So we put boron in the middle, three fluorines around it. How come I'm not putting a fluorine in the middle? Yeah, fluorine is always going to be terminal, it does not want to be anywhere else.

OK, so now we can look at part of the periodic table. We see here is boron. Right below it, aluminum. So that helps us remember those exceptions, they're right there. And now let's just calculate this Lewis structure and see about the octet deficiency.

So normally we would say boron has three valence electrons. And fluorine-- there are three fluorines, it has seven, then 24. OK, that actually would always be true. But now we're saying boron should want eight-- and we'll come back to that assumption-- to have complete octet. That's definitely how much it wants to have a complete octet, but doesn't really need a complete octet.

Fluorines also want eight. That's a total of 32. And now, if we subtract, we have eight bonding electrons. So we can assign two per bond first. Now we've used six, and we have two more. So we have two extras that we can put in, that gives us a double bond.

We can look at our extra electrons. We had 24, we used eight now to do bonding, so we have 16 left. And so we can put two on this fluorine that has the double bond. We can put six on the fluorine with the single bond, and another six on this fluorine. And that adds up, that's great.

And now we can assign formal charges and think about how good this structure is. So if we do the formal charges, let's look at boron first. So it had three valence electrons, it has no lone pairs, and it has half of eight bonding electrons, minus 1. Not bad for a formal charge.

What about this fluorine with the double bond? And that's a clicker question, I told you you'd be really good at formal charges by the end of class today. OK, 10 more seconds.

I think we can get in the 90's. Ah, it's killing me. All right, we have to keep working on it. There's going to be more clicker competition Friday. There will be a formal charge question on it.

And by the way, it's OK to sit in groups. We've had back-to-back wins of one recitation. I have noted that some of them sit in a group. Just saying that is allowed.

OK, so here, we have seven valence electrons for fluorine, and there were four lone pair electrons. Half of four bonding electrons, so we have a plus 1 charge there.

And then let's finish up. So our single-bonded fluorines, seven minus six lone pairs for those. And they have one bond, so they have half of two bonding electrons, and then there's zero. Overall, this is a neutral molecule. So we have plus 1, minus 1, that's a neutral molecule.

This all seems good, except that someone did an experiment and found that all three boron fluorine bonds were single bonds. So again, Lewis structures failed us. Experiment tells us it's a single bond. And this is in fact the correct structure here. Poor boron has an incomplete octet.

So it does not have all the electrons, but it's happy with that. It's OK with that because it's one of the exceptions. And if we look at the formal charges for it, now we have boron, it had three valence electrons, no lone pairs, half of six bonding electrons is three. So now it has a formal charge of zero. And all three fluorines, we have seven minus six, they have one bond, so half of two bonding electrons, they also have a formal charge of zero.

So most elements would not be OK with this. But boron, with its three valence electrons, thinks that this is just fine. So it's one of the exceptions. And again, we wouldn't have known this except for experimental data.

Lewis structures work 90% of the time, but there are some where experiment tells us that the structure we normally would've done with our rules of complete octets don't hold. OK, and we can rationalize this by the fact the formal charges are more favorable on this molecule.

One more exception-- valence shell expansion. This again, is not a property of just any atom. It needs to be elements that have been an n. What is n again? n stands for?

**AUDIENCE:** Principle quantum number.

**CATHERINE DRENNAN:** Principle quantum number, yes. You can't forget anything, we're coming back to it, we're coming back to all of it. Have a principle quantum number that's equal or greater than three. And what do we know about things, what kind of orbitals do we start talking about when we have principle quantum numbers of n that are equal to or greater than three, what happens?

**AUDIENCE:** d-orbitals.

**CATHERINE  
DRENNAN:**

We get some d-orbitals, exactly. d-orbitals-- I love d-orbitals. Closer to Thanksgiving, we're going to have a whole unit where we're talking about d-orbitals. We save that for a really special occasion. I love d-orbitals. d-orbitals allow for all sorts of craziness to happen, including valence shell expansion.

So this is most common when the central atom is large and it has a bunch of little small, electronegative atoms around it. And the transition metals, with their d-orbitals, they like this. And other things with d-orbitals are cool with this as well.

So the first example we're going to look at is phosphorus with five chlorines around it. Phosphorus is pretty large, and it has chlorine, which is a fairly small electronegative atom around it. And it has five of them around it.

So we'll put our phosphorus in the middle and we'll put our five chlorines around it. Now we need to count valence electrons because we need to draw Lewis structures. So phosphorous brings five valence electrons to the gain. The chlorines each have seven, and there are five of them. So we have 40 altogether.

Phosphorus, we think, wants eight. It would, for a complete octet. Also, chlorine wants eight, and there are five of those. So total, if we have complete octets, we need 48 electrons. 48 minus 40, the number needed for the complete octet minus the number of valence electrons gives you eight bonding electrons.

So we're going to assign two per bond, up to eight, and there we go. Now does that look like a good Lewis structure to you?

**AUDIENCE:**

No.

**CATHERINE  
DRENNAN:**

Yeah, it's pretty obvious that there's something wrong here. So this is not going to work out. We're not going to add chlorine to another chlorine because they don't like to do that. Halogens really like to be terminal. So that's not going to work. So we've got to use some extra electrons and make a new bond.

So we need to have five bonds, so that means we need to use 10. We need to have 10 bonding electrons. And when we borrow another two, we can make another bond. We had 40, we've now used 10. We had no choice, we had to use 10, so we have 30 lone pairs. And we have five chlorines that all want six lone pair electrons to complete their octet, and six times five is 30, so this works out beautifully.

So this is a very happy structure now. Phosphorus is OK, it's large. It has an  $n$  equal 3. It's OK being expanded, and chlorine is very happy. So the bottom line is there are certain kinds of elements that you can expand. They can have more than an octet. They can have five bonds. Others, carbon-- no, carbon is not going to have five bonds. But phosphorus is OK.

So some things can be expanded, some things can't be expanded. So you have to think about what the expansion would do and whether that would be allowed.

Let's do one more example. Chromium with four oxygens, minus 2 charge. We see chromium over here. It's got  $d$  electrons. Let's see what happens.

So here we have our skeleton structure. We put chromium in the middle and our four oxygens around it. Now we have a bracket around it with a little minus 2. Note the minus 2 because it has a charge on it. Don't forget about the charge. And now we need to see how many valence electrons.

So chromium is going to bring six. So we can look at where it is in the periodic table-- one, two, three, four, five, six. Our oxygen is up here. Also, have six valence electrons. And don't forget about the charge on the molecule. So when it's minus 2, you have to add two electrons. It has extra two electrons, so add those in, which gives you a total of 32.

What do you need for your octet? So eight for the chromium, four times eight for all the four oxygens. We need 40, then we can take our 40, minus 32, and we have eight bonding electrons. That seems good, two per bond. We'll put those on.

Then we'll see if we have any lone pairs, and we do. 32 minus eight gives us 24. The oxygens are going to want six, and there are four of them, so that just looks awesome. So maybe this doesn't need to expand.

Let's see. What do we do to test this? Experiments, or, if we don't have a lab, we do--

**AUDIENCE:** Formal charge.

**CATHERINE DRENNAN:** Formal charge. Yes, that's easier to do in the classroom. All right, so we'll calculate a formal charge. Chromium brought six valence electrons. It has no lone pairs, it has half of eight bonding electrons, or four bonds, plus two oxygens, have six valence electrons, six lone pairs, one bond, so half of two, or minus 1.

So the total charge here, because you have four of those, plus 2, is minus 2. So that's OK. But this has a pretty big charge distribution. Everything has a formal charge on it. And that doesn't make molecules very happy, they want formal charges of zero, maybe plus or minus 1. But this is a lot of formal charge.

So maybe we can do better. And as someone said, someone else did an experiment and-- yup-- they're not single bonds. So the experiment showed that it's somewhere between a single and double bond. So this is not the right Lewis structure. And one of the tip-offs could be, whenever you see plus 2, make sure there's not another possible structure, or minus 2.

So you can make double bonds here. And if you do that and calculate the formal charge then on chromium, it had six, no lone pairs, but now it has six bonds, so it has a formal charge of zero. The double-bonded oxygens had brought six valence electrons, they have four lone pairs, and they have half of four bonding electrons, now they're zero.

And the two single oxygens here are still minus 1. There are two of them, so that equals the minus 2. But this has much less charge separation. You have lots of zeros. You don't have any more things with charges of 2.

But this is not done. What else do we need here?

**AUDIENCE:** Resonance structures.

**CATHERINE DRENNAN:** We need resonance structures, that's right, because I just put the double bonds here. I could have put them there, or maybe somewhere else. And you can tell me how many other structures you need to complete this.

All right, 10 more seconds. Yup, this is a good one, I think, that helps when you do it in a team. Everyone sees different ones.

So there actually are four other ones. You can try to write that out and prove it to yourself. There are four other structures you can do. And you need all of those to get the correct structure. So these structures are correct, it is a resonance structure. There's less formal charge separation.

OK, so that's the end of Lewis structures. And we're going to talk about shapes and molecules on Friday. And problem set is due on Friday, and it has lots of Lewis structures in it, so don't leave it to the last minute.

