CATHERINE DRENNAN: So if we switch to today's lecture notes, we're going to talk today about applying some of the chemistry knowledge, with clicker questions and a clicker championship, to the issue of using CO2 to make biofuels. So first I just want to briefly review the course objectives, what I was hoping people would get out of this course. So I was hoping that you would know enough chemistry, have enough basic chemistry knowledge to do a UROP in the Chemistry Department without taking any other chemistry classes; that in UROP positions in other departments you would be using chemistry in your research; that you could also appreciate how chemistry is used to solve real world problems like we're talking about today, make informed decisions about your own health, the health of your family, environmental issues, energy issues, a lot of political decisions that are going on-- there's a lot of science actually in the news these days; and hopefully, make the world a better place by applying chemical principles to problems in science and engineering.

So those are my goals. And then if we just kind of look at the material that we've covered. The first half of the course, which will be Exam One, Exam Two material-- talked about the basic properties of matter, atomic theory, periodic table, bonding structures of molecules. And then thermodynamics kind of transitioned us from thinking about basic properties to thinking more about reactivity and how that material that we learned about in the first half, how those elements could come together and react to form molecules. And to think about how things react, we usually think about thermodynamics. We need to think about chemical equilibrium, acid base, oxidation, and sometimes, transition metals, because they are-- that middle part of the periodic table can do amazing chemistry-- and also kinetics and solubility. So all of these things are about how material reacts.

So we can't review everything. But I thought we would stick with this sort of carbon dioxide biofuels theme. And see how some of the things we've learned in this course would help us understand how we could approach this problem, how people are trying to solve this problem.

So what is the problem again? And Jingnan brought this up, CO2 is a waste product of combustion of fossil fuels. We want to remove it from our environment. It's a greenhouse gas. It's also leading to the acidification of the oceans. This is not a molecule we want around in the kind of quantities that it is around.

And I am personally very concerned about climate change. And after those of you who are freshman experience this winter, I think you will also be very concerned about climate change. So this is a problem.

What is the approach? Well, the idea, I think, is really great-- that you can take CO2 and not just get rid of it, but convert it into something we want, which is alternative fuels, like biofuels. So I think this is a really great thing.

So there are a few ways that one could do it. You could think about designing small molecule catalysts to do this. This is one thing people are doing. But there's really been a lot of energy on looking at how nature does things. So a lot of people are interested in nature, thinking about biological pathways that already do this.

They already remove CO2 from our environment and fix it. Form carbon carbon bonds and make it into multicarbon chains that can be used as biofuels. So but before we do any of this, before we can go and think about any of these solutions, we need to understand the basic properties of CO2, it's reactivity, and more about these pathways.

So let's talk about carbon dioxide, and let's think about how carbon and oxygen are bonded together. And we can use Lewis structures to predict what the Lewis structure of this should be, what the bonding will be. So let's go ahead with our first, our clicker question, and predict which of these, and we have a little bit of the periodic table, is the correct Lewis structure for CO2.

OK. 10 more seconds. All right. So we're going to go through and just look at what's wrong with some of these structures as a review. But first, can someone tell me for a t-shirt, what is the equation for formal charge? And Alaina will bring you the mic.

AUDIENCE: One half the number of bonds that are going on plus the number of loan pair electrons.

CATHERINE DRENNAN: Right. So I think we're missing one thing-- so formal charge, or maybe I didn't hear it. We have the number of valence electrons that we have, which for carbon was what? Four. So for carbon was four, and for oxygen is six, right. So minus the number of lone pair and then half of the bonding electrons.

So this is how we're going to do this. The first structure has zero formal charges. It's good. And that is, in fact, the correct structure. The second structure here, if we do it out we have oxygen in the middle and we have carbon on the end. And here we should have a formal charge of minus 2 on that carbon and plus 2 on the middle oxygen.

So it's not good, because it has charges, which is not good. But it's also not good because the negative charge should be on what type of atom? A more electronegative, so that's not true here. So that structure is not good for a variety of reasons.

OK, so if we look at the next structure, we have six valence electrons around one of the oxygens. We have two bonds to carbon and two lone pairs. And we have-- oh, actually we have the six around the other one as well.

So first off, if you counted, there's more valence electrons used here than you had. So that's not good. And if you look at the charges, it's minus 1, minus 2, and minus 1. So that's a lot of charge, but also, what else is wrong with that?

It should add up to 0, which it does not. And it doesn't add up to 0, because I put extra valence electrons in there that do not exist. So this structure is bad for a lot of reasons. Also the higher negative charge is not on the most electronegative atom. So this has many things wrong with it.

So then if we looked at number four-- so we have an oxygen with six around it, a carbon that has two lone pairs double bonded to an oxygen with two lone pairs. And this has minus 1 and also minus 1. So again charges don't add up. It has the wrong number of valence electrons. So that's bad.

And then the last one-- we have an oxygen with six lone pair electrons, a carbon with three bonds, no lone pair electrons, and an oxygen with two double bonds, two loan pair electrons, minus 1, plus 1. So this is not zero like that one is up there. But also something else is wrong. What else is wrong with that structure? What's wrong with the carbon?

AUDIENCE: Doesn't add up to 8.

CATHERINE DRENNAN: Right, so it has an complete octet. And so sometimes you can have an incomplete octet. Does anybody remember what two elements we mentioned are happy with an incomplete octet?

AUDIENCE: Boron.

CATHERINE DRENNAN: Boron and aluminum, right. And then some of them are happy with an expanded octet, but to be expanded you have to have an n number of what? Three or above. So carbon does not want to have a deficient octet or an expanded octet.

So many of these other ones had a lot of things wrong. And so this is something that could be useful to review. And again, Lewis structure is one thing that people go, oh, yeah, I know how to do it. But it's good to review the rules right before an exam.

OK, so here with our correct Lewis structure. And that Lewis structure stood well. That's a good structure. OK, so now that we know the Lewis structure, we can think about the geometry of the molecule, what its angles are, what it looks like in 3D. And we can use our friend, the Valence Shell Electron Pair Repulsion theory and Valence Bond Theory to predict things about this structure.

So why don't you tell me which ones of these are correct?

[CLASSROOM CHATTER]

CATHERINE DRENNAN: All right. 10 more seconds.

[CLASSROOM CHATTER]

CATHERINE DRENNAN: All right? OK, so let's take a look at that. So valence shell electron pair repulsion theory-- the AX, no AXE nomenclature. So X is the number of atoms bonded, and there are two here. So it's AX2.

If there had been lone pairs, which they're not on the carbon, we would have added an E to indicate the lone pair. And AX2 molecules are linear. So here we have our carbon monoxide. It just has a single bond. This model kit doesn't have double bonds, but we have a linear molecule there.

And again valence shell theory is really just about minimizing the repulsion between things. So the atoms, and especially those lone pairs that really take up a lot of room, try to position themselves around the central atom so it's the least repulsive.

So in valence bond theory leads to the idea of hybrid orbitals. This idea that the valence electrons are available for bonding. And that you're not really just having s orbitals and p orbitals separate, you're really forming these hybrid orbitals, which tell you about the geometry around individual atoms.

So the number of hybrid orbitals is the number of bonded atoms and the number of lone pairs. So carbon has two bonded atoms. So it's sp, and n equals 2, so it's 2sp.

And oxygen has one atom and two lone pairs. Again the number of bonds doesn't matter here. So it has one plus two or three, so its sp2 and again n equals 2. So 2sp2.

And then we can also have questions about the geometries, what are the angles for the different types of hybridization? So this really gets at what the geometry at every atom is like, whereas the vesper is really thinking about the overall shape of the molecule around the central atom and not so much about the individual atoms. All right, and remember that if we have a singly-bonded terminal atom, it's not hybridized. But this is not singly-bonded.

OK, so now we can also ask what is the polarity of this molecule, and that's one more clicker question. All right 10 more seconds. All right. So if the polar bear t-shirt had won, it would have given it away. But it didn't matter, you still remembered.

So, yeah, it does have polar bonds. Electronegativity difference greater than 0.4 does make it a polar bond, but because it is linear there's no net dipole. So the polar bond-- this cancels each other out with this linear geometry. Great. So non-polar molecule, even though it has polar bonds. So it's not just about the property of the bonds that's important. It's also about the overall shape of the molecule.

OK, so we have looked at some of the basic properties of CO2 now, which is the top part. And now let's move in to think about the reactivity of the CO2 molecule. So when we're thinking about reactivity we want to say is CO2 a stable or an unstable molecule compared to its elements?

And this is not a clicker question. So you can just tell me. To answer this question about stability of a molecule compared to its elements, what is the thing I want to know about?

Yeah, I want to know about delta G. In particular, I want to know about the delta G of formation of this molecule. But if you said delta G, that would be very good. So here the delta G of formation of CO2 is a negative number. It's a fairly big negative number minus 394 kilojoules per mol.

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So is CO2 stable or unstable? And you can just yell this out? It's stable, right. So the way we're thinking about this is with a delta G that's negative, it's spontaneous in the forward direction, which means it's not spontaneous in the reverse direction. So CO2 decomposing into its elements is not spontaneous. So that makes it a stable molecule.

All right, so let's kind of put all these things together about CO2 now. So according to the Lewis structure, it has double bonds. And usually a double bond means that it's harder to disassociate a big bond dissociation energy. And you don't need to know these, but in case you're interested, when you have carbon double bonded to oxygen, you have a bond dissociation energy of about 805 kilojoules per mol.

And it depends a little on the molecule in question, but a single bond is more like 358. And so double bond, it's hard to disassociate that. And it's also linear, non-polar, and stable.

All right. So we want to take CO2 and turn it into other stuff. We want to make biofuels and solve the energy problem. But this is a non-polar molecule, and it's very stable. It has strong bonds. This is a hard challenge.

And if it were an easy challenge, we would have figured this out. But this is not an easy challenge. It's a hard challenge, which is why it is a big area of research right now. So fixing CO2, i.e., putting these 1 carbon units together to make these long chain carbons like you saw in Jingnan's video, when she talked about these multichain carbons being used as biofuels. This is hard.

All right, so when things are hard, first thing that scientists often like to do is say, can someone solve this problem and can we steal an idea from them? Honestly, that's what we do. But it's OK when the people we want to steal from are not really people, but Mother Nature.

And so we look to Mother Nature and we look to some of the most intelligent life forms I know, which are microbes and bacteria. Oh man, can they do amazing chemistry that we cannot do. They are fantastic chemists, these little microbes.

So one approach is to look at a microbe that does a process called acetogenesis. And that is one of the six known pathways of CO2 fixation. So acetogenesis makes acetate, or what's known as Acetyl-CoA. That's Coenzyme A.

And this is considered the most ancient pathway of carbon fixation before origins of life kind of times, high CO2 environment, that maybe this was one of the first reactions that sort of generated metabolic fuel. And so here you have two molecules of CO2, one in blue, one in red, that are both converted to other carbons units that are then combined with Coenzyme A to make Acetyl-CoA, which then can go on to make biofuels.

So this is what we want to understand, and we want to use this and turn our CO2 into biofuels. So but before we do this again, we must understand how it works. And we can ask the following questions. Are there redox reactions involved? Yes, there are.

Is there acid-base catalysis? Why, yes, of course, there is. Are there transition metals involved? Is this hard chemistry? Yes, therefore pretty much guaranteed they'll be transition metals involved.

Are there challenging rate-limiting steps? Oh, there's always, something's always rate-limiting, absolutely. And what about the chemical equilibrium? What about our [INAUDIBLE]?

All right, so let's review the second half material thinking about the process of acetogenesis. First, oxidation reduction-- so you can tell me with a clicker question what is happening to CO2? And what's happening to blue CO2, and what's happening to red CO2? Are they being reduced or oxidized? All right. 10 more seconds. Great.

OK, so let's take a look at that. So that is right, the top reaction. So both of these are plus 4. It's the same molecule. And so in one case you're going to minus 2. So it's a 6 electron process.

And in the other, you're going to plus 2. But both of them are being reduced. And so that is what's happening in a lot of these carbon fixation pathways. You're reducing carbon dioxide and making it into hydrocarbons, which can be used for biofuel. And the precursor here is the reduced form of this 2 carbon molecule, this Acetyl-CoA.

All right, so it's being reduced. Now this is a fairly large reduction. Six electrons is a lot. Most of the reagents in nature that do reduction chemistry do one or two electron processes. So six is a lot.

And in fact, it requires five different enzymes to do this six electron reduction. So it's not just one enzyme, it's multiple enzymes that need to do this. So this raises a question then.

How are these carbon units, if you take one, you reduce it. Then you reduce it again and remove it to another enzyme, reduce it again and remove it to another enzyme, and reduce it again, move it to another enzyme. How does that happen?

How do the enzymes kind of pass things along? And I think about this as a problem like kindergarten soccer. So we have a bunch of enzymes. And we have a bunch of one carbon units. But the one carbon units do not get passed from enzyme to enzyme in an organized fashion.

And in fact, sometimes the enzymes don't really have control of those 1 carbon units. They can't grab it with their hands. That's not allowed. And we know enzymes do not have hands as such.

So how do the enzymes grab onto these one carbon units and how does an enzyme bring it from one enzyme to the next. And why-- you know it takes energy to reduce CO2. So you don't want to just reduce it and kind of pass it along, and then who knows what happens to that reduced molecule. You want to go to the next enzyme and the next enzyme and the next enzyme. You want to make your Acetyl-CoA.

So how does nature do it? It has a solution to the kindergarten soccer problem, and its solution is a B vitamin folic acid, also known as folate. And we talked about this before. This is why some people might want to drink Norwegian beer, lots of folic acid in it, or orange juice, or eat leafy green vegetables.

So here's folic acid in its large form. In your notes, it just has an R. This entire thing is abbreviated as R. And what these enzymes do is they grab onto R, to that arm. And they hold onto it and they bind their one carbon unit over here.

And then one enzyme does a reduction. And then it releases it, attached to folic acid. The next enzyme grabs onto the folate acid by the R group, reduces it again, lets go of it. The next enzyme grabs onto the folic acid by the R, reduces it again and this works.

This is a great thing. You have something small. You don't want it just fre floating in the cell, especially if it's not really all that soluble. So you use something else to hold onto it. You use a vitamin to hold onto it this is great.

But there's a problem. Well, first let's say, it holds onto it really well. You can pass it really well. This is great. But then when you get to the end, you're holding onto it really tight.

You get to the end-- how do you get the methyl group off the folic acid? Great vehicle, but you need a final step. You need to remove it when you're done.

So when the enzymes are done, how is this methyl group, CH3 group removed? And now we need to think about acid-base chemistry. So it turns out that the deprotonated form of folic acid, very hard to remove the methyl group. Whereas the protonated form of folic acid here, with the proton H in red, it's much easier to remove the methyl group.

So if the pKa of folic acid is 4.8, how much of folic acid will be deprotonated compared to protonated at physiological pH? All right. 10 more seconds.

Yeah. Yeah. So sometimes these things move around. The fonts change. So more will be deprotonated. I see that people are paying attention. And we can look at exactly how much more.

So if we're going to look at exactly how much more, what equation do I want to haul out? And Henderson-Hasselbalch. I should have a little approximate there, but still, there it is. So we have pH of 7.4. pKa of 4.8. And if we solve this, we have much more that is deprotonated. And again, the deprotonated form is nonreactive.

So this is true off the enzyme, just a folic acid. It is not in a state that's going to react very well. You're not going to get that methyl group off very easily. Most of it will be deprotonated and nonreactive. That's fine if you're just transporting it, and that's great.

Your body does this. You have methyl tetrahydrofolate in your blood right now. And you have an enzyme that takes off the methyl group. And you need an enzyme to catalyze it, because it needs to be a catalyzed reaction. It's not going to go on its own.

So again, just to remember our little pretty pictures. When the pH equals the pKa, you have equal number of moles of protonated and deprotonated. At pH's below the pKa, it's more protonated. And a pH's above the pKa, it's more deprotonated.

OK, so again we have the problem here that the removal of this methyl group is challenging, this is in fact a very challenging reaction both for humans and microbes. And so the solution, of course, transition metal and an enzyme. So you need both the transition metal, Vitamin B-12, bound to an enzyme to be able to do this really challenging chemistry. So this is one of the hard steps in this pathway.

So Vitamin B-12 we have talked about before. It's an example of a naturally occurring metal chelate. You have cobalt in the middle of this core and ring system. And you have cobalt in the plus 1 oxidation state is very reactive and it's capable of removing that methyl group from the folic acid and transferring it to itself, forming a methyl cobalt 3 species. And here's the little methyl group on top.

So we know about transition metals as well, and we can figure out the d-count. So we can look at the periodic table. And remember what about cobalt? What do we need to know from this? And so our d-count would be what then?

You can just yell it out , it's not a clicker question. So it was group 9? So we have 9 minus 1, or 8 d8. And over here we have 9 minus 3 equals 8? No, d6-- yes, there's a typo. d6 is right, the other math is incorrect, d6 system. OK, I was doing this at 3:00 in the morning.

OK, geometry around the central metal. And it's a little hard to see from this, so I'm going to help you out. So here there are no upper or lower ligands in the code one state. So you just have the ring system. So what is this geometry?

Yeah, so we have square planar geometry. And then in the code three state, you have a methyl group above. And now you're also interacting with this lower ligand. So now our geometry is what?

And what do we call this core and ring that has four points of attachment? Tetradentate. Right? Dent from teeth like claws grabbing onto your metal. OK so before we do our last chemical equilibrium, do we have a winner? We have a winner.

We have a winner. We do not need a tie breaker. OK, we'll announce that at the end. And if you're the winning recitation, please come down to collect your t-shirts.

OK so very briefly then, chemical equilibrium. So this B-12 enzyme which catalyzes the reaction, it not only uses this transition metal, but it also hydrogen bonds to the folic acid and lowers that transition state energy. And so here is the enzyme.

And this enzyme exists in multiple confirmations. So we can think about chemical equilibrium in terms of enzyme structure. Chemical equilibrium applies to so many processes, not just a plus b equals c plus d.

So here we have our B-12 enzyme, the B-12 is bound here. And this is the state, it's closed. B-

12 is highly reactive, so it needs to be protected. When you bind the enzyme that binds the folic acid, it opens a little. When you bind the folic acid, it opens a lot and it's able to do the methyl transfer reaction.

Then it needs to close up again to protect the methyl group. And then it needs to go on to transfer that methyl group to the enzyme that makes Acetyl-CoA. So you have all of these equilibrium, which are shifted by the binding of various things, the binding of the other enzymes or the binding of substrates.

So the important point is that enzymes are dynamic. Chemistry is dynamic. This is not about just chemistry in the solid state. Chemistry in solution is cool! And chemistry in solution can save the planet.

[APPLAUSE]

[MUSIC PLAYING]

CATHERINE DRENNAN: So if you appreciate this, this is how we're going to make biofuels and save the planet. All right. We have what I would consider as a bit of an upset. The winner of the 2014 t-shirt clicker competition is Jay's Recitation.

In second place, we have Lisa's recitation in second place. And in third place, which will also have a prize, we have Odin's Recitation. So good luck on the final. It's been a pleasure.