CATHERINE DRENNAN: Next hand out-- thermodynamics. Yes. Yes. I love thermodynamics. All right. So what is thermodynamics? So thermodynamics and kinetics I feel go together, but for kind of weird reasons we do thermodynamics now and we do kinetics at the very last unit of the semester. Part of the reason for this is that kinetics is often a unit that students can pick up really fast, and so I like doing it at the end when everything-- your world is sort of crazy and you have something that you can get a grasp on pretty easily for the last unit. So anyway, I'll tell you a little bit about kinetics now because we won't get to a lot of it until later.

So thermodynamics deals with energy change and spontaneity of reactions. And thermodynamics brings you three of my favorite things in chemistry, which are [MUSIC PLAYING] delta H, [CYMBAL CRASH] Delta S, and [DRUM ROLL] delta G. I love these. I live my life around these things. I believe entropy should always be increasing. And I love nothing more than free energy. That's great stuff. So today we're going to talk about delta H. Next week we have delta S and delta G.

What about kinetics? What does kinetics bring us? Well, kinetics brings us the rate or speed of a reaction. It can bring us fast reactions and it can bring us slow reactions. I like kinetics too. I kind of like the fast to be honest with you.

All right. So thermodynamics and kinetics. One. thermodynamics tells us whether something is going to happen spontaneously or not, but kinetics tells us the rate at which it happens. So let's just think of an example for a minute.

You may have heard-- this commercial happens a lot around Valentine's Day. Diamonds are forever. So actually, thermodynamically, graphite is favorable to diamonds. It's more stable. So graphite or coal-- thermodynamically, this is the stuff. Diamonds-- diamond is not forever. That's really a kinetic statement. It's there for a very long time, but you know it isn't inert.

So here's an important question. What is the best ring for one geek to give another geek? The thermodynamically stable one or one that is more kinetically slow to react, more stable, more

inert. Inert is reaction. What do you-- I should have a clicker question on this, I know. I don't know what you think. But actually, the answer is, in my opinion, neither of these.

Come on. There's only really one ring that any geek really wants. Green Lantern's ring has the power of chemistry at your fingertips. Who cares if something's inert? If you're the Green Lantern you can do whatever. So that's the ring. Anyway--

AUDIENCE: What about the one ring?

CATHERINE DRENNAN: Oh, one ring. Yeah. I like the Green Lantern ring, but I guess next-- maybe we should open a blog on this. It's a really important question.

So let's think about bonding for a minute. So thermodynamics is telling us about energy change. It's telling us about spontaneity. And so we need to think about energy that's going in. So kinetics is telling us about how fast. Thermodynamics is really telling us about stability. How stable is something? How much does it cost to break it apart?

So we're back to bond association energies. We have the change in the dissociation energy E to the little d. It's the energy to break a bond. We've seen this plot before. Now we have methane. We're breaking off a hydrogen from it, which is actually very hard to do. Scientists would love to break apart methane and make methanol, but it's a hard thing to do.

Up here we have unfavorable reactions. When the atoms are too close, then you have a sweet spot where the positions of the atoms are just right to form a bond. That's when you get methane. And then, if you put in energy, you can pull this off, is they go far apart with the radius this way. Your bond will dissociate. You always have to put energy in to get it to dissociate.

So now we can think about it-- we thought about this in terms of bond dissociation. We've seen this before, but now we can think about it in terms of a new term, which is delta H B, or bond enthalpy.

So bond enthalpy is the change in heat accompanying the dissociation of a bond and that's measured at a constant pressure. In fact, if we relate delta H to Delta E-- delta H equals delta E plus whatever change in pressure or volume. And often, this term is pretty small, so people often really think about reactions in terms of these being pretty similar to each other.

So for gases, the difference really is 1% to 2%. And if you're talking about a liquid or a solid it's

really a negligible difference. So we often really kind of think about these things in the same way. We think about the energy going into a system to break the bond, or we think about the bond enthalpies. And bond enthalpy, delta H, is often easier to measure, so it's very convenient.

So again, bond enthalpies You always have to put energy in if you're going to break a bond. So it's always going to be positive. It always takes heat. It always takes something to break a bond. And so breaking a bond is endothermic. Heat must be added. Whereas bond formation is exothermic. Heat is being released.

And so we can think about this-- again, when you form a bond those-- we saw with MO theory-- there's more electrons in lower energy in the bonding orbitals than in the antibonding orbitals. They're happy. This is a lower energy state. So if you're going to break that bond, breaking up is hard to do. And there's a song that verifies that statement. Breaking up is hard to do.

You always have to have heat. But when you go from that stable stay out-- when you form those bonds, it's like kind of the married couple, often get a little boring. They're in a low energy state. It's hard to get them out of the house and so they release all of their energy and they form this nice, little, happy, stable couple. So when you do bond formation that's an exothermic process.

So we can talk about standard bond enthalpies. When you see this little circle up there that means it's a value that's at standard conditions, where your reactants and products are in their standard states. And so we can think about what are some delta H or some bond enthalpies for different kinds of carbon hydrogen bonds.

So here's our friend methane. If you're going to pull off a hydrogen you have to put energy in to do that, and the bond enthalpy for that is 438. Now we can think about some other kinds of carbon bonds. We talked about this one. We have it here in the classroom.

So if we pull off a hydrogen from that, it's plus 410. So similar but not the same. If you now substitute three flourines for three of the hydrogens that changes your value a little bit, but not much. If you substitute chlorine it changes it a lot more. Same with bromine. So it depends. The bond enthalpy depends on what else is around that atom that you're pulling around. So it's not always the same value. It's different. It depends on what else is there.

So often you'll have a table that will report mean bond enthalpies. And they take all the bonds enthalpies and they get the mean value, and they're usually within 8% of each other. And for a carbon hydrogen bond it's around 412 is the mean bond enthalpy.

But when you're using mean bond enthalpies to calculate something, you have to realize that there can be some pretty big differences depending on what's around that bond that you're going to break. So those are some bond enthalpies.

Why are they important? Well, they're important because the difference in bond enthalpies between a product and a reactant can tell you about the enthalpy of that reaction. The enthalpy of the reaction of breaking of bonds and forming new bonds, or the enthalpy of reaction, which is delta H R-- sub R. And that is in the standard state in that case.

So let's talk about enthalpies of reactions. So we have this symbol again. Standard bond enthalpy for a reaction. So if it's a little B it's a bond enthalpy. If it's a little R it's a reaction enthalpy. If it's negative value it means it's an exothermic reaction, and if it's a positive value it means that it's an endothermic reaction. So we'll use these terms a lot and you'll get very familiar with them.

So let's look at some examples of reactions. And here is one of my favorites, and it is yes.

[MUSIC PLAYING]

It has it's own song.

- (SINGING) Photosynthesis Aah. Photosynthesis. Aah. Photosynthesis. Aah. Photosynthesis does not involve a camera or a synthesizer, although that's interesting too. Photosynthesis is how the plants take in light from the sun and turn it into energy. It's actually a thing on which most life depends here on the planet Earth. Photosynthesis. Aah.

CATHERINE DRENNAN: OK. That gives you an idea. Unfortunately, every time you will hear the word photosynthesis you'll go Ah. It happens. I'm sorry about that.

So photosynthesis. Amazing reaction. People right now are trying to duplicate it in industry to solve the energy problem. Good luck with that. But I know. I wish them good luck. That would be awesome. We use the opposite of that reaction for our energy. So we take sugar and use oxygen to break it down, which is an awesome thing because this has a really negative enthalpy of reaction minus 2816 kilojoules per mole. It's huge. And we store this in something

called ATP.

So since this is-- and I'm going to need the help of the TAs for a minute because we're going to do a very quick demo at the end of today's class. This reaction is exothermic big time. It's a big negative, which raises the question, if it's that exothermic-- really big value. We have sugar in air. Why we should feel heat? Heat should be released. So I think we should do this demo now and see whether that's true.

So I have a bag of sugar and it is sealed under nitrogen so there's no oxygen in there. And I forgot my safety glasses but I'll try to-- sorry about the front room. I should have had a stellar announcement that you might want to sit back. But I'm going to cut this open and let O2 in. So there should be a lot of heat coming out.

AUDIENCE: [INAUDIBLE] the things inside it individually wrapped?

CATHERINE DRENNAN: Oh, you know what? They are individually wrapped. All right, so this is not going to work. So I need the TAs to come down here, please, and you've got to help me unwrap them. Has anyone done the experiment yet? Do you feel heat coming out?

AUDIENCE: Yeah.

CATHERINE DRENNAN: You do?

[LAUGHTER]

All right. I better try it up here. Let's see. I'm going or unwrap mine. It's not working very well. So it turns out that heat should be released but this is very slow. So we don't feel the heat when we unwrap our Hershey's Kisses. I encourage everyone to try this experiment at least once. But the way that we harness this energy in our bodies is that we have catalysts, which are enzymes, that speed up the reaction. And that's how we get the full force of this reaction out.

So that is actually our introduction to thermodynamics. And next time we're going to talk about how we're going to calculate these delta Hr, these heats of reaction.

So we were talking about delta H, and so we want to pull out the handouts from last time. And we were at the bottom of page two with three different ways to calculate delta H. So our delta

H of reaction, delta Hr, the reaction enthalpy.

So I introduced you to bond enthalpies, and today we're going to look at how you use bond enthalpies to calculate reaction enthalpies. And remember, bond enthalpies-- sometimes it has nothing. Just delta H. Sometimes it's delta H sub B. Capital B for bond. And we're going to look at that.

Then we're going to look at how you can calculate delta H for reaction from the standard enthalpies of formation, and I'll introduce you to what that means. And then, also tell you about Hess's law where you can combine known reactions that have known delta H's to get a new equation and calculate a new delta H for that reaction. So three different ways.

So we're going to start with way one, which is bond enthalpies. So here is the equation for calculating bond enthalpies. So we have the delta H0 of the reaction equals the sum of all of the reactants bond enthalpies minus the sum of all the product bond enthalpies. And so this is bonds broken minus bonds formed.

And so let's think about this for a minute and think about what would be true. If you had stronger bonds in the products than in the reactants, what would be true? And this is a clicker question. All right. Let's just take 10 more seconds. OK Yep.

So now let's think about why this is true. So it's good news that most of you know that negative means exothermic and positive means endothermic. And let's look at why this is true. So let's look at both of these. So if we have bonds stronger in the products-- you can just think about the equation. So if you are bond stronger in the products this is a bigger number and that's the smaller number, which is going to give you a negative answer. And a negative value is exothermic.

And you can think about the equation stronger bonds here. A bigger number minus the smaller number. Positive or endothermic. But let's think for a minute about why this is the case and rationalize it because on an exam this is one of the equations that you're not given, so let's help you remember why this would be true.

We can think about this-- if you're going to break bonds-- and this isn't in your notes but people get confused by this, so I'm just going to write a little bit on the board. So if you're going to break bonds you need to put energy into the system to break bonds. And we talked about this before. And since we have exam two coming up we'll just do a little review of some of the

things that might be on the exam. So you don't have this in the handout we're doing right now, but you had this in the lecture nine handout. And something like this might be on the exam so we should be thinking about it.

So remember, if there was no energy that you needed to put in to break a bond-- if breaking the bond required no energy there would be no bond. So when the energy is zero there's no bonds. These two are not-- these things are not bonded together. And when you do form a bond, you go down an energy here so it's at a lower state. It's more stable. That's why it forms a bond. If it was less stable it wouldn't be forming a bond. But if it's more stable, lower in energy, a larger negative number, then a bond forms.

So to break this bond you have to put energy into the system. So breaking bonds always involves energy in. But forming bonds-- so if we're forming bonds then we're going to have energy out. So we're at a lower place here. So if we want to break bonds we have to put energy in, but if we're forming bonds then we're going to have energy that these guys had that is going to be released somewhere. So energy goes out of the system.

And the farther down we have the stronger bonds, the more energy you have to put in to break. But also, the more energy that comes out when the bonds form. So energy in to break a bond, but when a bond is forming it goes to a lower state and that energy is released.

So now we can think about what happens if you have a reactant with weak bonds. So if the reactant then has weak bonds, how much energy do you have to put in if it has weak bonds to break them? Not a lot. So we have just sort of a little bit of energy in. Little energy in to break those bonds.

Now in the products, if we have strong bonds, how much energy goes out if we're forming strong bonds? A lot. So energy out. We have lots of energy out. So that was the first case that we had. So we had something where the bonds were stronger in the product and we said that this was negative. So net here we have heat or energy out is released, and so that's an exothermic system.

Oh, the boards work today. And if we have the other-- if we have, say, strong bonds in the reactants, then we have to put a lot of energy in. Big energy in. And if we have weak bonds that are being formed, we're not getting much energy back so the net here is that you have heat in or heat absorbed. And it's an endothermic reaction.

So this is just one way to think about it. Remember, whenever you are going to break bond you always have to put energy in to break the bond. And when a bond is formed that energy is released. So we are thinking about the net of the processes, and that's why this equation works for us.

So keep this in mind. This is one of the points that people get confused on the exams. And sometimes like they say, oh, thermodynamics. I just don't understand it, and they're not keeping calm and sciencing on. They're getting all stressed by thermodynamics, and it's only this confusion. That's it. So if you work this out then thermodynamics will be your friend and you will love thermodynamics like I do forever. Just kind of keep this in mind and those diagrams in mind and you'll be all good.

All right. So let's do an example now. So we can use these bond enthalpies in this equation where we're summing up all our reactants. And sometimes you see some of a little i here for i reactants minus j products. So the sum of all of the products.

And it really is a lot here because we're talking about breaking every bond. We're talking about forming every bond. So this is not a huge molecule, but let's think about how many bonds we're actually going to be breaking here.

So these are all the bonds that are broken. They're not quite as many being formed here. So bonds broken. We have carbon hydrogen bonds, and we have seven of those. So 1, 2, 3, 4, 5-- let's see if I can count them-- 1, 2, 3, 4, 5, 6, 7. There it is. I need my glasses.

OH bonds. We have these guys up here. One, two, three, four, five. We have CO bond over a one double bond over here. So we also are going to have these ones here. One, two, three, four, five. We have the double bond over there. We have five carbon bonds. The one single bond here. And the carbon bond is one, two, three, four, five.

And we have OO bonds. We have six of those. Thank goodness. I didn't have to count anymore. It's already labeled. And then the bonds formed. So we're going to have these. So it's six of those, so we have 12 altogether and we have also 12 over here.

So first you have to count. And counting is not one of my strengths, so I don't like doing it this way and I'm going to show you two other ways to calculate the same thing. But we can take this and sum these all up. We can look up the mean bond enthalpies for every single one of these types of bonds, multiply them by the appropriate coefficients, and come up with a sum

for all the bonds for i number of bonds that you have in the reactants. And you can do the same in the products for j number of bonds that you have in the products and come up with these numbers.

So if you were told that you have to do it this way-- use bond enthalpies and you know how to do it-- or if it's an easier problem and you're only, say, breaking two things and forming two things this isn't a bad way to do it. For big molecules this is definitely a nuisance. And if we sum all of this up together-- and so for the total number we have reactants minus products. And so if we subtract this we get minus 2,740. And the actual value is minus 2,816. So it's not even the best agreement when you do it this way.

And the reason was, if you remember last time, we were talking about the bonds. Mean bond enthalpy is about 8% difference. So if you had, say, CH in a system that has all the rest of the atoms on carbon or H, that's a somewhat different value than if all of those other H atoms were substituted with bromine or if all those other H atoms were substituted with carbon. Then the bond enthalpy for that CH-- it depends on what else is bonded to the C. And so there's about 8% difference usually in the values.

And so overall, you're not going to get much better. You certainly are not going to get better than eight. So agreement of 3% is pretty good, but it's not all that precise because we're using these mean bond enthalpies, which don't depend on the actual value in that particular system.

So we can do better than this, and it can be also easier. And it'll be easier if we use standard heats of formation. So this is delta H sub f, f for formation. So the delta H sub f not for standard value is equal to the reaction, delta H, if you're talking about a reaction that involves one mole of compound being derived from its pure elements in their most stable state and in their standards state. So this is standard state 1 bar and room temperature.

So let's calculate for the same reaction glucose plus oxygen going to CO2 plus water and see if we can get a little bit more accurate value that way.

So let's think about what's happening in this reaction. So every time we oxidize glucose we're forming water. And so we can think about the heat of formation for liquid water. So again, this would be one mole coming from pure elements in their most standard state. So we have to think about where the hydrogen is coming from and where the oxygen is coming from.

So hydrogen in its most stable form is H2 gas, and oxygen in its most stable form is O2 gas.

So that's then the equation balanced for one mole of H_2O liquid being formed. And we can look up the delta H for this-- that delta H of formation-- for this reaction as written is the delta H of formation, and it's minus 285.83 kilojoules per mole.

So now let's consider what else that we're forming, water. And we're also forming CO_2. So CO_2 is derived from carbon in its most stable state, which is graphite as we discussed before, and also O_2, oxygen. And O_2 oxygen gas is the most stable state there. So for this reaction as written that is the delta H of formation of CO_2 gas and it's minus 393.5 kilojoules per mole.

So those are our products. We also have two reactants. One of our reactants is O_2. So it's what's doing the oxidation. And we're going from O_2 gas to O_2 gas. This is the most stable state. So what do you think the value is here?

AUDIENCE: 0.

CATHERINE DRENNAN: 0. Yes. So if you have an element already in its most stable state, its heat of formation is going to be 0. Because it's already the most stable state, so the heat of formation is 0. And every year, I think, on an exam someone's trying to see if they can calculate a delta H of a reaction and they're looking and they're like, oh, I want to use heats of formation because I know that's a lot easier but a value is missing from my table. And they're like, the value is missing from the table. And the TA doesn't know how much information or whatever to give.

And if you think you should have a value on an exam and you don't think about, is that element already in its most standard state? Perhaps it's zero and that's why it's not listed on the table. So keep this in mind. This can be very useful to remember.

All right. One more thing is involved in the equation. We have glucose. So we can think about the reaction that forms glucose from elements in its most stable state, and we've actually talked about all these already. We have O_2. That's in its most stable state. Carbon graphite. H_2 gas. And so this reaction as written-- it has a heat of formation of minus 1,260 kilojoules per mole.

So now we can calculate the delta H for the oxidation of glucose. The delta H of the reaction from these delta H's of formation. And here's the equation. Delta H of the reaction is equal to the sum of all of the delta H's of formation of the products minus the sum of the delta H's of formation of the reactants.

So this now is one of the sources of confusion because if you're using bond enthalpies it's

reactants minus products. If you're using delta H of formation it's products minus reactants. So that's why I spend a little time over here thinking about what's going on with the bond enthalpies, so hopefully no one will fall into this delta H pitfall over here and you'll keep the reactions-- the equations straight.

So now we can plug it in. If you remember the equations this is pretty easy. So we have our delta H of reaction. We have 6 times the heat of formation of our products over here. CO2. 6 times the first product and then 6 times the second product, which is water, minus the first reactant, which is our glucose, and we have one of those, and we have 6 oxygens. So products minus reactants.

Pay attention to the stoichiometry. You need to multiply the heats of formation by the number of molecules so then we can put in the values that we just saw. C02 minus 392 for our water minus 285 minus-- and here we have a minus 1,260 for glucose. And again, 6 times 0 because the oxygen is already in its most stable state. And if we do the math correctly, you get minus 2,816 kilojoules per mole, and that is exactly the experimental value. And it's because the heats of formation are also experimental, so this is a very precise number. When you use the heats of formation you're going to get a much closer value to experimental. And this was a bit easier than thinking about every bond that would be broken and every bond that would be formed.

One more way that you can do this. And this takes advantage of something known as Hess's Law and the fact that enthalpy is a state function, which means that it's independent of path. So if you were climbing a mountain and you wanted to go from point A to point B, you could climb all the way up to the top and go back down or you could just go right from A to B and it wouldn't matter. Your delta H would be the same in both cases because it's independent of path. So it only matters what the values are for your reactants and your final products. It doesn't matter how you get from the reactants to the products. Delta H is going to be the same.

And because of this, you can take different routes if their equations for different parts of your reaction that are already known with values of delta H-- you can add those equations together and then add together the delta H's to get a new value.

So Hess's Law-- if there are two or more equations that are added to give another chemical equations then you can add up the delta H for the reactions of each of the individual equations

to get the sum for your new equation. So let's do this now, again, for glucose and oxygen.

So if we have these three equations here-- this one is showing glucose plus oxygen being broken down to the elements that are in the most stable state. So graphite, H2 and O2 for glucose. And then our 6 O2s are there on both sides because it's already in the most stable state. We're going to be forming CO2 from the elements in the most stable state and also water.

So we can add these together, paying attention to the stoichiometry. So we need to multiply this equation by 6 and this equation by 6, and then we should be able to do some canceling and make sure that we're getting our equation of interest. So we can cancel these 6 O2s with these, we can cancel these O2s with these, and we can cancel this H2 with this. And that leaves us with glucose plus 6 oxygens going to 6 CO2s and 6 waters. So this is going to work now.

And now, since we added this together to get this, we can add our delta H of reactions together to get a new delta H of reaction. Oh, sorry. I forgot to cancel my graphites. There we go. Now we're good. Didn't notice them there.

So our delta H for reaction. We saw before that the formation of CO2 from elements in its most stable state was minus, so now we've just changed the sign because now we're going the opposite direction. So we have a positive value for that delta H of reaction. Now we have 6 times the heat of formation of CO2 and 6 times the heat of formation of water because that's what those equations are. Those are the heat of formation reactions. And if we add this all together then we get the number that we saw before. So it doesn't matter what path we take. We're going to get to that same answer.

And this one, since we're using information that all has to do with heat of formation, it's not really very different from the one we did before. But you can use Hess's Law for delta H of reactions that are not heats of formation. If equations are available that can be added or summed to get your net reaction, then you can add or subtract these values to get a new delta H. Don't forget kilojoules per mole.

So we have our three different ways-- bond enthalpies, heat of formation, and Hess's Law.