CATHY DRENNAN: So now, we're going to move on to talk about spontaneous change. And so this is today's handout. So spontaneous reaction is a reaction that proceeds in the forward direction without any kind of outside intervention, like heat being added, for example. It just goes in that direction.

So we can talk about the following reactions are spontaneous at constant pressure. And we'll see later that temperature can make a difference between whether something's spontaneous or not. But constant pressure, here's an example, iron plus oxygen. And what is this in layman's term an example of?

AUDIENCE: Rust.

CATHY DRENNAN: Rust, yes. And many of you are probably aware of this, rust is a spontaneous process. It's something that people try to do something about.

You don't want your car to rust. If you're new to New England and you're from a part of the country that doesn't get so cold, you'll look at people's cars and you're like, wow, look at all that rust all over them. Yes, rust happens, especially in New England.

And delta H here is negative. Is this endothermic or exothermic?

AUDIENCE: Exothermic.

CATHY DRENNAN: Exothermic, minus 824. Here is another spontaneous process. This molecule is ATP. And it will hydrolyze, which means react with water, forming ADP.

So ATP is triphosphate. ADP is diphosphate. So one of the phosphates-- and here's the phosphate-- comes off. It hydrolyzes off. And this is a spontaneous process. And we also have a delta H0 of minus 24 kilojoules per mole.

And remember, when we oxidize glucose in our body, we store that energy in ATP. And we want that ATP to be around. And then when we break ATP apart, it releases the energy. So

this is a very important biological process. And you have a negative value, exothermic reaction.

But there's a few other examples of spontaneous reactions. One of them is this one. And we've probably all experienced this.

If you're from New England, you've seen snow melt or ice melt, solid to liquid. If you're from a hot part of the world, you probably had ice cubes in your nice, refreshing drink with maybe a little umbrella on the top. Anyway, everyone, I think, has seen ice melt. But here, delta H0 is of positive value. It's endothermic.

Also, if you have ammonium nitrate, this will just come apart in a spontaneous reaction. Delta H here is plus 28 kilojoules per mole. So is delta H the key to spontaneity? It is not-- plays into it, but it is not the determining factor.

So if delta H0 is not the key to spontaneity, what is? It is free energy, yes, particularly Gibbs free energy, or delta G. And I'm really happy they decided to add the Gibbs free energy, because another thing of energy would be a lot. So having this free energy having abbreviation of G, I think is a good thing-- so Gibbs free energy.

So Gibbs free energy depends on delta H. But it also depends on another term, which is T delta S-- temperature and delta S, change in entropy. So delta G is the predictor of whether a reaction will go in the forward direction in a spontaneous fashion or not.

So let's just think about the sign of delta G and what it means. So again, at constant temperature and pressure here, delta G less than 0, negative delta G, is that spontaneous or not?

AUDIENCE: Spontaneous.

CATHY DRENNAN: Spontaneous. Positive delta G is not spontaneous, non-spontaneous. And delta G equals 0. It's one of the other things that I am very fond of, which is equilibrium.

So delta G indicates whether something is spontaneous or not. Negative value, spontaneous in the forward direction. Positive value, not spontaneous in the forward direction. And equilibrium, the thing we all try to reach in our lives.

So let's look at an example and calculate what delta G is going to be. So we saw this equation

already. We have a positive delta H0. And now, I'm telling you that delta S0 is also a positive value. So we can use this equation.

And this is really one of the most important equations in chemistry. Figuring out this equation was really a crowning achievement. And you'll be using it a lot. Not just in this unit, but pretty much in every unit from now on, you will be using this equation.

So room temperature, pretty much we're not doing-- occasionally, we'll do something not at room temperature, but we like room temperature. And we like it in Kelvin. So delta G0, so we plug in our delta H value. So it's going to equal delta H minus the temperature. And if the temperature isn't given in a problem, you can assume that it's 298.

And now we need to plug in delta S. But I left a blank here to make a point, which is that delta S's are almost always given in joules per kelvin per mole. But everything else is given in kilojoules. So you want to make sure you convert your units, or you're going to come up with very funky answers at the end.

So from joules to kilojoules, so now plus 0.109 kilojoules per kelvin per mole. And we can do this out now. So we have plus 28 minus 32.48. And why don't you tell me how many significant figures this answer has. 10 more seconds.

So at least some people got it right. We've identified once again a weakness, so rules of adding and subtracting. So we have 28 here minus 32. There are no significant figures after the decimal point here. So we're just left with 4.

So when we're doing multiplication or division, we consider the total number of significant figures. But with addition and subtraction, you gotta pay attention to where the decimal point is. And when we get into the next unit, there are logs. And those have special rules of significant figures. Yes, very exciting.

So delta G0 is negative here, although delta H is positive. So this reaction is spontaneous. It's not hugely. It's a pretty small number, but still, it's spontaneous.

So let's consider our friend over here that we've been talking about-- glucose being oxidized to CO_2 and water. You practically should have the delta H memorized for that at this point. Now, I'm telling you what the delta S0 is. And it's positive 233 joules per kelvin per mole.

And we can plug this into our equation to calculate a delta G0, again remembering to convert

joules to kilojoules to do this. And so now, we see that it has a very negative delta G0 here, minus 2,885 kilojoules per mole at room temperature. So at room temperature, this reaction is spontaneous but slow. We saw that with the candies that had glucose in it. We opened them up, and no water or CO2 were obviously being liberated in this reaction, because it is slow.

And now, a clicker question. I want you to tell me whether it would be spontaneous at different temperatures or not? 10 more seconds.

Yep. So it is spontaneous at all temperatures. Not all reactions are, but this one is. So if we go back here, the reaction is spontaneous at all temperatures. And that's because, to be spontaneous, you want a delta G that's negative.

If delta H is negative and delta S is positive, then you'll have a negative minus a negative. So it doesn't matter what temperature is. This will always yield a negative delta G0.

So other reactions, that might not be the case. But if you have negative delta H and a positive delta S, it will be spontaneous. So negative delta H, again, exothermic, heat release.

And a positive entropy is a favorable thing. Entropy is always increasing. So if this reaction has increased in entropy, it will be much more likely to be spontaneous.

So let's talk about entropy. So entropy is a measure of disorder of a system. Delta S is the change in entropy. And delta S, again, is a state function.

So one example of entropy in New England are these stone walls that do not look absolutely beautiful. There are often stones falling everywhere. And it doesn't matter if these stone walls that were probably built in 1600s or 1700s in New England fell totally apart and were rebuilt, now we just care about how the wall is compared to the way it started.

So delta S, again, is a state function. It doesn't depend on path. And so if you get out and walk around and go like on the Minuteman Trail and see some of the historical sites where Paul Revere rode his horse along a lot of stone walls, there's a New England poet who writes about this, Robert Frost. And he said, "something there is that doesn't love a wall." And that something is entropy.

AUDIENCE: [LAUGHTER]

CATHY   Entropy does not love a wall. Entropy does not like order. Another example, those of you who

DRENNAN: are learning more about me as a person know that I am a fan of dogs. This is my dog Shep. Shep does not like going to the groomers, does not like it.

And I think that this is because he's been at my office hours and he knows that increasing entropy is favorable, decreasing entropy is not. And he says, really, this violates the laws of thermodynamics, what you're doing to. Me and you should cease and desist. But anyway, he still get haircuts.

So entropy, again, is this measure of disorder of a system. You have a positive delta S, which is going to be an increase in disorder. And a negative delta S is going to be a decrease in disorder. And disorder, you can be thinking about this as internal degrees of freedom in your molecule, thinking about this as vibrations. All sorts of different things can lead to increase or decrease in entropy.

But we often think about changes in entropy depending on if the reaction is changing in phase. So gas molecules have greater disorder than liquid. And liquid has greater disorder than solids.

And so a solid has all its molecules lined up. And liquid can move around a little bit more. But gas really can spread all out. So in terms of entropy and changes in entropy, we can think about the phase change that's happening and even predict if something's going to be an increase in entropy or not.

So let's just look at one example. So without a calculation, predict the sign of delta S. And this is a clicker question. Let's just take 10 more seconds. And can our demo TAs come down?

Yep, good. So you predicted positive, which is the correct answer. And so here, we're going from a liquid to a liquid and a gas. And so going to the gas, that will increase the disorder of the system. So delta S will be positive.

So now, we're actually going to do a demo of this particular reaction. And so we have hydrogen peroxide, which can just be bought at a CVS or local drugstore. And it will go to liquid water and also oxygen gas.

And so how do you see a gas? And you can see it by putting it in with soap bubbles. So as bubbles of oxygen form, the soap bubbles will bubble out. And so you can see it.

And you can also add some kind of food color. And we have yeast as a catalyst to make it go a

little bit faster. So let's see if we can actually see disorder increase. I don't want the mic. If you want to just say-- if you want to talk at the same time, here's a mic.

AUDIENCE: I might do that.

CATHY DRENNAN: You're not going to do that, OK.

AUDIENCE: Yeah, we will.

CATHY DRENNAN: Oh, you do. OK.

AUDIENCE: Is this on? This on? Yes, it is. OK, great.

So what we have going on here is we've got this container. It's filled with water. And what I did was I added about 4 teaspoons of yeast. The yeast, as Cathy said, is going to act as a catalyst. It's actually a biological species. It's a living species that's actually going to catalyze this reaction.

What Erik is doing is Erik is pouring some hydrogen peroxide. He added some soap. So as you see in the reaction, the H2O2 is going to break down into water and gas-- the gas being oxygen.

And what we don't want to happen is we don't want just the gas to escape, because then you guys can't see it. So what Erik is doing right now is he's adding some soap. The soap is actually going to catch, if you will, the escaping gas and turn it into a foam. And what we should be able to see is the foam kind of escape from this container.

You ready? OK. So hopefully, this will work. We should put on our goggles.

[LAUGHTER]

Smells really bad. OK, ready? And-- get out of there, look at that. Hey! Wow, that worked a lot better than we thought it was going to work.

CATHY DRENNAN: And so this is sometimes called the elephant toothpaste demo, because that is sort of, if you were an elephant, what you would probably be brushing your teeth with, I don't know. Yes. So this is--

--entropy increasing. So let's just see if we can quickly talk a little more about entropy and then we'll end. So entropy of reactions can be calculated from absolute values. And again, we can use this equation here.

So we have a delta S for a particular reaction, can be calculated from the delta S's of the product minus reactants. So again, we have products minus reactants. The absolute value, or an absolute delta S, S equals 0 for a perfect crystal at a temperature of 0 kelvin.

You never really talk about S by itself. It's always really delta S. And S of 0, this is like the saddest thing for a crystallographer, because you know you're never going to have a perfect crystal, even if you go to 0 kelvin, I feel like at least experimentally. So S equals 0, to me that's kind of sad.

So if we just put in for this reaction that we just did, we can put in our values here. And we can put in we're forming liquid water. And we're forming O2 gas. And we're using two molecules of hydrogen peroxide-- H2 O2 here.

And so now, we can calculate what that delta S0 is. And it's a value of 125 joules per kelvin per mole. So again, products, water and gas, minus reactants, pay attention to the stoichiometry, and you can get your delta S value.

And why is it positive? Again, we already talked about this. It's because it's going from liquid to a liquid plus a gas.

And then, if we plug these values in again to see if it's spontaneous, we can use this equation and plug in our values, making sure we change our units. And we can see that, in fact, this is a spontaneous reaction, because it's negative here. But you already knew that, because you watched it go spontaneously.

So most of the time, you can't do the demo. So then you can use this awesome equation right here. So that's where we're stopping for today. And we'll see you all on Friday.

So if you take out your Lecture 16 notes, the bottom of page 3, we had an example about the melting of ice at room temperature. So we did a little demo for you at the end of class last time and calculated that the reaction was spontaneous for hydrogen-- hydrogen peroxide is pretty reactive. And we watched the O2 bubble go.

And we did that calculation. So we're thinking about, not just delta H, but we're thinking about delta S. And we're now thinking about delta G as well and how they all play together.

So when we started last lecture, we had talked about the fact of some reactions that were spontaneous where delta H was negative, where it was exothermic, where heat was released. But then we also gave some examples where delta H was positive and said, but these are also spontaneous reactions.

We all know that at room temperature ice will melt. We know that that's a spontaneous reaction. But the delta H for that reaction is actually a positive value. It's an endothermic reaction.

So when we're thinking about these reactions and spontaneity, we have to be thinking about delta G, no just delta H. And delta G has to do with delta H and delta S. So sometimes, delta S is the driving force behind whether a reaction is going to be spontaneous. Whether the delta G will be negative or positive, delta S is making that determination.

So we can calculate what a delta S for reaction is if we know the entropy values for the products. And it's the sum of the entropy values for the products minus the sum for the reactants. So when we're doing heats of formation, we also had products minus reactants. But we have one exception to this products minus reactant rule, and that's when we're using what? What thing are we going to do reactant minus products?

AUDIENCE: Bond--

CATHY DRENNAN: Bond?

AUDIENCE: Bond enthalpy.

CATHY DRENNAN: Enthalpy, right. But here, we're products minus reactants. So we can plug those numbers in. Our product is our liquid water. Our reactant is our solid water, or our ice.

And we can calculate what the delta S0 is for this reaction. We can put in our values. And we get a positive value, positive 28.59 joules per kelvin per mole. And delta S's tend to be in joules. Everything else is in kilojoules. So keep that in mind.

And why do you think this reaction has a positive value? Why is delta S greater than 0? What

would be your guess for that? What's happening?

AUDIENCE: [INAUDIBLE].

CATHY DRENNAN: Yeah, so we're going from a solid to a liquid. So we're increasing the internal degrees of freedom. The molecules of water can move around more in a liquid than they can in a solid.

So this is increasing the disorder of the system. You're increasing entropy here, because the water molecules can move around more. There's more freedom of motion. So delta S is positive. It's increasing.

And then we can use that to calculate delta G0, Gibbs free energy. We can plug in our delta H value minus T, room temperature, times delta S, which we just calculated, making sure that we convert from joules to kilojoules. And then our units will be kilojoules per mole.

And here, delta G0 is a negative value. So it is spontaneous. We all know it's spontaneous. We've observed this happening. So even though delta H0 is positive, it's an endothermic reaction. Ice melts at room temperature, because the delta G is negative.

So let's talk a little more about delta G. So let's talk about free energy of formation and the last page of this handout. So free energy of formation, delta G sub f. And so this is analogous to delta H of formation-- so the change in enthalpy of formation.

So again, when you have a little value here, this is standard Gibbs free energy of formation for the f here. And that's the formation of 1 mole of a molecule from its elements in most stable state and in their standard states. So we can have tables in your book of these values.

So your book, in the back, if you haven't explored, the back of your book gives lots of tables of things, including information about delta G's and delta H's and bond enthalpies and all sorts of other things. Redox potentials, we haven't talked about yet, lots of tables. So you can look this up.

Or if you have already, say, looked up your delta H of formation, you can use this handy equation-- delta G equals delta H minus T delta S. But if we plug in our delta H's of formation, we can get our delta G's of formation. So how you're going to calculate delta G of formation depends on what information you're given.

So let's think a little bit about what it means for particular delta G's of formation-- if they're

positive or if they're negative. So let's look at an example. And we saw this before. This is the formation of carbon dioxide from elements in its most stable state, which is graphite carbon and O2 gas. So these are the elements in their most stable state, forming CO2.

Now, I'm telling you that the delta G0 is minus 394.36 kilojoules per mole. And we can think about what this information tells us, that this is a fairly large negative number. So if delta G of formation is less than 0, what's going to be true thermodynamically? And this is a clicker question. Let's just take 10 more seconds.

Interesting. So let's think about why this is true. This might be a deciding clicker question. We'll see.

So if it is negative value for delta G, a negative value for delta G means that it's spontaneous in its forward direction. So here, the formation from the elements in their most stable state, if this is spontaneous in the forward direction, it also means that it's non-spontaneous in the reverse direction. That means once CO2 forms, it's going to be stable compared to the elements from which it came, because it's non-spontaneous going in the reverse direction, or at least that's the way that I like to think about it. So relative to its elements, it's stable-- spontaneous forward, non-spontaneous in reverse.

So this is kind of bad news for us, because there's too much CO2 in our environment right now. It's a greenhouse gas. And wouldn't it be awesome if we could just encourage it all to go back to its elements, form more oxygen, which we could breathe. How lovely? Make some nice graphite. Maybe compress it, make some diamonds.

But no, it is quite stable compared to its elements. So CO2 is in our environment causing global warming. And it's going to be hard to solve that problem, not easy to solve that problem. So this is unfortunate news that thermodynamics gives us.

So then we can look at the other. If you have a positive value for delta G of formation, then it's thermodynamically unstable compared to its elements. So it's spontaneous going in the reverse direction. So it's unstable.

So thermodynamics tells us whether something is stable or unstable. And kinetics tells us about whether things will react quickly or not. So something can be kinetically inert-- it might take a long time to react. But thermodynamics tells us stable, unstable.

So thermodynamics is great, but it doesn't tell us anything about the rates of reactions. So

nothing about the rates, and that's kinetics. So really thermodynamics and kinetics are very important for explaining reactions. And we'll talk about more kinetics at the end.

So to calculate a delta G for a reaction, it depends, again, what you're given. You can sum up the delta G of formation of your products minus your reactants. Or you might use this. You'll find yourself using this equation a lot.

This, again, was a crowning achievement of thermodynamics, that delta G equals delta H minus T delta S. So, again, whatever information you're given, you can use that to find these values.

So we're not done with this equation. We're going to switch handouts. But we're going to continue with that exact same equation.