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CATHERINE DRENNAN: Yeah, let's show the answer. All right. For a special treat, special benefit-- I'm not sure what to call it-- something special later in the class, does someone want to tell me why that's the right answer?

AUDIENCE: Well as we did last lecture, we crossed off the k_2 because that's the slow step. So it doesn't matter as much.

CATHERINE DRENNAN: Yeah. And so when you get rid of that, when the k_{-1} is really fast compared to k_2 , k_2 is very small compared to that. So you get rid of it. And that simplifies the expression.

So temperature-- today's lecture is largely about temperature. But we're going to tie in all sorts of other things we've learned over the course of the semester. So I'm very excited. Some of my very favorite topics are coming back today.

So effective temperature, we talked about this a little bit when we were talking about making bread, adding your baking soda and about rates and why you put things in the oven. And we talked about it has to do with also the spontaneity, whether you change the temperature and what your ΔH and ΔS are. But we also talked about rates and that increasing the temperature often increases the rate.

So many of us have observed this. You increase the temperature, you increase the rate. But today we're going to talk about how you can quantitatively say how much the rate might be changed-- the rate constant might be changed if you increase the temperature.

So in 1889, it was a wonderful day for Arrhenius. He had been trying to plot different values of rate constants versus temperature to see what would happen. And then he tried natural log of the rate constant k versus inverse temperature. And he got a straight line.

And scientists always get very excited when your data falls on a straight line. It means you figured out some relationship between two values. So here is the Arrhenius plot. And we'll

introduce some terms.

So again, we're plotting the natural log of k versus $1/T$ over temperature, $1/T$ over inverse kelvin over here. And here is our plot of this straight line that Arrhenius found. Natural log of k on the y-axis versus $1/T$ gives you a slope then of minus the activation energy-- so E_a is activation energy-- over R , our good friend the gas constant.

And then the y-intercept over here is the natural log of something called A . We have a lot of different A 's in this particular unit of kinetics. This one is factor A , sometimes called the Arrhenius factor, A for Arrhenius. It has a couple of different names. But importantly, it has the same units as k , our rate constants.

So what this plot told Arrhenius back in 1889 was that rate constants vary exponentially with inverse temperature. So this was the first kind of connection between rate constants and temperature that could be used to kind of come up with quantitative numbers. So factor A , this Arrhenius factor, and the activation energy, E_a , depend on the reaction being studied. So they have to be measured for the particular reaction.

So it's a clicker competition. So we'll have a bunch of clicker questions today. And why don't you tell me if you think factor A is temperature dependent?

All right. 10 more seconds.

Yep. The answer is no. And so what is this factor A ? If we think about this in terms of the plot, what it is is the rate constant when $1/T$ is equal to 0. Because it is the y-intercept.

And when $1/T$ is equal to 0, what has to be true about T ? Yeah. Infinitely large. So factor A is the rate constant at an infinitely large temperature, at a huge temperature. So it's the fastest that particular reaction could ever go at this infinitely huge temperature.

So that's what factor A is. And of course, we can't plug things in and say, how fast is this at an infinitely huge temperature? So conveniently, you can get that value out of plotting your data. You measure a bunch of rate constants versus temperature. And you plot it this way, and you can calculate this sort of maximum rate constant possible for this reaction if you had this infinitely huge temperature.

What about activation energy? Do you think that's temperature dependent?

All right. 10 more seconds.

So no, it isn't. And so if we sort of just think about it back here, the answer is no. Again, you plot the rate constants over all these temperatures to get one value out of the slope. So it is largely independent of any kind of temperature. You get one activation energy for the reaction in question.

But it does depend on the reaction, for sure. There isn't just one value for this for everything. It depends on the materials.

All right. So let's look at some other ways that we can express the Arrhenius equation. So we have the Arrhenius equation written as a straight line. And we can also do something very, very simple to it, which is switch these two terms. And that gives us what is officially known as the Arrhenius equation.

So natural log of k equals natural log of A , this Arrhenius or factor A , minus the activation energy over the gas constant times temperature. And of course, if you want to solve for k , you take the inverse log of both sides. And so then k is going to be equal to this factor A -- again, measured for every reaction in question-- e to the minus E_a , the activation energy, over RT .

So here is our equations. These will be on equation sheets, so you don't have to memorize them. But you already, if you've been studying your equation sheet for exam four, realize that there's a lot of symbols that are very similar in these units.

So we have a , in nuclear chemistry, activity. So just keep in mind what equation is what. When you're talking about nuclear decay, you don't have your activation energy term. So that should give you somewhat of a clue. So one of the challenges in the final is making sure you know which equation is which.

So let's look at an example now where if we're given some of the information, we can solve for other things. So an example, this is classes at lunch time. So we can think about the hydrolysis of an average lunch of sucrose to form a molecule of glucose and a molecule of fructose as part of the digestive process.

So some of you might have eaten already. You might be digesting sucrose-- it comes in many different forms-- right now. So using the information about activation energy, we can predict

what the rate constant is going to be at a different temperature.

So some kind person measured the activation energy for this digestive process at 108 kilojoules per mole and also figured out that the k observed, observed rate constant, for this reaction is 1.0×10^{-3} per mole or per at normal body temperature. And so now we're asked to calculate what that rate constant should be at lower temperature, 35 degrees Celsius, somewhat below body temperature. So how are we going to do that?

Well, let's remind ourselves of our equations, our Arrhenius equation. So we know what E_a is. We were not told what our Arrhenius factor A is. We don't know that.

But we do know one of the rate constants at one of the temperatures. So if we combine these two equations, then we have an appropriate number of variables to solve for the rate constant at the new temperature. So let's combine those two equations.

So we have natural log of k_2 , our rate constant, at temperature 2 minus the natural log of the rate constant at temperature 1, which can also be expressed as natural log rate constant 2 over rate constant 1. And our natural log of the Arrhenius factor drops out. And so we have minus E_a , our activation energy, over our gas constant times $1/T_2$ minus $1/T_1$ over the first temperature.

So we can put in our values that we're given. So we have our first rate constant down here, the rate constant at the first temperature. We put in our temperatures, making sure we convert them to kelvin because our gas constant is in kelvin.

And also, we are going to convert our activation energy from kilojoules to joules because we want to cancel our units. So now we can cancel joules. We can cancel moles. And we can cancel kelvin.

And so that gives us a new rate constant, 7.6×10^{-4} per mole or per second. And this is a lower rate at a lower temperature. And in fact, that is often true. You have a lower rate at a lower temperature.

And this is one of the reasons why it's a really good idea to keep your body temperature at body temperature. And around this time of year, people come in to MIT from warmer climates. And they do not have appropriate clothing. And so your body does not work well in the cold.

The rates slow down. You're not digesting things. Your body is really not doing anything at the

rate it's supposed to be doing these reactions because they're nicely tuned to the appropriate body temperature. So go out and buy a winter coat.

So this now, this equation that we just derived shows us the relationship between rate constants and temperature. So again, $\ln k_2/k_1 = -E_a/R(1/T_2 - 1/T_1)$. And if we look at this equation, we'll realize that if we have a very large value for this activation energy, this E_a term here, that's going to mean that the rate constants are very sensitive to temperature.

If this is small, there won't be a big difference between k_1 and k_2 . But if the activation energy is really big, there will be a big difference between k_1 and k_2 . The rate constants will be very sensitive to temperature.

All right. So now let's think about rates and temperature. And let's think of a cold temperature. Let's think, for example, of liquid nitrogen temperatures.

What do you think happens to an enzyme? You have enzymes in your digestive process that are hydrolyzing sucrose that you might have had for lunch. What do you think happens to enzymes if you put them at liquid nitrogen temperature?

They will slow way down. One would say they would stop working entirely. They would just sort of be, we call it frozen.

And in fact, I use this all the time in my research. So one thing we do, we study the structures of proteins. And so we grow these lovely protein crystals. And what we can do, we take these-- a lot of times, the proteins or enzymes in the crystals are active. They're able to convert reactants to products.

And so we can soak in reactants and then take our crystals and dunk them in liquid nitrogen and then determine the structure of that. And if we do it at different time points, you can actually kind of walk through the mechanism of the enzyme. Watch what happens at various different states.

So this is a very common thing that's used. We like to do things at liquid nitrogen to see things sort of-- we sort of pause it when it's dumped in liquid nitrogen. It stops what it's doing. And we can capture its structure.

What do you think about non-enzymatic reactions? Do you think they're also going to be

slowed down? I don't know. Should we do an experiment and find out?

AUDIENCE: Yeah.

**CATHERINE
DRENNAN:** Yeah, I think we should. So we now have-- let's bring out our demo TAs. We now have glow sticks. Glow sticks are in fact chemicals in there that when you break them, you have a chemical reaction.

So we're going to do this. And we're going to break them and watch them glow. Let's break them and put them in here first. And then we're going to cool them down and see what happens to the chemical reaction.

Here, let's have a little help over here. Please break some of these.

AUDIENCE: How do you break them?

**CATHERINE
DRENNAN:** You break-- see, you just kind of snap them and then shake them up. And I think we'll bring down the lights so you can all see these pretty well.

So now the chemical reaction is going. And so we can see the chemical reaction. That's what's wonderful about glow sticks. You can observe the chemical reaction because it causes it to glow.

Move so everyone can see. Now we're going to see what happens to the chemical reaction when it slows again. When the chemical reaction is slowed down, you won't see it anymore. So it'll stop glowing.

That should be good. We'll do all of them, and we'll see. It'll take a little bit of time. But it should not be too long.

And hopefully, it'll slow down faster than the liquid nitrogen destroys the plastic cups. Yeah, I think you can see it with the first one now. Mary, why don't you come down here? We have something else for you to do.

Let's put some liquid nitrogen in here. Let's bring up the lights because our glowing has stopped. So another thing that liquid nitrogen changes the properties. So Mary will demonstrate to you what happens to a flower.

And just like right now, the flower does this. But let's put it in liquid nitrogen and see what happens. Give it a decent soak.

And now smash it.

[LAUGHTER]

Thank you very much, our lovely assistant. I will brush off my computer later. We have more flowers, and apparently there's a broom somewhere. So if we finish class, for some lucky other individuals, you can come down and smash the rest of the flowers.

So liquid nitrogen really changes the property of things. Sometimes it's used by dermatologists to remove warts or other things. They'll dab some liquid nitrogen on you. And I always feel like paying a lot of money to go have that done-- I have liquid nitrogen around my lab.

But then I'm like, yeah, I probably have enough liquid nitrogen burns on my fingers already that I don't want. Crystallographers who use this a lot, they'll often be in a situation where you have this liquid nitrogen. And it's sort of dripping on you. But you have your crystal, and if you let go, then you'll destroy your crystal experiment.

So you'll have liquid nitrogen sitting in your palm. And you're like, OK, I'm going to get a burn. Or I'm going to lose my crystal.

And so you decide how important that is. And so sometimes a crystallographer will walk up to you and go, see that scar? That's 1.2 angstrom data, baby, right there. So we suffer for our science sometimes.

So liquid nitrogen is very-- changes the property. Cold things are different than warm things. Buy a winter coat. So everything slows down in the cold, in terms of elementary reactions. Our rate constants slow down.

So now let's think about a reaction and what's called a reaction coordinate and consider what's happening in a reaction. And then we're going to come back to thinking about the effect of temperature, where temperature really makes a difference. We'll quiet down a little.

So considering the reaction coordinate, reaction coordinate the reactions of-- you bring your reactants together and form your product. So two things coming together to form something

else, that is a reaction. And as you go along in the reaction, that's your reaction coordinate. And we're going to also introduce this term of activation complex or transition state.

So two molecules can collide. Two molecules colliding, bimolecular. But every time those two molecules come together, they're not necessarily going to form a product. Why?

So only when that collision energy is greater than some critical energy-- which is sometimes called E_{min} , this sort of minimum energy to get this reaction to go, or as I like to call it, the activation energy, E_a , that's what we've been talking about, our activation energy-- will you get a reaction. So you need to have enough energy in your two things coming together. Those two things coming together need to have a critical energy for them to react.

So why is this true? You need to have that critical energy. But why? Why is this necessary?

So it's necessary because before this reaction takes place, even if it's a very happy reaction, things need to occur. So the two things coming together need to often distort. Bonds might have to be broken. And new bonds need to be formed.

And while that is occurring, while there is distortion of the bond or bonds are breaking, you need to have some potential energy to do that. You need some energy to make that reaction go. So the potential energy of the system increases first while these distortions are happening.

So the encounter then between them, you form some activated complex, or what's known as a transition state. And that activated complex, it can go on to form a molecule. Or from that activated complex, the two molecules may just go apart again.

So what determines whether they're going to go on happily to form their complex or going to depart from each other, never to form a larger molecule? And the thing that determines the fate is that critical energy. So only those molecules with that sufficient energy to allow for those bond distortions and rearrangements will be able to go on and make this.

And you can think about this, I think, in terms of a couple, a relationship, that there's always some work that has to go into it. It's never perfect. And if you put in this effort and this work, you can go on. And if you don't really have it in you and you're like, ah, you walk away.

You don't have that critical energy. You don't have that special overcome, that activation energy, and you go back. So let's just take a look at some molecules checking each other out and figuring out if they have what it takes, if they have that critical energy.

Let's watch and see what happens. Here they come. They're finding each other. They're circling each other.

And oh my goodness. They had the critical energy necessary. And they formed a bigger yellow molecule. There they go. What a happy ending.

So only those molecules that have that critical energy can go on and form their complex. And so here is where temperature comes into play. Here is where temperature becomes really important.

Because they need to have a certain amount of energy. And there's a relationship between the kinetic energy of molecules and their temperature. So let's take a look at this plot over here.

So this is, on one axis, fraction of molecules. And on the other axis, we have kinetic energy. So if you're at low temperature over here, most of your molecules are going to have a low kinetic energy. But it will tail off.

And there will be some molecules that will have a higher energy. And if this line here represents that minimum energy, that critical energy or that activation energy, in blue here we have those low temperature molecules. Only a very small fraction of those will have the energy to react, will be able to overcome that minimum energy, that critical energy needed.

Now if you're at high temperature, more molecules have a higher kinetic energy. And if you see over here shaded in orange, way more molecules have that critical energy, have the energy necessary to distort those bonds and go on to make a molecule. So here's where temperature is important. So kinetic energy, pass it on. So let's draw some reaction coordinates and think about what's going on. Yeah.

AUDIENCE: For this idea of collision, could it also apply to the association reactions? Because that's [INAUDIBLE] molecule. Or are [? they still into ?] each other? [INAUDIBLE]

CATHERINE DRENNAN: Yeah. So if you're talking about the forward reaction and the backward reaction of things, whether it's two molecules that are coming together to form things or molecules breaking apart, there's a critical energy both directions. And we'll see that, actually. It's a good question. That kind of leads us in to our reaction coordinate diagram.

So most of this is in your notes. There's a few things that are not. But let's look at a reaction

coordinate diagram.

And by that, I mean we have Potential Energy, or PE, on one side. And on the other axis, we have what's called just the reaction coordinate. So if you're asked to draw a reaction coordinate diagram on a problem set or an exam, asking for potential energy versus reaction coordinate.

Now our reactants are going to have a particular amount of potential energy. And in this case, it's up here. And our products are going to have some potential energy down here.

And there will be a difference in energy between these, our ΔE . But these reactants aren't just going to be able to go to products without overcoming some kind of critical energy. So before they can go down there, they need to go up here.

So we have the activation energy, E_a for forward direction. Also, if you're down in products and you want to go back to reactants, there's also a barrier that you have to overcome. And it's not just this. It's all the way up here.

And so this would be the activation energy of the reverse reaction. And this dashed line on the top is our transition state or our activated complex. Both are two expressions that are used kind of interchangeably.

So this transition states, some kind of weird mixture where they've come together, and they're sort of breaking and distorting. It's not our final products. That's down here. But you need to go up in energy, overcome an activation energy barrier. So the transition here, you need to go up, and then you go down.

So now let's think about all of these energy terms. And what's true is that the change in energy-- this change in energy between reactants and products is equal to our activation energy for our forward reaction minus the activation energy of the reverse reaction. And this ΔE over here can be measured from a calorimetry experiment.

And you might recall back when we were talking about thermodynamics that E is kind of closely related to ΔH . So we had this equation at one point that ΔH is equal to ΔE plus the change in PV . And we said that for gases, there's about a 1% to 2% difference between ΔH and ΔE . But for solids and liquids, it's pretty much the same. So you can think about this ΔE like you were thinking about ΔH , for the most part.

So now for this, if we have some of the numbers-- if you know activation energy in the forward and the reverse, you can calculate delta E. If you know delta E and one of the activation energies, you can calculate the other. So I'll tell you for this particular reaction what these values are.

And I was going to bring colored chalk, and somehow that didn't happen. So the activation energy in this is not in your notes. So I'll write it down. Is 132 kilojoules per mole. And I'll also put it here, a little bigger, 132 kilojoules per mole. And for the reverse reaction, it's 358 kilojoules per mole and minus 358 kilojoules per mole.

And so if we do the math here, we will calculate that delta E is equal to minus 226 kilojoules per mole. So would you expect that to be an endothermic or exothermic reaction? Exothermic. Right. And we can put that value also in here, minus 226 kilojoules per mole.

So what's really important here, even though it's exothermic reaction, it's not going to just go without having those molecules have some critical energy necessary to overcome this activation energy barrier. You still need energy. You need to go up here before you can go down there.

So just sort of thinking about this in layman's terms, this idea of these activation energy barriers, for me whenever I sit down to write a grant or write a paper, I think, wow. I sit down at my computer, have my cup of coffee. I know that we're about to get scooped on this data. So I really should write this paper, a little stressed about it.

Then I think, wow. I could write a lot better if my office was clean. Now I hate cleaning my office. But compared to writing a paper, it's pretty good. I don't mind doing it.

So then clean the office. Then walk the dog. Maybe do later some laundry. Lots of things happen.

And then eventually, you hear from the collaborators. They're like, I need this paper now. And you're like, oh man.

And so that stress gets you over that activation energy barrier, just catapults you over. Or you wait to a grant-- you start six months early. And then the week before it's due, suddenly you have that nervous energy that gets you over that.

So many of you have probably experienced this. And you know, if you need some extra help

with an activation energy barrier to do the rest of those extra problems for exam four, you can come talk to me. And I'll stress you out and get you right over that activation energy barrier.

But the thing to keep in mind is that look at this slope in this case down here. So often it's just that little something to get you over. And then it's smooth sailing.

So you can work these games with yourself. You've just got to get over it and know that once you're over that barrier, it's all going to be good. So you can get yourself over. You should never forget about activation energy barriers.

There's always a barrier. Am I right? There's always some kind of barrier. Anything you're going to do that's worthwhile has some barrier associated with it.

So now let's think about the results of these barriers, again, coming back to this idea of temperature. So for an elementary reaction-- again, that's a reaction that occurs exactly as written. It's a step in an overall reaction mechanism. There's always a barrier, always a barrier.

Barrier is always positive. It's always there. And so if you increase the temperature, you're always going to increase the rate of that reaction. It's always going to help get over that barrier.

But increase the temperature, increase the rate. But for an overall reaction, temperature is a little more complicated to predict. So if you increase the temperature, it's not always as clear what's going to happen to the rate. Because you can have a lot of different steps involved.

It can be exothermic and endothermic. A lot can be happening. Changing the temperature, you're changing k . So to think about an overall reaction, we need to understand reaction mechanisms.

And that's really convenient because we just talked about reaction mechanisms on Monday. So you all know how to write out reaction mechanisms. So let's just practice.

So for this example, we have two molecules of NO plus O_2 going to 2NO_2 . Step one, fast and reversible. NO plus NO , going to an intermediate. Then the intermediate is reacting with oxygen going to two molecules of our product.

So we can write the rate of formation of product based on the slow step, or if we didn't know the slow set, on the second step or the last step. So two molecules, again, two molecules are

being formed. k_2 times the concentration of the intermediate times the concentration of O_2 .

But we have an intermediate. So we need to solve for the intermediate in terms of rate constants, reactants, and products. But now we're told we have a fast step followed by a slow step. So we know how to do this.

And remember, when you have a fast, reversible step followed by a slow step, this first step approximates an equilibrium reaction. There is not much of the intermediate that's being siphoned off in the slow step. So pretty much, when you form the intermediate, it's going back and forth just like you have in an equilibrium situation.

And just to emphasize this, I'll share a little picture here of the beach in the summer when you don't need your winter coat. And here we have my daughter and her best friend. And they are trying to empty the ocean with this princess bucket.

And one can ask the question, is this going to affect the tides? Is the ocean going to be different? But the rate at which my daughter and Aiden fill up their buckets and bring them over here, that's a really slow step compared to everything that's going on in the ocean.

So when you have a very slow step like a kid and a long distance with a princess pail, you don't really need to worry about that. And you can think about the fast step as being an equilibrium. This is not being siphoned off enough to worry about it. And so that makes it easier to solve for your intermediate because then you can just do it by an equilibrium expression. So in the clicker question, tell me how I can do that.

AUDIENCE: I think you're good.

CATHERINE OK. 10 more seconds.

DRENNAN:

So let's just take a look at that. So again, we're writing our equilibrium expression for the first step, products over reactants. And then we can rearrange it to solve because the product here is our intermediate. So we can solve for the intermediate in terms of K_1 and our reactant.

And then we can substitute it in. And that gives us this. So we had the $2k_2$ here. Now we have our K_1 and our $N O$ squared. And here we have our oxygen there.

So now we have a rate law that doesn't include any intermediates. I'm just going to put that back up here if you didn't get it written down. Now let's think of what happens with temperature.

So this is an elementary rate constant, little k_2 . So you increase the rate when you increase temperature. And here is our expression again that tells us about that change.

So now for the equilibrium constant, the effect of temperature depends on whether the reaction is exothermic or endothermic. And does anyone remember what the name of the equation is that tells us about temperature effect with equilibrium constants? Yes. The van 't Hoff equation.

I told you that some time in the future I'd ask you for the name of this equation. And that time is now. You don't really need to know it. But it's just fun. There's not many names for equations in general chemistry.

Look how similar these equations are. These are very similar equations. So we have the natural log of rate constants here.

Here we have the natural log of equilibrium constants. Here we have our activation energy. Here we have ΔH .

So if the reaction is exothermic, if we increase the temperature, what happens to our equilibrium constant? Does it increase or decrease? You can just yell it out. It decreases.

Now let's think about what happens here. So our k_{obs} now has an elementary rate constant term, which is going to increase with temperature. And it has an equilibrium constant term, which is going to decrease with temperature for an exothermic reaction. So we have these going in opposite directions.

So overall, we want to think about the magnitude of our activation energy term for our rate constants. And we want to think about the magnitude of our ΔH term in terms of the equilibrium constants. So for the particular reaction in question, you can look up.

The activation energy is a small number. And ΔH , again, it's exothermic. And it's a big number.

So then if you're thinking about that, if E_a is small and positive-- E_a is always positive. There is

always a barrier, always positive. Then the rate constant is only going to increase a little bit. But ΔH is a big negative number, so the equilibrium constant is going to decrease a lot.

So for this particular reaction, increasing the temperature actually decreases the K 's. And so for any reaction, it depends on the magnitude of E_a and the magnitude and the sign of ΔH . So again, large E_a means very sensitive to temperature. Large ΔH means that the equilibrium constant is very sensitive to temperature.

For an elementary rate constant, it's always going to increase with temperature. Because E_a is always positive. There is always a barrier to overcome. Temperature always increases a rate constant.

But for an equilibrium constant, it can increase or decrease because ΔH isn't always positive. Like the activation energy barrier, it can be positive or negative. So the magnitude of ΔH , how big a number it is, tells you about the magnitude of the change, how much the equilibrium constant will change.

Will k_1 and k_2 be almost like each other or really, really different from each other, those equilibrium constants? And the sign of ΔH , whether it's positive or negative, tells you the direction of the change. Will it increase or decrease?

So I just want to show where we're going with this because it's just super exciting. Yes. We're back to Le Chatelier. This is what I was so excited about. Remember, Le Chatelier told us, when we apply a stress to the system, the system responds in such a way to minimize that stress.

So if we increase the temperature, according to Le Chatelier, what direction will the reaction shift, in the exothermic or the endothermic direction? What is it? The endothermic.

So you increase the temperature. You add heat. It shifts in a direction to minimize that or to use up that heat. So we'll end with one last clicker question. And we'll finish this concept on Monday.

But we want to think about how Le Chatelier and what we've known already applies here. So why don't you tell me which of these diagrams is exothermic and which is endothermic? Because we're going to tie this all back to temperature and Le Chatelier.

AUDIENCE: We don't have that question.

CATHERINE We don't have that question. OK. Then we will not do that question.

DRENNAN:

AUDIENCE: [INAUDIBLE] the question.

CATHERINE OK. So I'll just give you the answer to that. And then we'll see who the winners are. So that

DRENNAN: one is endothermic. And this one is exothermic. And we'll finish the rest of this on Monday.

But for now, can you tell us who the winner is? No, it's not coming up.

AUDIENCE: It's Dan.

CATHERINE Top two.

DRENNAN:

AUDIENCE: Dan and Jay.

CATHERINE Dan and Jay have beat out the other folks. So we know who's in the playoffs. All right. Friday

DRENNAN: exam. See you Monday in class to finish the handout.

All right. Let's take 10 more seconds on the clicker question.

So let's take a look at this. 56% do you have the right answer. So rate constants always increase with increase of temperature. That's our little k 's. Because there is always some activation energy barrier to overcome. There is always a positive barrier.

Whereas, for equilibrium constants, K , you can have a reaction that's exothermic or endothermic. And so that will change. It either increases or decreases because ΔH can be positive or negative.

But activation energy barriers are always positive. There's always a barrier. Always a barrier to doing anything that's important. I've got to calm down.

Le Chatelier tells me that when a stress is applied to the system, I should respond in such a way to minimize the stress. It's a very calming rule in chemistry. Reactions don't like stress. And they'll respond in a way to minimize it.

So we've been talking about Le Chatelier for a lot of the semester. And we've talked about the

effect of temperature on reactions previously. So if you add heat to a reaction, it will want to respond in such a way to minimize the heat or absorb the heat. So it shifts in the endothermic direction.

So we've already talked about this. And nothing is new here today. But today, I'm going to give you a different way to rationalize why that happens. So we're not changing what happens. We're just going to come up with a new way to rationalize the why.

So we ended last time with these two diagrams. And we identified one as endothermic and one as exothermic. So these, again, are our reaction coordinate diagrams. We have PE on one side. What does PE stand for again?

Potential energy. It stands for other things too, but in a reaction coordinate diagram, that's what it is. And then the reaction coordinate going this way. So we go from reactants to products along the reaction coordinate.

So here in this endothermic reaction, we have our reactants down here, our products up here, and a very large activation energy barrier for the forward direction, a much smaller activation energy barrier for the reverse direction. With the exothermic reaction here, we have a smaller activation energy barrier for the forward direction and a bigger one for the reverse direction. So let's look at the one equation that will be on the exam that will not be on your equation sheet. I think this is-- for this unit, this is the one that will be not on your equation sheet.

This change in energy is equal to the activation energy for the forward direction the of reaction minus the activation energy for the reverse reaction. And again, this is our ΔE here. And this is our ΔE here.

ΔE is like ΔH . If you're talking about a gas, it's 1% to 2% different. If you're talking about a solid or a liquid, it's negligibly different.

So if we look at this endothermic reaction here, we have a big forward activation energy barrier minus a small reverse activation energy barrier. So that's going to give us a positive value for ΔE . And it'll be an endothermic reaction.

And if we look at this equation again and fill it in for the exothermic reaction, we have a small barrier in the forward direction, a big barrier in the reverse direction, and a negative value for ΔE and ΔH . It's an exothermic reaction.

Now let's think about what happens when we increase the temperature. So if we increase temperature, it's a lot easier to overcome this forward activation energy barrier, the big one. And that's going to shift it to products.

And this is because the small activation energy barrier, it's not that hard to get over something that's a small activation energy barrier. It's not hard. But if it's a really big barrier, it's hard to get over that barrier. You need a lot of kinetic energy. Increasing the temperature will give that kinetic energy to overcome that barrier.

Remember that when molecules come together, bonds are distorted and formed. The potential energy goes up first. And only those molecules with that critical energy that can overcome that activation energy barrier can go on to products. Increase the temperature, that allows you to overcome the big barrier.

Now if we look in this side, this is a small barrier. They weren't really having-- molecules were probably not having a huge amount of trouble with that barrier. The barrier that was hard was for the reverse direction.

So now you increase the temperature of an exothermic reaction. It's easier to overcome this big barrier, the reverse barrier. And you have a shift toward reactants.

So this is what we had seen before. You increase the temperature of an endothermic reaction. You go to products. You increase the temperature of an exothermic reaction. It shifts to reactants.

So these are the same things we saw before. But now there's a new rationalization behind it. Now we can think about this in terms of activation energy barriers.

So the important points to remember, big activation energy barrier, rate constant very sensitive to temperature. If you have a big barrier, increasing the temperature makes a big difference. If you have a small barrier, doesn't really matter that much.

Most of your molecules can get over that small barrier. So big barrier, increasing the temperature, more molecules can go. And so you're going to shift in the direction of the big barrier.