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Catherine Drennan and Elizabeth Vogel Taylor, *5.111 Principles of Chemical Science, Fall 2008*. (Massachusetts Institute of Technology: MIT OpenCourseWare). <http://ocw.mit.edu> (accessed MM DD, YYYY).
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5.111 Principles of Chemical Science, Fall 2008
Transcript – Lecture 34

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PROFESSOR: So, let's finish up new material today, new material Monday, and then we're done with the kinetics unit. So, we're going to talk about temperature, collision theory, and activated complex theory today.

So on the first day, we talked about kinetics, we talked about factors affecting the rates, and this was in your handout on that first lecture, but just to kind of review for a minute what we have talked about so far and where we're going. So these are some of the things we came up with are factors affecting the rates of reaction. People said mechanism affects the rate of reaction, so we talked about mechanism. Concentration of material, nature of material -- that pretty much fits in in every lecture. We've been talking some about that, say, if it's first order or second order, if you have a concentration term in there, or if you don't have a concentration term. The nature of the material, we're going to talk more about that today. Temperature is going to be the number one topic for today, and on Monday the number one topic is the use of catalysts to speed up reactions. So, by Monday we'll be done with this list.

So, what about temperature. So temperature, when I said what affects the rate of reaction, temperature was one of the things that you yelled out at me, and that's very much true, it has one of the biggest effects on the rate of reactions. So when we were talking about the gas phase, there was an observation made that the reaction rates tend to increase as the temperature increases. And most of you can think about this and are aware of it, and today we're going to talk more about the quantitative affect of this, how much does the rate of a reaction increase when the temperature increases, how do you know what equation do you use.

So, this idea has been around for awhile. So in 1889, Arrhenius plotted rate constants versus temperature, and he found that if he plotted the natural log of those rate constants versus inverse temperature, then he would get a straight line. So let's look at the plot that he had. So, he found that if he plotted natural log of the rate constants versus $1/T$, so units of $1/K$, that he got a straight line. Which means that the rate constants are varying exponentially with inverse temperature. So you have to use a natural log to get a straight line, if you don't use natural log, you wouldn't get a straight line here.

So, let's look at some of these terms that we have here, and here's our equation for the straight line, the natural log of k equals minus e_a -- e_a is activation energy, which we're going to talk a lot about today -- over R , R is our friend the gas constant, and T is temperature, plus natural log of A . So what is A ? A is called factor

a or sometimes it's called pre-exponential factor, and had has the same units as k, k being the rate constant.

So, let's think about this equation and this plot, and about factor A and this other term, activation energy. So, factor A and activation energy depend on the reaction being studied. So, it depends on the nature of the materials involved. So I said we'd talk again about nature of the material. So one kind of reaction's going to have one activation energy, another one will have a different one.

So, let's think about this term, factor A. What is it exactly? Do you think it would be temperature dependent? What do you think? How many people think yes, it would be temperature dependent? How many people think no? Some people are not going to commit. The answer is no. So, let's think about what factor A is. So, factor A is the rate constant at some really, really large temperature. So, if we look at this plot, the natural log of k equals the natural log of A, or k equals A if you're along this axis here. If you're along that axis here, that's at zero, so that's when 1 over temperature equals zero, then the rate constant equals factor A. What would be true about the temperature for 1 over temperature to equal zero? Very big. So, at the biggest, hugest temperature you can imagine, the rate constant's going to equal A. And so, factor A depends on the nature of the material being studied and you would have to determine what that value is. But it's definitely not temperature dependent. It's the value of the rate constant at an enormous temperature.

So, what about activation energy? Do you think that's temperature dependent? Why don't you tell me what you think. All right, let's take 10 more seconds.

All right, so I'd like you to discuss this amongst yourselves and see whether you're happy with this answer. All right, go ahead and vote again. All right, 10 more seconds. And the correct answer is? So, I think most of you will remember this answer. So the activation energy is not temperature dependent. You can calculate what the activation energy is by plotting the rate constants versus 1 over temperature, and then you get it from the slope of the line. So, activation energy depends on the nature of the material, but it isn't temperature dependent. So, we're going to talk a lot more about that today.

Before we leave this, I just want to say one thing about a clicker question. So, at the end of last time, we had our first repeat winner for a clicker competition. So, we thought that we might have an opportunity for recitations to see if they can -- if some other recitation can get a second win. So on Monday we're going to have our final clicker competition, and if somebody else does tie, one section, that we'll have a final one-time clicker question that'll be a run-off. And whatever recitation wins, we have special prizes for the members of that recitation. So that's on Monday. So you may want to review catalysis on Monday, if you feel that you're in the running for the grand champion clicker recitation.

All right, so let's go back to this. So we found out that no, activation energy is not temperature dependent.

All right, so what are you going to see on your equation sheet on the final, you may see a couple of different forms that are all equivalent to each other. So here is the plot of a straight line. It will often be written with just natural log of a and e a over r t terms reversed. So that's as a straight line, and this is often what you see for the Arrhenius equation. You can also get rid of the natural logs and have the term here

exponential, so you have k equals factor A times e to the minus, activation energy divided by $r t$. So, those are the equations, they're all equivalent to each other that you might see on your equation sheet.

So, it's also true that non-gases can exhibit this kind of behavior, and let me just give you one example of a non-gas that exhibits this kind of behavior and you tell me what this is. What is that? Crickets. So crickets exhibit Arrhenius behavior. They will chirp faster as the temperature gets hotter. So if you're out camping, sometimes it can be in the summer, it can be actually be quite deafening, and you were very happy to go back to the city where you only have ambulances and cars going, and you don't have this incredible racket at night. You can actually calculate what the temperature is by counting the number of chirps of the crickets and using a little equation. I think it's you count for 14 seconds and add 40 and that's the temperature in fahrenheit or something like that. So, not only gases do this kind of behavior.

All right, so activation energy, we're going to be talking a lot about this today. So, what is it exactly. So let's think about two molecules coming together. So when two molecules come together, you have this bimolecular process going on, but every time two molecules come together, they're not going to go on and form a product. You're only going to form a product when those molecules have a critical amount of energy. When they have the energy which allows them to react, that activation energy. If they have enough energy when they come together, they will go on and form products. So, that's what activation energy is, it's this critical amount of energy that they need to react with each other.

All right, so let's just think about what affects that critical amount of energy, and of course, temperature is going to be involved. So let's think about that. So if we have fraction of molecules on one side, and we have kinetic energy down here, let's think about how temperature is involved in this. So, at a low temperature, the fraction of molecules that are going to have enough energy to react is going to be less. And let's think about at a higher temperature, go like this, so this is high temperature, and we have low temperature up here. And then over here we would have our activation energy, the energy needed for a reaction. And you see, if you're at low temperature, only a small number of molecules are going to have enough energy to react, but if you're at higher temperature, a large number of molecules are going to have that critical energy to react. So, at low temperature, not many can react, at higher temperature, many more will have that energy -- will be able to overcome that activation energy, will have it and they can react.

So, temperature plays a big role here. So we can use this idea of activation energy to predict a rate constant. Let's look at an example. So, often people have sucrose in their diet, and the hydrolysis of sucrose will form glucose and fructose as part of this digestive process. And we can think about the rates at which that would happen in the body. So normally, we're at 37 degrees, that's normal body temperature, and we have the observed rate constant for that is $1 \cdot 10^{-3}$ per molar per second. But what happens if your body temperature is lowered, what happens if it was at 35 degrees, and to be able to answer that question, you need to know what the activation energy is for this process, and here it's 108 kilojoules per mole. So, we want to ask the question, what is the new rate constant at 35 degrees?

So, we can take our Arrhenius equations, and we can put a 1 by the rate constant for temperature 1, and a 2 for the rate constant at temperature 2. Now we can combine

these equations. Natural log of a cancels out, it's not temperature dependent so it doesn't stay in here. And so we can solve, we can subtract these two, or that's equivalent to dividing them, and so natural log of rate constant 2 over rate constant 1 equals minus the activation energy over the gas constant times this temperature term. Does this look at all familiar? Does this look like some other equation you saw once upon a time? Do you remember what that equation was called? Van't Hoff equation, right. And there we were comparing what instead of rate constants? Equilibrium constants, and instead of e^{-a} , what term did we have here? Δh , right. And it's good you remember that because we're going to come back to that at the end of today's class.

So, we can use this equation and plug in the values. We put in our activation energy, and remember to pay attention to units, because if you're going to cancel your joules with a gas constant, you want to make sure you've converted your kilojoules to joules, and then we can plug everything in and solve for k_2 .

So, here k_2 is 7.6×10^{-4} per molar per second, so it's slower. And this is one reason why it's really nice to have your body temperature stay the normal temperature. If you get too cold, your body processes, your enzymes are not functioning, everything is slowed down. And if you get too hot, that's not good either. So you really want to maintain it, and so for some of you who come to MIT from warmer climates, let me introduce you to the L.L. Bean catalog, they sell coats, they sell boots, and all sorts of things. So, this winter, when you come back for IAP, or for the term, you're well-prepared, and you don't have to prove that it's not good if your body temperature goes below 37 degrees.

All right, let's think about what else this equation tells us, and the other thing it tells us is that if you have a very large activation energy, if this e^{-a} is a very, very big number, that means that your rate constants will be very sensitive to temperature. So if this is really, really big, there's going to be a big change in your rate constants as temperature changes. And keep that in mind, we're going to come back to that later.

So, what do you think happens to the rate of an enzymatic reaction at liquid nitrogen temperatures? We looked at going from 37 degrees to 35, liquid nitrogen is pretty cold. So, not a whole lot happens at liquid nitrogen temperatures as far as enzymes go, and I'll just mention, so it slows way down, that this is a trick that I use in my research. So we have crystals of enzymes, and we can try to get structures in particular states by taking the crystals that have enzyme in it, and starting a reaction, and then dunking the crystals in liquid nitrogen to kind of stop it at a particular stage, and then you look at what the structure looks like. So that's one use.

So, we're going to also take a look at other reactions, we don't have any enzymes here, but some other things, and look at what happens when we get things to be very cold.

[EXPERIMENTING]

So, Dr. Taylor is pouring out some liquid nitrogen.

PROFESSOR: All right, so what we're going to look at is a reaction that we can see pretty easily here. Have any of you used glow sticks before, maybe trick or treating

or some other point. So basically, you may or may not know how they work. There's two compartments in glow sticks that have two different chemicals in them, and they're trade secrets so we can't put them on the board. But basically, what we have here is a reaction. A lot of reactions we know give off heat, or they give infrared light. Here we have a reaction that gives off energy as visible light. So would you call this an endothermic or an exothermic reaction here? Yeah, so this is an exothermic reaction.

So just as Professor Drennan was talking about with slowing down enzymatic reactions we can think about if we can slow down this reaction. So, we're just going to put it in the liquid nitrogen -- so, keep an eye on this, we'll do several controls of different colors here. So, see if an orange glow stick works the same. What we're looking to see is if we can slow down this reaction. What would we see if we slowed it down or even if we stopped it? Yeah, we're not going to see anymore color. So are you starting to see color loss in this first reaction here? So, we'll try green, and yellow. So, it looks like this first one might have stopped already, you see there's no color anymore here.

What would you expect if this heated back up to room temperature? Yeah, so hopefully, if you just keep your eye on this, we'll continue on with the lecturing, because I don't know how long it will take for it to warm back up the room temperature. But keep an eye and we'll see if we get the temperature back high enough to see the glow again.

And since we do have a liquid nitrogen here, it's too hard to resist freezing a flower. This has nothing to do with kinetics -- we can't even try that connection. But we will be freeze a flower. OK, she will try making -- good catharsis pre-exam.

PROFESSOR: So, has anyone had liquid nitrogen applied to them? It's used in doctor's offices, if you want a little something removed perhaps, put a little liquid nitrogen on and burn it off. Good premed training for you. I think we're pretty frozen here.

So it looks the same, but as you can see -- [INAUDIBLE] -- So I think that's all we can do [LAUGHTER] [APPLAUSE]

PROFESSOR: So I actually heard something interesting on NPR about liquid nitrogen removing warts and things like that, and they were talking about how there was something that was actually better than liquid nitrogen for doing that. Did anyone hear the story about what the thing was that was better than liquid nitrogen?

It was duct tape. And so some scientists had looked at what all the uses of duct tape are. And since most of you are planning on being scientists or engineers, duct tape will probably be an important part of your life in the future. And so, duct tape worked better than liquid nitrogen for removing warts. And they found that duct tape worked really well for a lot of things. There was only one thing they tried that it did not work well for. Anyone want to guess what that was? Repairing ducts, yes. Not really good -- there were many, many, many better ways to repair ducts than with duct tape, but I guess they decided that calling it wart removal tape was just not quite as catchy as duct tape, so it's still referred to as duct tape.

OK, so when you lower the temperature, things tend to slow down. But if molecules are going to react, they need to have enough energy, they need to have a high

enough temperature to overcome this activation energy. So that critical amount. So again, when the molecules come together, and let's just look at these for a minute, when they're coming together to react, and if they're going to react, there needs to be some energy associated with this, because you're probably going to have to break a bond, and that's going to take something, and then you may have to form a new bond, for example. So there needs to be a critical amount of energy, you need to be able to overcome that activation energy barrier for the molecules to react. So it always takes some energy for things to react and so you need to have enough energy.

And so, if those molecules have that energy, they'll come together, react, and you'll form products. If they don't have that energy, they're just going to go back to what they were, unchanged reactants. So you need to have sufficient energy to overcome that activation energy barrier.

So, this is just a little movie that shows two molecules coming together, and if they have enough energy to react, you will see a spark, and then the molecules will react. So, here we go. Molecule in red, in green, they're checking each other out. Do they have enough -- they had enough energy, and they reacted, and went on to product.

All right, so let's talk about this activation energy barrier and these activated complexes. OK, so in this example, you have NO_2 plus CO , and they can come together and form NO plus CO_2 . And that's going to take some amount of energy to react. And so, I'm drawing something that's called an activated energy diagram, and we have potential energy on one axis, and on the other we have what's called a reaction coordinate. And so, the reactants are going to have a certain amount of energy, so our reactants are going to have some amount of energy, and our products will have some amount of energy. But even though in this case the change, the products are lower in energy, and you have a ΔE for the difference between the reactants and the products, they can't go directly to products. They have to overcome an activation energy barrier. So they have to overcome some kind of barrier before they can react.

So, only ones that can overcome that barrier, that have enough energy to overcome this activation energy barrier, so the activation energy for the forward reaction, only those will be able to react. There's also an activation energy barrier for the reverse reaction on this side. So, if you go from products to reactants, you have to overcome that activation energy barrier. And up here, this is called the activated complex, so you have some kind of activated complex or transition state, so the molecules will come together, they'll form some kind of transition state up here, and then go down into products.

OK, so most of you are sort of familiar with the concept, I think, of this activation energy, we've been talking about it, but the idea of an activation energy barrier, I think is something that probably all of you can personally connect with. So, for me, one of the things that I find really hard to do is get started writing a long National Institutes of Health grant. They're about 25 pages long, they're single spaced, font 11, and they have point 5 margins on every side of the page, and it's really dense, and it takes a long time to sort of get going on that. And so, there is deadlines, and MIT is very particular, you need to have it to the Office of Sponsored Research five full business days before it's due at the National Institutes of Health, and then the Department needs to sign off on it. And I'll be looking at my calendar and I have those dates marked, and checking how many days I have left, and eventually, just

like getting started, it's like oh, there's so much to do, I have to read the literature, the new stuff that's come out on my topic. And I have to think about what projects I'm going to do in the future, and I have to write about the progress that I've made so far, which is not really what I want it to be. And so, I think a lot about how -- it's just overwhelming.

But then eventually something happens. Either it's tremendous fear that there's so few days left and you just have to do it. Sometimes it's going and getting an enormous cup of coffee and sitting down. You know, people have been known to sort of chain themselves to their desk, like they're not going to get up until they've written the introduction to the grant. So, a lot you can connect with this. That any new thing you start, there's some barrier that you have to overcome to get started with it. And often once you're started it's not that bad, and some of you may be thinking, exam 1 was a long time ago, I recall there was a lot of material on exam 1. And it seems really scary. But then the fact that I mention the final exam over and over in class is helping you get that energy that you need to overcome that activation energy barrier and start studying, because once you start studying you go, Oh yeah, I remember this, this wasn't so bad. So you just need to get over that activation energy barrier and you're all set.

So, molecules have to do the same thing, and the ones that have higher temperature have an easier time getting over that barrier. So, here we can talk about this general process. We can look at the individual numbers involved. So in this particular case, there's an activation energy for the forward reaction of 132 kilojoules per mole, and there is an activation energy for the reverse reaction of 358 kilojoules per mole. And there's also a Δe for the reaction, which is this line, from reactants to products, which in this case is minus 226 kilojoules per mole. So do you think this reaction is endothermic or exothermic? What do you think, exothermic or endothermic? It's exothermic, and if you look back in your notes, we talked a little bit about the relationship between Δh and Δe . And they're actually pretty similar. A Δh usually equals Δe plus a change in $p v$. So, for gases it's about 1% or 2% difference, and for solids, there's really negligible difference between Δe and Δh . So, they're pretty similar types of values.

So, we can think about what Δe really is, and so Δe in terms of activation energy is going to be equal to the activation energy for the forward reaction minus the activation energy for the reverse reaction. And in this particular case, we have 226 kilojoules per mole is our Δe , and for our forward reaction, we have 132 kilojoules per mole, and for the reverse reaction, the activation energy for the reverse reaction is 358 kilojoules per mole, and so these should all equal up to each other. And so, if you know two of these values, you can calculate the third. And this is one of the equations that you have to memorize for the final, because it has, it's sort of a conceptual thing that you need to understand what this diagram says, that this plus that is equal to that, that these all add up to each other. And if you have a negative value here, that means it's an exothermic reaction.

So, this Δe is a change in internal energy of the system, and you can determine that value experimentally, say, with a calorimetry experiment.

OK, so let's keep this in mind and go on and take a look at how this connects back with some other things that we have already talked about in this course. So, for an elementary reaction, and I think for all of us, there's always some activation energy barrier to overcome. There's always some positive activation energy to overcome.

And because there's always this activation energy to overcome, increasing the temperature is always going to increase the rate of an elementary reaction. It's always going to make it easier to get over that activation energy barrier. But for an overall reaction, increasing the temperature may not increase the rate of the reaction. So let's consider why that would be true.

So, here is a reaction that we've talked about before, we talked about this proposed mechanism where we have a fast reversible step and a slow second step. So we learned last time that we can write the rate of product formation from the second step, there are two molecules of NO_2 being formed, so we have $2k_2$, the concentration of NO_2 , and the concentration of O_2 . But this is an intermediate, so we need to solve for that intermediate.

So, in this case, we have a fast reversible first reaction and a slow second reaction. So this intermediate is going to build up, and it's going to be more or less an equilibrium with the reactants, because this is very fast, and only a little bit of this is siphoned off to make product, and so this creates an equilibrium type situation. So why don't you solve this intermediate for me, this is a review from the last class. OK, let's just take 10 more seconds. Very good. So, we can solve for this, equilibrium constant for the first step, products over reactants, and then if you solved for this, the intermediate here, which is the product in the first step, then it would be equal to $k_1 \text{NO}^2$. We can take that term and we can plug it in, so over here, we can substitute it into this equation, and so we have $2k_2$, big K_1 times NO^2 .

All right, so here is our rate then. And if you missed some of this, this was in the notes from before. So now let's think about the effect of temperature. So, k_2 is an elementary rate constant, and so its temperature -- if you increase the temperature, its rate will increase. So here again is our equation, the activation energy is always positive, there's always some barrier to overcome. So if you increase the temperature, you're always going to increase the elementary rate. Well, what about equilibrium constant? So we've talked about this back in chemical equilibrium that the effect of temperature on the equilibrium constant depends on whether the reaction is endothermic or exothermic. And you told me before, the equation, and that's the Van't Hoff equation shown here. And so look how similar those equations are. So for an elementary rate constant, we had e^{-E_a} , and for equilibrium constant, we're talking about $e^{-\Delta H}$.

So, if you have, here the reaction is exothermic, and if you increase the temperature of an exothermic reaction, what happens to k ? It decreases. So, again, it would shift, then, to the endothermic direction, decreasing k . So let's look at this then. So we have in this k_{obs} term, we have an elementary rate constant and an equilibrium constant, so if you increase the temperature, the rate constant increases, but the equilibrium constant is going to decrease.

So, the magnitude of the increase or decrease depends on the size of the activation energy or the size of ΔH . So for this particular example, there's no way that you would know this so I'm telling you, that the activation energy is a small number, or you might be able to look it up in your book, and ΔH is a very big number and it's negative, it's an exothermic reaction. So if you have a very small number for E_a , that means that the rate constant will increase only a little bit, it's not that sensitive to a change in temperature, because E_a is a very small number. But if ΔH is a

big number, then the equilibrium constant would decrease a lot with temperature because this is a big number here.

So in this particular example, increasing the temperature actually decreases the observed rate, because ΔH is, in this particular example, a much bigger thing. So if you were given either numbers or some information like that, you should be able to rationalize what might be true about the rate of the reaction.

so, a large activation energy means that the rate constant is very sensitive to changes in temperature. A large ΔH means equilibrium constant is very sensitive to changes in temperature. And, as we've talked about, E_a is always positive, so the elementary rates always increase with temperature, whereas ΔH can be positive or negative, so equilibrium constants can increase or decrease with temperature. And here, the magnitude of ΔH indicates the magnitude of the change, how much k will change, will it be a big change or a small change, whereas the sign of ΔH indicates the direction of the change.

So, just want to review one thing and then we'll stop for the day. So when a stress is applied to a system, an equilibrium, the system tends to try to minimize that stress. So we're back to LeChatelier's principle.

And so, just one more clicker question and we'll stop for the day. So increasing the temperature is going to do what again? Again, thinking back to LeChatelier. And just 10 more seconds. Very good. So, we're going to finish up these notes on Monday. We're going to think about LeChatelier in a new way, we're going to think about it in terms of activation energy, which is really fun, because we tie back what we learned in the middle of course to what we're seeing now in the end of the course.

All right, have a great weekend, everybody.