PROFESSOR: All right. So today we're starting the last unit of this class, which is kinetics. So, we're moving toward the end of the semester, and today will just be an introductory lecture on kinetics. So, again, kinetics are the rates of chemical reactions, and so we're going to talk about, we're going to introduce you to rate expressions and rate laws.

So, when you're considering a chemical reaction, we've been asking so far in this class whether the reaction will go spontaneously. So we've been talking a lot about thermodynamics, we've been talking a lot about delta g. But we also need to consider how fast a reaction goes, and that's kinetics. So, a kinetic experiment is one in which you measure the rate at which something's happening. The rate at which a concentration is disappearing or whether the rate at which a concentration is forming. You're measuring some kind of change of a reaction, change in composition versus time.

So, I'm going to give, for an example, of why kinetics are important talking about the oxidation of glucose. And I'm going to ask -- we're going to do a little experiment, and I'm going to ask the TA's to help me. Everyone needs to have something to do an experiment with, something that might have some glucose in it to do this experiment. So, if the TA's could help me hand out the ingredients for this experiment. So, don't open your experimental apparatus until I give the OK. So, just collect it and let me set up the experiment for you while we're handing things out.

So you're all familiar with this reaction, so we have glucose and oxygen go to c o 2 and water. And so we've talked a lot about delta g for this reaction, and delta g again, is equal to delta h minus t delta s. So for this particular reaction, we have a negative delta h nought, so what does negative delta h mean about this reaction? It's exothermic. Delta s nought is positive, what does that mean, if delta s nought is positive? What's increasing? Entropy or disorder of the system, which is favorable. So, our delta g nought is a big negative number.

So, in terms of thermodynamics, what does this mean? Is this reaction spontaneous? Yes, it's very spontaneous, it's very thermodynamically favorable. Now, when glucose in products are wrapped, they're often wrapped under a nitrogen environment, so, oxygen is not sealed up in this container, in the wrapper, and they do that to prevent bacterial contamination and things like that. So, the glucose that would be in a wrapped candy is not exposed to oxygen. And so if you look at this thermodynamic information up here, one might imagine that if you ripped this open, and oxygen came in, that there might be some kind of level of explosion with c o 2 coming out and water coming out.

Now, you know, you might say well, if you have one sort of little thing it might not, but now if everyone has one, and we all open it at the same time, what do you expect to happen? Let's try it. Oh, we need some more down here. Anybody else need any?

All right, so I'm trying mine, and I'm not really noticing anything happening. So the situation is the following, It is a spontaneous reaction, but it's slow. So here, kinetics are very important.

So, how many of you are having Thanksgiving with a small child around, younger siblings or something like that? When you see them eat a lot of sugar, which can happen over Thanksgiving, it sometimes seems like an explosion has occurred, that there's all of a sudden hyper energy running around. But that could be due to this reaction biochemically, getting a lot of energy into the system, but probably you will not see c o 2 and water coming off of the small child as they run around.

So, let me introduce you to a couple of terms, if you haven't heard these already. So people are often talking about compounds being stable or unstable. When they're doing this, they're talking about the thermodynamics of a system, the tendency to decompose, whether the reaction is spontaneous or not. Then you can also hear people talking about whether the compound is labile or non-labile or inert, and this refers to the rate at which that tendency is realized. So you might have a very unstable compound, thermodynamically it wants to decompose, but it also might be very non-labile, it might be fairly inert, that kinetically that decomposition is going to take such a long amount of time, that you're not going to notice the tendency to decompose. So, these two can play off each other. So, you can have materials that are very unstable thermodynamically, but you won't really see them decompose because the rate is just way, way too slow.

So, you know for this particular reaction, this is how we get energy -- we make ATP's of energy for the body. So it's slow, but in the body we have to do something about that because we need energy to keep going, and so to be a useful energy source, the oxidation must be fast enough. So, does anyone know in the body what happens to make that reaction faster? Enzymes, right. So, enzymes are catalysts and they will speed up the reaction.

So, let me just give one more example. Some of you may have heard the commercial from deBeers, "a diamond is forever." If you haven't, you will probably hear that quite often between now and the Christmas season. This is a very popular time, I guess, for people to buy each other diamonds. But if you look at that the thermodynamics of this, graphite is actually much more stable than diamonds by 2,900 joules. So, one could argue that graphite is forever, not that diamonds are forever. Of course, here kinetics are on the side of the diamond, they're relatively kinetically inert, it's a huge activation energy barrier, which we're going to be talking about in this unit for the conversion. So, diamonds do, in fact, stay around for a long time. One could still argue that, perhaps, a better gift would be a graphite ring than a diamond ring, but I have a feeling that probably even if the person receiving said

ring was a chemist, they might still not a 100% appreciate that gesture. So, it's important, the thermodynamics are important, but kinetics are also really important to understand what kind of chemical reactions are going to occur.

So, let's think about what are some factors that would affect rates of reactions. So let's write down, and you can think about what are some factors affecting rates. What's one thing people can think of that might affect the rate of a reaction?

STUDENT: Temperature.

PROFESSOR: Temperature, definitely. And this is used quite often in cooking to get things to occur. What else affects the rate of a reaction? OK, yeah, so pressure could -- if you're changing things, applying pressure to sort of switch things around. That will depend, say, for pressure on the nature of the material and things like that of what you're talking about. So let's make that a bigger category and put nature of the material. What type of material it is. And also, along with that, if you're thinking about a particular reaction and how it's going to go and how you might get it to sort of push one way or the other, you're also thinking about the mechanism of that reaction. So what's reacting with what will make a difference. I think I also heard someone talk about concentration, how much of it you have. And you told me the last one that we're going to talk about in this unit, when we were talking about how the body gets the oxidation of glucose to go, what was necessary there? A catalyst, right.

So, those are all the things we're going to talk about in factors affecting rates of reaction in this next unit.

So now, chemistry is an experimental science, and so a lot of kinetics are involved with measuring the rates of reactions. So let's talk about how one might measure the rate of a reaction. So here's a particular reaction, we have n o 2 plus carbon monoxide, going to n o plus carbon dioxide, and one could measure the rate of decrease of the reactants or the amount of increase of the products. So let's just look at one of the products. So one might be plotting a change in the concentration of one of the products versus time. And you may find that it goes up, and then maybe starts to level off a little bit over time. And now, how are you going to measure a rate out of this, the rate at which this reaction is going?

Well, one could measure an average rate, which would be some change in concentration over some change in the amount of time. And you could express that as the change in concentration over the change in time. So, you could pick a particular interval, say, we want to measure the average rate from time is 50 seconds to time equals 150 seconds, and we'll look at how much the concentration has changed over that time interval.

So, we can do a little calculation of the average rate and get a number, 1 . 2 8 times 10 to the minus 4 molar per second, and that's an average rate. But if we had picked at different interval, we would have gotten a different

number. So the average rate depends on the time interval, so that's not always ideal. You don't always want to know an average rate, which might be different depending on which particular unit you pick. So often, when you're talking about rates, you talk about instantaneous rates. So the rate at a particular instance of time. And so let's look at instantaneous rate.

So, we have the same reaction, same plot, but now we're going to be considering instead of the average rate, the rate at a limit when your time interval is going to zero -- at a very, very small time interval, so the rate at the particular instance. And so this can be expressed as d times the concentration of a product, n o, over d t. So, as delta t approaches zero, the rate becomes the slope of the line tangent to the point, that particular time point that you're interested in.

So, let's find an instantaneous rate at 150 seconds. What is the rate of this reaction at 150 seconds? So we can look for 150 seconds, we can have a point on the curve at 150 seconds. And so as our time interval approaches zero, the rate will approach the slope of this line. So we can draw a slope that's tangent to the curve at the time t, it's time 150 seconds, and then we can calculate the slope of that line. And so we can do that math, calculating the slope, and here we find that at an instantaneous rate that time equals 150 seconds, change in -- this is the slope of the line -- the change in concentration over change in time, and that gives you 7 . 7 times 10 to the minus 5 molar per second. So, that's instantaneous rate at a particular time.

What do you think the instantaneous rate is called at time equals zero? Any guess? Initial rate, yeah. So, initial rate, instantaneous rate at time equals zero seconds. So that's instantaneous rate.

So now, let's talk about rate expressions, and then we're going to talk about rate laws. So, same equation. Again, you can monitor how much your reactants are disappearing, you can monitor the amounts of your products being formed, and you can express this in the following way. So we could say that the rate is going to be equal to the decrease in one of the reactants, so minus d times the concentration of n o 2 over d t. We could also express it in terms of the second reactant, so minus d times change in the concentration of the other reactant over time. Or we can express this in terms of the products being formed, so here there's no negative sign, so we have d concentration of n o over d t, or our last product, d times the concentration of c o 2 d t.

So this would be a rate expression, and these would all be equal to each other, if we make the following assumption. We're going to make the assumption here that there's no intermediate species that's being formed, or that if there are intermediate species, that their change in concentration is independent of time. So if there were some other really complicated thing going on here, then those rates may not be equal and we might have something else in the mechanism that would cause one thing to disappear a lot faster than something else that's being formed. But these should all be equal if you assume no intermediate species, or make assumptions about

those intermediate species.

So, then the general expression for a rate expression, if we have an equation, a plus b going to c plus d, where we have coefficients of the reaction, small a, coefficient small b, coefficient small c, and coefficient small d. So we could express the overall rate then, minus 1 over a times d a t t minus 1 over b, d b d t, 1 over c, d c e t, 1 over d d d d d t. That was not easy. All right, so that's the general form for the rate expression.

So just to make sure that everyone's on the same page, why don't you do a rate expression for me for this one. OK, just 10 more seconds. Excellent. So you just have to pay attention to your minus signs, your stoichiometry. So, it's minus for the disappearance, stoichiometry 1 over 2, and then no negatives for your products of things that are appearing. Very good. Rate expressions, not that complicated.

All right, so now we're going to talk about rate laws, which are slightly more complicated than rate expressions. So, a rate law is -- you come up with a rate law experimentally, and it's the relationship between the rate and the concentration. So we have -- we're going to introduce a term called the rate constant, which is the small letter k. And so the rate constant is going to tell you about the relationship between the rate and the concentration of your reactants in a reaction.

So, if we had that same reaction here, we could also write that the rate is equal to a rate constant times the concentration of your reactant, a, raised to a power m, and b raised to a power n. So here, m and n are the order of the reaction with respect to a and b respectively, so m is the order of the reaction in a, and n is the order of the reaction in b, and our small letter k here is the rate constant. So that would be an expression for rate law. And so, now I'm going to tell you a lot of things that are true about rate laws.

So, a rate law, again, comes from experiment, so you can't just look at the stoichiometry of the reaction and predict the rate law. So m is not the stoichiometry of the reaction in terms of the a, that is, unless the reaction is what we call an elementary reaction, or a step in a reaction, and we're going to talk more about that next week -- then you can, if it's an elementary reaction, then you can use stoichiometry to predict. But for other reactions you can't, and that'll become more clear next week when we talk about this in detail.

So, rate laws are not limited to reactants, sometimes a product will show up. It's not that common, but it's possible, and again, it's experimentally determined. So the experiment would have to tell you whether that term is going to be there or not. So, occasionally you'll see a product term in a rate law.

So, in terms of m and n, the orders of the reaction, m and n can be integers, they can be whole numbers, or fractions, negative or positive, lots of options for m and n. And let me tell you about all the options for -- we're going to use m here. So, you have this table in your notes, most of it is blank, some of it is filled in, and we're

going to fill in the parts that are not filled in right now. So we're going to start in the middle where the order of the reaction is one here, m equals 1, and that's called a first order reaction. So these names are pretty much intuitive when you look at them.

So here, the rate law for a first order reaction would be our rate constant, k, times the concentration of a. So let's think about what that rate law would mean. Say you double the concentration of a, what would happen to the rate of the reaction? How many people say double, raise your hand. Good, that's what happens. All right, so it doubled the rate of the reaction.

So now let's think about m equals 2. See on your handout that that's called second order -- again these names make sense. The rate law for this would be k times the concentration of a squared, so m equals 2, and that's shown over here. If you double the concentration of a, what would happen? So you should quadruple the rate. So what about if you tripled the concentration? Why don't you go ahead and tell me if you triple it for m equals 2, what would happen to the rate? OK, let's just take 10 more seconds. Excellent. That's right, 9 times. So, you're definitely getting the hang of this.

All right, so let's move down and talk about m equals minus 1. If you think of a good name for this let me know, because no one ever calls that anything, so we can leave that blank. And go ahead and talk about what the rate would be there and how we would write the rate law. And so, the rate law, then, would be k, our rate constant, times the concentration of a raised to the minus 1. All right, if we double the concentration here, just yell out what you think would happen. You would 1/2 the rate of the reaction, or you can think about as 2 to the minus 1, 1/2 the rate of the reaction. And you will have problems on problem-set 10, which will be due a week from Friday where you're going to be given experimental data, and you have to look at it and see, OK, what happened to the rate, and then what does that mean about the order of the reaction. So this is a lot of what the problems are like in this unit.

All right, also there is no name that I'm aware of for when n equals minus 1/2, but we can write the rate law. So that's just going to be k times the concentration of a raised to the minus 1/2 -- again, for the order of reaction, they can be integers, they can be fractions, they can be negative, and they can be positive. So, tell me for doubling the concentration here of this one, what's going to happen to the rate? OK, let's just take 10 more seconds. Yup, so most people got that right.

So, if we go back here, 0 . 7 times the rate, you could think about this as 2 raised to the minus 1/2. These get a little more complicated and are some of the harder ones on the problem-set to recognize the relationship. So if you remember all the possibilities, it's going to help you think about what's going on when you see the experimental data.

All right, so let's go up to m equals 1/2 here, and this one sometimes does have a name -- anyone want to guess what that one might be called? Half order, very good. So, half order, and so here our rate, then, is going to be equal to k times a to the 1/2. So, if we double the concentration here, what happens to the rate? Someone want to yell it out? So, 1 . 4 times the rate. And m equals 0 -- any guess of what that's called? Zero order. And the rate law here, the rate is going to be equal to what? K, and that's it. So the rate equals k. So what does that mean -- if you double the concentration, what happens to the rate? Yup, no effect on rate. So that's zero order -- the concentration term, it doesn't matter what the concentration is, and there will be some that you'll see on a problem-set like that, so if there's no effect on rate, you have a zero order.

So those are the possibilities that you will see for the order of reactions, and again, you'll be given experimental data and have to figure out the order of the reactions. And often, it's not just as simple as one thing, there'll probably be two things in there, so you'll have to figure out the order with respect to both of those two things. So that makes it a little more complicated.

All right, a couple more things that are true about rate laws. So the overall reaction order is this sum of the exponents in the rate law. So then, if you had this rate law, rate equals k times a to the 2, second order, and b 1, the overall order for this would be? 3. So, we have third order. Sum of 2 plus 1. So for this particular one, your second order with respect to a, first order with respect to b, third order overall.

Units. Units for k are a lot of fun. So it depends on what the reaction is, and often, for a problem, you'll have to figure out what the units for k are, depending on are we talking about molar per second or what's going on. So just pay attention to the units for k, they can vary. And sometimes one of the problems will be what are the units for this particular k, so you'll have to figure that out per problem.

So now, again, kinetics is experimental -- we determine rate laws experimentally, and sometimes this is not easy, because sometimes there'll be very small changes that you're looking at, or those changes will happen really quickly, so the interval of time is very short. And sometimes when you're trying to measure these changes, the reaction's happening faster than your equipment can record those changes. So this can be technically very difficult, and so one thing that scientists do is they use integrated rate laws. So in this way, you can express concentrations directly as a function of time and you don't have to worry so much now about measuring those small amounts of changes that occur are very, very quickly. So let's talk about integrated rate laws. And here, we're going to start a derivation of an integrated rate law.

So here's -- we're told this is a first order reaction, and so we're going to do the first order integrated rate law. And in this reaction, a is going to b -- we can write a rate expression for this. so we can talk about the disappearance minus d a over d t. We can also now write the rate law for a first order reaction, and we know that that is our rate

constant, small k, times the concentration of a. So we know we can write the rate expression, and we can write a rate law for this first order reaction.

So now, we can do a derivation. So, in this derivation, we're going to separate our concentration terms and our time terms. So we're going to move everything with concentration to one side, and things with time to the other side. So, on one side, then, we can have 1 over the concentration of a, we're going to bring that down here. We have d a over here, and then we have our negative sign, and our k over here, and move d t also over to the other side. So now we have concentration terms on one side and time terms on the other side.

And now, as you might have guessed from the name integrated rate laws, we can integrate, and so we can look at the interval from the initial concentration or original concentration of a, to concentration of a at some time, t. And we can also look at from some time, 0, to the time, t, in question.

So there's that expression again. Now you can write this expression also in terms of natural log. So we can re-write this in terms of the natural log of the concentration of a at time, t, minus the natural log of the concentration of a at our original time, or the original concentration, equals minus k t. And you can also express it in this term, so you can just bring this guy over to the other side of the equation, and this is one expression for the integrated rate law that you will see. There's also another expression that you'll see, and let's show you what that is.

So you can also take the natural log and bring these two terms together. So natural log of your concentration of a at time t, over your original concentration of a equals minus k t. And now you can take the inverse natural log of both sides, so just your concentration at time t over your initial concentration equals e to the minus k t. And that expression is often written in your book or on equation sheets as a concentration at a particular time equals the concentration of the original material, e to the minus k t. And these are the two expressions that you'll see the most often. This one is often referred to as your integrated first order rate law, whereas this one is the equation for a straight line. So these two are the ones that you will see the most often for integrated first order rate laws.

So one was an equation for a straight line, so let's come up with a straight line. So if you plot your data, if you've measured your concentration of a at various times, you can take the natural log of those concentrations that you measured and plot them against time. And if you do this, and it is, in fact, a first order reaction, you should get a straight line. So here, we can look at this in terms of a straight line, so on y-axis, we have the natural log of the concentration of a at a particular time, and that's plotted against time, over here in seconds. And so, what does that mean in terms of what is this, what is the intercept here? Yup. So the natural log of your initial original concentration of a. And what is the slope of this line? The slope is negative k, and so the slope is really what people are after. So often what you want to do is measure rate constants for particular reactions, and if you can then measure the concentration of a at particular times and plot it this way, you can come out with your rate

constant. And that's what you want to know, and those are some of the problems that you're going to see. Are you going to see experimental data for what happens to rate at particular concentrations, and you can come up with values for your rate constants.

So, let's talk about one other thing, which is half life. So people are often very concerned with half life. When do you hear about half life a lot? Does anyone know? Yeah, when we talk about radioactivity, which we'll be talking about next class. They're very concerned about the half life, which is the time it takes for the full amount of your original material to be reduced by a 1/2.

So we can look at an equation that we had up above for our integrated first order half life, and we can think about this in terms of a half life expression. So here, t has a particular special meaning -- we have t, 1/2, which is the abbreviation for half life. And so half life by definition is the amount of time it takes for the original concentration to be reduced by 1/2. So here we have our final concentration, concentration of a at a time t. So when we're talking about half life, we're going to have 1/2 as much as we had when we started. So our a t is going to be our original divided by 2, 1/2 the amount we had in the beginning. And so, now t has a special name, it's t to the 1/2 here.

So now we can simplify this expression to come up with an expression for half life for a first order reaction. So, the a to the 0, our original concentrations cancel out, and so we have the natural log of 1/2 equals minus k, our rate constant, times t 1/2. The natural log of 1/2 is minus 0 . 6 9 3 1. We can get rid of our negative signs and solve for t 1/2, because this is a half life expression, so t 1/2 equals 0 . 6 9 3 1 over k. So that's an expression just for a first order half life. And notice that half life does not depend on concentration here. That term dropped out. So half life depends on our rate constant, k, and k depends on the material in question. So, for radioactive material, some radioactive materials have short half lifes, so their k's are very different from each other, and so that can be very important, especially when you're thinking about storing radioactive waste.

So, using that value, tell me, for the same material then, does it take longer to go from 1 ton to a 1/2 ton, or from 1 gram to 1/2 gram? Let's just take 10 more seconds. Yup, it takes the same amount of time.

And then just to finish up here, we have one more thing to do and then we're done. So here, in a plot for a first order half life, the concentration of the material at the first half life has dropped by how much? 1/2. At the second half life is what?

STUDENT: 1/4.

PROFESSOR: And the third half life?

STUDENT: 1/8

PROFESSOR: Yup, so that's first order half life.

All right, everybody, have a happy Thanksgiving.