

The following content is provided under a Creative Commons license. Your support will help MIT OpenCourseWare continue to offer high-quality educational resources for free. To make a donation or to view additional materials from hundreds of MIT courses, visit MIT OpenCourseWare at [ocw.mit.edu](http://ocw.mit.edu).

**CATHERINE  
DRENNAN:**

All right. So enzymes, of course, are catalysts, and that leads us to our next unit, which is kinetics. And it's our next unit and, in fact, our last unit of the semester. So we're going to be talking about kinetics for the rest of the semester, which sounds like a long time, but it really isn't. All right. So we'll switch to today's handout.

So kinetics and thermodynamics is a sort of yin-yang. You really have to think about both of them at the same time. So when you're thinking about whether a reaction will go forward spontaneously, you're thinking about thermodynamics. And you're thinking about how fast that reaction is going to go, you're thinking about kinetics.

So let's just do a little review. We've talked about this before, but it's a clicker challenge. So today, let's think back to thermodynamics and tell me what stable/unstable refers to, thinking about thermodynamics and kinetics now. OK, 10 more seconds.

OK. So most people got stability. When you're talking about stable/unstable, you're not talking about rate. You are talking about  $\Delta G$ . You're talking about the spontaneous tendency. A chemist, if it's around a long time, would talk about it not being stable, but being inert.

And in terms of this one here, if you're thinking about the  $\Delta G$  for the decomposition into its elements, that versus the  $\Delta G$  for formation, if that's negative then it would be stable. But we want to be positive for the decomposition. All right. So let's just look at this up here. So again, it refers to  $\Delta G$ . And labile and inert refers to the rate. And again, when you have a negative  $\Delta G$  of formation, then that makes something stable. OK.

So thermodynamics, kinetics. We want to think about, is the reaction spontaneous? But we also need to think about how long it's going to take. So rate is important. And so if we think about the average rate of a Ferris wheel-- I looked it up. It is 31.4 seconds to spin around if you're at an amusement park.

And you can think about your experience-- or sorry, that should say imagine-- one revolution for every 5 seconds or every 5 hours would be a very different experience. Five seconds

would be way too fast. You'd probably be throwing up everywhere. In 5 hours, you'd be like, oh, my goodness, get me off of this thing. So rate matters.

And chemical kinetics doesn't measure the rate of Ferris wheels, except maybe it does if the ferrous is ferrous iron. Then we might be talking about its rate if it's spinning around doing things in a chemical reaction. So we might think about the concentration of ferrous iron changing with time. So chemical kinetics experiments, you measure concentrations and think about how fast they're changing with time.

So let's think about some of the factors that are going to affect the rates of chemical reactions, and we'll write some of these on the board. So what's one thing that you may have observed that will affect, either speed up or slow down, say, a chemical reaction? What's one thing you can think of?

**AUDIENCE:** Temperature.

**CATHERINE DRENNAN:** Temperature. What's another thing you can think of?

**DRENNAN:**

**AUDIENCE:** [INAUDIBLE].

**AUDIENCE:** Catalysts.

**CATHERINE DRENNAN:** Catalysts. So right, so changing the sort of environment. So it depends a little. It could be pressure. It depends on what you're talking about, what kind of nature of material you're talking about. So possibly pressure could have an effect. And that brings us to the nature of the material, whether it's gas or solid or other things.

And that also comes to the other issue, which is, what is its mechanism? Oops, sorry, mechanism. So does it have one step? Does it have many steps? Do the steps involve changes in phase? What's going on in the mechanism? And so those are all some good things.

One other thing that I'll put on, which also only applies in some cases, depending on the type of mechanism and type of reaction, would be the concentration of the material, which kind of also gets to this pressure idea, depending on what it is. How much do you have in there? All right. So those are some of the things, and we're going to talk about most of these in the next unit.

All right. So let's now think about one example of a chemical reaction, and this chemical reaction is called the oscillating clock. And before we see the demo, we're going to think about what's happening. So this demo, as with most chemical reactions, involves thermodynamics, chemical equilibrium, kinetics.

It also has some acid-base. You have to have some acid in there to get it to go. It's also an oxidation-reduction reaction. And it has colors, and we'll see that the colors change depending on what the oxidation state of the material is and also what its liganded state is.

So basically, in one demo, you get every unit that we've had in the second half of the course. And that's kind of true about any chemical reaction. Every chemical reaction, if you're interested in it, involves thinking about all of these things that we've been talking about.

All right. So oscillating clock reaction. It's a fairly complicated reaction. It has many steps, and we're just going to break the overall reaction shown here down into two steps today. As with many reaction mechanisms, there are multiple steps. But here is step 1 that we'll talk about, and here is step 2 that we'll talk about.

And step 1 occurs when your  $I_2$  concentration is low.  $I_2$  here is a product of the reaction, and when it builds up too much, then that reaction will stop. And so in this reaction, we have acidic conditions. You'll see our  $H^+$ . And under those acidic conditions, we're going to change a clear solution-- so  $I^-$ , iodide, in its certain oxidation states is clear. But when it goes to  $I_2$ , it turns an amber color.

In the second reaction, which will only occur when  $I_2$  is high-- so this will build up, shutting off reaction a and starting reaction b. In this reaction, you have a complex being formed, and that's going to change the color. So we're going to go from amber to a blue complex.

All right. So before we see this happen-- and I should say that once you get over here, you find the blue complex. This will consume the  $I_2$ , which will cause that to drop to be low again. And then you're going to start reaction a again, which, when your concentration's built up too much, you'll start reaction b again.

And so reaction a, then reaction b, then reaction a, reaction b. And you'll notice that the product of one of the reactions is a substrate here, product here, substrate here. So this goes back and forth, hence the name oscillating clock.

All right. So before I show you something pretty, I'm going to make you do work and think about the oxidation-reduction reactions that are occurring that you're going to see that lead to these specular color changes. All right. So here we go, clicker question. All right, let's just do 10 more seconds. All right. So somebody asked once, like, how will I know that it's a peroxide? So I tried to help you out and said reaction with hydrogen peroxide. Let's see how many people-- some people definitely noticed that.

All right. So let's just take a look over here at what's going on and fill in our chart. So here the oxidation state is plus 5. So we have now this oxygen is its normal minus 2. So minus 2 times 3 minus 6 equals the whole thing. Charge needs to equal minus 1. So we need plus 5 there. And I<sub>2</sub> is 0. The next one, I<sup>-</sup>, is being oxidized to I<sub>2</sub>, minus 1 to 0.

The oxygen in hydrogen peroxide is being oxidized. So it's minus 1 here because we have plus 2 for H and two oxygens. So that's minus 1 each to 0. And then, again, minus 1, and oxygen and water is minus 2. So there's lots of oxidation-reduction reactions going on. And in fact, this occurs in multiple different steps. So there's even more different reactions going on that I didn't even show you.

All right. So we have one more clicker question to answer before we do the demo, which is that if I told you-- you want to think about iodide you're using because it's changing color. Why are you using the hydrogen peroxide? So tell me what is true about hydrogen peroxide using the information given. All right, 10 more seconds.

All right. So if we look over here, the large positive value. And again, it's a large positive value of the standard reduction potential is a big value, which makes it a good oxidizing agent. The reduction is spontaneous. So if you have a large positive E for the reaction written as a reduction, that means that delta G for that reduction is going to be negative, which means it's spontaneous. So things that like to be reduced are good oxidizing agents. Actually, hydrogen peroxide is a really good oxidizing agent, and that's why it's used in a lot of things.

All right. So let's look at this demo now. So again, clear to amber, amber to blue. And the reaction rate is also sensitive to temperature, and you told me temperature does affect reaction rates, and it does in this case. All right. Let's see it.

**AUDIENCE:**

OK. So we've got the hydrogen peroxide. Eric's got that in his hand. He's going to take that off before he actually unscrews it. Yay. OK. Hydrogen peroxide, as we said, it gets reduced really easily, which is actually the reason why we kept it in a plastic bag, because even the presence

of oxygen can cause it to react. So he's going to add solution b. That was solution a. Solution b contains the iodate, which is going to provide the-- huh?

**CATHERINE** Oh, sorry.

**DRENNAN:**

**AUDIENCE:** Yeah, I got it stirring.

**CATHERINE** All right.

**DRENNAN:**

**AUDIENCE:** It's going to provide--

**CATHERINE** I forgot to turn this on.

**DRENNAN:**

**AUDIENCE:** --the iodine for the solution. And as you can see, it's turning kind of yellowish, which is what we were expecting. So now the iodate is starting to produce the iodine. And when he adds solution d, we can see it changing. Yay, it works. It's always a struggle whether these things will actually work, but this one usually works very nicely. I'm going to turn this up a little bit more. And it will actually continue to do this for quite a while, I think, right? So--

**CATHERINE** Yeah.

**DRENNAN:**

**AUDIENCE:** Yay.

**CATHERINE** Awesome.

**DRENNAN:**

**AUDIENCE:** Awesome.

**CATHERINE** [LAUGHS].

**DRENNAN:**

[APPLAUSE]

**CATHERINE** Yeah. So we can move this off to the side, and now we're going to see the effect of  
**DRENNAN:** temperature.

**AUDIENCE:** Actually, we'll move that in a second. So as Cathy mentioned, affecting temperature will affect the rates of reaction. So this guy will continue to go. And what we have here is we have all three solutions again, except they've been put in ice. So we're going to see if we've kept this a little bit cold again. You should have taken the thing off.

All right. So that's the peroxide. We've got solution b. You got it? OK. And yeah, we're going to stir in a second, after b. So as before, you saw the temperature change kind of quickly. This time it's not really changing that much.

So before, you saw temperatures change pretty quickly. This is probably going to take a while to actually change, and it might not change at all. It's because the reaction was so cold that you won't have that second step. And also I can't-- there we go. So it happens really, really slowly, as you can tell, whereas this one happened very, very quickly. So yay.

**CATHERINE DRENNAN:** Yeah. So example of many things. So we had chemical equilibrium. We had thermodynamics, talking about which reactions were spontaneous. So spontaneous until making the amber. And then when it's made too much of the iodide, the  $I_2$ , then we see the next reaction going until we now have too little.

And then we switch back and forth. And yeah, this, I think, very clearly demonstrates that the temperature is very different, has a very different effect. It's a much, much slower reaction. All right. Thank you. We can leave them-- do you want to just leave them up here?

**AUDIENCE:** I'm going to leave this one up here.

**CATHERINE DRENNAN:** Yeah, OK. We'll leave the fast one up there. It will eventually stop. So it's good probably, I don't know, maybe five minutes or more or a little longer. And then eventually it just kind of stays this more dark brown. Maybe it's already happened. We'll see if it switches again.

All right. So let's talk about measuring reaction rates then, because we just saw this reaction going in another reaction rate. We saw the effect of temperature. And let's think about how we would actually go about measuring some of these. So we can think about measuring two different kinds of rates-- an average rate and an instantaneous rate.

And so first let's talk about measuring average rate. And to do that, I should switch back over here. OK. So let's consider a different reaction now, one that's a little less complicated and kind of made up, but it's a good example.  $NO_2$  plus  $CO$  goes to  $NO$  plus  $CO_2$ . And so if you're

measuring a rate, you could think about measuring the decrease in either of the reactants or the increase in concentration of either of the products.

So in this case, let's consider that we're measuring the change in NO. And usually people pick the thing to measure based on what's easiest to measure, what kind of handle you are. Does it have a spectroscopic signal or something else that you can easily measure?

So here we have concentration versus time. And so we should see none in the beginning, and then we should see it increase and then level off. And we can calculate an average rate, which is just going to be the change in concentration over the change in time.

We can also express the average rate as  $\Delta$  the concentration of NO over  $\Delta t$ , the change in time. And we can calculate what that would be. We can pick an interval, say, from 50 to 150. We can measure some concentrations there and then calculate the average rate-- the change in concentration from the time 150 to the time 50 concentration over that time interval. And it will give us an answer, in this case,  $1.3 \times 10^{-4}$  molar per second.

All right. Well, that could be useful to know. But the average rate depends on the time interval I picked. If I picked a different time interval, I might have gotten a different rate. So instead of calculating average rate, a lot of people want to calculate instantaneous rate, where you're asking, what is the rate at a particular time point?

So now let's talk about instantaneous rate. We'll have the same equation up there. Now, instantaneous rate is defined as the rate where you have a limit of  $\Delta t$ , the change in time, going to 0. You're comparing concentrations at time  $t$  and time  $t$  plus the interval  $dt$  over this time change, again, as you approach 0.

You can also express this as  $d$  change in concentration of NO  $dt$ . And so as that change in time approaches 0, then the rate becomes the slope of the line tangent to the curve at time  $t$ . So if we wanted, say, find the instantaneous rate at 150-- here's 150-- we can draw a line tangent to the curve at that time. So this would be the point at 150, and then we can calculate the slope to tell us the instantaneous rate.

So let's do that. We will calculate the slope. We have to look what the concentrations are, what the times are. And then the instantaneous rate at 150 would be the slope of the line, this change in concentration, over that time interval. And to the correct significant figures-- there

should be an extra 0 in there--  $7.70 \times 10^{-5}$  molar per second. So that would be the instantaneous rate, again, the slope of the line tangent to the curve at time 150.

So you could ask, what is the instantaneous rate at 100 seconds or 200 seconds, and get that instantaneous rate. People are often talking about initial rate. And by initial rate, they mean the instantaneous rate at time equals 0. So again, we have two different rates. We have average rate and instantaneous rate.

So now let's think about rate expressions and then rate laws. All right. So keeping with that same reaction, again, we could monitor NO forming or CO<sub>2</sub> forming, or we could monitor either of our reactants disappearing. And if we assume that there's no intermediates or very slow steps, then we could say that the rate of the reaction should be equal to the disappearance of the concentration of NO<sub>2</sub>, or decrease in NO<sub>2</sub>, one of our reactants, over time.

It should also be equal to the disappearance of CO, our other reactant over time, and also equal to the appearance of NO with time, and also equal to the appearance of CO<sub>2</sub> with time. And again, for these all to be equal to each other, we are assuming here there are no intermediates being formed, or that if we are forming them, then they're independent of time.

In other words, if, say, there was a large, slow step somewhere in here, we might see all the reactants disappear. But there'd be a lag before the products would appear, because more steps and things are going on. So these are all equal to each other if you have no intermediates or the intermediates are not affecting the overall rate.

So we could think about this for a generic equation. So if we consider A plus B going to C plus D, when we're talking about the rates of disappearance or appearance, we have to remember the stoichiometry of the reaction. So if we have a stoichiometry of little a, then we would say minus  $1/a \, dA \, dt$ , stoichiometry of little b for reactant B, minus  $1/b \, dB \, dt$ . Then formation of products,  $1/c \, dC \, dt$ , and our other product,  $1/d \, dD \, dt$ . I got through it. OK.

So let's look at an example reaction, and why don't you tell me what the rate is equal to.

I didn't announce whether this would be in the program or not. Why don't you look at the results and make a decision? OK, 10 seconds. All right. Still haven't gotten much into the 90s, but still I'm happy. All right. So here, again, we're talking about the disappearance of our reactant. So it will be minus  $1/2$ , and the formation of one of our products and the formation of

the other product as well. All right. So don't forget about the stoichiometry of the reaction.

So these are called rate expressions, and you don't want to get that confused with rate laws. So a problem might ask, write the rate expression. This is what it's looking for. If it says write the rate law, it's going to be looking for the following thing. So a rate law is a relationship between rate and concentration, and they are related by a proportionality constant, little  $k$ , which is called the rate constant. So big  $K$  is what?

**AUDIENCE:** Equilibrium.

**CATHERINE DRENNAN:** Equilibrium constant. Little  $k$  is a rate constant. All right. So let's look at a reaction. And so reaction of A plus B going to C plus D, the rate law could be expressed, rate equals rate constant  $k$  times the concentration of A to the  $m$  and B to the  $n$ , where  $m$  and  $n$  are the order of the reaction in A and B respectively, and  $k$ , again, is our rate constant.

All right. So let's look at what I call the truth about rate laws. So the first thing, you cannot just look at the stoichiometry of the equation and say, oh, it's going to have this  $m$  for A based on its stoichiometry, unless it's what's called an elementary reaction.

And we're going to get to that on Wednesday after Thanksgiving. Make sure you come Wednesday after Thanksgiving. That's the lecture on mechanism. It's a really important lecture in kinetics. So we'll learn about elementary reactions. So you can't just look at the stoichiometry and write the rate law. You need experiment.

So the rate law is not just limited to reactants, although largely it's true that the rate laws will just have reactants. It can also have a product term, like C could appear in the rate law. How would you know this? Well, it would be experiment would tell you whether this was true or not.

So for this rate law, we saw this already, the order of the reaction in A is  $m$ , and the order of the reaction in B is  $n$ . And  $m$  and  $n$  can be integers. They can be fractions. They can be positive, and they can be negative. So now we're going to think about all these different orders of reaction and think about what-- and we'll do it just for A-- what  $m$  is equal to.

So we're going to fill in this table here. And some of these things are in your notes, some of them you need to fill in. So we're going to start with  $m$  equals 1, and this is called a first-order reaction. The rate law for this, the rate would equal the rate constant times the concentration of A. And now let's just think, if this is a first-order reaction that just depends on A, if you

double the concentration of A, what do you expect will happen to the rate?

**AUDIENCE:** It'll double.

**CATHERINE** What?

**DRENNAN:**

**AUDIENCE:** Double.

**CATHERINE** It will double, right. So in a first-order reaction, you double the concentration of something, and  
**DRENNAN:** the rate will double. And this is how you figure out what the order of the reaction is. You double the concentration of something, leaving everything else the same, and see the effect on rate. So again, these are experimentally determined.

Now let's consider  $m$  equals 2. And notice the blue went away here, but it's still there. So you can see it. All right. Second order-- what does the rate equal? So it would equal  $k$ , our rate constant, times the concentration of A, and now we have a 2. So it's raised to the power of  $m$ , and that's 2. So that's how we would write the rate law for something that was second order in A. So now let's think about if you double the concentration of A, what you would observe for the rate? What would happen?

**AUDIENCE:** Quadruple.

**CATHERINE** It would quadruple, right. Now, what about if it triples? Why don't you tell me what would  
**DRENNAN:** happen then. All right, 10 seconds, very fast. 90%, yes! OK. So yes, 9 times. All right. And in problem set 9, which is already posted, there's all sorts of problems where you see the effects, and you can figure out what the order of the reaction is.

All right. So now let's consider  $m$  equals minus 1 over here, which is often not referred to by any name. The rate here would be equal to  $k$  concentration of A to the minus 1. And if we double the concentration of this-- you can just yell out-- what would happen to the rate?

**AUDIENCE:** Half.

**AUDIENCE:** Half.

**CATHERINE** Half, yes. All right. Now,  $m$  equals minus 1/2. So the rate here would be  $k$  equals  
**DRENNAN:** concentration of A raised to the minus 1/2. And now if we double, that's our last clicker question on this sheet. So why don't you tell me what happens, and this should be fast too. All

right, 10 more seconds.

All right. So going back over here, right, we have 0.7 times, which is 2 to the minus 1/2. And when you're looking at the effects of the rate on concentration, you'll see the concentration double. And you're like, what on earth happened to the rate? Keep in mind this minus 1/2, because it's very hard to think about what the relationship is. So again, they can be fractions, positive, or negative.

All right. So back up here now, this actually is called half order. So we would have a rate that is equal to  $k$  times the concentration of A raised to the 1/2. And if we double that-- you can just yell out-- what would happen?

**AUDIENCE:** [INAUDIBLE].

**CATHERINE DRENNAN:** So 1.4 times the rate. And finally,  $m$  equals 0. What do you think that is likely to be called?

**AUDIENCE:** Zero order.

**CATHERINE DRENNAN:** That is zero order. So at least some things are pretty easy to guess. And if we think about the rate, what would the rate be equal to?

**AUDIENCE:**  $k$ .

**CATHERINE DRENNAN:** Just  $k$ , right. It's just going to be equal to  $k$ . So zero order, the A term is not there. So if we double the concentration of something that is zero order, what happens to the rate?

**AUDIENCE:** Nothing.

**CATHERINE DRENNAN:** Nothing, right. No effect on rate. The concentration term isn't part of the equation. So the problem set 9 will have a lot of experiments, and you need to figure out by looking at what is happening what the order of the reaction is. Is it doubling when you double the rate? Is it quadrupling? Is it doing some weird thing that seems to be a negative-- an inverse fraction? And that will allow you to figure out what the order is. OK.

So once you figure out the order of the reaction, then the next truth about rate laws is that the overall order of the reaction is just the sum of the exponents in the rate law. So for example, if we had this reaction, what would be the overall order? You can just yell it out.

**AUDIENCE:** 3.

**CATHERINE DRENNAN:** Yep. It would be a third order. The order would be 3. Now, some people get this wrong on the test. It's like, no, you want to save your points for something that's hard. 2 plus 1 is 3. So remember that. OK. And this would be then second order in A. You would say that's first order in B, overall third order. So if you're going to lose points on an exam on this material, I recommend losing them determining the units for the rate constant, because that's much more complicated than figuring out the overall order of the reaction.

The units, it depends on the order. You can have squared. You can have molar squared, quadrupled, molar to the minus fractions. All sorts of crazy things happen in your units of rate constants. So save your points if you're going to lose some. And I think it would be great if everyone got 100, but if you're going to lose some, lose some on that. That's harder.

OK. So we'll end there for today. And Wednesday, we're going to be talking about integrated rate laws, half-life for first order, nuclear chemistry. It's going to be very exciting and slightly radioactive.

So where were we? We were talking about the fact about how you measure instantaneous rates and average rates. And one of the issues of doing kinetics experiments, it's all experimental. You want to measure things. But it can be very challenging to measure initial rates, because you're often talking about a very small change in concentration.

And so it can be helpful sometimes to use integrated rate laws, which allow you to measure a lot of different concentrations as times elapses and plot that data to get out rate constants and things like that. So we're going to talk about integrated rate laws. And so the alternative, then, is to use this integrated rate law. Again, expresses concentrations directly as a function of time and gets at this small changes problem. All right. So we're going to talk about first order now, and then we'll talk about second order in a little bit.

So for a first-order equation, we have A going to B. And we learned last time that we can write a rate expression for a first-order process, or for this process here. So we could talk about the rate expression as the disappearance of A minus d concentration of A dt. We can also write the rate law for a first-order equation, and that would be k, our rate constant, times our concentration. So the rate expression has the d dt, and the rate law has k, our rate constant, in it.

All right. So using these two things that we learned last time, we can do a derivation to get our integrated first-order rate law. So in this derivation, we're going to separate our concentration terms on one side and our time terms on the other side. So we're going to bring over our concentration of A over here. So we'll divide by the concentration of A.

We have our d concentration of A term from here. We're going to take our minus sign, put it on the other side. And we're going to take our dt, our time term, and put it over there as well with our rate constant. So we have the terms that have concentration of A on one side, and we have our terms with rate constant and time on the other.

Now we can integrate both sides, and we will integrate from our original concentration of A. So that's A to the O, for our original concentration, up to concentration at whatever time t we stop the experiment and through all the times in between, over 1 over the concentration of A dA. And on the other side, we have our minus rate constant k, and we're looking at the time from time 0 to time t, when we stop the experiment.

All right. So we can take this expression now and move it up, because I have more derivations to go. So I'm going to put it on the top of the screen. And now I am going to solve it. So this integral solves to the natural log of the concentration of A at time t minus the natural log of our original concentration of A, on the other side minus kt, our time.

So there are two ways we can rewrite this equation. We can write it as the equation for a straight line. And all I did was take this natural log of A<sub>0</sub>, or A original over here. And we could also rearrange this term. Instead of minus, we have natural log of the concentration of A at time t over our original concentration. And now we can take the inverse natural log of both sides. And so we get rid of natural log here, and on the other side we have e to the minus kt, again, the rate constant times the time.

And then I can write it-- break this out here, moving the original concentration of A to this side. And now this is the equation for the integrated first-order rate law, where you have the concentration of A at some point t equals its original concentration times e to the minus k, the rate constant, times the time.

So if you know a rate constant and how much time has elapsed, and you know how much you have of something originally, you can figure out how much you should have now. Or if you figure out how the concentration changes over time and how much you had originally, you can calculate the rate constant for that particular material.

And you can do those calculations for rate constants by plotting, using this equation for a straight line. So here I'm going to plot natural log of A. So I measured the concentration of A at various different times against time. And we have an equation for a straight line. So we should get a straight line if this is a first-order process. And so what would this be up here? What is the y-intercept? What is it?

**AUDIENCE:** Natural log of the original concentration.

**CATHERINE DRENNAN:** Yeah. So that's the natural log of our original concentration. And this you can yell more loudly-- what is our slope?

**AUDIENCE:** Minus k.

**CATHERINE DRENNAN:** Yes. It's a little bit easier to yell loudly. Minus k. So you can experimentally determine the rate constant from this. So if you measure how the concentration of A changes with time, plot your data, natural log of those concentrations versus time, get a lot of data points, from the slope you can measure the rate constant. And so rate constants for a lot of different materials have already been measured in this kind of way.

All right. So for a first-order process, these are important equations. But also for first order, we spend a lot of time talking about half-life. So half-life is the time it takes for half of the original material to go away. So it's a really easy thing. I like it when things are called what they are. And here the time involved has a little special abbreviation,  $t_{1/2}$ . So whenever you see  $t_{1/2}$ , that's talking about a half-life.

So we can derive this expression as well for the first-order half-life using the expressions that we just looked at, so from the expression we had above, where we had the natural log of the concentration of A at time t over our original concentration equals minus the rate constant k times time.

And now we can substitute in. So we're not interested in just any old time. We're interested in  $t_{1/2}$ , so we're going to want to put a  $1/2$  in there. And that is the time it takes for the original amount to go to half, so to be divided by 2. So we can put that in. So now our  $A_t$ , our concentration of A at time t, is our original concentration divided by 2, and our t is  $t_{1/2}$ .

So you'll see that the  $A_0$  terms are going to cancel out. And you're going to end up with natural log of  $1/2$  equals minus k times our half-life,  $t_{1/2}$ . And so then we can put in our value for the

natural log of  $1/2$  and get rid of all those minus signs and rearrange it. And so then our half-life for this first-order process is going to be equal to  $0.693/k$ , the rate constant.

So you'll note a couple of perhaps important things about this expression. And one of the important things is that half-life doesn't depend on the concentration. So the concentration term has dropped out. So what does half-life depend on then if it doesn't depend on the concentration? Again, this is for first order.

So it's going to depend on  $k$ . That's all that's in there. There's only one thing that's in there. There's a number, a constant, and there's  $k$ . So half-life depends on  $k$ , this rate constant, and the rate constant depends on the material in question. So different materials will have different values of rate constant. And we just saw how you can calculate a rate constant. You can measure it and get the slope of the line and tells you about what  $k$  is.

All right. So let's use this expression now. And why don't you tell me for the same material, which of these events will take longer. All right, 10 more seconds. So it takes, in fact, the same amount of time, because the concentration doesn't show up in there, and it was the same material.

All right. So before we move away from this, you can write same amount of time in your notes. Let's take a look at this plot on the bottom of the page and just think about what's happening. Because you can talk about a first half-life and a second half-life and a third half-life. So we can just fill this right in. So for a concentration at your first half-life, how much is left? So what's this number? The concentration is what? Half. Second half-life, what do we got?

**AUDIENCE:** 0.25.

**CATHERINE  
DRENNAN:** 0.25. Third?

**AUDIENCE:** 0.125.

**CATHERINE  
DRENNAN:** 0.125, right. So this is pretty easy to think about. But sometimes when you have data and you're looking at it, you have to remember what the sort of possibilities are. OK. So that's first-order half-life, and that's the end of this lecture. But we're not really moving away from the topic, because now we're going to talk about an example of a first-order process, which is radioactive decay.