PROFESSOR: So last time, there was a question that was asked about the order of magnitude rates. You asked the question about the concentration of the catalysts. So the rates that I gave you, which were the rates of reactions are basically order of magnitude. They're estimates and odd numbers that, they obviously depend, as you pointed out, depend on the concentration of the catalyst. Depends on the concentration of the reactants. Depends on where you are on those concentrations. As we saw when we did enzyme catalysis, is that depending on KM, the Michaelis constant, and the substrate concentration, if your substrate's concentration is much higher than KM, you are in the maximum velocity limit, where the rate depends on k2 times the initial concentration of enzyme. In that case the rate of the reaction depends just on the concentration of enzyme, and not on the concentration of substrate. But if you are at the small concentration of substrate relative to KM, then your rate depends linearly with the concentration of substrate. And the same thing happens with the non-enzymatic catalyst, that there will be some sort of mechanism that goes along with it. And most likely it's going to be second order in the catalyst. And the reactant if it's just the two body process. But it could be more complicated. So definitely those concentrations will go in there. But a priori, it's not clear how they will go in there. But the orders of magnitude are roughly right. And the basic idea is that you change your rate of reactions by 15, 18 orders of magnitude with the right catalyst, especially if it's a biological catalyst.

One concept that I didn't go through last time, which is also quite useful, it's called the turnover number. Turnover number. And this is useful for any kind of catalyst. But for enzymatic, or enzyme catalysts, the turnover number is k cat. The number per second. It's a rate per second. How many times does a reactant get, the number of times that a reactant turns into a product per second, per catalyst.

So let me write it out. So it's the number of product formed per second, per second, per enzyme, per molecule of enzyme. OK, so if one enzyme is going to be there, there's going to be some substrate going in. Coming in, the pocket coming out. Coming in, the pocket coming out, so the number of cycles of this process per second. is the turnover number.

And so if you are where the concentration of substrate is very much larger than the Michaelis constant, where are you are at the saturation limit, then this turnover number doesn't depend on the substrate concentration. It's just k cat. So that's why k cat is important. As this turnover number in the maximum velocity limit. Because in the maximum velocity limit, then the process that's dominant is the second process, ES goes to enzyme plus product.

The first process here is not the rate limiting step. This is the rate limiting step. Because the substrate concentration is very high. So this first part goes very high, goes very fast. And the number of product formed per second, per molecule of enzyme, the number of molecules formed for second, that's the rate of product formation. Rate of product formation per second. Divided by the concentration of the enzyme. If you normalize by the number of enzyme. So this becomes rate of product formation in moles per second, divided by moles of enzyme. It's the same thing as what we're saying here in words. And so the rate of product formation is dP/dt, and you divide that by the concentration of enzyme, which you can write as E0. dp/dt, and the maximum rate limit is k max. It's a constant divided by E0. And k max is k cat times E0 divided by E0. The E0's come out. And this is k cat. Which is basically k2. So that's the turnover number. Any questions on this turnover number? You see that a lot in catalyst literature and especially the enzymes. I have to get out these lecture notes. Send these back.

OK, so the last topic I want to talk about is oscillating reactions. It's sort of like an interesting topic. And it's applicable not just to just chemistry, but it's basically playing with the differential equations. And you'll see this sort of stuff later if you keep doing science that involves coupled differential equations. It's just all over the place.

So normally we have an equilibrium process. A goes to B, B goes back to A. And if you start out with something which is out of equilibrium, then you will eventually reach equilibrium at a rate which is dependent on those two rates. k1 plus k minus one. So B will to come up to some B equilibrium. And A will, if you start out with a lot of A, and a little bit of B, and concentration of A, will come down smoothly, monotonically, to the equilibrium state. But sometimes, if you're out of equilibrium, and this doesn't have to be chemistry. It could be anything that's out of equilibrium, your emotion's out of equilibrium. Stock market is out of equilibrium. Population dynamics are out of equilibrium. The weather. Whatever.

So, you're out of equilibrium, let's say this is equilibrium for A, this is equilibrium for B, let me try to keep them somewhat the same as here, I messed up. You're out of equilibrium, you start down here for A. And you, instead of going linearly down or monotonically down, exponentially down to the equilibrium, instead you overshoot. And you keep going back and forth. Like a spring. And then B does the same thing. Overshoots, comes down. Overshoots, comes down. Like a pendulum. A lot of things work like that. The heart is something that works like that, right? It beats. It's not in equilibrium. Good thing it's not in equilibrium. So the heart is one example of something that oscillates, back and forth, back and forth. And so there are actually many examples of complicated processes that involve chemistry, that aren't at equilibrium, that instead go back and forth, in and out, of on one side or the other of equilibrium.

Now, there's an important feature of, if you want to build a chemical process that looks like this. It's often very useful to have a particular step in the mechanism that's called an autocatalysis step. And that provides feedback. It's like, if my microphone here, the speaker which is here, I were to stand right in front of the speaker and my

microphone would pick up the volume from the speaker, it would get amplified, and I get feedback. And that would be a bad thing.

So this is a form of feedback here. You need some sort of feedback that the reaction knows that you're building up, that this is going too fast. And then there's a feedback process that brings it back up. And a feedback process that goes back and forth. And the way you get this feedback is by having a step in the mechanism that has both a molecule as part of the reactants and as part of the product. It's not the same as a chain reaction, where we talked about an intermediate being recycled and building up. This is an actual reactant and an actual product that's part of this step here.

So this is an autocatalytic step. And let's just see what that step looks like. Suppose we just have that step. So we want to find out, as a function of time, if you start out with some A and B, what happens to the concentration of B as a function of time. The time dependence of that. Clearly it's going to build up. But how is it going to build up? So we need to solve for B as a function of time. So let's go ahead and write down our rates. The rate of the reaction is $d[A]/dt$, is, let's put a rate constant here. k, k times $[A]$ times $[B]$.

Now, $[B]$ and $[A]$ are related to each other through stoichiometry. The concentration of B is the concentration of B that he started out with, $[B]_0$, then every time you destroy an A, you create 2B. So it's plus two times the amount of A that you've destroyed, $[A]_0$ minus $[A]$, $[A]_0$ is what you started out with. This is what's left over. So the difference is what you've destroyed. But every time you destroy an A to form 2B, you also destroy a b. So you have to subtract away the B that you've destroyed. Which is $[A]_0$ minus $[A]$. This is the 2B that you created by destroying A, and this is the B that you destroy by having to destroy A, for the reaction. You've got to bean-count correctly. Keep track of everything.

So $[B]$, then, is just, I'm going to drop those brackets. B_0 plus A_0 minus A. So you can plug that in here. And is equal to k times A, times B_0 plus B_0 minus A. And now you have a differential equation that only contains A and time. B_0 is a constant. And the way you solve that is by partial fractions. Use partial fractions, solve for this. And I'm not going to go through the math of solving for it. It's not that interesting. Let me give you the answer. You end up with $[B]$ as a function of time, is this function A_0 plus B_0 over one plus A_0 over B_0 times e to the minus k times A_0 plus B_0 plus time.

And that's where the time component comes in. Whoops, I'm sorry. Usually I don't have this on, let's turn this off. That's where the time dependence comes in. And clearly, at t is equal to infinity, t equals infinity just goes to zero. So you have B as A_0, plus B_0, everything goes through to the product. t equals to zero, this is equal to one. And B is equal to just B_0.

Alright, and so the curve looks something like this. This is what it turns out to look like. We're starting with B_0 here.

There's an induction period where very little happens. It's like the dormant stage. So, locusts that are sitting in the ground for seventeen years waiting for something to happen. Dormant stage, the induction period. And suddenly something starts to happen. There's an inflection point. And you get to A0 plus B0. The locusts wake up. And go to maximum concentration.

So there's an s-like shape that has an inflection point and an induction period. That's pretty typical of an auto-catalytic reaction.

OK so let's apply it to a process now. And again, this is going to be coupled differential equations. Broadly, broadly applicable, the example that I'm going to give you. This mechanism has been used for all sorts of things.

So what do we have here? We're going to have an island. In the ocean. Island here. And it's going to be sunny, so let's get some yellow chalk here. There's the sun. And every now and then it's going to rain. We need some white chalk for the rain. There's a cloud that comes in. That's going to be one of the reactants. And then some seeds blow in from the continent, and grass starts to grow on the island. Grass. And then there's a shipwreck and a couple of rabbits get on the island. And now we have rabbits. Rabbits. A little tail on the back. I hate rabbits. I have a little vegetable garden, a little tiny vegetable garden. And there are rabbits. And I have to fence in my vegetable garden and make it impermeable impenetrable to rabbits. And rabbits are very clever. And my vegetable garden looks like a fortress. It's got a green fence. Heavy duty things. It's terrible. Rabbits are awful. They're very cute but they're awful.

Alright, so now what happens. Well, given the rain and the grass, it turns out that this island can only support 25 rabbits. If there are more rabbits than that, then they all eat too much. If there are less rabbits then that's fine. But 25 is about the maximum that can support on this island. The rabbits, unfortunately, are not that smart. They don't know that. They don't know that only 25 rabbits can live there. So, what happens is that the Year one, Year one there are ten rabbits. And the food condition is great. Lots of food, number of rabbits. Lots of food. So the bunnies, the rabbits make bunnies. Lots of rabbits. Year two, they kind of went overboard. Now there are 50 rabbits. The food is lousy. Terrible. Well, there's a feedback here. Feedback and rabbits start to die off. Don't reproduce as much. Year three, we're back to ten. Great food. Rabbits don't notice. They multiply. Food is terrible. And they just don't learn.

Humans are a little bit like that. Except our cycle isn't one year, it's usually on the order of 30 years. It's like the memory of a generation disappearing. And we have to relearn the mistakes of the previous generation. Science is like that too. Science goes in cycles. 20, 30-year cycles. Topics that were out of fashion 20 years ago, 25 years ago, come back. And suddenly everybody's excited about them. And all the ideas, of course we make progress. We go a little bit further than we did 20 years ago. But all the ideas that were out of fashion 20 years ago come

back. People get really excited, and they relearn all the mistakes that people made at the beginning. Technology has improved, we know more, and therefore we go a little bit further this cycle than we did the previous cycle. But it's really interesting to look at history of science and see this sort of cycle.

So let's write a mechanism. Let's write a mechanism here. So we have rain plus grass makes more grass. At the rate k1. That's autocatalytic. It provides some feedback. Then we have grass plus rabbits make more rabbits. OK, let's do more because I don't know how much, more, more. Also autocatalytic. Then we have rabbits. Eventually, unfortunately, rabbits become dead rabbits. Rate k2 k3, and that's the termination of the process.

OK, so now let's put some chemistry on this. Let's assume that instead of having objects, live objects here, we have chemical molecules. So A plus B goes to 2B. That's the first step. Then we have B plus C, C is the rabbits. And then C goes to some sort of products. Soil. This is a very famous mechanism. It's called the Lotka-Volterra mechanism. It's also called the predator-prey mechanism. In my case here, I made it sort of warm and fuzzy. I didn't have a predator in there. But you could change this. Instead of having rabbits and grass, we could have rabbits and foxes. Where A is the grass, if you take A to be the grass. B to be the rabbits. And C you be the foxes. Works the same. You have grass plus rabbits makes more rabbits. Rabbit plus foxes make more foxes. Eventually the foxes die off. Same idea.

So now, let's solve this. Let's assume that A, the rain here, it's constant. There's a steady supply of rain. It doesn't go away. That makes sense in my example here. So the concentration of A is kept constant. In order to get oscillations to keep going, that turns out to be important. To have one of the reactants just keeping being reintroduced in the system. Because it gets used up. And when all the reactant gets used up, then you're done. So in the case of the heart, we have to keep feeding ourselves to produce energy. Otherwise the heart would stop.

OK, now we want to know what is the concentration of B and C as a function of time. So we write down our kinetic equations. dB/dt gets produced through the first step, k1 A times B, gets destroyed in the second step. k2 B times C. dC/dt, C gets produced in the second step, k2 B times C. Gets destroyed in the third step. k3 times C, got to do your bean-counting correctly. And the strategy here that we're going to use to solve the problem is to assume that we're at steady state. We're going to find the solution at steady state. Then we're going to perturb away from steady state a little bit. And see whether this creates an oscillation.

First we need to find out what the steady state solution is. So first, let's find steady state. Then perturb away from steady state. We're looking at a harmonic response, if you've heard that term. When it's going to look like a spring, close to its equilibrium state.

That means that we're going to set it these two things equal to zero, for this steady state. Things are not

changing. Concentration of B and C are not changing. A is not changing on purpose here. And so all these guys here are then steady state concentrations. If we set it equal to zero. We solve for A in this. For C in this process here. The B's cancel out here. We divide by B. And you solve for C as a function of A. So this one here gives you C steady state is equal to k1 over k2 times the concentration of A. And this one here, now you put in the C and you solve for B, B steady state, is equal to k3 over k2.

So the next step is to perturb away from equilibrium. Or from the steady state, rather. This is not equilibrium, it's not equilibrium because we keep adding A. We have to put some input into the system. So here we are. We've got some concentration of B here at the steady state. We have some concentration of C at the steady state. And now we're going to add some delta B to the system, or delta C. Or both. Delta C, we're going to ask the question, given our system here, how is it going to respond? It has a number of choices. It could respond by going back to the steady state in a monotonic fashion. Without overshooting. This is kind of like an overdamped system. It's like having a shock absorber on your car. You go over a bump, the car doesn't oscillate up and down. It's sort of damped. It's a damped oscillator. It goes back to the steady state.

Or, you could, there we go, there's B, C. Or you could perturb, and it could just stay where it is. That could happen too. That's an inelastic response. Kind of like the supply and demand with oil. The price of oil goes from $10 a barrel to $120 a barrel. The use of oil doesn't seem to be affected very much by the increasing price. You're still using just as much oil. There's an inelastic response. What we're looking for is something that has an elastic response, or a harmonic response. We perturb it, it tries to get back to steady state. But because of feedback, and not being over-damped, if it's an oscillator, it goes up and down. Like a scale that is not well, well, like a car that has bad shock absorbers, all it has is the springs. Up and down. So what we want is, we want to solve for dB/dt as a function of time. We want, well, I'm going to do everything in green. Since I lost my white chalk. We want delta B, delta C as a function of time. So, that means that we start with B is B steady state plus delta B, C is C steady state plus delta C. And we put that in our equations. For dB/dt and dC/dt. So now dB/dt is the same thing as dB steady state plus delta B dt, which is d delta B / dt. Because this is a constant here. And that's equal to k1 times A, times B steady state plus delta B. Minus k2 times B steady state plus delta B times C steady state plus delta C. And then you have the same thing for dC/dt, it's going to look exactly identical. d delta C / dt. Thank you much, this is magic. k2 times B steady state plus delta B, times C steady state plus delta C, minus k3 times C steady state plus delta C.

So these are two differential equations. And there are coupled differential equations. Because delta B is occurring here, here, and here. So the time derivative of delta C depends on delta B. And the time derivative of delta B depends on delta C. It's a coupled system. And if you actually expand this out and take away all the terms that cancel out, you end up with something that looks much simpler but is just as hard. d delta B / dt is equal to minus k3 delta C and d delta C / dt is equal to k1 A delta B.

And then you really see that it's coupled, because the time derivative of delta B depends on delta C. And the time derivative of delta C depends on delta B. And there's the feedback sitting right here. And that's what you do. You learn how to solve in 18.03. So I'm not going to solve it here, I'm just going to give you the solutions. Because that's what we're interested in. After all, you're not expected to learn how to solve this equation. Although you should be able to put the solutions in and make sure that they do work out.

And so the solutions are harmonic solutions. Delta B is a function of time is equal to delta B0. The amount of the perturbation times the cosine of omega t, where omega is the frequency of the oscillation. Minus some pre-factor here, k3 over k1 A to the 1/2 power. Times delta C0 sine of omega t. And then delta C looks the same. The same frequency. Delta C0, cosine of omega t. Plus k1 over A times k3 to the 1/2 power. Delta B0 sine of omega t, where omega, the frequency of the oscillation, is these rates. k1, k3 and A. So obviously, keeping the concentration of a constant is important because we don't want a time dependence here. The rain is constant.

And then if you do that, then you have this oscillation. Up and down and up and down with this frequency here. You get exactly what we're trying to get. Which is this process right here. So let me give you an example of this. And the best way to do is to actually go and see a movie of a reaction that looks like this. This is the reaction that was optimized and created for demonstration purposes. So it's a pretty complicated reaction. There are ten steps to the mechanism. And if we gave you that mechanism to solve for the final exam, you would still be here probably two weeks form now. It's pretty complicated. You'd need a computer for sure. So, ten steps, well, that's what's known. There are probably more than that. It's probably more complicated than what we really know in terms of fishing out intermediates.

And the basic reaction is, you start out with an oxide of iodine, which is clear. You create I2, which is going to look gold. In solution, and then it creates Ii minus, which is going to look deep blue. And then it'll feed back and start again. So we're going to have this cycle of products. And amongst those ten steps, or more than ten steps, there are a few autocatalytic steps, which provide the feedback.

So now I have to start it. Let's go ahead and read. Alright. So here we go. So, there are two solutions, A and solution C. Actually, we mix three solutions together. The potassium iodide is what is going to give rise to the different colors. And now we're in the gold phase of the reaction. It's important to stir, otherwise it wouldn't, and then it turns deep blue. And then there's an induction period, where you wait for a while. And then eventually it should go clear. So it goes clear. And then it turns gold again. And then deep blue, and there's the oscillation. And then a long induction period, and then it goes through that cycle over and over again. And the recipe can be found pretty easily. And if you ever are in a lab, have access to doing this, it's a pretty easy reaction to put together.

The only problem is that unless you use fresh hydrogen peroxide, it doesn't work. Because hydrogen peroxide

tends to go bad over time. If you're going to do this, buy your hydrogen peroxide immediately before you try to do the experiment. And then it'll work. So what happens is that as long as there is a steady supply of hydrogen peroxide in here, it'll keep oscillating. But as you've used up the hydrogen peroxide, this is going to start to die. And eventually it'll have this pale blue solution. And it's like the heart stopping. If you want to start it up again, add more hydrogen peroxide and it'll start up again.

OK, any questions? There's like an infinite number of these oscillating reactions that people have discovered. And optimized, that you can find in different places. Questions? Questions about the final. I didn't get to do a review, but you'll get that done with the TAs. Yes.

STUDENT: [INAUDIBLE]

PROFESSOR: Because there's enough of the equivalent of A, of the rain here. So it'll oscillate and there'll be some damping. So what will happen in this reaction is that the induction period will get longer, and longer, and longer. Because the w, this term right here, the frequency which depends on the concentration of A, that well get slower and slower. And eventually it'll just die. OK?