CATHERINE DRENNAN: All right. So 10 more seconds. OK. Let's quiet down. So that is the-- you got the 70% with the right answer. If people can just yell out what was wrong with number one.

AUDIENCE: Sig figs.

CATHERINE DRENNAN: Sig figs. And what about numbers three and four? What equation was that using?

AUDIENCE: Second order.

CATHERINE DRENNAN: Second order. That's right. So this is a good clicker question for a problem that's going to be coming up on exam four and also on the final exam to a larger degree. On the final exam we have equation sheets that have all the equations from the whole semester, and so you need to figure out and remember which equation goes with which problem.

It doesn't say, oh, here is the expression for first order. Here's the equation for second order. You need to look and remember which equation goes with which thing. But in terms of first order, what's a way that you can remember what a first order equation would be? What's missing from first order? Yeah, the concentration in the material. So for first order it's independent of the original concentration in the material, which is why we can use first order equations for nuclear chemistry. Because the rate of decay of radioactive nuclei are independent of the nuclei around them, so it's a first order process.

So when you think a little bit about these equations, you should be able to identify which equation goes with which problem. And so you can identify the type of first order problems also. And for the second order it almost always says, for this second order process, which gives you a nice hint that that's a second order process. And then you just have to identify the equation.

OK. So today is more kinetics. So we're in the kinetics unit. We'll be in the kinetics unit for the rest of the semester. It's our last unit. So today I think is one of the most important lectures in

terms of the kinetics unit because we're talking about reaction mechanisms, and that is really an important part of kinetics.

So investigating reaction mechanisms. So if you're going to describe how a reaction takes place-- often reactions don't occur in one step. It's really uncommon for reactions to occur in one step. So you want to describe the different steps. And you describe those steps, which are also called elementary reactions. So you break down a complex reaction into a series of steps, and then you try to figure out if that mechanism, if those series of steps, are consistent with the data that you've collected on this particular reaction.

And over here I just show you some steps in the natural biosynthesis of a vitamin biotin. Biotin is important vitamin for us. It's also used a lot in feedstock. And so people buy a lot of biotin to put in feed stock, and so there's a huge market of biotin. Now right now it's made by what is estimated to be a 13 step organic synthesis which produces-- that's a lot of steps. It's really expensive, and there's a huge amount of organic waste associated with making biotin. And we're talking about in the tons level of waste. So researchers have been trying to figure out the mechanism by which nature makes biotin because that would be a lot more environmentally friendly.

So when you're thinking about this, what you want to say is, OK, if we write out a mechanism is it consistent with the experimental data and are there fast and slow steps? Because if there's a step that's really slow maybe you can do something about it. Maybe if you're talking about an enzyme you could re-engineer the enzyme so it would be a better enzyme.

Maybe natural selection didn't particularly work. Maybe the cell doesn't really need as much biotin as we do commercially, so there was no need to make it fast. But now we have a need to make it fast, so maybe we can do some evolution of this enzyme and design something to be better.

So when you're talking about reaction mechanisms you want to know what's fast, what's slow. And if you want to use that product for something, you want to figure out how you can change things to have a better mechanism-- maybe avoid some really slow steps so that you can do better.

Today is also World AIDS Day. And understanding the mechanism of HIV protease was really essential in designing inhibitors against that enzyme. And if you inhibit the enzyme you stop the development of the disease. So this was a very important thing, and we have some pretty

good molecules to treat AIDS right now. And some of the challenges have moved on to other things, like less good health care in parts of the world where this has affected.

So I feel like AIDS has kind of taken a backseat to hearing about Ebola recently, but AIDS is still a very important problem and one that smart people like you could address. So again, understanding reaction mechanisms is very, very important.

All right. So let's go to a simpler problem and a simpler reaction mechanism. We'll go to our friend over here where we have two molecules of NO reacting with one molecule of O2 going to two molecules of NO2. So someone measured some rates for this and came up with the following rate law where you have a rate constant, which is just called k obs for observed. And we'll talk about that more in a little bit. And they discovered it is second order with respect to NO and first order with respect to O2.

So there's a couple of things right away that we can ask about this. One is, what is the overall order then of this reaction from this experimental data? What would that be?

AUDIENCE: Three.

CATHERINE DRENNAN: Three. Again, if some of you missed it. 2 plus 1 is 3. This is not where you want to lose your points on the exam. There's going to be some tricky significant figures in the kinetics units. Save your points to lose there. Count 2 plus 1 and get 3. So is one step likely to have three different things come together at the same time? So how likely is it that all three things are going to merge in one step? No, it's not very likely, so it's no.

But if it did work that way, what would it be called? What molecular reaction? Do you remember?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: So if you have three things it's a termolecular. So they're rare. So that's not how this works.

All right. So let's look at some rate laws and try to write a rate law for a reaction. We're going to take our overall reaction, we're going to divide it to two steps and write a rate law for that and see if that's consistent with the experiment.

So we finally got this up here. Sorry the handwriting isn't perfect. I got here early but then-- the

first time I'm going to use the boards a lot today. Squeegee was gone. There's always something. So we're going to break this reaction down into two steps. So in the first step we have our two molecules of NO coming together to form an intermediate N2O2. And this is a reversible step.

So in the second step of the reaction we have our O2 molecule coming in, reacting with our intermediate and forming two molecules of NO2. And so this is really pretty common that when you have a multistep reaction that you form an intermediate and your intermediate goes away.

So now we can think about how we would write the rate law for this particular mechanism. So starting up here. This is being written as a series of steps, which were also called elementary reactions. And for an elementary reaction it occurs exactly as written. That's its definition of an elementary reaction or a step. So now we can write the rate law for the forward direction of this exactly as it is written.

So that would be writing-- and these are my little K's for rate constants. So we have K1 times the concentration of NO to the 2. So we're writing it exactly as written. I said that for an overall reaction you can't just look at the stoichiometry. You have to think about experiment. But for an elementary reaction you can write it just from the stoichiometry, and so this is how we would write it just from the stoichiometry.

So what would be the order of that reaction? Just the forward reaction? 2. And that makes it a what kind of molecular reaction?

AUDIENCE: Bimolecular.

CATHERINE DRENNAN: Bimolecular. Bimolecular. OK. So let's write out the rate law for the reverse reaction now. And again, exactly as written. So we're going to have K minus 1 times the concentration of our intermediate N2O2. And that would be the rate law for the reverse reaction.

So what would be the order for this reaction now? 1. Right. We only have one thing in here. And what do you call an x molecular when there's one thing?

AUDIENCE: Uni.

CATHERINE DRENNAN: Uni. Unimolecular. For step two now you're good at this. Let's do a clicker question. All right. 10 more seconds. Yup. So we're just going to write this exactly as written. It doesn't say it's a reversible reaction. So it's K2-- and I'll put this down here. K2-- our rate constant for the

second step-- and then times the reactants. So we have O2 and our intermediate N2O2.

So what would be the order of this reaction or this step? Two? We have two things in there. And again, we call that bimolecular. So we have uni-, bi-, and ter- molecular reactions for order of 1, 2, and 3.

All right. So we've written this out. Now what we want to do is we want to write out an overall rate law for this. So we've written out the rate laws for all the individual steps. And we'll put that-- Yeah, I guess I can put it-- maybe I'll try to write it down here. I was going to have this all organized but then the boards weren't cooperating today.

So I'm going to write the overall rate. Let me try it here. And this is for formation of N2O2. And we're going to put a 2 in there, and I'll explain that in a minute. Then our K2-- so we're just writing this now from the last step-- times O2 and our intermediate N2O2.

So the overall rate of forming NO2 is the 2 because 2 moles are formed. So as these guys disappear-- as O2 and N2O2, our intermediate, disappear-- and O's going to form twice as fast because there are two of them being formed. So we put a 2 in there. And then we just have a rate order or rate law for the last step, K2 O2 intermediate.

So you can always write the rate for the overall reaction from that last step. Although sometimes we'll see if they're fast and slow steps you can also write it from the rate determining step. But we're not done here because we have an intermediate in this expression. And in a rate law you cannot have an intermediate in there. You need to solve for the rate in terms of your rate constants, your reactant concentration, and your product concentration. So we need to get rid of this. We need to solve for this.

So how are we going to do that? How are we going to solve for this? So we want to think about now, what is the net rate for this formation? How is that intermediate being formed, and how is it being consumed given those steps up here?

So it's only being formed in the forward direction of the first step. And let me just grab this. So the forward direction of the first step, which is K1 times NO to the 2. And so this is where our intermediate is formed. Our intermediate is going away in two different steps. So it's going away in the reverse direction of step one. So it's decomposing in that step. And so it's decomposing at the rate of K minus 1 times its concentration.

The intermediate is also being consumed in the second step. It's reacting with oxygen and

being consumed. So here it decays and here it is consumed. And it's being consumed by the reaction K2 times the concentration of O2 times its concentration. So that's the second step.

So now we just need to take that equation and solve for the intermediate N2O2. But we don't know net rate over there. We have too many variables right now. So at this point we have to use what's known as a steady state approximation.

So steady state approximation and pretty much everything-- I'm talking about reaction mechanisms-- we're going to use the steady state approximation. And that is that the rate of formation of intermediates equals the rate at which they go away. So the net rate is 0. So we can set this whole thing now equal to 0. So steady state approximation net rate is 0, or the rate at which an intermediate forms equals the rate at which that intermediate decays.

So I can rearrange this equation now, and I'm going to bring the terms that have the intermediate to one side. So I'm going to put them over here. So we have the term at which it decays-- K minus 1 times our concentration of our intermediate. And it had a negative but I brought it over here to this side with a 0, so now it's positive. And I'm going to bring the same for the rate law at which it's consumed over. So that's K2 times our intermediate concentration and our oxygen concentration. And now on the other side we'll have the rate at which the intermediate is formed, which is K1 No to the 2.

So this is another way to express the steady state approximation. The rate at which the intermediate goes away equals the rate at which it's formed. That's the steady state. There's no sort of flux in the intermediate. It's being formed and going away at equal rates. So now we can use this to solve for the intermediate. Now we're set. Now we can solve for the intermediate. And so let's do that over here.

So I'm going to pull out-- I had a straight line here. This one's a little crooked. I used to write a lot on the board and used to evaluate professors by their good handwriting and my ratings were always-- my overall rating was limited by my handwriting to a large degree and so I stopped writing on the board. But now they've got rid of that as a criteria, so I can write on the board again.

So I'm going to pull out the concentration of the intermediate-- our N2O2. and I'll pull it out of the expression leaving K minus 1 and K2 times O2. So I just pulled out the concentration of the intermediate over here. And then we leave the other side the same. Our K1 times our NO

squared.

So now I can solve for the concentration of the intermediate. N2O2 equals K1 times NO squared over K minus 1 plus K2 times O2. Great. So we've solved for the concentration of the intermediate now. Now we can take this and bring it back over here and put that whole term into this. And then we'll have a rate law that is expressed only in terms of our rate constants and our reactants and/or products.

So let's do more on the PowerPoint here. So this is what we just came up with. So the concentration of our intermediate K1 times NO-- one of our reactants second order-- over K minus 1 plus K2 times the concentration of oxygen.

Now I'm going to plug that into this expression, which we just got from writing the rate law for the last step using a 2 because we have two molecules of product being formed. So we're going to plug it in there, and that's going to give us this. So we have our 2, we have a K1 from here, a K2 from here, we have our oxygen concentration, we have our NO overconcentration second order over K minus 1 plus K2 times concentration of oxygen.

So that might be the complete answer to some problems but here we were given an experimental rate law, which was second order in NO and first order in O2. That does not match this. Term has an O2 at the bottom. This one doesn't have an O2 at the bottom. These are not the same. So that must mean that the mechanism has fast and slow steps and that we need to reconsider this expression in terms of fast and slow steps.

So let's go back now and think about our mechanism. And so if we come over here-- let's say that the first step-- let's bring this down again. Let's say the first step is fast. And we already said that it was reversible, but we'll put that down too. Is fast and reversible. And step two is slow.

So I'm just going to propose that these are true, and then we will recalculate what the rate law would be if you have a fast reversible step followed by a slow step and see if that agrees with experiment.

So to do that we have to consider what it means if we have a fast step followed by a slow step. So let's introduce a term-- very important term-- which is the rate determining step. Also known as the rate limiting step.

So the slow step of a reaction, if it's truly a very slow step, is going to govern the overall rate of

the reaction. So let's think about this a minute. So I told you that the extra problems for exam four are long. They're very long. Sorry about that, but there were a lot of problems and I wanted to get you ready for exam four. You also have problem set nine due tomorrow. So you've got a lot of problems to do.

So after class today I feel that many of you are going to be really inspired to get started on those problems. And you may run out of here. You might leap over the chair in front of you and race out the door. You may clear the table on the way out because you're in a real hurry to start those extra problems. You will run to the library to look for a table, but all the tables will already be taken. How did your classmates get out of class so fast to get all of the tables in the library? And they're already finishing problem set nine and starting on the extra problems.

So you race back to your dorm, but all the tables in the downstairs of the dorm are also filled with 5.111 students. So finally, on the fifth floor of one of the dorms you find an empty table, and then you're really fast. You got the problems out, you got your pencils out, you got your calculator out, you've got old equation sheets out, and ready to go. It's like two seconds.

So it took you 40 minutes to find a free table at MIT that didn't already have a 5.111 student sitting and doing those extra problems and problem set nine. So it was 40 minutes plus 2 seconds to actually start doing the problems.

So the rate determining or rate limiting step was finding your table. 40 minutes plus 2 seconds is pretty much 40 minutes, and that's what happens in these reaction mechanisms. If you have a really slow step that governs the overall rate of the reaction.

Now a lot of you know also about rate determining steps because some of you may be the rate determining step in your group of friends. The rate at which you get to dinner and eat is determined by you being ready to go. Some are in the room like me, yeah, that's me. You know who you are.

So I'm saying that what you gotta do to not let yourself be that person-- that rate determining person, the RDS in your group of friends-- you need to get sleep and you need to eat well and you need to make sure you got your ATP. And that means, of course, to get enough sleep you gotta start problems sets early, especially the extra problems because they're long. Rate determining steps. Very important.

So let's get back to our example. And we made a proposal. We made a proposal that step two

was going to be rate determining. That was slow. We made the proposal that step one was fast and reversible. Step two was slow. So what that's going to mean then is that our rate law for the first step-- that's fast. That's a big number. The rate for the second step is slow. Rate determining.

So that will mean then that K1 is going to be greater than K2 times O2, so we can drop out our concentrations here to think about them. They're going to be the same. So what's left? That means the rate constant for that reverse step is very fast. It's a big number. That's going to be big compared to K2 times O2.

So now we can go back and look at our expression for the intermediate. And we note that K minus 1 is in the bottom as well as K2 times O2 is in the bottom of the expression. So if K minus 1 now is really big compared to K2 times O2-- again, that's the fast step; that's the slow step-- then this term pretty much doesn't matter and it can drop out. Because this is really small compared to that.

And if we drop out this term we can rewrite the expression like this. The concentration of our intermediate rate constant K1 NO squared over K minus 1. And now we can rearrange this equation, bringing the concentrations to one side and our rate constants to the other side. So we have our intermediate N2O2 over NO squared equals rate constant K1 over K minus 1.

What does rate constant K1 over rate constant K minus 1 equal?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: It equals the equilibrium constant K1 for the first step. So if you have a fast reversible step followed by a slow step, the first step is basically in equilibrium. We can make that approximation that it is in equilibrium and solve it by thinking about equilibrium expressions. Fantastic. We can be back to equilibrium expressions.

So let's think about this a little bit more. Here I have a pretty picture for you. So here we have our reactants forming our intermediates. The intermediates are also going back and forming our reactants. Reactants are forming the intermediates and then back again. Fast reversible.

Every once in a while an intermediate gets siphoned off to products, but if this is a really, really slow step it doesn't happen very often. It doesn't really affect this very much. And so basically, this is in equilibrium. It's like this part doesn't even really matter. It doesn't play in. So when we

have a fast reversible step followed by a slow step, we can assume the first step is in equilibrium and we can solve for our intermediate using equilibrium expressions.

So let's do that. Let's take our equilibrium expression for the first step and now plug it in to our rate law. So we can substitute this step now or we can have rate constants or we can have an equilibrium constant. You can write either. These are equivalent. And we can put those back into this, which was our original overall rate that we wrote. We weren't done though because we had an intermediate. So we can plug this now in for our concentration of the intermediate.

And so now we get 2 times K1 K2 O2 NO squared over K minus 1. Or we could just put that with the big equilibrium constant and get rid of our little K1 over K minus 1. Both of those are equivalent. And now we can take all of our K terms and call them K obs. So K obs is just the experimental rate constant. It's the collection of rate constants that are measured.

And we often-- when we measure things, we can't distinguish K1 from K2. We sometimes try to do that, and that's a little more complicated. But in this case, all that was given was an overall K observed. And this was our experimental rate law K observed times O2 first order NO second order. And now we see this expression agrees with this rate.

So the fact that we have a good agreement means that a mechanism with this fast reversible step followed by a slow step gives rise to a rate law that's consistent with experiment. It doesn't prove that's the right mechanism. It's very hard to prove mechanisms are right, but at least it's consistent. So we can say this is a good guess, a good proposal, for our mechanism.

So let's look at another example. So in this example we have NO again. We have two molecules of NO, and now we have Br2 going to two molecules of NOBr. And we're told that the experimental rate is K obs times NO first order, Br2 first order and asked, for this proposed mechanism, which would be the slow step to give rise to that experimental data?

So the first thing that we would want to do with all of these is to write the rate laws for each individual step. So for the forward step we have one molecule of NO reacting with Br2 with rate constant K2. So we get rate constant K1 times the concentration of NO times the concentration of Br2. Again, this is a step or an elementary reaction, so we write the rate law just based on the stoichiometry here.

Now we can do the same thing for the reverse rate. So we have K minus 1 times the concentration of our intermediate. So in step two our intermediate, which is formed in step

one, is reacting with the second molecule NO, forming our product. And we can write the rate for this as well. K2 times the concentration of our intermediate, NOBr2, times the concentration of NO. So again, these are steps. They're elementary reactions so we can write the rate law based on the stoichiometry in that proposed step.

So now we can write the overall rate law for the formation of NOBr, and we can just write it from the second step like we did before. Again, this is an example. We're forming two molecules of product so there's a two in there. We have K2. It's basically just this. K2 times our intermediate, NOBr2, times the concentration of NO.

But once again, we're not done because there is an intermediate in the expression and you can't have an intermediate in your rate law. You need to solve for the rate law in terms of rate constants, reactants, and products. So we need to now solve for our intermediate in terms of things that are allowed in the overall rate law. And so we want to think again about what is the change in concentration of our intermediate So we can do the same thing that we did before?

So the intermediate is being formed in the first step. So we have the rate law for the first step. K1 times NO times the concentration of Br2. The intermediate is also decaying in the reverse part of the first step. So that's minus the reverse rate minus K minus 1 times the intermediate here. And then it's being consumed in the second step. So it's going away by the rate K2 times the concentration of the intermediate times the concentration of NO.

So again, this is exactly what we did with the first example. We think about the change, how it's being formed, and the two different ways that it's being consumed. We can again use a steady state approximation and set all of that equal to 0.

So let's do that and we'll solve again for the intermediate. So on this next slide now-- I just put those things up there. This is what you were just copying down. If you didn't finish it's still here. And here is the steady state approximation. So again, the steady straight approximation is the net rate of formation of your intermediate equals the net rate of it's going away. Net rate is 0.

So rearranging then we can bring the two terms that involve the decay or the consumption of our intermediate on one side and then set them equal to the rate at which that intermediate is formed. And then, we can pull out our terms for our intermediate. So we pull out NoBr2, leaving K minus 1, leaving K2 and NO, and set it equal to the rate law for the first step in the forward direction. We can solve for the intermediate. Take this, divide it by this term. So we have K1 times NO times Br2 over K minus 1 plus K2 times NO.

Now we can take this. We are done solving for our intermediate. We have no more intermediates in there, so we can now plug this back in to the expression we had before. So we can take this, plug it in here, and that gives us this formation. So we have 2 times K1, NO times NO-- NO squared-- Br2 on top, K minus 1 on the bottom plus K2 times NO.

Now we were asked, what are the fast and what are the slow steps? So now we want to take this and think about, if there's different fast and slow steps, is it consistent then with the experiment? So first, let's consider if the first step was slow and the second step was fast-- or i.e., if we have K2 NO greater than K minus 1. And this is a clicker question, so why don't you tell me how this then, using this, changes?

OK. 10 seconds. OK. Let's now think about why that's true. This involved doing a couple of steps in your head. So if we have a first step that's slow and a second step that's fast, the second step involves the K2 times the concentration of NO. That's the second step. That's fast.

That's going to be a big number compared to K minus 1. So if we look, both are on the bottom here. And if this term, K2 NO, is much, much bigger than K minus 1, then we can say K minus 1 goes way.

If we get rid of K minus 1, we can simplify the expression even more. We can get rid of our K2s and we can get rid of one of our NOs, which gives us this. So saying that the first step is slow and the second step is fast gives us a very different equation. A lot of things cancel out.

So we can also write that expression as K obs times NO times Br2. And the overall order of that reaction would be what? Yell it out.

AUDIENCE: Two.

CATHERINE DRENNAN: Yes. So this is what we would get for a first step that's slow; second step that's fast. Now let's consider if the first step is fast and the second step is slow. So if the first step is fast that means K minus 1, the rate constant for the reverse step, is going to be a lot bigger than K2 times NO.

And so now we can look up at this expression and say, OK, if this is much bigger than this then that cancels out. And then we're left with this expression, which I can put down here. So that leaves us-- we can't cancel any more at this point. So that leaves us with 2 times K1 times K2--

these-- NO squared Br2 over K minus 1. So assuming different things about how fast and slow the steps are gives you very different rate laws.

We can also write that to make it look a little simpler as K obs, but you'll note that the overall order is very different. So what's the overall order here? Three. Right. So let's remind ourselves what the experimental rate law was. And it was NO first order Br2 first order. So that means that this one would be consistent. So the mechanism is likely to involve a slow first step and a fast second step.

And so that's how you do a lot of these problems. You think about what is going to change when you have different fast and slow steps. One of them will be more consistent with the experimental data and one of them will not be consistent.

OK Let's do one more fast example. Here we have rate law for two molecules of ozone O3 going to three molecules of O2. And ozone has been in the news a lot recently. So we want to keep our ozone layer. We don't want it to go away.

So we have O3 going to O2 plus O, and you're forming an intermediate O. That intermediate is reacting with O3, forming our two molecules of O2. So let's just write out what our rate is for the forward reaction. So we have K1 times the concentration of O3. For the reverse we have K minus 1 times concentration of O2 times the concentration of our intermediate O. For the next one we have K2 times our intermediate O times the concentration of O3.

So now we're told that there's a fast reversible step and a slow step. So the rate will be determined by the slow step. So we can write out the rate of formation of O2 based on the slow step, which happens to be the second step, which is what we've done all along. So there's not really a huge change right now.

So the formation-- again, two molecules of O2 were formed so we have a 2. We have K2 times the concentration of our intermediate O times the concentration of O3. But again, O is an intermediate so we need to solve for it in terms of our products reactants of rate constants.

But now we're told something about fast and slow steps right up front. And so if we have a fast reversible step followed by a slow step, how can we solve for our concentration of our intermediate in a simpler way than we've been doing? What do we use? Or what can we use?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: We can use the equilibrium expression. So we can put that in. We can say our equilibrium expression products over reactants equals little K1 over K minus 1, or equilibrium constant K1. Solve for O and get either big equilibrium constant K1 or our little rate constant K1 over K minus 1, and we have O3 over O2 here. So this was a lot simpler than doing all of that.

So again, if you have a fast reversible step followed by a slow step you can solve for the concentration of your intermediate using an equilibrium expression which you all know how to write. So that makes your life easier.

Then we can substitute that back in and we are able to put this back. And we'll solve it for O and we'll plug in our K1 over K minus 1. O3. We had an O3. So that's squared over O2. Or we could write that in terms of K obs O3 concentration to the 2 over O2.

So let's end with some fun, thinking about what we would observe here. First, the order and then what would happen if we double things. So what is the order with respect to O3? You can yell that out.

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: Yup. What is the order for O2?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: Oh, sorry. I had something here. Double this what happens?

AUDIENCE: [INAUDIBLE].

CATHERINE DRENNAN: The rate. Well, four times. Order here. Some people yelled it out. Oh, no. Oh, man. It's a clicker question. I forgot about that. Don't listen. But luckily, everyone yelled out different answers. All right. 10 more seconds. OK. Yup.

So it's minus 1. And so if you double it, it will half. And then finally, the overall order would be 1 because again, the overall order is the sum. So 2 minus 1 is 1. And last clicker question. All right. 10 more seconds. I know you're really in a hurry to do those extra problems for exam four. I'm the rate determining step. I am with my clicker question. I admit it.

AUDIENCE: Yay.

CATHERINE DRENNAN: All right. All right. See you Wednesday. Remember, final clicker competition of the year before the finals.