PROFESSOR: Please note that this is a clicker competition, perhaps the last of the year, before you put in your vote for this particular clicker question. And the defending champs are recitation three, and I believe that no recitation has won more than once. Is that true? Is there a recitation that has two victories? So, this might be your last chance if your recitation has not won, or if you want to be decisive victors in the clicker competition to have a repeat victory, this is your chance -- no pressure. But go ahead and put in your clicker response. OK, let's just take 10 more seconds to click in.

OK, the answer here is b, and the trick was to recognize which is the equation for first order half life, and which is the equation for second order half life. Most people got this right. And we picked this clicker question to demonstrate a point that will, for the final exam, which is that you will have an equation sheet of all the equations. There'll be a few you have to memorize, we'll let you know what they are, but that's a lot of equations. So, so far on each hour exam, you've had an equation sheet that's been related to that particular material.

On the final, you of an equation sheet that has the equations from exam 1, exam 2, exam 3, and also the fourth exam material. And so, it doesn't say on them, oh, first order half life equation, colon, and then the equation, it just has all of the equations.

So one thing that you have to do is recognize which equation can be applied where. And this is something that people, occasionally that's part of knowing the material is to know/recognize the equations. You don't have to memorize them, but you do have to be able to recognize them and know when to apply them. So that's something you should be thinking about as you're reviewing the material for the exam. And we're just going to at jump right in and talk about reaction mechanisms. So this is the last type of question that's on problem-set 10.

So, when you're investigating reaction mechanisms, you often will have an experimentally determined rate law, and then you want to try to come up with a mechanism that's consistent with that rate law. So, for this particular reaction, we have 2 n o plus o 2 going to 2 n o 2 gas. And experimental rate laws determined there was a rate constant called k obs, for k observed, the observed rate constant that was calculated. And we know that it's the order of the reactions here. Overall, what is the overall order at this particular rate law? Three. So we have second order in n o and first order in o 2. So if it's overall order of three, is it likely to occur in one step? No. What would it be called if it did occur in one step -- if three things came together at the same time to form a product? Yeah, thermonuclear. And we learned last time that thermonuclear reactions are rare. So it's unlikely that those

three things, the two n o's and the one o 2 are going to come together at the same time to form product, so it probably has more than one step.

So, on the board here and on your notes, we have a two-step proposed mechanism, and let's talk about these two steps and come up with a rate law that's consistent with this mechanism, and then see if that agrees with the experimental rate law that was determined.

So, in the first step of this reaction, we have 2 n o's coming together. There's a little rate constant, k 1, above the first arrow, and for the reverse direction, we have k minus 1, so this is written as a reversible reaction, and it's forming an intermediate n 2 o 2. In the second step, we have the o 2 coming in, reacting with that intermediate with a rate constant, k 2, and it's forming two molecules of n o 2.

So now we can write the rates for each of these individual steps. We can write the rate for the foward reaction here, and so that's going to be equal to k 1. And we have n o, two n o's, so n o squared. And again, this is a step or an elementary reaction so we can write the reaction exactly as it occurs. We can write a rate law for that step using the stiochiometry of the reaction. For an overall reaction, you can't do that, it has to be experimentally determined. But for an elementary reaction or a step in a mechanism, you can do that. So we write it exactly as it occurs.

So, what would be the order of this particular reaction as written here? Two. And what about molecularity? It would be bimolecular. So we're just getting you used to some of these terms.

All right, so then for the reverse direction, the rate of the reverse direction would be equal to what rate constant? k minus 1. Times what? Yeah, n 2 o 2. So what's the order here? One. And what's this called? Yeah, so that's called unimolecular.

All right, what about step 2? What would be the rate here, and that is a clicker question. OK, just 10 more seconds. Yup, so we write it exactly as written, so we have a k 2 times the concentration of o 2 times the concentration of n 2 o 2. All right, so what is the overall order here? Two. And again, that would be the bimolecular.

All right, so we have our two steps, and we've written rates for all of those particular steps. Now we're interested in writing the rate of the overall reaction that forms n o 2. So, let's think about what the rate of n o 2 formation is. So, in the last step, we're forming n o 2, and we can just use that last step to write this out. We're forming two molecules of n o 2. So we're going to put a 2 in there, because the rate at which the concentration of this will increase twice as much as will decrease this amount. And the book is somewhat inconsistent in its use of 2's in these equations. If you're forming two molecules in your last step, there should be a 2, but 2 is not always in the

answer key. So what I've done in the past is if you put a 2 and there should be a 2, great, but if you don't put it, that's OK, too, so I have not taken off for this because the book is not been completely consistent in its use of that. But, if you see a two, and 2 things are being formed, you know where that comes from.

So, 2 times k_2, that's the rate constant of that last step, and that we're talking about the concentration of O_2 and the concentration of N_2O_2. So we're writing out just that last out there with the 2, because two molecules of NO_2 are being formed. But we're not done with this, we can't use this, because it has an intermediate term in there. And if we're going to write the rate of a reaction, the rate of product formation, we can't have any intermediates in our equation. We need to solve it in terms of products and reactants. So, we need to solve for N_2O_2. So we need to solve for the concentration of N_2O_2, and substitute that into our equation. So we need to solve for it in terms of products and reactants. So, we need to think about how this intermediate is formed, and we need to think about how the intermediate is decomposed, and we need to think about how this intermediate is consumed.

So, the net formation of N_2O_2 is going to be equal to the rate at which it's formed. So the rate at which it's formed. What step is it formed in, the intermediate formed in? It's in step one in the forward direction, so the rate at which its formed is k_1 times NO squared. So that's the forward rate of the first step. Then we need to think about the rate at which its decomposed. What step does the intermediate decompose in? Right, the reverse of the first step. So we're going to put a minus sign here, and k_{-1} times the concentration of the intermediate. And then we also want to think about the rate at which it's consumed. And it's consumed in the second step, so that's k_2 times the concentration of the intermediate times the concentration of O_2.

So that's the net formation. And now we can use something called the steady state approximation, and the steady state approximation is used in all sorts of kinetics, including enzyme kinetics, and it can be phrased two different ways, which are equivalent. You can say that the steady state approximation is that the net formation of the intermediate equals zero -- i.e. this is the net formation of the intermediate, so this entire equation equals zero. Another way to say it is that the rate of formation of the intermediate equals the rate of decay. So that's saying the same thing, that this term is going to be equal to those two terms. That's saying the same thing.

So, if we can set this whole equation equal to zero, then we can solve for the concentrations of the intermediates in terms of the rate constants and the concentrations of the reactants and the products, which is what we need to do. So, let's do that. So we can rearrange this expression now that we have set equal to zero, and so we can bring N_2O_2 over to one side, so we have our intermediate on one side. And then we are going to have k_{-1}, and our little k_2 times the concentration of O_2. And so, that is the rate in which the intermediate is decomposed and consumed, and that's going to be equal to the rate at which it's formed, which is another way of expressing the steady state approximation. So we've just moved the decomposed and consumed to one side, and we have the rate at which it's formed on the other side, and now we can easily solve for the concentration of the N_2O_2, so

we're going to do that over here. So that's now going to be equal to our k_1 times n o squared over k minus 1 plus k_2 times the concentration of o 2. So now we've just solved for N_2O_2, our intermediate, in terms of our rate constants and in terms of our reactants. So that's good.

Now we need to take this and substitute it back into here. And if we substitute it back into here, let's do that over here, so now we'll have k, 2 times k_2, we'll also have a k_1 term. We're going to have, we have n o squared. We also have an o 2 term from over here, and this is all going to be over k minus 1 plus k_2 times our concentration of o 2. So we've just substituted that term in here, and now we have a new expression for the rate of our product formation, and that's lovely. Except that it doesn't agree with the experiment. So we have a problem. In the experiment, there's n o squared and o 2, but there is no o 2 in the bottom, so something is going on. So that means that our reaction as written, which didn't have any fast steps or any slow steps is inconsistent if you write a mechanism for this, if you write a rate law for this, it's inconsistent with the experiment. So we need to do more to our proposed mechanism. We need to add fast steps and slow steps until we can write a mechanism that agrees with the experiment. And so, if we want to do this, we're going to assume, now we can try that the first step is fast and the second step is slow.

So let's talk about this slow step and what happens if you have a slow step. So I'm going to introduce this term of rate determining step. So the slowest step in an elementary reaction is going to determine the overall rate. If it's slow compared to the other steps. And so, the overall rate, it can't be any faster than that slow step, and that slow step is going to govern how fast the overall reaction is.

All right, so let me give you an example of this. I know they're you're all very anxious to complete problem-set 10, the last problem-set that will be graded in this course. And you know, because I told you at the beginning of class, that after today's lecture, you will know all the material that will allow you to complete that problem-set. So some of you are going to get really antsy at the end of class thinking OK, I can go and do that problem-set. So, you're going to be ready, you may have already started packing up your backpack as the class is winding down, you see we're getting close to the end of the handouts saying, all right, I've got to get out of here, I've got to get to the library and finish the rest of problem-set 10.

All right, so let's say it takes you five seconds to pack up and be out the door. Or maybe there's some people coming in, OK, maybe ten seconds to get out the door. Then you're running down toward the library and you're moving pretty fast, you're jumping over people that are stopping and talking to their friends, you're moving very quickly, you might slide down the banisters to get to the first floor, and you get to the library, but you were too slow. Even though you did it really fast, all the tables are busy, everyone else is completing problem-set 10. So you go up and down, you're looking for a table, there's no tables, they're all busy, everyone has their chemistry textbooks out and they're going.

All right. So, then you have to leave the library, you go to building 2, that's close by, they're classrooms, they're not in use, the first couple you check there's recitations going on. Finally you find the one that's empty. When you find it that's empty, your backpack is off, your books are out, your calculator's out and you're going. Right, maybe another ten seconds. But it took you about 20 minutes to find that free table. So, maybe ten seconds to get out of this classroom, ten seconds to get your books out of your backpack, but then 20 minutes overall to find that free table. So that's the rate determining step, that 20 minutes to find that table is going to control the overall rate of the reaction. And so, many of you have probably experienced rate determining steps in your life, some of you may have friends that are always your rate determining step, and so you know about this. You know about this. And so rate determining steps allow us to come up with different kinds of mechanisms and simplify different expressions.

All right, so let's look at what this does for us here. If we make assumptions now about a step being fast and a step being slow. All right, so we're going to be able to -- this expression here, we're going to be able to simplify. All right, so we're going to ask the question then, here, we're assuming that we're going to say, all right, let's just say the first step is fast and the second step is slow. We're going to see whether that gives us an answer that's consistent with the experimentally determined rate law. So here, if we say this is fast and this is slow, basically we're asking the question, is the decomposition of the intermediate or it's consumption faster? So as we wrote this, then, we're saying decomposition is fast. The first step is fast and reversible, so the decomposition is fast. The second step is slow, the consumption of that intermediate is slow. So that allows us to change our rate.

So, what we're then saying in terms of the here's the words, here's sort of the equations, we're saying that this term here, this k minus 1 times the intermediate term, is a lot bigger, because this is faster than this. This is slow, the rate of consumption is slow. So k minus 1 is going to be a bigger number than k 2 times o 2.

So, if we say that, if we say this is fast, that's a big number, this is a fast step, k 2 is a small number, it's slow, if this is a lot smaller than k minus 1, and these are both appearing in the bottom of the equation here, that allows you to get rid of this term. So if you have something really big and something pretty small, on the bottom of this equation, the really small thing is kind of insignificant. And so we can get rid of that here. So we can get rid of this term. So that allows us to simplify this expression. Now we have k 1 times n o squared over k minus 1. We can also rearrange that and bring our concentration terms on one side, so we have our intermediate over our n o squared and have that now is going to be equal to k 1 over k minus 1. What is little rate constant k 1 over rate constant k minus 1? Big k, right. So that's another way of saying the equilibrium expression. So it's the equilibrium constant for the first step is equal to k 1 over k minus 1.

So basically what we're saying then, if we have the first step being fast and reversible, and the second step being slow, we're saying that the first step is really an equilibrium. So what allows us to say that? Well, if you have a fast

reversible step followed by a slow step, that means that not much of your intermediate is being siphoned off by the second step, allowing you to reach equilibrium. So you can think about that in terms of this plot here. If you have reactants going to intermediate, and this is fast and reversible, so they're going back and forth, fast, reversible, and very little of that intermediate is getting siphoned off, this is very slow. So very, very little of this is being siphoned off to products. So that allows that first step to really reach equilibrium conditions, because this doesn't really factor in, and so you reach an equilibrium here. And that allows you to simplify your expressions.

So now, we can go back with our simplified expression, and we can express it as rate constant k_1 over rate constant k_{-1} times n_o squared, or we can write it as the equilibrium constant 1 times n_o squared, and we can plug that in solving for our intermediate. And so, if we put that now back into this expression, we have the $2k_1$, k_2, we have our oxygen concentration and our n_o squared over k_{-1}, or we can have equilibrium constant 1 with our k_2 in our 2. And now, we're consistent. If we realize that the k observed that was given in the experimental rate law is a combination of all of our k terms. So it's a combination, you can't, at least in this experiment, you weren't able to come up with the individual rate constants, they just came up with overall observed rate, and so that's all of our terms in there. And so if we put that in here, we realize that this is consistent with the experiment.

And in doing these problems, it's OK to leave your little rate constants, it's OK to use equilibrium constants in there, you should show all of your work, so that if you have a k obs in your final answer, we can look back and see what that was equal to. So it's hard not to show all your work as you're writing through all of these on a test, but you can end your answer, it would be correct end your answer here or here or here. So I don't care which k is in your final answer, but definitely show all your work. So that agrees with the experiment.

All right, so let's look at another example now. And now we have, again, a 2-step reaction, and the first step is fast and reversible, and the second step is slow. So, with those predictions of the mechanism, let's just go right through and try to solve for the rate here without going through all of the steps we did the first time and see if we can do this more efficiently. And again, this is a reaction with ozone, and depletion of ozone is a major problem that will be facing us, that has faced us, and will continue to face us in the future.

All right. So lets first think about the rates of the individual steps. So the rate of the forward reaction here is going to be what? Just yell it out. Yup, k_1 times the concentration of o_3. What about for the reverse step? Yup, it's like clear and then it gets mumbly. k_{-1} times the concentration of o_2 times this concentration of o, which is an intermediate. All right, so let's look at the second step here. So the rate here is going to be k_2 times this intermediate -- concentration of this intermediate, o times the concentration of o_3.

All right, so now we know that this second step is going to be controlling the rate, it's a slow step, at least that's our

prediction that we're going to write a rate expression based on. And so, that's going to be our slow step, our rate determining step. And again, we're forming two molecules of o 2 in this step. So we can have a two in there. And that the rate of formation of o 2 in this last step, 2 times k 2 times our intermediate o times o 3. Are we done? Was it that easy? Are we done? No. Why isn't this finished? There's an intermediate. Intermediates will not be your friend in doing these problems.

Yes, we have an intermediate so we're not complete. We need to solve for o in terms of products, reactants, and rate constants. So we're not done. So we need to get rid of the intermediate. But now, we can do that more simply because we've set this up that we have a fast reversible step followed by a slow step. So we can solve for the concentration of that intermediate in terms of equilibrium expressions. So, if you haven't learned how to write an equilibrium expression yet, remember you need it for the unit on chemical equilibrium, the unit of acid base, the unit of oxidation reduction, and here you need it again in kinetics, so definitely want to be able to write those for the final. So we can go ahead and write those. So, for the first step, again, it's products over reactants. You can also express that in terms of rate constant k 1 over rate constant k minus 1, and that's all equal to our big k, our equilibrium constant, k 1. And so now we can solve in terms of o, our intermediate, and so here, we pull that out, here we've solved for it in terms of k 1 times o 3 over k minus 1 times o 2, so we just brought those to the other side. You could have also used the equilibrium constant here instead of the rate constants, either one is OK.

So, now we've solved for it here, and we can put it down into this expression here. So we are going back to our overall expression that we wrote. So the expression that we wrote based on this was 2, k 2 times the concentration of our intermediate, times the concentration of o 3. Now we substitute in for the intermediate, so we have 2 times k 2, k 1, we have o 3 and an o 3, so that squared, over k minus 1 times o 2.

And this can also be expressed in terms of k observed, putting those terms together, o 3 squared over o 2. And that would be the answer to what the rate is for that particular proposed mechanism.

So, let's think about if that's true, what we should expect if we do some experiments, what we should expect about the order of the reactions, and what would happen if you double concentrations of things and look for the effect. So if you're going to test this proposal, what would we get? So, what is the overall order of this rate law here. Oh, sorry, the order first let's do of o 3. 2. So if we double the concentration of o 3, what would you expect to see in terms of the rate? It will what? Yup, quadruple. What is the overall order of o 2, or order of o 2, and that is a clicker question, actually. So you know what some people think. And not only tell me the order, but tell me the effect of doubling. OK, let's just take 10 more seconds. Very good.

All right, so the overall minus 1, that's what it means if it's on the bottom of that equation there. And so if we double it then it should half. So overall then, what is the order of the reaction? It's 1. And so, remember you can

sum up the order of the individual ones to get the overall order, so the overall order is 1. And what about if you double both things, what's going to happen to the rate? OK, let's just take 10 more seconds. OK, people are doing quite well on this. All right, so you double both and you double. So, everyone's in very good shape on these types of problems, which is excellent because this is worth a lot on the final.

All right, so let's do a final example, and in this case we're given an experimental rate law, which is up here, k observed times the concentration of n o and the concentration of b r 2, and we want to figure out from this, we'll look at if we have one step is being fast and the other step is being fast, and see which would be consistent with this experimentally determined rate law. So these are some of the types of problems you have, your given experimental rate law and say tell me which step has to be fast and which has to be slow to have a rate that's consistent with the observed rate.

So, in this reaction we have 2 n o plus b r 2 going 2 n o b r. So if we write this in the first step, we have n o plus b r 2 going to an intermediate, n o b r 2 with forward rate constant, k 1, and reverse rate constant, k minus 1. And in the second step we have the intermediate interacting with another molecule of n o forming two molecules of n o b r, our product. So let's consider what the rate of the forward reaction is here, and so that would be -- you can yell it out. k 1 times -- yes, excellent. And for the reverse reaction then we're going to have our k minus 1 times our intermediate concentration.

Now we can look at step 2 where our intermediate is being consumed, and the rate would equal then k 2 times the concentration of the intermediate, n o b r 2 times the concentration of n o. All right, so we know nothing now about fast or slow steps, so we can write the formation of our product just in terms of this second step. And again, there are two molecules being formed, so we have a 2, and 2 times this rate for this second step, k 2 times intermediate times n o. So again, now we have an intermediate that we have to get rid of. We can't have an intermediate in our final expression. But we can't use the equilibrium constant right now because we don't know anything about what are the fast or the slow steps. So we're going to write it the long way with no assumption about fast or slow steps. So to do this, so we have our intermediate, and so we're going to solve for it in terms of products and reactants. So we're going to write about the change in the concentration of that intermediate. So, the intermediate's being formed in the first step. So we first write the rate at which it's being formed. So it's being formed here, so that's k 1 times n o times the concentration of b r 2, so this is how it's being formed. And then we're going to consider how it's being decomposed, and you told me before it gets decomposed in the reverse of the first step.

So we have a minus sign, because this is a negative change in concentration, it's being decomposed, and it's being decomposed with a rate constant of k minus 1 times the concentration of that intermediate. And the intermediate's also being consumed, so that's decreasing the concentration of the intermediate, and it's being consumed in this second step. So it's being consumed here with the rate constant of k 2 times the intermediate

times n o. So that second step. So this is how we write it if we don't know anything about the rate at which -- what's slow and what's fast. So this will always, always work to write things this way. So that's the overall change in the concentration of the intermediate, how it's being formed, decomposed, and consumed.

Now we can use the steady state approximation, and you can always use the steady state approximation in these problems, and that says that this net change is going to be equal to zero. So the steady state approximation, then, let's you set this entire term equal to zero. And sometimes, a question you might get is to say what the steady state approximation is. So you should be able to articulate that in words as well as use it on a problem. So now we can set this all equal to zero, and we can solve for our concentration of our intermediate.

So, rearranging this then, bringing our intermediate terms on one side of the expression, and again, here's the rate at which it's decomposed and consumed being equal to the rate at which it's being formed. And we can pull out our intermediate, so then that's times k minus 1, k 2 times n o, and that's equal to the rate at which it's being formed. And so now we can take that, divide by that term, and we get an expression for the concentration of the intermediate in terms of our reactants and our rate constants. So now we need to plug that back in to the original equation that we had.

So this is what we solved for, and now we can put it into here, and if you rearrange that, we have the 2, we have the k 1, we have the k 2, we have an n o here, we have an n o there, so it's squared, b r 2 here, and then on the bottom we have k minus 1 plus k 2 times n o.

OK, so that's great, but that's not consistent with the experimentally determined rate law, so something has to be fast and something has to be slow. So let's first consider if the first step is slow and the second step is fast, which would mean that the second step is bigger, it's faster, that's k 2 times n o would be bigger than k minus 1. So the second step then is fast, faster than this. So now why don't you go ahead and tell me how this simplifies if that is true. All right, let's just take 10 more seconds. Yup. All right, let's look at why.

All right, so that's the answer and let's consider why. So that means if this is much bigger than this term, that cancels out. If that cancels out, what else cancels? k 2 also cancels, and what else cancels? one n o cancels giving you this expression. And that is consistent with the answer up there. So you could also see that as the k observed. So that's consistent. And let's just quick -- oh, first tell me the overall order. 2.

And now let's just look at what would have been true if we had done it the other way around. So if we did it the other way around, we'd say that the first step is fast so that's a lot bigger than this. If this is a lot bigger than that, we'd cancel out this second term here. Can anything else cancel? No. So, we're left with this expression, and that is not consistent with this up here, because we have this squared term. So even if you write it as k observed, that's not consistent. And so, the overall order for this would have been 3, which is not consistent with the experiment.

All right, so now you know everything you need to know to finish problem-set 10. Don't let anything be your rate determining step.