PROFESSOR: So last time we were starting more complicated mechanisms and we looked at series reactions. A goes B, which is an intermediate. Goes to C with rates k1 and k2. And we solved the problem exactly. Which turned out to be a little bit complicated. And then we were looking at special cases. And I left the special case of k1 equals k2 to do as a homework problem. And then on the board we did k1 much greater than k2. Which looks like, if k1 is much greater than k2, the rate into k1 is much greater than k2, so using the analogy of buckets and pipes, it's a big pipe between k1 and between A and B. And a little pipe between B and C and you started with a bunch of liquid on top. And you basically dump it into here. And then you slowly drip into C here. So the first thing that happens is that A gets dumped, it becomes B very quickly. With a rate constant k1. In a first order fashion. So A is A0 e to the minus k1 times time. Then B comes up sharply. And then drops down with rate constant k2 slowly. So B is approximately A0 e to the minus k2 times time. And then C has a very small quadratic rise, followed by the exponential rise to saturation that you'd expect. So C is approximately a0 times one minus e to the minus k2 times time. The rate constant k2 dominates the long times. And everything it's looking like it's pseudo first order at long times.

So you can do this either by thinking about it, solve the problem by thinking about it, which is perfectly fine. Or you can do it by solving it exactly, as we have done last time. And then putting in the right approximations. Which in this case was Taylor's approximation, if I remember right. And know just by looking at the equation and putting the right approximation, you get it out. And a third approximation, which is the opposite one, k2 much less than k1, so k1 much less than k2, the way that that's going to look, we can do it by inspection.

So basically if we think of buckets and pipes, that's a very thin pipe connecting the bucket for A and B, so we drip from A to B, then we have this very fat pipe connecting B and C. So as soon as a little B gets in there, it immediately becomes C. So, the rate determining step is the first one, A goes to B. And so k1, we expect that to be the rate that dominates the long time. And we never expect to get any significant amount of B to pile up in the middle bucket, because this pipe is much bigger than that one here. Therefore, what we expect to see is a slow decay in A, with rate constant k1 dominating the long times, A is approximately A0 e to the minus k1 times the time. We don't expect B to amount to very much at all. It'll rise up a little bit at the very early times, and it'll pretty much stay very, very small. Not quite constant. And in fact if you look at the full result, and you put in your approximations, and I'll let you do that, you would find that B is essentially related to A through a constant term where k1 is very small compared to k2. So this is a very small number here. B is equal to a very small number

times A. So it basically follows A, but at a very very, low level. And then you would find that C rises up in approximately e to the minus k1 times t, so with rate constant k1. One minus e to the minus k1 times the time.

So the dominant rate is k1, and in this case here this is an approximation that we're going to see again. We're going to revisit this approximation here when we get to more complicated mechanisms, it's going to become this steady state approximation. Where the amount of the intermediate, or the concentration of intermediate, is low at all times. And doesn't change very fast. The slope here is very slow. Because k1 is so slow coming down, and B is related to A, which means it's related to this slow decrease in A, the amount of B is small and the rate of change in B is also very small. And hopefully we'll get to that very soon in this lecture.

OK, so that's a summary of what we did last time. Any questions?

So the next thing now is to go to the next mechanism. Which is, so far we've looked at reactions that proceed all the way. We haven't looked at equilibrium yet. But we know thermodynamics is all about equilibrium. So now we're going to connect kinetics and thermodynamics. We're going to look at a mechanism which is an equilibrium mechanism. Equilibrium or reversible reactions. Where you have A goes to B, with summary constant k1, but you can have the reverse process B goes back to A with the rate constant k minus one. Or you can write is as A k1, k minus one to B, where k1 could be k forward and k minus one could be k backwards. Also written as k sub f, and this is also written as k sub b.

So now we have more information than we had before. Because now we know this is an equilibrium problem. And we already know about equilibrium from thermodynamics. And we know that at equilibrium, in addition to all the rate laws that we're going to write down to solve the problem, we also know that at equilibrium, the equilibrium constant is related to the equilibrium concentrations. To the ratio of the equilibrium concentrations. This is something additional that we have.

So let's write down everything we know. And our goal is to find out the time, the dynamics of this problem. Suppose you start at some time t equals zero, at a certain amount of A0 in your pot, a certain amount of B0, how do you get to equilibrium. What's the rate, what does it look like?

So the first thing is to write down the rates. So the forward rate minus dA/dt, which is the forward rate, R sub forward is equal to k1 times A. And the backwards rate, minus dB/dt, which we can write as R sub backwards, that's k minus one times B. At equilibrium, we have no dynamics. Or no ensemble dynamics. The pot looks constant. It doesn't look like anything's going on in there. The concentration of A doesn't change. The concentration of B doesn't change. They're constant at the equilibrium concentration. So that implies that the rate of formation of B must be equal to the rate of destruction of B. Or, in other words, that the rate forward at equilibrium has to be equal the rate backwards. Otherwise, there'd be changes in concentrations. So if that's true,

then that means that at equilibrium, k1 A equilibrium has to be equal to k minus one B equilibrium. Which means that we can get this ratio of B to A. And see that this is equal to k1 over k minus one.

So we've just, this is pretty major here. Looks pretty simple, but we've taken an equilibrium property here. And related to kinetics. To a rate property. So here we have kinetics. Here we have thermo.

And this is going to turn out to be, this kind of ratio between forward rates and backwards rates, related to equilibrium constants is going to be valid, not just for this very simple mechanism we have here with just two species. But it's going to be valid for more complicated. And we have two species reacting to form another species, or bimolecular stuff, et cetera.

OK, so now we've laid the groundwork, let's look at the dynamics. Let's look at the time evolution. So that means that we need to take, well this is not quite right. I shouldn't write minus dA/dt. This is minus dA/dt rate forward in the absence of reverse process. It says just the destruction of A and not the creation of A. So if you look at the full kinetics, the full mechanism, this also, the rate backwards is minus dB/dt, in the absence of forming B back through the reverse process. So both of these are in the absence of their reverse process. The full kinetics, for the destruction of A. A is the rate backwards, or the rate forwards, which is k1 times A, and then the rate backwards, which is the creation of A. That's the two rates together. Minus k minus one times B. There's the formation of A here, this is the destruction of A. This is the full differential equation for the full mechanism. Not just one part of it. This one here is just for the first step, and that one here is for the second step. This is what we need to solve.

But now we have a lot of help by what we've already done. So, what we can do is well, the problem here is that's it looks hard because there's B included in here. This is not just A, there's B in here. But there's only two species. And stoichiometry is going to help us out. Remember last time, or a few times ago, we said the last species is the easy one. Because it's always related to the concentration of all the other species by stoichiometry. And the last one here is B. So we know that B is related to A. B is whatever you started out with. Plus whatever you used up for A. That's one way of writing it. So you start with this amount, and you create this amount. By having A react. This is what you started with, A, and this is what's left. The difference has to go into B. So stroke stoichiometry give you a relationship, which you can use to plug into your differential equation here.

And now, after rearranging your differential equation, putting B in there, you can rewrite this as k1 plus k minus one times A minus k minus one times B0 plus A0. Something which depends on A, something which is constant here.

OK, and what else do we know? We know something about equilibrium. We know something about when we reach a state where the rate forward is equal to the rate backward. When the rate forward is equal to the rate backwards, the rate of change of A is zero. A is not changing. The concentration of A is not changing. So at

equilibrium, dA/dt is equal to zero. And just like in this example here, this is going to turn out to be related to an approximation called the steady state approximation, which we're going to see later this morning. Writing at equilibrium that the change in the concentration of one of the species is equal to zero, we're going to use that as an approximation also later, when we get to more complicated mechanisms.

This is going to be the equilibrium approximation. And this is going to be the steady state approximation. Let's keep going with our, we're solving this guy here. So at equilibrium, dA/dt is equal to zero. And then we can replace our concentrations here with, and so if you write equal to zero here, then we can write it as equilibrium right here. And we'll be able to solve for A equilibrium in terms of k1, k minus one, B0, and A0. And then if you do that, you get A equilibrium is equal to k minus one over k1 plus k minus one times B0 plus A0. And we're going to need that. Because now we're going to be able to plug this, so there's A0 plus B0 sitting here. And we're going to replace A0 plus B0 in terms of A equilibrium. There's a minus sign here. And between this A and this A equilibrium here, so by rewriting, by plugging in A B0 A equilibrium instead of B0 plus A0, we can rewrite that equation as dA/dt is equal to k1 plus k minus one times A minus A equilibrium.

This is nice because, this quantity, A minus A equilibrium, describes the difference between where are you are and where you want to be. It's a nice variable to have. It's going to change in time and at infinite time, this is going to go to zero. A is going to go to equilibrium. A equilibrium is a constant. Now we have a differential equation that relates A to this difference. But A equilibrium is a constant. So there's nothing that forbids us from just writing minus A equilibrium here. d of a constant dt is zero. So I'm just basically subtracting zero here. So and I have something of the form dx/dt is equal to constant times x. And I know how to write that. That looks just like a first order process. I know the solution is A minus A equilibrium is equal to my initial A, my initial state. A0 times e to the minus k1 plus k minus one times time. And I've solved the problem.

I've described how, as a function of time, how A, the concentration of A, gets equilibrium. And if you want to know B, it's just the same thing. You replace B here and B0 here. You put k minus one here, k1 here, but it's the same thing.

So if you were to sketch it out as a function of time, there's, eventually you'll get to the concentration A equilibrium. If you're above it, you're going to decay in a first order fashion, with a rate constant k1. A minus A equilibrium is A0 minus A equilibrium e to the minus k prime times t, where k prime is k1 plus k minus one. And this is when A is greater than A0, A equilibrium. A0 is greater than equilibrium. And if you start below, you're going to come up like this. A0 is less than A equilibrium. And both rates come into here, in a very simple way. Just the sum of the two.

So experimental, if you want to find out these rates, you can measure their equilibrium concentrations. Measure k equilibrium by obtaining the equilibrium concentrations of B and A. And that gives you the ratio of k1 plus k minus

one. And then you can just start the process with some concentration of A. Which is different in equilibrium. Then watching it in time, extract out, observe and measure k1 plus k minus one. In this kinetic equation. At kinetic relation. And then you have two results, two pieces of data. You've measured k prime, which gives you the sum of the two. And you've measured K equilibrium, which gives you the ratio of the two. And you've got your two rate constants out. OK, any questions for the equilibrium problem? We're slowly -- yes.

STUDENT: [INAUDIBLE]

PROFESSOR: There is not yet a relationship between k1 and k minus one. It depends on the problem. And we're going to study the, when we get to potential barriers, we look at, we'll look at this issue. OK, it's a good question. We're going to do that probably next time.

So let's get going, then, with reversible reactions. So now we have, let's make it a little bit more complicated. Let's, instead of two species, let's make it three species. So we have A plus B goes to C, where the rate constant k1, and then C goes to A plus to B with a rate constant k minus one that you can rewrite as A plus B goes to C, k1, k minus one, and then you write down your, you want to solve this. So the first thing you do is your write down your differential equations. dA/dt is equal to, put all the rates in there. k1 A B minus k minus one times C. And at equilibrium, we set that equal to zero. So you can write equilibrium here, equilibrium here, equilibrium here.

And when you bring this term over to the other side, you find, then that at equilibrium the ratio of the forward rate to the backward rates is equal to C equilibrium divided by A equilibrium. The equilibrium, which, you know is the equilibrium constant. So again, for this slightly more complicated problem, the ratio of the forward and backward rates are related to the equilibrium constant.

So now you want to solve this. Well, we're not even going to try. Because it's going to be too complicated. So as soon as you get away from first order kinetics and go to second order kinetics with multiple steps, it's a mess. So instead you try to find approximations. In this case here there's one we can use. Or a limiting case, at least. One we can use, which is an obvious one, which is flooding. As a limiting case. If we want to isolate a small part of the problem, we can use flooding. Because we can overwhelm the system with either A or B. Take B0 much greater than A0 and C0. So over the course of the reaction of the process, the concentration of B hardly changes. And so when we write our kinetic equation, our rate law, k1 A B minus k minus one C, we could put a little naught here, because we know the concentration of B is not changing. And so now we're left with the problem we had before. Which was a reversible first order process which we have just solved.

And you go through the experiment and you extract out k1 times B0 and k minus one. You do the experiment again with a different concentration of B0 to start out with. And you can extract out k1. So this is a process of getting the rates by using a simple approximation here. Simple limiting case.

Any questions? So we've just finished putting all the building blocks together now. Let me remind you what these building blocks are. We have a bunch of approximations under our belt. Flooding, we've looked at rates being much faster than others. And we have three simple mechanisms, we've looked at parallel reactions. We looked at series reactions. And we've looked at reversible reactions. So a complicated mechanism will basically put these three building blocks together in a series. And they'll all be happening at the same time somehow. And obviously, since it was, since we threw up our hands, just with a simple reversible process like here, it's clear that we're going to throw up our hands a lot. When we write down these mechanisms. So we're going to need approximations. We're going to need something that we'll automatically go to, and say this is going to be too hard. I'm not even going to try. Let's do an approximation. And two approximations that we're going to talk about are ones I already mentioned at the beginning. Which is the steady state approximation, where one rate, the rate to go into the intermediate is very slow, or the rate to get out of the intermediate is very fast. And the equilibrium approximation where the system sets up a very fast equilibrium and you're allowed to use thermodynamics to help you out in solving the problem. These are the two approximations that we'll use when we put these things together.

OK, so let's look at the first, simple, more complicated mechanism. To see where these approximations come in. So the first one is going to be a series. We're going to start putting these things together. First one is a series reversible. Those two together. Series reversible. So we have first, a reversible process. Everything is first order here. k minus one goes to B. And then B goes to C with some rate constant k2, all first order. If we were to turn the crank, we'd say, oh, I've got to write down all my rate laws here. Minus dA/dt is all the ways that I destroy and create B, so there's a k1 times A minus k minus one times B. dB/dt, all the ways that create and destroy B is that you create it through destruction of A. I destroy it through the backwards rate to make A. And I destroy it by making the product, C. There's the intermediate. And then for C, that's pretty simple. There's only one channel into C, and that's the destruction of B to form C, k2 B. All the rate laws. I write everything I know here. Couple of differential equations. We know it's going to be hard to solve.

So, let's remind ourselves of what I just erased. Which was the case where the intermediate concentration was always very small and didn't change very fast. And the process was dominated by k1 here. That was the rate limiting step. Remember that our first example this morning.

So this is where the concentration of B is roughly constant over time. It's small. And over any small time period, it's roughly constant. Which means that dB/dt is roughly equal to zero. If you look at a long term, obviously it's going to change as you go from this point to that point. In fact, there's a relationship between A which is changing in time and B. But A is also changing in time very slowly. Because the rate k1 is very small. So dB/dt, which is related to this rate k1, is going to be very slowly changing in time. We can approximate it at zero.

What are the ways in terms of matching these rate constants that we can get to the approximation. To a diagram that looks like that? But we don't want B to pile up. That means we have to have the rates out of the intermediate to be much faster, at least one of the rates out of the intermediate to be much faster than the rate that creates the intermediate. So the different ways of creating that approximation are if, and the length of the arrows now is going to be proportional to the rate. We want it to be very hard to make B. And as soon as we make B, we want it to go away. So one of the ways to do that is to have the reverse rate much faster than the initial rate. And we could have a slow rate into C, that's fine. We could have, again, a very slow rate into B. We could have a slow reverse rate and a fast rate into C. Perfectly fine. We could have both. Fast rate out of B through A, or out of B through C. As long as this first rate into the B is small compared to one of those two rates, we're never going to pile up B. It's going to go away as soon as we make it. So in all these cases, $k2$ plus k minus one is much bigger than $k1$.

When we have that situation, then we can make the approximation up here. That the rate of change in B is very small. Almost zero, which means it's basically a constant. And instead of writing B in this case here, we're going to write it as B steady state. Which is basically a constant in terms of solving the differential equations. And that's going to make our life much easier. Because instead of having to solve these coupled differential equations, we're just going to have to solve coupled algebraic equations. Which is really messy, but less hard. If you're a bean-counter than this is heaven.

So now we're going to put steady state, this is going to be a constant. And this is going to be equal to zero. And then here this is going to be steady state here. This is going to be steady state here. And the first thing to do now is that we've eliminated this differential equation. We now have an algebraic equation where we can solve for B steady state. So if you recognize that you're in this situation here, forget about trying to solve. Immediately go to the process of putting in a constant for B. Setting dB/dt for the intermediate equal to zero. And then starting to turn the crank on the algebra.

So let me go ahead and turn the crank here. Go through the steps, which is basically typical of these problems. So you turn the crank. You solve for the steady state concentration. You get, in terms of A, over k minus one, plus $k2$. Then you plug this back in here. And you get a new differential equation, minus dA/dt is equal to $k1$ times A minus k minus one times B steady state, so we plug this in here. And you get, so there's A sitting here. A sitting here. It's going to be of the form, effective rate times A. It's going to be basically a first order form. Which is what we'd expect from sketching the diagram just like that. So you get minus dA/dt is an effective rate. $k1$ times $k2$ over $k1$ plus $k2$. Times A. This is k prime.

So if you were to do an experiment under these conditions, you'd find that A behaves, it's basically a pseudo first order problem. With a funny rate that contains all the elementary rate constants as part of it. And when you do the same thing for C, dC/dt, you find that depends on A. It's $k1$, you plug these steady states in here. $k1$ $k2$ divided by

k1 plus k2 times A. This is k prime again. So the problem, and it's first order. So the problem looks like effectively you're going from A to C. Forget about the intermediate. With an effective rate k prime. Where k prime contains these rates.

So this is steady state approximation. It's the prototypical problem. Questions on steady state, before we go to the next approximation.

Alright. So now, as promised, the next approximation is that where are set up the fast equilibrium. And you can use thermo to help you out. Equilibrium approximation A goes to B. This is a fast process. And then k2 out of B is a slow process. Little arrow here, and two big arrows here. You put your A in your flask. Immediately you set up the equilibrium. And you slowly dribble out of that. If you want to do it as a function of buckets and, so you have a big pipe connecting two buckets that are just offset from each other. So there's, in this case here B is favored over A. Because it's a little bit lower than this guy here. And then there's a little bucket, there's a little tube, comes out of here. So there's a little dribble into C over time.

First thing that happens is you set up your equilibrium. And then you slowly extract stuff through a little tube into C.

So what do you expect this to look like? Well, you expect A to really slowly come out. Because the rate limiting step is the rate from B to C. So k2 is going to be the way that A is going to come out. You expect it to slowly go away. You expect B to get created very fast, to some equilibrium amount. And then also to follow the same rate k2, slow k2, to disappear. And you expect C to come up. You're basically in a first order process to saturation of A0. So when you expect the dominant rate to be k2, and the fast dynamics to happen at very, very early times, and then everything to follow first order kinetics.

So now let's do the math and make sure that it agrees with what we've just assumed that it's going to look like. So equilibrium is happening. You can assume that at any time after the initial very fast process of getting equilibrium. So after some initial time, the ratio of B over A is always going to be a constant. The dribble out of B here is not going to be fast enough to change that ratio. As soon as you get a little bit of B out here, immediately the ratios, the amounts rearrange to keep the ratio constant.

So now when I look at the rate of the reaction, the rate of formation of C, k2 times B, well, in terms of A, it's k2 times K equilibrium. Times A. Which is k2 times k1 over k minus one times A. And you can immediately see that C is behaving, or the reaction is behaving, like a first order process. With an effective rate which contains all three rates in this ratio here. So it looks like A goes to C, with some k prime where this is k prime. It looks like A goes to C with an effective rate constant k prime. OK. Questions? We're going to do some examples. And then we're going to do chain reactions next time. We're one lecture behind.

Alright. Let's do some reactions. Some examples.

I'm going to skip the first example, which is the example with the chaperone, in the notes. And I'm going to go directly to the gas decomposition. The two examples are basically very similar in their use of the steady state approximation. So I'll let you read over the first example.

So this example here is going to give us the Lindemann mechanism, for which Mr. Lindemann got a Nobel Prize many many, years ago. Basically, it's looking at decomposition of a gas phase molecule. Where you have a molecule, A, that breaks down into products. And the observation before Mr. Lindemann got around, was that it looked like a first order process. It looked like A is just falling apart on its own into these products. Mr. Lindemann got around and said, well, why would A just want to fall apart. There's something a little bit odd about that. Stable molecule, why would it want to fall apart. And so he hypothesized a mechanism. And it went like this. That A actually collides with another molecule, which could be a bystander. Could be a chaperone molecule that just happens to be there. Or it could be another molecule of A. There's a collision. There's a collision that creates a vibrationally excited version of A. Of A sitting there. It collides. It suddenly starts to be really vibrationally excited. Bonds vibrate all over the place. Atoms wiggle. There's the collision partner that goes away. So kinetic energy is transferred from M and A to the vibrational loads of A. In a process which is reversible. k1, k minus one, because this excited A, this vibrationally excited A, could also collide with a molecule and cool down. The energy in the vibrations could be transferred back to kinetic energy for a reverse process.

But if you wait long enough, or if this vibrationally excited A, with these atoms widely moving around, that has more of a chance of falling apart than this guy here. So A star could fall apart into products. With a rate k2. So he said, this is actually an important step. It's not that A just suddenly falls apart. But this has to happen. So all the observations that supported a first order process, which basically only supported one elementary reactions, might not be right.

So let's assume his mechanism, and let's look at what we need to do as an approximation. And where that leads us in terms of trying to experimentally confirm that this mechanism is plausible. Not prove it, but just to make sure that it's consistent with, the data's consistent with the hypothesis.

So let's compare our rates here. So we have a collision. A and M collide, and there's a certain probability on the collision that kinetic energy will be transferred to vibrational energy. That turns out to be a moderate probability. So k1 is reasonably fast. The reverse process, you have something that's vibrationally excited colliding with a molecule. There's a probability that that excitation is going to get turned back into kinetic energy. And then these two molecules will fly apart with high velocity. And that tends to be much more highly probable then the first process. So this is faster. Then the excited molecule's waiting around. And there's a probability that there's it's

going to just fall apart. And that turns out to be really slow. So we're going to assume that the last step is a slow step.

So what does it look like? Well, we have the creation is fast. So the intermediate is fast. But the destruction through the reverse process is much faster. We have at least one step, out of the intermediate, which is faster than the step into the intermediate. That's all we care about. It doesn't really matter that this is slow in terms of using the steady state approximation. We just want the step getting out of the intermediate, a backwards step in this case here, to be faster than the state into the intermediate.

So this allows this, this fact that this is faster, that allows us to use a steady state approximation. So now we can go ahead and solve the problem. So we write down all the rates minus dA/dt. It's k1 A. Let's start with the rate of the action. Let's take a product. Let's take C. Let's say this goes to product C here. So dC/dt is equal to k2 times A, that's the rate of the reaction. And we're going to look at this rate of reaction. And see how it changes. What it looks like under limiting conditions. The rate of reaction. Let's look at the intermediate. Because this is what we're going to solve first, because this is going to turn out to be an algebraic equation. Because we're going to apply the steady state approximations. Intermediate d A star / dt is, we can create it through the forward process. We destroy it through the backwards process. A star times M. And we destroy it through the final process. A star. We apply the steady state approximation, steady state, steady state. We solve for A steady state algebraically. k1 A M over M times k minus 1 plus k2. And then we plug that back into the rate of the reaction. The rate of appearance of C. Which is what we're measuring experimentally. We're looking at the products. Measuring the appearance of products. So they're destruction. This is also equal to the destruction of A.

And so we plug this into the, we write our rate of reaction. Which we measure, experimentally. We find this is k1 times k2. Times, we plug in for, and here, what we do here, we solve A in terms of A steady state. A is equal to something A steady state. Well, let's see, A is equal to M k minus one plus k2 times, well this is actually, I have this wrong up here, this is d A star. So we don't need to do this here. The appearance of C is, A star here. So we plug in A steady state here. A star steady state, and this is A star steady state. The intermediate is what we're solving a steady state for. So this is k1 k2 A M over M k minus one plus k2. We just have the extra k2 that appears when we multiply A steady state star with the k2 there. And then we can look at the limiting cases.

There are two limiting cases, which we can tell by looking at the denominator. If we have one term bigger than the other. Only two choices here. So the first case is where M k minus one is much bigger than k2. Experimentally, what does that mean? It means that this in the gas phase now. It means that regardless of what these rates are here, we've managed to make the concentration of M high enough so that this becomes true. There's always an M that's going to be high enough so that the multiplication of these two is going to be bigger than that. What does that mean? It means that the pressure is high. Concentration of M is high. This is a high pressure case.

And then the other one is M k minus one is much less than k2. M is very small. Low concentration, low pressure. The partial pressure of M is very low. This could be A. M could be A, or it could be some other molecule that's in the mix. And by high pressure we mean something on the order of one bar, let's say. That by low pressure we mean something around 10 to the minus 4 bar.

So now we can go and put these limiting cases in our equation here. k minus one is much bigger than k2, so we can ignore k2 here. And then we have something that looks like the M's disappear. We have something that looks like k1 k2 over k minus one times A is the rate of reaction. First order. Looks like it's first order in A. This is what people had observed. Great. The problem is that they didn't know to go to low pressure. They were doing all their experiments at atmospheric pressure. They were getting a first order rate. They thought they had solved the problem. It's just A falling apart by itself. Until you go to low pressure, where now this term dominates the denominator. Or rather, this one dominates the denominator. And now you have something of the form k1 A times M. This dominates, this term goes away. The k2 goes away and you have k1 times A times M left over as the rate of the reaction. Second order. There are two species here. A times M. M could be A or it could be some chaperone. A squared. Second order process. So if you're at low pressure, you see something at second order. You've discovered something about the mechanisms you didn't expect. And then you get a Nobel Prize. Alright, next time we'll do chain reactions.