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PROFESSOR: So, any questions from last time? We started doing reaction mechanisms. We did first order parallel reactions. So one of the things that we'll be stressing is that the mechanisms that we write down are ways to try to understand a complicated chemical process. And you take data, you can find intermediates sometimes. And you get rate laws from the data. You infer rate laws. And from these rate laws, you think up of a reaction mechanism and you make sure that what you measure is consistent with your mechanism that you make up to explain the complicated chemical process. And one really important thing to remember is that when you come up with a mechanism and you've got a bunch of data that supports it, it's great. But it doesn't mean that you've solve the problem. It doesn't mean that you've proven that the way that the chemistry proceeds is really the way it proceeds. Because there's always the possibility that there's an intermediate somewhere in there that you haven't been able to measure. And a lot of people got tripped up over the course of the last century, of making up mechanisms, getting a lot of data that supports the mechanism and missing something really important. So it's a common mistake, that people think they've proven a particular chemical mechanism just because they have data that supports it. It's up to a certain point that you know what you have. And we'll see examples of that today, probably. And then certainly next time when we start making approximations in our kinetics. And see where things can really go wrong if you don't have enough data. If you don't try to fish out really, really, tiny intermediates somewhere along the way.

So last time we did then parallel first order reactions. And today we're going to march through and do parallel first and second order. So one is first order, the other one is second order. Things are going to get more complicated. And what you're going to get is a flavor of how to solve the problems. Setting up the problems. We're not going to do a lot of the algebra here on the board, because otherwise we would spend the next three weeks doing algebra. And that would be no fun at all. That doesn't mean that you're not going to be doing any algebra on the homework. Because part of it is figuring how to do it.

So, we have a reaction where A goes to B plus C. And the first thing we did was, the first mechanism we wrote was a parallel mechanism where we had A goes B and A goes to C. That's the mechanism. And one other way to write it is A goes to B or C, in a way that is more, sort of describes the branching process, that when we talk about a branching ratio, the ratio of amount of B to C, this looks like the branching out of two different paths.

And this time we're going to do where this is first order and this is second order. With the rate k_1 and a rate k_2 .

And the way that you do all these problems, you have to be very systematic about it. The first thing you do is you have to write down all your rate laws. And make sure that you include everything. So you start by writing the rate law for the destruction of A. And then the rate law for the appearance of B and for C. So for a, we have dA/dt . And again, I'm dropping the brackets around the A, because I don't want to carry around all these extra symbols.

So we destroy A by making B. So that's going to be first order. And then we also destroy A by making C, and that's second order. So we have two paths out of A. To get rid of A. Then we write down the appearance of B, dB/dt . It's only through one path, first order in A, and then the appearance of C, only one path which is second order. And these are all our differential equations. And now the trick is, how do you solve these three differential equations in a way that you get meaningful information out.

Well, the first thing to do is to, so these two here depend on A. So the appearance of B depends on A, the appearance of C depends on A. But this one here only depends on A by itself. So this is the first one you're going to start out with. Because you can put all of the A's on one side and all the time on the other side and integrate. So then you solve, and you can rewrite this as $-dA/dt$ is equal to $k_1 A$ plus $k_2 A^2$. And then you put all the A's on one side, all the t's on the other side. And integrate from A_0 to A minus dA over A times one plus k_2 over k_1 times A. That is equal to k_1 from zero to t dt.

And then you have to solve this integral here. And there's a reason why I factored out the A here. It's because this is of the form you can use to use the trick of partial fractions, which we mentioned this before. So you use partial fractions to solve this. And I'm not going to do it on the board. You turn the crank, you basically write one over A times one plus k_2 over k_1 A is equal to n_1 of A plus n_2 over this part here, and you solve for n_1 and n_2 and you plug it back in, and you redo your integral, et cetera. And you get your answer. Which I'm going to write down because I'm going to use it later. $k_1 A_0$ over e to the k_1 times t, k_1 plus $k_2 A_0$. So one of the things we immediately see is even though this mechanism isn't very complicated, just two paths, one first order, one second order, the solutions start to get not so simple pretty quickly.

So it depends, there's an exponential on the bottom here. Depends on the initial concentrations and both rate constants are in there. The first thing you want to do is you want to look at limiting cases. Just like before. We did, and the first limiting case we're going to look at, so interesting to look at is this guy right here. k_1 and $k_2 A$ here. If one is bigger than the other, then things will cancel out. And we can get some intuition. So the first limiting case we're going to look at is where $k_2 A_0$, this term right here, is much smaller than k_1 .

Now, we want to make sure that in these limiting cases that when I write something like this, that the units actually make sense. That I'm not saying, three apples are less than four oranges. So k_1 , it's first order, so the units are one over second. k_2 , it's a second order rate constant, so the units are one over second molar, times moles per

liter. So the moles per liters cancel out and I have one over our second is less than one over second, so things are great. It I'm making the right kind of approximation here.

What else is this approximation saying? This is saying that the rate into B, so this one is the faster one. k_1 , the rate into B, is the rate into, is k_1 , is faster than k_2 times A, which is basically the rate into C. So this is saying that the rate into B, to form B, is faster than into C. So we can write down a sketch. We can sketch what we expect this approximation to be, then. And we know it's going to look something like this. We know that A is going to come down, exponentially. Without any structure to it. It's going to go either into B or into C, in some branching fractions. And we know that the rate into B is faster than into C, so B is going to come up like this. And C is going to come up, but slower.

And there's going to be a ratio between these two guys. So we know the slope here is going to be slower than the slope for B. And we can check that out, within our approximation. We can write, at t equals zero, find out what these initial slopes are. For the creation of B and C. So dB/dt is the slope of the creation of B at the beginning. At t equals zero. And that's just the rate law. dB/dt at t equals zero is $k_1 A_0$. And dC/dt , the initial slope, t equals zero, is $k_2 A_0$ squared. Or $k_2 A_0$ squared, rather.

So I'm going to write it as $k_2 A_0$ squared, like this. We said k_1 is much bigger than k_2 times A_0 . There's the same A_0 here. So we see, just by writing this down, that our intuition that because the rate into B is much faster than into A, that it should look like this. Well it's borne out just like this very simple sort of looking at the initial rate where the slope here is much smaller than the slope here.

And then we can take the approximation in here. And see what it implies. So let me do that here, let me just use my green chalk here. So $k_2 A_0$ is much less than k_1 . So this is going to go away. $k_2 A_0$ is much less than k_1 . Well, this is building up from zero. So this is always bigger than one here. So I can get rid of this as well. Because there's the k_1 sitting here. And k_1 is much bigger than $k_2 A_0$.

Once I got rid of all these two guys, then the k_1 's cancel out. And this is looking very nice. Because now I can take that e to the $k_1 t$ and put it upstairs. A is equal to approximately $A_0 e$ to the minus k_1 times time in this approximation. It looks like it's first order coming down, with a rate constant k_1 . It looks like basically the branching into C is nonexistent as far as, at least in this approximation, as far A is concerned. It's going to look like this thing here. It's going to look like first order A goes to B with rate constant k_1 . So if you didn't know, if you didn't know that there was another substance, C, that was being formed along the way, if you didn't measure it, if you didn't do the analytical chemistry and sort of fish it out, and you just looked at the two major components, A and B, in this case here, you'd measure a rate out of A, it would look like it's first order. It's great. Got my mechanism. A goes to B, period. And you would know there was a minor component that was being formed at the same time.

OK, let's do another approximation. Let's do the other case, where $k_2 A_0$ is much bigger than k_1 . And, in this case here, you have to be a little bit more careful. You have to add that you're going to look at this at early times. And we're going to see why early times is important here. In just five minutes. And early times, and how you define early times. What does it mean for things to be close to time equals zero? Well, we have to have a reference time scale. The reactions, I'm going at a certain rate. And one second may be very slow. Or it may be very fast. Depending on the rate of the reaction. So k_1 here defines the time scale of the problem. It's one over second, unit of one over second. And early times means that the times that I'm looking at compare to this rate, it's very small. So $k_1 t$ is less than one.

That means that the time, during the time period that I'm looking at, hardly anything has happened to the branching of A to B. That that's what I mean by early time. So B is hardly being built up yet. k_1 is our reference time. k_1 is units of one over second. This has units of seconds. So it's all working out fine. In other words, I would have no idea how to define early times. I could say, it's in a year, it could be, if you're looking at plutonium decay, it's a 100,000 year half-life. A year would be an early time. So it would be really fast, compared to the process. But if you're looking at a reaction that takes a few nanoseconds than a year would be very, very long. So you really need your reference time somewhere in there.

So this approximation means that essentially, no B is being created. While we're looking at the process. And so we might then very well expect that if we look at A and C, that the answer is going to be that we're going to see something that's second order. So we expect that the form of A, the way to write it is going to be one over A equals $k_1 t$ plus A_0 .

So let's go ahead and take our complete solution and write it in the way that we might expect the answer to be. In terms of one over A rather than A here. So let's just invert it. e to the k_1 times time, k_1 plus $k_2 A_0$, minus $k_2 A_0$ over $k_1 A_0$. This should be a minus sign here. There should be a minus sign here. It didn't matter for our approximation because we got rid of it anyway, but it would be a proper sign here is minus.

And so now we need to make our approximation and figure out what this here. So if we take the approximation that $k_1 t$ is small, less than one, then what that should trigger in your mind if that if you have e to the something that small you should use a Taylor series. And expand this into a Taylor series. So we're going to see this multiple times. So we take e to the $k_1 t$ and expand it out as one plus $k_1 t$ plus et cetera. We're going to keep the first order terms in there. So we're going to plug this approximation into here. That's this approximation there. And then we're going to expand it out. So plug it in here, and, keeping it to first order in time, and multiplying it out, and I'm not going to do the intermediate steps, I'm just going to give you the stuff after doing the multiplications, we get $k_1 t$ squared. So that's basically k_1 times one plus $k_1 t$, and then you have plus $k_1 k_2 A_0$ times t . That's this term here. $k_1 k_2 A_0$ times t times that. And the $k_2 A_0$ times one gets subtracted out from this minus $k_2 A_0$ here. So

that's all we have on top. And then there are terms of higher order in time. But we're not going to worry about this. We're going to stick to first order in time. Divided by $k_1 A_0$.

And now you do your cancellations. We have our approximation at k_1 times time is much less than one. So here we have k_1 times k_1 times time. So this term here means it's much less than this term here, because of our approximations. So we can get rid of this term here. Get rid of that. There's no reason for us to get rid of this one here. Because we've got $k_2 A_0$ there, which is much larger than k_1 . And so when you expand this out, all the k_1 's cancel out here. So so k_1 cancels out that k_1 , we have one plus one. So this is basically one over A_0 . And then we have plus $k_2 A_0$ time over A_0 , so this ends up being equal to one over A_0 plus k_2 times time.

Exactly what we expected. That if you put in the right approximation in the math, it behaves as your intuition would tell you. Which is that the branching into B nonexistent. And that you're looking at everything going to C. It looks second order in C. But in this case here, it's only early times. So if you keep going, what happens? If you keep going in time, beyond the time scale of this first order rate constant, and you wait long enough, then the amount of A keeps decreasing. Keeps getting smaller and smaller. So if you start the clock again, a little bit later, where A is much smaller, then k_2 times the amount of A you have there, is no longer going to be much greater than k_1 . At some point along the way, k_2 times A is going to be much less than k_1 . So at some point along the way, it's not going to be this approximation any more. It's going to be the previous one that we did. The one up there. So at early times we start with something that may look second order for A. Time goes on, time goes on, time goes on, A gets depleted. A gets depleted, and the rate k_2 times A, which is sitting right here, this part here becomes smaller and smaller. And pretty soon this part wins. And it becomes first order.

So what you'd expect to see, then, is if you were to plot as a function of A, you expect to see something that starts out as first order and then as A gets depleted, switches over to second order. Something that's second order here. And first order. This is the concentration of A. So if you were to plot it, here you're plotting the concentration of A. If you were to plot the log, of the concentration of A, at long times you'd expect it to be first order. So something linear. But at early times you'd expect it to be second order. So you'd expect to see something that's nonlinear, then switching to something linear. And if you were to plot it as one over A, then you'd expect to start off with something that's linear, at second order, early times. But instead of keeping, being second order, as you deplete the amount of A, the branching into B becomes important. And you become second order. So this is second order at the beginning. And this becomes first order.

So, any questions here? The importance of doing this problem here was to lay out basically a systematic way of looking at the problem. You lay out your rate equations. Like this. You solve what you can, in this case you solve for A. And it's complicated. So you want to learn something about what the data might look like. And you look at limiting cases. Two obvious limiting cases. One rate is faster than the other. You pick the first one first, then go

through it. And then use your intuition. Every point along the way, your intuition can tell you what you expect the result to be. So in this case here, our intuition told us that if we took the rate into B to be much faster than that into C, than we expected to see something that was largely first order. And when you use the approximation in our exact solution, in fact it does look like it's first order. So always use your intuition. Because the math is going to get pretty hairy. The algebra might make it complicated. And it's really easy to make a plus sign into a minus sign somewhere along the way. Just like I did here. So if I hadn't fixed my mistake here, and I had gone and put in my Taylor series here, I would have gotten in trouble. Because this minus sign would have been a plus. And these $k_2 A_0$'s would not have canceled out. And I wouldn't have gotten the right result, which my intuition had told me should be a second order process. And so if you have a problem, let's say you're on an exam and you're doing algebra, you're trying to, and you end up with a result that doesn't match what your intuition tells you, and you don't have time to fix it. Tell us. You know, I know this is wrong because I know it's supposed to be second order. But I don't know where I went wrong. And that's really important. Just tell us. That means that you're thinking. Let's get a little bit more complicated. Any questions?

Consecutive series reactions. These were parallel reactions and now. Basically what we're doing here is we're building up a toolkit of simple mechanisms. And then we'll be able to put these mechanisms together to make something more complicated. So the next kind of mechanism, series mechanism, series reactions, so we have our reaction. Which is A goes to C. And the mechanism that's been thought for this reaction is that there's an intermediate. That first you have A goes to B, some intermediate, which gets used up to form the final product, C, with a rate, k_2 , here.

And we can either write the mechanism in two steps. Or we can write it as A goes to B goes to C, like this. And see both ways of writing it. And we want to solve this. And we want to look at special cases, and we just want to understand the implications of this mechanism.

So the first thing to do, just like we did before, is to write all the rate laws. Before we got going solving anything. So we start with A, minus dA/dt . There's only one way that gets used up. Through the formation of B in a first order process. Easy. This is easy to solve. We know the answer is going to be exponential in it. For B, dB/dt is equal to, well it can be formed through my first order in A, so that's k_1 times A. But it also could get destroyed by forming C. So we've got to get all the paths out of A, here on the right side of this equation. So it can be destroyed in a process, which is first order in B. So we're going to take both k_1 and k_2 to be first order initially. Then we'll make one of them second order and things will become very complicated and we'll throw up our hands.

But for now, let's not throw up our hands quite yet. OK and for dC/dt , there's only one way it can be formed is first order by destroying B. And we have a couple of differential equations here. This differential equation for C, depends on B here. The differential for B depends on A here. So that means that things are going to get a little bit

more complicated. The easy one to solve is always the first one here. That's first order. So we just write down the answer. A is equal to $A_0 e^{-k_1 t}$. We know the answer to that one.

Then we have to work on B . So we want to find out integrated rate laws for every one of these chemical species. And always there are tricks involved. Partial fractions, whatever. So we write down B now. $\frac{dB}{dt} + k_2 B = k_1 A$. Let me rearrange it a little bit, plus k_2 times B , putting the minus $k_2 B$ on the other side here. Is equal to k_1 times A . But I'm not going to keep this A there, because now I know what A is in terms of time. And a constant. k_1 times $A_0 e^{-k_1 t}$.

OK, that's my differential equation for B . Got to solve this thing. Well, the last time I did differential equations in college was a century ago. And I wasn't kidding. It really was last century. In fact, it was last millennium. That was a long time ago. So how do you do this? Well, the trick here, there's a trick. And the trick is to multiply the whole thing, both sides, by $e^{k_2 t}$. And you multiply this side by $e^{k_2 t}$ and you multiply this side by $e^{k_2 t}$, to solve this equation.

So once you do that, then you have $e^{k_2 t} \frac{dB}{dt} + k_2 B e^{k_2 t} = k_1 A_0 e^{-(k_1 - k_2)t}$. This side here. And then you have is equal to $k_1 A_0 e^{-(k_1 - k_2)t}$.

OK, so the reason why this trick works is because this guy right here can be nicely written as $\frac{d}{dt} (B e^{k_2 t}) = k_1 A_0 e^{-(k_1 - k_2)t}$. It's in nice simple form, so when you integrate, it'll be very easy to integrate. And then the other side, you still have $k_1 A_0 e^{-(k_1 - k_2)t}$. So now you integrate both sides with respect to time, The integral of something $\frac{d}{dt}$ with respect to time, it's just going to be itself right here. So it's very simple. So you integrate both sides from zero to time, dt . Zero to t , dt on both sides. And on this side here, you end up with $B e^{k_2 t} - B_0 e^{k_2 \cdot 0} = \frac{k_1 A_0}{k_2 - k_1} (e^{-(k_1 - k_2)t} - 1)$. Just taking the upper limit minus the lower limit. And that's just equal to B_0 , at time to equal zero. And so, and at time to equal zero, B_0 is equal to zero because we haven't made any intermediates. So this goes away. And then we have an equals sign. And on the other side, we have $k_1 A_0$ over $k_2 - k_1$, it's just the integral of this thing, here with a $k_2 - k_1$ goes in the denominator. $e^{-(k_1 - k_2)t} - 1$.

So now you have your integral form for the amount of B that gets created at any time. And I want to keep that on the board. Because I'm going to use it later. $k_1 A_0$ over $k_2 - k_1$ times $(e^{-(k_1 - k_2)t} - 1) + B_0 e^{k_2 t}$.

OK, we're two thirds of the way through. Now we've got to find C . And for the last component, you don't want to be doing this kind of stuff. You don't want to waste your time solving differential equations, because stoichiometry can help you out. At the end of the day, you know that everything that started out as A , in terms of quantities, is going

to end up at C. You know that if you end up with a concentration A_0 at the beginning, at the end of the process the concentration of C, at infinite time, is also going to be A_0 . If you know that there's a correlation, there's a stoichiometry that relates A and C together. And B. You have conservation of mass here, basically. Conservation of atoms. That has to come into play

So, for C, we're just going to do algebra instead of calculus. So let's write down the stoichiometry here. The amount of C at any time is what it's going to be at the end. Which is A_0 , very end of the process. It's going to be A_0 . But before we get to the end, there's still stuff that's left in A and B. And that's going to decrease the amount of C. So minus whatever's still in A and B. That's the stoichiometry. That's one way of writing it. You could also write it in a different way. Which is that the amount of C is equal to the amount of A that you have used up. A_0 is what you started out with. A is what's left over. So this is the amount of A used up. It's not all quite in C yet. Some of it is stuck in B.

So it's the amount of A used up, minus the amount that's stuck in B. Those two are the same. I hope. A_0 minus A, yeah, that's right. Minus B, yeah, that's right. So this is used up. And then stuck in B. That's the hard part. Putting down the stoichiometry. Once you've done the hard part, then if you solve the other two then it's easy. You just plug in. It's just algebra. And you get something complicated. C is equal to complicated. It's in the notes, I'm not going to write it down.

So we've solved the problem exactly. And now you're going to do an experiment. And the experiment you're going to do is not going to follow this whole thing, exactly. It's going to look at limited cases. That's what you can do. And so the first thing to look at is to look at the initial times. The very beginning of the process, how are things appearing. And then we'll look at the late times.

So initial times. Near t equals zero. Well, every one of these things has an exponential in it. And whenever we see exponentials and we look at something at the early times, times that are faster than one over k_1 , or faster than one over k_2 , it tells us use a Taylor series. So use the approximation e to the minus kt is approximately equal to one minus kt plus kt squared over two plus et cetera. And keep as many terms as you need in the Taylor series to get something sensible. So if everything comes out of zero at the end, you know you haven't kept enough terms in t . Things have canceled out too much. And you want something that is time dependent. Because you've got a change in time, right? It's a very common mistake to say only keep one here and then everything cancels out you get zero, and you say, well, B is equal to zero at all times. That's nonsensical. And I don't know a priori how much time to keep. So let's go to second order.

So if you plug this Taylor series into A, and get something that's time dependent, you only need to go to first order. One minus k_1 times time plus et cetera. Plug it into b, plug your Taylor series into these two guys here, get

$k_1 A_0$ over k_2 minus k_1 , you only need it to go to first order. The one's cancel out but the times don't cancel out. Minus k_1 plus k_2 , that is, unless k_1 and k_2 are the same. So we're making the approximation that k_1 is different than k_2 . Times the time.

And when we look at C, this complicated thing that I didn't write down, if you were just to stop at first order in C, you get C equals zero. You know that can't be right. You know that C is going to increase in time. It can't be equal to zero at all times. So we have to go to second order for C. And it's approximately equal to A_0 times $k_1 k_2$ over two times the time squared.

Let me rewrite this a little bit closer in, because I need some room here. So c is approximately equal to $A_0 k_1$ is k_2 over two times time squared.

OK, and then we can start plotting out what this is going to look like then. So we have the concentrations time on the axis here. Let's start with the concentration of A. A is dropping down linearly in time. It's dropping down linearly in time here. B is increasing linearly in time, at the beginning. So B is going up linearly in time, like this. And C is increasing quadratically in time. So it's pretty flat, coming up first. And then it starts to curve up. It's our first approximation.

Then, we go to late times. t equals infinity. So t equals infinity where am I going to write this? Have to move this up. Let's go, t goes to infinity. Well, here I know that I'm allowed to go to zero. Or allowed to go to constant, because infinity is forever. So at t infinity, I know that I'm going to use up all of A. So I know that A is going to be equal to 0. I know I'm going to use up all of B. So I know B is going to go to zero. Somehow. And I know that C is going to go to A_0 . So C is going to go to A_0 at infinity.

So now on my graph here, I know that at infinity, A is going to go down to zero like this, somehow. Probably exponentially, because it is exponential in time. So it's going to go to zero exponentially. B is going to go down to zero exponentially. There are the exponentials right here. So B is going to go down to zero exponentially. Something like this. And C is going to saturate to A_0 . Exponentially rise up to A_0 . So this was A_0 right here. It's going to go like this. So then I connect the dots. And I know that C is going to start quadratically. And then it's going to rise up an exponent like this. I know that B is going to start off linearly, and then it has to go to zero. So it has to go through some sort of maximum. And A is going to go down exponentially, exponentially like this.

So the interesting part of this diagram is that B goes to a maximum. There is some point, there's some time, that we can call $t_{B \text{ max}}$, where B is a maxima. And that's an interesting point. That's something that we can try to figure out experimentally what it is. And we could get some parameters, we could maybe extract some information. There's a maximum B, concentration of B, that gets formed. And how do you solve that? You set dB/dt equal to zero. So you have your equation for B right here. You set it equal to zero. and you solve. You get

your maximum time. It's made up of rate constant. You get your maximum concentration, which is also made up of rate constants. And you can get rate constants out of this. Question.

STUDENT: [INAUDIBLE]

PROFESSOR: Yes.

STUDENT: [INAUDIBLE]

PROFESSOR: That is a coincidence. That is my poor sketching. It should probably be somewhere like, in the middle here. Actually, it completely depends on the rates. And we're going to see limiting cases where this maximum can occur here, or it can occur somewhere down here. So this is the complete case.

So, limiting cases. the important limiting cases. We've made an approximation along the way that k_1 is different than k_2 . So that has to be a case that needs to be worked out. And it's likely to be easier than the full solution. So one of the limiting cases is k_1 is equal to k_2 and I'll leave that for homework. You can do that yourselves. It's good exercise. What about another limiting case? Well, you have two other limiting cases. One, you've got two rates. So, one is bigger than the other. No information on this board here. You start off with one case. So k_1 greater than k_2 . k_1 greater than k_2 . What does it mean? k_1 greater than k_2 . It means that the rate determining step, or the limiting step, in this reaction, is the second step. k_2 is very slow compared to k_1 . And sometimes I like to think of these things as pipes. And connecting vessels. So let's say we have the amount of liquid in the top vessel is the concentration of A. The amount of liquid in the middle vessel, let me get my color scheme to be consistent here. Then we have a middle vessel, which is the concentration of B, and a final vessel, which is the concentration of C. And we start out with some sort of amount of A in here. Started with a lot of A, and then these vessels are connecting with pipes. So there's a very thick, big pipe that connects A and B together. The rate is fast, going from A to B. And the rate going from B to C is slow, so there's a skinny pipe connecting B and C together. Then I turn on the system, I set time to equal zero, poof, what happens? There's the big pipe connecting A and B. The whole amount of a here gets transferred to B, suddenly. Then it gets stuck here. And then it dribbles out from B to C.

So what do we expect, if we were to plot our quantities as a function of time. What we'd expect then, then we're going to make sure that the math works out, is that A is going to decrease really fast. It's going to go, poof. First order in time with a very fast rate. And all of this is going to go straight into B. So we expect B to go linearly. Remember, at the beginning it's linear. Linear goes up. Almost all the way up to A_0 . Because it can't hardly get out. Reaches its maximum, then it goes from B to C through this skinny, skinny pipe. First order rate, with a rate k_2 , so we're exponentially going down, slowly, slowly, slowly, with a rate k_2 . And then C starts quadratically. And then very quickly, once everything's into B, A is forgotten. A doesn't matter any more. Basically what you're looking at is a transfer of B into C through this little pipe. And you know that's going to be a first order of rate. First order of

process, B to C's first order of process with rate k_2 .

So you expect, then, C to go up in the first order process to A_0 with rate k_2 . There's the rate k_2 here. And the rate k_1 here. So when you turn the crank on your approximation in the math, what you'd better see is that at the end, B as a function of time should look like a first order process with rate k_2 . C as a function of time should look like a first order process with rate k_2 , going to A_0 . And you can write the answer, you should be able to write the answer, for C, it's going to be C is approximately, it's going to go to A_0 , there's no other choice. Everything that was in A gets transferred to B, so at time is infinity it's going to be A_0 , and it's going to be a first order process with rate k_2 . One minus e to the minus k_2 times times. I don't even have to do the math. I know that's the answer. If you don't believe me, then do the math. You should do it. But that's the answer. It has to be the answer. And if you look at B, the answer has to be that it's approximately looking like B is disappearing with a rate constant that's k_2 , e to the minus k_2 , and the maximum here is very close to A_0 . So I'm going to be putting A_0 here. Close enough.

So as long as I ignore the very initial time where A suddenly dumps into B, then everything after that very early time here is just looking like B goes to C. This is not zero, this is t . And A just disappears quickly. And we can write it as A is equal to $A_0 e$ to the minus k_1 times the time. That's an easy approximation. And you've just got to make sure that this fits. So the other limiting case, which I'm also going to leave as a homework, because it's so straightforward, is to have k_2 greater than k_1 , and you should make sure that you can predict it. and that the math works out.

OK, any questions? Next time we'll do reversible reactions. And some more approximations.