PROFESSOR: OK. So last time you started kinetics which is a completely different topic from thermodynamics. They're related and we'll see a relationship at some point. And you did first order kinetics. And today we're going to move on and go ahead and do more complicated kinetics and hopefully get to some interesting stuff in a couple lectures. Right now we just have to do the review of stuff that you've probably seen before. And so we're going to go reasonably fast. So you saw first order reactions. Today we're going to do second order reactions. At least begin with second order reactions. Second order kinetics. Of the form, and then there are two kinds. There's first order, rather, second order, in one reactant of the form A goes to products. And then you have first order in two reactants first order in two reactants. So I'll have the form A plus B goes of products. Where that's first order in A and first order in B, and this is second order in A. So you can think of this as A plus A goes to products if you want. And there's some rate constant k, associated with this reaction. And we do the rate analysis. We write the rate of this process. Minus dA/dt.

And for the purpose of writing on the board, and you might want to do this also in your homework, when you're tired of writing. I'm going to skip the brackets. The little brackets that we usually put for concentration. I'm going to skip those, because it's just too much work to write them. And you can understand that A is a concentration of A. So this is equal to k A squared. Second order on A. And the units for k, it's important to keep track of your units, at the end of the calculations, often you want to make sure your units work out. So the units for k are going to be of this, A is in moles per liter. The units for k, you're going to have to be able to match the units on this side here. So the units for k are going to be liters squared per mole squared per second. To make the units match.

Then you integrate this, on both sides, from zero to t, or from A0, the initial rate, to A. Or from zero to t and this doesn't go like this. So integrate with A0 to A. You've got dA over A squared, you put all the A's on one side, all the t's on the other side, from zero to t dt with a minus k on this side here. And then you get your rate equation, integrated rate equation for this. Which gives you one over A is equal to kt plus one over A0. So this gives you A as a function of time. And this is a convenient way to write it, because it's linear in time. So you always try to get things to be linear in time. Because then you can plot them as a straight line. Plot on this axis here you plot one over A. on this axis here you plot t as a function of time. And then you get a straight line where the slope is k. Gives you the rate, and the intercept is one over A0. Yes.

STUDENT: [INAUDIBLE]

PROFESSOR: k is moles per liter squared per second. You're right, liters per mole per second, yes. That is correct. because it has to work. Otherwise it doesn't work. So I need to turn on my brain. OK, think. Liters per mole per second. Thank you.

And the other thing that you want to know is the half-life. What is the half-life. So you set 2 A0. So A0 over two, you look for the time where you get to A0 over two, so you put A0 over two in here. And that's going to be equal to k times t 1/2 plus one over A0. So you solve for the half-life and you get a half-life of one over k A0. So the half-life is inversely proportional to the amount of stuff you started out with. Unlike the first order reaction, where the half-life was independent of the amount that you started out with.

So this was the easy one. The next one is a little bit more complicated. Which is when your first order in each of two reactants. Then your rate, your differential rate equation, looks like this. Because the k times A times B, and now you don't know what to do with B, a priori. So you want to rewrite this equation a little bit differently in terms of the amount of A that's used up. So you define A, x is equal to A0 minus A, this is the amount of A that's used up. This is what you started out with, this is what you're left with. And so the difference is what's being used up. And dx/dt is minus dA/dt. And by stoichiometry, what you've used up, of A, is also what you've used up of B. Because for every A that reacts, you have to use up one mole of B. For every mole of A that reacts, you use up one mole of B. And so you also have x to B0 minus B. So, you can plug this in here. And get a differential equation which is purely in terms of one variable, which is x. Right here, it looks like it's in terms of two variables, which makes it complicated. By doing this change of variables, you see that A and B actually related. Because of the reaction stoichiometry. So you can rewrite that as dx/dt is equal to k times A0 minus x times B0 minus x. And now you have a differential equation in one variable, which with some tricks you can solve. So we want to have the integrated equation. So we take an integral of both sides. We put in all the x's on one side. All the times on the other side. We'll go from x equals zero to x, dx, A0 minus x times B0 minus x is equal to k from zero to t dt. And now you have to dig back into the last time you took integration calculus, which for me was about two centuries ago. And figure out how to do this integral here.

And the trick for doing this integral is to use partial fractions. So you use partial fractions to do this integral here. Which means that if you take this ratio, one over A0 minus x times B0 minus x and rewrite it as some number, n1 divided by A0 minus x, plus some number n2 divided by B0 minus x, you solve for n1 and n2, and you find that n1 here is equal to one over B0 minus A0 and n2 is minus one over B0 minus A0. And so you plug, now, this in here. And instead of having this complicated denominator, you have a sum of two integrals that you know how to do. Because they're basically of the form one over x.

And in doing this, you also realize that you have to be careful because when A0 is equal to B0, when you have the same amount of A and B, then things blow up and you're in trouble. So that's going to be a special case. So always look out for special cases for these things. So you assume, then, that B0 is not the same as A0. And then you can go forward with solving it. So you integrate, and at the end of the process, I'm not going to go through it, it's really complicated, you get something that looks like this. A0 minus B0 log of A B0 over A0 B. And you have your equation here.

Now, we don't really have a good way to plot it against one variable. And the usual thing is look at specific cases. And limiting cases. And there's one limiting case we already brought up. Which is when you started with the same amount of material. What does it look like if you have the same amount of material to begin with? So if you have A0 equal to B0, you start out with the same amount of stuff, but if you start out with the same amount of stuff, then this doesn't look so different from, at least mathematically, from this one right here. If you start out with A0 is equal to B0, and for every mole of A that you use up you use a mole of B, then throughout the whole reaction, the concentration of A and the concentration of B are going to be the same. So for the whole reaction, if you started with this, A is equal to B for all times. That makes it easy. Because now you can go back and instead of writing A times B, you can write A times A, which is A squared, which is what we had here. And then you have the whole thing solved.

So in that case here you just have minus dA/dt is equal to k A squared, and one over A is equal to kt plus one over A0. You don't even have to do any math, you just look at it. So that's one case.

Another case is if one of the reactants is in much higher concentration than the other reactant. And that's called flooding. You basically flood the system with one reactant. And that's something that we'll use again, hopefully by the end of class today. Let's say that we take, so this is another limiting case. Let's say we take A0 to be much bigger than B0. So we flood the system with A0. As a result, the concentration of A doesn't change very much in my pot. It's hugely concentrated in A, there's a little bit of B around. Again, with the process. If I use all of the B up, the difference in A is going to be very small. So at the end of the process, I'm basically still going to have A0 left in the pot.

So during the whole process, during the whole time period, I might as well assume that A is equal to A0. And that makes my life much easier. Because now if I write my differential equation in terms of B instead of A, so the rate of destruction of B, k A times B, instead of writing A here, it's pretty much constant for the whole time. I'm just going to write A0. So now, if k times A0 is a constant, and this looks awfully like a first order reaction. So I can solve for it. And I get that, so I can just write the answer because I've done this already. I don't have to do it again. The concentration of B then goes like B0 e to the minus k prime t, that's the first order reaction. Where k prime here is this new rate constant, this new number, which is k, times A0. So that's easy to solve also.

So always go to the limiting cases, because they tend to easy. And if you were to go to the full solution and put in this limiting case, then you'd find that you get the right answer this way as well. You can directly go to the easy way of doing it, or you can go through the whole process of solving it and putting the approximation in there. And do the cancellations and get this. But this is much easier. Just writing the answer down is always much easier. So it's a pseudo first order reaction. We call this a pseudo first order reaction.

So we're done with the simple stuff now. Any questions on first order and second order reactions?

So the next step is, you've got a reaction. It could be a gas phase reaction, it could be a solution phase reaction. There's some quantity, some property, of the solution that's going to change. That's going to allow you to follow it as a function of time. And that property could be many things. It could be spectroscopic. It could be that there's an absorption in the visible that changes as the concentration of one of your reactants changes. Or one of the products could have an absorption band that you could follow in time. Or you could using infrared spectroscopy to follow it in time. Or if you have a reaction in the gas phase, and you have more products or less products than the reactants, and the pressure is going to change in time if you have a finite volume. So there's usually some quantity that you can use to follow the reaction in time to extract out data. And then from that data, that you want to know what are the kinetics of this reaction. Because eventually you're going to try to find a mechanism. You're going to try to find a mechanism that's consistent with the data. So you get data. Then you want extract out of the rate constants and orders.

So let's assume that you've found a way to get data. And now you've got to analyze your data. And suppose that you've found a way to measure the reactant concentration as a function of time. And let's say that in the first case, the simplest case is that you have one reactant. So you have one reactant, A. So A goes to products. And you've managed to extract A as a function of time. Well, the obvious thing to do is to plot A versus time and see what it fits like. So you take A versus time, and you plot it. And you know that if you plot log A versus time and it's a straight line, well, that's going to be a first order process. Plot log A versus time in a straight line, you know that's going to be first order. If it doesn't go to a straight line you know it's not first order.

So then you go ahead and plot one over A versus time. And if it's a straight line, you know it's second order. And if it's not second order, it's not a straight line. It's not a straight line, you look for some other order. So that's one way to do it. And you've got to have enough points on your graph, because if I were to plot a, let's say this is my data point, if I have a second order process, at the beginning it's going to look an awful lot like a first order process. It's not until after a while that it's going to start to deviate. So you've got to have enough points down in time to make sure that you can differentiate between a straight line and a line that's not straight. And usually, that's often a mistake that experimentalists make. They look at the beginning. They say, oh, it's a straight line, work is done. Go home. But usually you need to have a good amount of the reactant consumed before you can tell the difference between first and second order. So you'll have an opportunity to do this on the homework. This kind of exercise of extracting the order of a simple reaction.

Another way to do it if you have a simple reaction is to look at half-lives. That would be the half-life method. If you can measure A as a function of time, then you know when you've gotten A over two. So, you know that if I look at the half-life versus the concentration, the initial concentration, of my reactant, that tells me something about the order. Because we saw that for our first order, t 1/2 was independent of the initial concentration. And that for a second order, t 1/2 was proportional to one over the inverse of the initial concentration.

So if you plot t 1/2 versus A0, or have a few A0 versus t 1/2s, then you can tell the difference between first order and a second order reaction, and see which one fits. Sometimes to get even more solid numbers, because from here you can also extract k. If you have a bunch of points, of t 1/2 versus A0, you can extract k, the rate constant. Not just the order, but also the rate constant out of this data. You can use multiple lifetimes if you have enough data. Multiple lifetimes. So you can define, you can define a t 3/4. Which is the amount of time it takes for the concentration of A to be 1/4 of what you started out with. So 3/4 is gone. And then you can put that into your first order rate law. So when you have log of A over A0 is equal to minus kt, you get that t 3/4, we can solve for t 3/4, and you get that that's equal to two log two, over k. And then you can do the same thing for a second order process. So this is first order. You plug in t 3/4 and A is equal to 1/4 A0, and you solve for t 3/4 for a second order process. And you get that this is equal to three over A0 times k. So it's the same functional form as these two. But there's a pre-factor that's different here. So here there's a two that comes in there. And here there's there's a three that comes in there. And so there's an obvious way to tell, then, if you have the t 1/2 and the t 3/4 signs. Basically, you follow, instead of having many reactions, instead of having many reactions to do, with different A0's here you can do one reaction. If you do one reaction and you watch the reactant go away, and you time it. When 1/2 of it is gone, that's one time, then you keep going, like 3/4 is gone, that's another time. Then you can take the ratio of those two times. Of t 3/4 versus t 1/2. t 3/4 versus t 1/2. And if it's a first order process, the ratio here is just two. And if you take t 3/4 over t 1/2 and it's a second order process, the ratio is three. So with one experiment, then, you can extract out the order. You can't extract out, well, you can extract out the rate constant. If you know the order then you know which equation fits, and you can extract out the the rate constant, with a big error bar. You're always better off doing many multiple lifetimes of different A0's or many of these just to get more statistics in the result.

So this is the simple process. And you always try, if you have something complicated, you always try to bring it back to a one component process by doing something like flooding. So if you have five different reactants, if you make four of them in very large quantities and keep one of them in very small quantities, then all the four that are in large quantities are basically constant over the process. And you basically are looking at only one reactant going away. And then you can use these methods to figure out what the order is for that one reactant. So, questions about simple one reactant sort of processes.

It's pretty straightforward. So now, let's say we have more complicated reactions. There are two ways that we can deal with that. The first, I already mentioned, which is the flooding which we'll get back to. And another way is called, so we have some complicated reactions. Complex reactions, with multiple reactants, that's A plus B plus C goes to products. And there could be some stoichiometry in front of there. So one of the ways to deal with that is called the initial rate method. We want to find out orders and rate constants. Initial rate method.

So if I look at minus dA/dt, one of the reactants or the rate of the reaction near time t equals zero. That's the initial rate. Right as the reaction starts. I mix everything together and I, just as after I mix it together, I watch the process of A disappearing or B disappearing or C disappearing. And so in reality what I'm doing is minus delta A / delta t near t equals zero, where delta t is a small interval. So there's not much change in delta A. Experimentally that's what I do. And that's pretty much, essentially getting this number out. And we're going to call that the initial rate. And the initial rate is k, and at the beginning I haven't used up anything. So all the initial concentrations are there A0 to the alpha, B0 to the beta, C0 to the gamma. Et cetera if you have more reactants.

So you measure this. You measure this R0, and then you repeat the same process with a new concentration of one of those three reactants. So with A0 prime, let's say. And then you get a new R0, R0 prime. Then you take the ratios of these R0 and R0 primes, R0 divided by R0 prime. So R0 is k A0 to the alpha, B0 to the beta, C0 to the gamma, then you have k A0 prime to the alpha. B0 to the beta, C0 to the gamma, and the k's you disappear. The B0's disappear. The C0's disappear. The only thing that we've changed is the concentration of A0 to begin with. So the ratios of these initial rates is the ratios of the A0's to the alpha power, to the order in terms of A0.

So if you're clever about your choice of ratios, then you can get alpha pretty easily. So if you choose, so if you now choose A0 prime to be equal to 1/2 A0, then you measure R0 over R0 prime. And if you get one, then you know that that alpha's zero. Alpha has to be zero here. Then you know alpha is zero, that gives you the order. It's a zero order reaction. If you get that R0 over R0 prime is square root of two, or rather 1/2, then a square root of two, square root of 2, then you know that alpha is 1/2. And that's a half order. We haven't seen any half order reactions yet, but we will. Those are indicative of a complicated mechanisms. But that's what you would get out of this experiment. If you get that it's equal to two, if you get that this ratio is equal to two, then you know that alpha is equal to one, et cetera. So it's a pretty easy way to get the order. Then you repeat the experiment. Now instead of changing A0, you keep A0 constant and you change B0. Or, you can use flooding or isolation, which is the next process to get the other orders. And eventually you get the rate constant. Once you have all the orders, and you have R0, then you have the rate constant. OK, so that's one way of doing it.

And a second way of doing it is the way we already mentioned. To solve the second order reaction in two components. Which is to flood the reaction with everything except for one. So this is called flooding or isolation. Basically, you isolate one reactant and watch it. You're trying to get back to a system, which is a simple system. Which is a system of one reaction. So let's say you take A0 to be much smaller than all the other species. You flood with B and C, and you isolate A0. And then your rate minus dA/dt, it's going to be A to the alpha. And instead of B, well, during that process B's going to say pretty much constant. Because it's hugely concentrated in B. You can replace B with B0. You can replace C with C0. So now you have an effective constant, an effective rate constant, and then you have a process which is effectively, or pseudo, one reactant. Then you can use these methods here, you can plot A versus time, you can find path lines, et cetera, to gather the order for it. Then you can get alpha and k prime. And if you can change B0 and C0, then you get k out of this.

So this is basically all fairly straightforward, just tedious experimentation to get all these numbers out. OK, any questions on this? You'll get experience on the homework. There's likely to be a question on the final where you're given data and asked to extract out orders and rate constants.

So let's move on now. So, so far we've looked at first and second order elementary processes, and we've looked at taking data and extracting out rate and rate constant. And the next step is to build mechanisms. So a mechanism is when you take a complicated reaction, like A plus B plus C goes to D plus E. And you break it up into elementary steps. What's an elementary step? An elementary step is a step which happens in a single reaction. So I could hypothesize that this complicated reaction happens in three steps, where I need to have a molecule of A and a molecule of B collide with each other to first form an intermediate F. Then I want a molecule of F plus a molecule of B to collide to form intermediate G plus a product D. Then have the intermediate G plus reactant C collide together to form the product E. So this set of elementary steps, where at each step you have a collision of two or three molecules together, three is not so common but two is very common, those elementary steps are called the steps of the mechanisms.

And these elementary steps you can define something called molecularity, which is the number of species that you need to collide with each other in one of these elementary steps. So the molecularity here would be two, you need two molecules to react. Here it's two, here it's two. If I have an elementary step which is a zero order in one reactant, then the molecularity would be one. Or I could have A plus A, the same molecules have to collide with each other. Molecularity would be two. And the molecularity and the order of the reaction are connected. So if you have something which is a molecularity of one, then it's going to be a first order reaction. One reactant is just sitting by itself, falls apart, like in radioactive decay. Molecularity of one, that's a first order of process. If I need to have two molecules come together, then it's a second order process. If I have to have three molecules collide at the same time together, molecularity of three, then it's going to depend on the concentration of all three at the same time. That's called a ternary reaction, and those are really quite rare. Termolecular reactions, you need to have your concentrations very, very high to statistically get an event happening where all three molecules collide together. So three body reaction is hard and anything higher than three body is essentially impossible. So that limits your choices, which is nice.

So that's the mechanism. And so what we're going to do next is go through some mechanisms. Some simple mechanisms and build up the complexity. Any questions about mechanisms here? What we're doing here is, we're formulating a framework. Where we can go back and look at things that are more complicated, like chain reactions or explosions or enzymatic reactions, and know when to apply approximations and et cetera. So we basically, here, are just laying down the ground rules.

So let's go to our first example of a mechanism, a more complicated reaction. And what we're going to do is we're going to extract out integrated rate laws out of all these mechanisms. And see what it looks like, as a function of time.

So the first one we're going to do is called parallel reactions. Simple mechanism. In this case here I have one reactant, and that reactant has a choice. You can think of it as a radioactive decay, an atom decaying in two different channels. So it can decay into B, or it can decay into C. There are two rate constants, k1 and k2. So you can write it like this, or you can write it as A goes to B plus C. This is how you would write a reaction. And this is how you would write your mechanism. A goes to B and A goes to C. Each elementary step, these are the elementary steps and this is the complex reaction, each elementary step is unimolecular. It's a first order process.

So in all of these examples, the first thing you do is you write your rate law. The rate at which A gets created or destroyed. And there are two paths. It gets destroyed and into B, with a rate which is proportional to the concentration of A, and it gets destroyed into C, proportional to the concentration of A. So you write down all the ways that A can get destroyed. There are two ways here. Two channels. This one happens to be fairly easy to solve. k1 plus k2 times A, and you've seen this before. It's minus dA/dt as a constant times A. That's a first order process. So you can just write down the answer. You don't need to do any math here. You recognize that we just call this one k prime. And that the rate is A as a function of time. This is A0 e to the minus k1 plus k2 times t. And everything you've learned about plotting first order processes et cetera, is applicable here, where the rate constant is the sum of these two.

So that's for the reactant. The products are also interesting to plot as a function of time, to see how they are related to each other in terms of their concentrations. So let me go through this also. When things get more complicated we'll quickly go and make approximations. But for now, we can still do everything exactly. So you write down your rate law for the product. dB/dt is equal to k1 A. dC/dt is equal to k2 times A. The formation of B depends linearly on A. The formation of C depends linearly on A, because they're both first order processes. To make B and C. And you integrate. You integrate here from zero to B, dB. Is equal from zero to t, A dt, k1. A is a function of time. And we've already solved for that. It's this exponential up there. So you plug in here A of time. And you turn the crank and you integrate, and it's an exponential. So it's not so hard to integrate. And you get that B is a function of time is k1 times A0 over k1 plus k2 times one minus e to the minus k1 plus k2 times the time.

Things are already starting to get a little bit more messy in the math. And then to get C, you actually don't need to do anything. Because you notice that the only difference between B and C here is replacing k2 with k1. So don't worry about doing any math. Just write down the answer. k2 A0, you interchange k1 and k2 at every step. One minus e to the minus k1 plus k2 times the time. The only difference is up here in the k2 term. And those are your equations for k1 and k2. And what you find, is the ratio of B to C is a constant. If I divide B by C, everything cancels out except for the k1 and the k2 here. Is equal to k1 over k2. And that is called the branching ratio.

The branching ratio, because there are two branches out of the reactions. And this gives you the ratio of which one is more likely to happen than the other one. And so if k1 is much bigger than k2, the rate is per unit time. The units of k1 are per second or per minute or per hour. So if this is big, if k1 is big, then mostly you're going from A to B, and only a little bit of C is formed. And the ratio of B and C is always constant. And so you can plot, then, you can plot the result. You can sketch out the result.

So you know that A is going to come down exponentially. Time on this axis here, concentrations on this axis here. So this is A as a function of time. That's that equation up here, in exponential decay. And the quantity of A. And B and C are going to come up in time, also, with this exponential format here. B is going to saturate at this ratio right here, k1 A0 divided by k1 plus k2. C is going to saturate at this quantity here. So they're going to start both at zero. And B is eventually going to go to k1 A0 over k1, plus k2. And C, eventually, will go to k2 A0 over k1 plus k2. And this, and the ratio of these two lines at every point is k1 over k2.

So, a simple question, for instance, that you might be of the type that you might be asked to look at is, suppose that k1 is 1/10 of k2. Which would you expect? Would you expect to have, let's see. So C is in green here. C, B. Or do you expect, so A comes down. B comes up. C comes up like this, or do you expect the last choice, I'm going to put the last choice here, so this is, let's call this choice number one. Choice number two. Choice number three. So k1, the rate k1 is 1/10 of the rate k2. That tells you something about the branching ratio. So do you expect this one here to be the right one? How many people think this is the right one? What about this one here? How many people think this is the right one? One person. What about this one here? So the branching ratio is the ratio of the two. It's 1/10. So this is approximately, in my sketch, poor sketch, granted, but this is approximately 10 times bigger than this. So that's the ratio that you'd expect. And it's the right, here k1 is the rate into B. It's slower than the rate into C. So, you got it right. So for more complicated, we have a more complicated process, we're going to ask you the same sort of stuff. And it won't be as straightforward. Any questions on this beginning here? Next time we're going to finish with the parallel first and second order processes. And hopefully we'll get done with the complex reactions and mechanisms and move on to, I forgot what's next on the list. But some explosions or chain reactions.