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PROFESSOR: So, now we'll start on the last of the main topics in the course. So we've finished most of our macroscopic thermodynamics, and our microscopic approach to it through statistical mechanics. And now, our final topic is kinetics. Kinetics is really a very different kind of topic. Because unlike thermodynamics, thermodynamics tells you all about equilibrium properties. A huge part of the work of this term has been to figure out what equilibrium is. What is the equilibrium state, given some situation. You've got some phases present. Different then, you could go from solid to liquid to gas. Or you've got different chemical constituents together that can react and go back and forth. What are the equilibrium concentrations?

But we haven't worried at all about how long it might take to get there. And that's what kinetics does. Kinetics is concerned with rates of reactions, primarily. How long it takes to reach equilibrium. And of course it's super-important. Because if you look at that window glass, it's not in equilibrium. It's silicon dioxide, the equilibrium state would be a crystal. It would be crystal and quartz. Nevertheless, none of us is very worried that on the moment it's likely to suddenly, spontaneously turn into a crystal and be opaque and scatter light and do all that sort of stuff. And in lots of other situations, certainly if you look at any living biological system, including yourselves or your friends or any other one, it's certainly far from equilibrium. And you probably would hope for it to stay that way. So there's an enormous amount of chemistry and processes we're concerned with. Which depend intimately on kinetics in order to work the way they work. They also do depend on thermodynamics and where equilibrium states are. But that doesn't mean they necessarily reach equilibrium states.

So we're going to go through kinetics, starting with the simplest examples and working our way up to more complex cases. And just see how we can describe elementary chemical reaction rates and processes. So that's our concern now, is dynamics. How long things take to get to equilibrium. And actually just like macroscopic thermodynamics, kinetics does take an empirical approach to the topic. In other words, it's based on experimental observation. Of macroscopic rates. How long it takes a collection of stuff, a mole of stuff to change chemically. And undergo reaction. And so forth. We often infer molecular mechanisms based on kinetics. And it's hugely important and valuable to do that. But it's also important to recognize that what kinetics can do is show us how we can formulate microscopic mechanisms that might be consistent with our macroscopic kinetics models. But the kinetics models by themselves don't prove the mechanism. And there are all sorts of examples where mechanisms that were proposed and accepted because they were consistent with macroscopic kinetics results turned out to fail. There are other ways to prove mechanisms. You might be able to design direct spectroscopic

observations of intermediates and so forth. And in that case, it often becomes possible to distinguish between different mechanisms. Which might all satisfy the macroscopic kinetics equation. So we use kinetics to infer a mechanism but not necessarily to prove it. Not generally to prove it.

We also use kinetics to describe an enormous range of time scales. So, the fastest things that we're sometimes concerned with that might take place on femtosecond time scales, 10^{-13} seconds or so, or 10^{-15} seconds, even. So, if we look at the range of time scales we might be concerned with, might go anywhere from about 10^{-15} seconds at the fastest, and might go to enormous scales on the other end. All the way out to maybe 10^{10} seconds, which is on the thousands of years. Could be longer than that, sometimes even millions of years. And the formalism that we'll set up applies equally to the full range of time scales. So it can describe an enormous amount of chemical activity. More commonly, for stuff that we're going to compare to, you might measure in the lab. Common time scales range from roughly 10^{-6} seconds out to about 10^5 seconds. That is, microseconds to about a day. But there are plenty of examples of going either faster or slower, depending on the need and the experimental equipment available.

Let's define a few terms. Let's talk about how we're going to just formulate chemical reaction rates. So, let's just imagine any simple reaction of this sort. So $A + B \rightarrow C$. There's some rate at which it happens. Note, by the way, it's an arrow in one direction. It's not an equals sign like we've seen before, or a double arrow. So the point I'm emphasizing here is when we talk about reaction rates, unlike equilibria, we're talking about a particular direction. Later on, we will talk about reversible reactions. But there, too, the arrow going this way refers only to one of the chemical reactions that can take place. Namely, in this case, the changing of what was the product now, would be the reactant, C, back into A plus B and it has nothing to do with the rate this way. Measured independently and so on.

So the rate, we can look at the rate of disappearance of A. So it's just negative $d[A]/dt$, where the brackets indicate concentration. Usually in moles per liter. If it's in a gas, then it would be p_A , of pressure. So negative $d[A]/dt$ is our rate. And note that that's generally a positive number. We're looking at reactions going, if it's a reaction going in this direction. A is gradually disappearing. So we're going to define our rate this way. To be a positive number. The rate for C is going to be plus $d[C]/dt$. It's also going to be defined in a way that makes it positive. Because in this case, since the reaction's going this way, we're looking at the appearance of C.

Now, by stoichiometry, in this case, of course whenever a molecule or a mole of A disappears, a molecule or a mole of C appears. So because of that, in this case, the stoichiometry tells us that that $d[C]/dt$ is equal to negative $d[A]/dt$. And also equal to negative $d[B]/dt$. And any of those can be used to define the rate of reaction.

Now, this is a particularly simple case because I've chosen the case where all of the stoichiometric coefficients are

equal to one. So now let's just look at any case that's different. Let's look at $2A + B$ goes to something else, $3C + D$. And just look at the reaction rates that we might see there. So here now, the appearance of C is going to be three times as fast as the appearance of D, for example. And also three times as fast as the disappearance of B. So if we write negative $d[B]/dt$, we expect that's going to be negative $1/2 d[A]/dt$. In other words, A is going to disappear twice as fast as B. Every time a molecule of B reacts, two molecules of A do. And that's going to be plus $1/3 d[C]/dt$, and every time that happens three molecules of C get formed. And it's going to be plus $d[D]/dt$. One molecule of D gets formed. And so, the reaction rate could be defined in terms of any of these. But the important thing is to keep track of stoichiometry so that the rate as it pertains to each constituent is accounted for correctly.

So to generalize, if I have little a of A, and little b of B, going to little c of C, and little d of D, then the rate of reaction can be written as minus one over $a d[A]/dt$, or minus one over $b d[B]/dt$, or one over $c d[C]/dt$, or one over $d d[D]/dt$.

So, experimentally, lots of measurements of reaction rates have been made. And now to start on what's seen empirically, basically the following result is extremely common. The rate is equal to some constant times the concentration of A to some power α , times the concentration of B to some power β , and so on. For all reactants. Multiplied together, each concentration taken to some power. Notice no products. Again, we're only looking at a reaction going one way. And if we look at the rate, this is typically what's found. α is called the order of reaction, with respect to A. β order with respect to B. And so on. And little k is our rate constant which, just to make clear, since we've been using it extensively in the past few lectures, is completely not equal to the Boltzmann constant. Absolutely no connection between them.

Now, α and β , what they are, what they turn out to be, is typically what's determined as a result of kinetic measurement. Typically they're small integers. So, just sort of a typical example, if you look at the reaction of NO and O₂, to make NO₂, simple reaction, and you look at minus $d[O_2]/dt$, use that as a measure of the reaction rate. What's found is that it's a constant times NO concentration squared, times O₂. Simple, right? One of the exponents is two, the other's one. Doesn't seem so surprising mechanistically. But it's not always the case. Even when you have small integers, it's not always the case that the most obvious mechanism you would infer is the real mechanism. And sometimes those exponents don't turn out even to be integers.

But here's another example. If you just look at CH₃CHO going to methane and carbon monoxide, seems like it would be a pretty straightforward thing, too. So if you measure, for example, the rate of appearance of methane, what you discover is that it's equal to a constant times the concentration of the starting material to the $3/2$ power. Not obvious mechanistically why that should be the case. Usually it's telling us something. It's telling us that the reaction mechanism is complicated. It's a multi-step process. Sometimes there could be chain reactions and so forth. So again, seeing things like this certainly helps us to infer molecular mechanisms. Again, they don't prove

molecular mechanisms. But they certainly can be very helpful in suggesting them. And then other means can be used to try to prove them. Including, above all, direct observation of the intermediates that you would expect on the basis of one mechanism or another.

Now let's just go through some elementary examples of kinetics one at a time. So let's start with the simplest possible case. Actually, a very rare case, but one that'll help us just set up the formalism of, and the mechanism for us to proceed. So let's talk about zero order reactions. Actually very rare. So, what this means is something like A goes over to products. Make a measurement of $d[A]/dt$, and discover that it's k times A to the power of zero, that is, it's just k . There's no dependence on the concentration of A. Or anything else. And you have some rate of its disappearance. So here's an example of it.

You could have oxalic acid, and it just turns into hydrogen carbon dioxide and carbon dioxide. Things break apart, forms these products. Make a measurement of the disappearance. Seems to have nothing to do with the concentration of it. At least under certain conditions. Now, turns out that there's another element that helps understand this. Turns out that light is needed, it's a photochemical reaction. And then it's easy to see how this can happen. Let's say we have an abundance of the starting material, and not very much light. So every now and then photons bleed in, and every now and then when they're absorbed, it leads to dissociation. In that situation, you'll be limited by the photons, but not by the concentration of the molecules. And in fact, strictly speaking although this is zero order in terms of the chemical constituents, it's not zero order in the photons. So in some sense, in this sort of situation, the photons should be considered one of the reactants. You could write this as this plus $h\nu$ plus one photon, goes over to these products. And then if you measure the rate and things are under circumstances like I described, you would discover that in fact yes you'd be photon limited. The rate would depend on how many both photons are coming in. Still, ordinarily, chemical rate equations aren't formulated in those terms. So in the usual formulation, this would still have the appearance of a zero order reaction.

Now, how do we write and formulate a solution? So it's simple. We've we've written a differential equation here. It's a pretty straightforward one. Minus $d[A]/dt$ is just a constant. So we can solve it. And typically we'll solve it by rewriting in integral form and then doing the integration as long as we can do the integration. So from here we can write the integral from starting concentration $[A]_0$ to some other concentration, $[A]$, $d[A]$ is equal to minus k integral from zero to t dt . So all we've done is integrate on both sides.

And we've assumed a starting concentration. We've assumed an initial condition. And we've also assumed an initial time, which usually we can just call zero. And this is, of course, something we can solve for straight away. So we just have that $[A]$ minus $[A]_0$ is negative kt minus zero, which is minus kt . So $[A]$ is minus kt . Plus $[A]_0$. In other words, the concentration of $[A]$ at any time is given by the initial concentration, minus the rate constant times time. It decays linearly in time. So we can sketch that. This is our initial concentration. And then it's just going to decline

with time after that. And there's our solution.

In lots of cases, it's useful to define what's called a half-life. It's just useful. Because it provides some timeframe, a single number that's a timeframe on which the reaction occurs. So, the half-life is just the time that it takes for half of the reactants to disappear. $t_{1/2}$ time to react half the reactants. OK, so in this case it's straightforward to see when that happens. In other words, that's the time at which this concentration of A is just equal to $[A]_0$ over two. So we have $[A]_0$ over two is minus $kt_{1/2}$ plus $[A]_0$ or $t_{1/2}$ is equal to $[A]_0$ over $2k$. $[A]_0$ over $2k$.

So there's our half-life. So if we go over here, we can put that in. $[A]_0$ over two, and this time is our half-life. So that's zero order reactions. And, again, zero order reactions are rare. But the procedure we're going to use to solve for kinetics is outlined in this way. And we'll use that again and again. Let's look at first-order kinetics. Let's go over here.

Now, first order reactions are quite common. Much, much more common than zero order. So here, you have A goes to products. That's the simplest case. But this time if we measure $d[A]/dt$, we discover that it's equal to a constant times the concentration of A. There's an important point to note here. What are the units of k , in this case. What do they have to be? Yeah, reciprocal seconds right? The equation has to work. This is concentration per second. This is concentration. This better be per second.

Let's just, before we move on completely, look at this. What are its units? Here's the equation. What are the units of k ? No, not unitless, because, look at this. This is some concentration unit, typically moles per liter. So this is moles per liter per second, right? It's disappearance of some concentration for time. That's got to be here. All that is here. Moles per liter per second. So in every case, the units of k , the rate constant, have to be figured out on the basis of the specific rate equation. Doesn't have the same units. When the kinetics are of different order.

Now, let's solve this using the same approach as before. Namely, this is still a pretty straightforward differential equation. So let's just integrate both sides. So that is going to tell us the integral from $[A]_0$ to $[A]$. But now we have $[A]$ on this side. So here we just had a constant. And effectively, I didn't write it out. But we effectively wrote this, rewrote this, as $d[A]$ equals minus $k dt$, and then went from here to the integral. We're going to do the same thing here, except now there's this. So really we're going to have $d[A]$ over $[A]$ is minus $k dt$. That's what we're going to integrate on both side. We need to have the variables distinct on each side. So we have $d[A]$ over $[A]$. Equal to minus k integral from zero to $t dt$. And so, of course, you know how to do this integral. It's going to look like \log of $[A]$. And again, it's taken at $[A]$ or, at $[A]_0$. So we have \log of $[A]$ over $[A]_0$. We're going to have \log of $[A]$ minus \log of $[A]_0$ coming out. And that's equal to minus kt .

So now the kinetics are quite different. We have $[A]$ is equal to $[A]_0 e^{-kt}$. Very important, very common sort of result. It's saying we start with a certain amount of material, and there's an exponential decay of

it. So very different from kinetics here, which are just linear. And again the kinetics here, if you imagine that situation where you've got starting material and bleeding in gradually are photons, presumably at the same rate, then sure that material you're going to see the disappearance of it linearly with time. Just depending on the rate at which the photons are coming in. Here it's very different because, presumably, A is required in order to do this reaction. It'll depend on how much. Because of course if there's more of it, you'll just have more at any given time decaying over to products. So you have an exponential decay.

So let's plot that. Here's [A], let's make that $[A]_0$. There it is. Now, let's look at what happens to the product. So let's imagine that it's A going to B, so of course $-\frac{d[A]}{dt}$ is just equal to $\frac{d[B]}{dt}$, and the rate of appearance of B has to match the rate of disappearance of A. Let's assume that we don't have any of B present at first. So let's make $[B]_0$ equal to zero. Well then, [B] just has to equal $[A]_0$ minus [A], right? All the stuff that's left, all of the A that has disappeared, that's given by this difference. Is just equal to B. So that's just $[A]_0$ minus concentration of A, but that's just given by that. Which is $[A]_0 e^{-kt}$. Or in other words, [B] is just equal to $[A]_0$ times one minus e^{-kt} . So at t equals zero, this is zero and this is one. In other words, this is going to be zero at first. And then it's going to grow in with the same exponential form that this decayed. So, [B] is going to do the exact opposite. It's going to be like this. So this is [B] of t and this is [A] of t equals $[A]_0 e^{-kt}$.

Now, it's always useful to, whenever possible, to plot these things linearly. Find a way to plot these as straight lines. And of course in this case it's straightforward to do that as a log plot. So if we take the log of both sides, we know of course that the log of [A] is just $-\ln[A]_0 + kt$, plus the log of $[A]_0$, so now let's look at that. Make this the log of $[A]_0$ and this is the log of [A] on the axis. That'll be time. So there's just some linear decay now. And the slope is $-k$. So experimentally, of course, this'll be done typically as a simple way of determining it.

Now, we also can usefully look at the half life, in this case, in the case of first order kinetics. So we have an expression in general for [A]. So if we let [A] equal $\frac{[A]_0}{2}$, at t equals $t_{1/2}$, that tells us that $\log \frac{[A]_0}{2}$ over $[A]_0$ is $-\ln 2$ plus kt to the $1/2$. But this is just the log of two, or $\ln 2$ is over k is t to the $1/2$. And so t to the $1/2$ is just $\frac{0.693}{k}$. So we can write that just generally, completely independent of whatever [A] is, also independent of what $[A]_0$ is, and that makes sense. So the point is, if you have something that just spontaneously decays into products, maybe it's just gradual chemical decomposition of something. Spontaneously, without the participation of other constituents. There's a general half-life that can be associated with that. That'll just be related directly to the rate of the decay. So it's knowable and measurable in a simple form.

And again, the half-life is always useful. Because it just gives a simple, one-number measure of the rough timescale for things to change. So if we go back to this plot, and then once again here's our half concentration. And here's our $t_{1/2}$, just a useful way of summarizing in a simple way, what happens. Yeah?

STUDENT: [INAUDIBLE] PROFESSOR: Ooh. Well, I didn't think about it. But it isn't necessary that that'll happen. Sure seems like it must be. When one is half decayed, the other must be half formed as long as there wasn't any B present at first. So yeah, thank you. Well, given that, something needs to move. But let's pretend like I got it right at this intersection. Even though it doesn't look that good. So really it should be there. Thank you.

So the single most common example of first order kinetics of this form is radioactive decay. You've got some radioactive isotopic that can spontaneously decay into some other nucleus. And of course, this is measured and half-lives have been tabulated for lots of cases of this sort. So a simple example.

Let's look at carbon-14. It's got a nuclear charge of six. It can decay into nitrogen-14 through the loss of an electron. Happens. First order kinetics. Now, in the atmosphere, what happens is this will end up, the ^{14}C ends up getting replenished.. Because from cosmic rays, what can happen is in the atmosphere, you can have your nitrogen plus a neutron will come and form ^{14}C plus a hydrogen atom. So in fact, the overall concentration in the atmosphere of ^{14}C tends to be constant over time. But stuff that's formed down here on Earth, with carbon, its content of ^{14}C decays over time, and it doesn't get replenished. So, let's think back some long time ago. Here's a tree. we can make it pretty. So it's got some concentration of ^{14}C that came from carbon dioxide in the atmosphere. That's what it started with. That's our starting point. At some point later, through natural occurrence or human intervention, that tree became horizontal. Then, and although we're looking back here, let's call this our t equals zero. And our ^{14}C concentration at the time is our concentration at zero.

Now let's say, shortly after that, either right after because of deliberate action, or shortly after because it was just discovered, somebody decides to build something using that tree. So, early human craft. And then let's say lots later, depending on your definition of lots, modern human, which can be denoted by this style of hat, makes exciting discovery. Terrific. And would like to know how old is it. How long ago did all that stuff happen. Let's assume this is also approximately t equals zero. Well, so a log of $[^{14}\text{C}]$ over $[^{14}\text{C}]_0$.

So this carbon dating, all it's really doing is measuring that. It gives a number for it. And we know this because we're assuming it hasn't changed any in all those years. In the atmosphere. It's different down here, because the tree or the boat wasn't replenished. Not nearly as many cosmic rays fell on it. So that's minus log of t . And it turns out the $t_{1/2}$ is 5,760 years. Amazing, that this can be known down to ten years. But it is. So that says, k is 0.693 divided by $t_{1/2}$, which is one over 8,312 years. So there's our answer, then. The time, how long ago that happened, is just minus 8,312 years times the log of $[^{14}\text{C}]$ in the artifact. Divided by the log of, by $[^{14}\text{C}]$ in the air. And the assumption again is that this is the same now as it was back then. And there's a bigger number than this, so it's a positive number overall. So in a fairly straightforward way, we'll use first order kinetics to determine the lifetime of something like this. Because we know the rate constant. And everything else follows.

Let's see. Next there's going to be second order kinetics. But let me just stop here and say just a word about the exam on Wednesday. So I've handed out an information sheet about it. But I don't have anything very different to say this time than I've had to say about previous exams. Solve lots of problems. Go over the homework. Go over practice problems. Try last year's exam as a sample exam when you're ready to do it. Try it under test conditions. There's nothing on the exam that you're going to look at and say oh my God, how was I supposed to know that we ought to study that. There won't be any surprises. Most of the exam questions so far, not all have been easy, but I think they've been more or less plain vanilla in the sense that they're right more or less down the middle of what we're trying to teach. And not very many are taking off little peripheral elements of the class. And it's not going to be any different here. So if you can just do the problem solving and get familiar enough with it that you're just good at it, so that you can do it with a reasonable speed, you're going to be fine.

Also try to work on just understanding the underpinnings. Especially of statistical mechanics. That's where when you have these true-false or multiple choice questions, these sort of thought exercises. Those are really hard. Because they go a little bit beyond problem solving. If you could do the problem solving, you're going to do fine. But it's always useful if you can also formulate things. And for that, it's never easy to just tell you here's what you have to do, to get good at this. Because you have to think about it. And it's always hard. But to be sure, if you can just try when you review the statistical mechanics, especially, and you review the expressions that you use and how you solve problems with them, the next step in studying is to try to think, OK, do I really understand where that expression came from. And why it makes sense physically. And if you can do that, then so much the better. Then you'll be in an even stronger position. The info sheet gives a handful of equations that we do expect you to come in with those on your fingertips. There are not very many. Mostly we'll provide expressions that you'll need, and the important thing is that you know, understand, where they apply. And how to use them. So, good luck on Wednesday.