CATHERINE DRENNAN: So radioactive decay is kind of a classic example of a first-order process. So we are doing one little tiny section of the chapter on nuclear chemistry, and we're doing that all today. And so all we're really covering is problems associated with first-order processes. So this is just a small introduction to this idea.

So radioactive decay has a lot of applications. There are medical applications, including imaging organs and bones, including the heart. And so there is a compound that you already saw called Cardiolite. And so we talked about this in transition metals because you have a transition metal. And what is the geometry of this compound? Octahedral, and we have cyanide ligands, which what kind of field strength? Strong. Yeah.

So this compound was designed in part by an MIT professor, Alan Davison. You could go talk to him about this incredible discovery and invention. It's used about seven million times a year or to image various organs and has been for a very long time. It's off patent now.

But this patent made Allen Davison, MIT, and MIT Chemistry Department an enormous amount of money. And so you could go talk to him about it, except he's happily retired living in one of his homes.

[LAUGHTER]

So you can't really do that. But anyway, so this uses an isotope of technetium, which is metastable isotope. And so it's 99. It's an isotope of the normal 98 atomic mass. And so the next challenge, you're always looking for the next great thing, the next great imaging agent. So this is still a very active area of research, and there's actually a talk just this week on campus about work in this area.

So this is transition metals combined with radioactivity. So it's two topics here in the class. So another, of course, important use is the potential of nuclear energy and the current use of nuclear energy. This has many challenges, and I don't want to go on record of what I think about nuclear energy. I think it's a complicated problem.

There are a lot of challenges. But one I'd like to bring up, because I think it's particularly interesting to me, is what to do with the waste. And so one story that I heard about actually there was a documentary made about this.

Finland had this idea to create this three-mile long tunnel, and they wanted to store 12,000 metric tons of nuclear waste. And they wanted the containers to store it for 100,000 years. And this documentary asked a number of questions about this idea, such as, what kind of container do you use, and how do you know the material you design your container is going to last 100,000 years?

As experimental scientists, we like to test how long things last. But you can't really do this experiment. Also, it kind of brought up the idea, do you guard this facility for 100,000 years? Because you can make bombs out of a lot of this radioactive waste. So you kind of need to protect it.

But maybe you should just bury it and then no one knows it's there so you don't have to guard it so they can't find it and use it. But then what if someone stumbles upon it and releases all of this radioactivity? So that would be bad.

So do you put warning signs for people who will be around 100,000 years from now, saying, hey, don't go in here. It looks like a pretty tunnel. But, hey, the half-life of the thing stored here are 100,000 years. So this is pretty radioactive still. Don't go inside. And if you write this sign, what language do you put it in?

So the documentary pointed out that Neanderthals existed like 40,000 years ago. So 100,000 years from now, what's going to be going on? How do you write a sign to people that long in the future?

Anyway, I just think that these are sort of interesting ideas and brings up the point that as scientists and engineers, we need to think not only about the science and engineering of what we're doing, but the ramifications to society and the sociology as well as politics involved in some of this science. So this is an interesting area for that intersection of the social sciences and the natural sciences and engineering.

So radioactive decay-- definitely a useful thing, dangerous and useful all at the same time. Oh, look at that. You know the clicker question's coming up at the bottom of the page. We're not

there yet. It's OK. We're not there yet. I just added that at the end and apparently didn't animate it well.

So the decay of a nucleus is independent of how many nuclei are around it. That's what makes it a first-order process. So because it's a first-order process, we can apply those first-order integrated rate laws that we just derived.

So we had our rate log of the concentration of something A equals its original concentration to the e to minus k, which is our rate constant times time and also our half-life equation that we just used. So instead of concentration of A, though, we're going to have a different thing to express what we're interested in here, which is N, the number of nuclei. So we can just write that same expression down.

But instead of concentration of A, we're just going to use capital N. So N, the number of nuclei at some particular time, equals how many nuclei were present originally times e to the minus k. And here it is a rate constant still, but it's a decay constant in that the rate you're measuring is radioactive decay. So it kind of has a special name. Although, if you use rate constant for that, that is what it is, so that's OK.

t is still time. And yes, N to the o is the original number of nuclei. So we're just going to do a clicker question about how one goes about calculating the number of nuclei. 10 more seconds.

So someone want to tell me for one of the Green Lantern T-shirts, what is wrong with the other answers? I think I saw your hand up first. Sorry, folks.

AUDIENCE: Let's see. So answers one and two, they have the wrong-- what was it-- the molar mass of technetium. Is that technetium? Yeah And answer four does not multiply by Avogadro's number. So that's going to give you the number of moles of the particle.

CATHERINE DRENNAN: Right. Great job. It's Thanksgiving. I thought we needed a good prize today. So right. So one thing you also want to remember make sure that your units are good. And it's really important in doing this-- you can take this back-- to remember to use the number that is here, this atomic mass number, not the one from the periodic table in calculating the problem.

Actually, the periodic table disappeared from that. Oh, well. So if you use the periodic table, it's a close answer but sometimes. Sometimes it won't be so close. But remember, when it tells you about the isotope, it always has the atomic mass that you should be using in the problem as part of the questions. So keep that in mind. And yeah, you definitely want to remember

Avogadro's number. And the answers are such that it's hard to tell that you messed up.

With the wavelength, it's really easy to tell you messed up if you didn't use Avogadro's number because it doesn't make any sense. With these, it's a little harder. So remember to use the isotope's atomic mass and also remember to use Avogadro's number when doing this. And then you should be fine.

So this is really similar. It's really similar, depending on whether you're talking about chemical kinetics or nuclear kinetics in doing these problems in terms of the equations. But in chemical kinetics, you're measuring the concentration. Whereas with nuclear kinetics, you're measuring decay events. And so usually how do you measure decay events? And the most common way is here, our Geiger counter.

So I just want to-- it's always important every once in a while at MIT to double check that the rooms that you're teaching in have not been contaminated by some wonderful experiments. So, so far, we're good. So here, this is working. You can hear the chips, I think.

This is pretty good. You don't have to be concerned about this. There's always some background level. It's fine. So there are gases in here that will get ionized by radiation, which gives off. Then that's translated into that clicking noise. So that's what is happening.

So it's measuring, with our thing, whether there are any radioactive events going on. And this is called a Geiger counter. And we use X-rays in my lab. So I went and stole this from our X-ray facility before I came here. Luckily, it's almost Thanksgiving, so no one was collecting any data. So no one will get in trouble for taking this right now. And Hans Geiger is the person who came up with this idea and this device.

Does anyone remember where we heard that name before? Think back class two. So he did that amazing gold foil experiment. And so our ping pong balls that we were throwing were duplicating the experiment that he did as a graduate student. And luckily, I think he was smart enough to realize that when you're working with things-- he was working with a lot of radioactivity at that point-- that once you know exactly how much radioactivity you're working with-- and so these were very early day experiments. And he came up with this device that helped him know how safe he was. And this is still sort of the standard thing to have these around and double check that there is no radiation leaks in places like that.

So the Geiger counter-- all right. So also a couple of more terminology things. Decay rate is

also called activity or specific activity. So you're talking about how active your substance is. That's really how radioactive is it. And activity also has the letter A.

So we were talking about the concentration of A. Now we have A again. There's a lot of A's in this unit. So that's the change now in the number of nuclei over time- that's the rate expression, or the rate law-- k, the decay constant, times the number of nuclei. And because activity is proportional to the number of nuclei, we can also take this expression that we had before that had the N's in it and rewrite it with A.

So now it's really just like that first-order expression we had but without the concentration term. So we have the activity at some time equals the original activity of the material times e to the minus kt. And all of these equations are going to be on your equation sheet.

But if you mess up and use the wrong equation for this, it doesn't matter, as long as you're using the first-order equation. Whether it's concentration or activity, it's the same idea that you can determine, if you know the rate constant or the decay constant, how much material is left, how much activity is left, how many nuclei are left after a given amount of time.

So I know what you're all thinking now. You're thinking, this is fantastic, but what about the units? We musts here about the units. So the SI units for activity are the becquerel, BQ. And one becquerel is one radioactive disintegration per second. And this is the newer unit.

The older unit was called a curie, and sometimes you will still see this in the literature. And a curie, one curie, was 3.7 times 10 to the 10th disintegrations per second. So it was a much larger number than the current SI unit. So this was what one gram of a radium specific activity was.

So they used this big number. But it was not really practical because you want to tell people like how much radiation would be safe for them to have in a year or something like that. And you didn't want to use this giant number for that. So we've moved to here.

So does anyone know or want to guess who the older unit was named for of radioactivity? One might think Marie Curie. But a lot of the evidence suggests it was actually her husband, Pierre Curie, who it was named after. It's a bit controversial.

But they both worked together, and they worked with Henri Becquerel. And they all won the 1983 Nobel Prize for discovering radioactivity. Three years later, Pierre Curie was killed

crossing the street. He slipped when it was raining, and a horse and wagon, I guess, ran over him and killed him.

So this is, I think, an example of someone who's so brilliant, but you say, they're so brilliant, but do they look both ways before they cross the street? So you are all very brilliant. And I encourage you look both ways before you cross the street.

Anyway, so he died. And some of the stories are that they named the unit after him as a tribute. Others say, well, it's really for both of them. But in any case, now it's named after the third person, Henri Becquerel.

So radioactivity, I'm going to tell you a little bit about radioactivity. This chart is not in your handout because you're not responsible for knowing all this information, so I just didn't put it in there. But you can look this up.

There's a couple of points I did make in your handout, which is there are different types of nuclear radiation. We have alpha particles, alpha decay, beta decay, gamma decay. Some of those involve a mass change. So like an alpha particle is the same as a helium-4 nucleus-- two protons, two neutrons.

Beta decay involves an electron. Gamma is a photon. So there are definitely different types. Some mass change, some not. There are also really dramatic differences in half-life. So again, half-life depends on the material in question. It depends on that decay constant, that rate constant. And if we look at this table, we can see things from milli seconds. And if we look at some of these, d is for a day. a is for year. y is also for year.

So sometimes you'll see y for year. Sometimes you'll see a. I think most people guess that y is for a year. That a is for year, I don't really know. But anyway, in this table it's a. So if you see that, don't be confused. And Ga, that's giga years, so 10 to the ninth. That's where the Finland 100,000 years comes from, that we need to keep the stuff safe for a very, very, very, very, very, very long amount of time for giga years.

So in some decay processes, such as uranium-238, you have more than one type of nuclear radiation going on. And it can involve a very long and complicated series of different events. So here at MIT, we spend most of our time talking about science and engineering.

But I feel like every once in a while we should throw in some poetry into our science classes. So once a year I like to read a chemistry poem to enrich our lives. And today is that day in

2014. And the poem I'm going to read to you is called "The Days of Our Half-Lives," and it is by Professor Mala Radhakrishnan.

She got her PhD here at MIT in the Chemistry department. And she wrote this book, which she wanted me to point out is available on Amazon if you're looking for a Christmas present for a very, very geeky friend of yours. And it's illustrated by another MIT chemistry PhD, Mary O'Reilly, who actually did the illustrations for the videos that I've been showing you in class.

So MIT chemists, just really multi-talented individuals. So I will read you this poem now. And as I read it to you, I will point out what is happening in this decay process because all of Mala's poetry is scientifically correct. So "Days of Our Half-lives."

"My dearest love, I am writing you to tell you all that I've been through. I've changed my whole identity. But loved, I can't pretend to be. When I was uranium-238, you were on my case to start losing weight. For 5 billion years I'd hoped and I'd prayed, and finally I had an alpha decay.

Two protons and two neutrons went right out the door. And now I was thorium-234. But my nucleus was still unfit for your eyes, not positive enough for its large size.

But this time my half-life was not very long, because my will to change was really quite strong. It took just a month, not even a millennium, to beta decay into protactinium. But still, rejected me right off the bat-- protactinium, who's heard of that? So beta decay I did once more to become uranium-234.

Myself again but a new isotope, you still weren't satisfied. But I still had hope. Three alpha decays 'twas hard, but I stayed on through thorium then radium and then radon. I thought that I would finally please you. My mass was a healthy 222.

But you said, although I like your mass, I don't want to be with a noble gas. They dress so well. You had a point though. I wasn't reactive. So in order to please you, I stayed proactive.

A few days later, I found you and said, two more alpha decays, and now I am lead. But you shook your head. You were not too keen on my mass number of 214. I had a bad experience with that mass before, and an unstable astatine walked right out the door.

So in order to change, I went away. But all I could do was just beta decay. My hopes and my dreams started to go under, because beta decay does not change a mass number. To

bismuth and polonium, I hoped and I beckoned. My half-life was 1 6 4 microseconds. And then finally, I alpha decayed. And then I was lead with a prize worthy mass of 210.

Got to admit, I was getting quite tired, and my patience with you had nearly expired. You were more demanding than any I'd dated. And much of my energy had been liberated.

But you still weren't happy, but you had a fix. I really like the number 206. So I waited for years until the day which began with another beta decay and then one more. And finally, in the end, I alpha-ed to lead 206, my friend.

To change any further. I wouldn't be able-- not longer active, but happily stable. It took me a million years to do, but look how I've changed, and all just for you. Wait, what did you say? I've gotten so old that you'd rather be with a young lass of gold?

Well, I give up. We're through, my pumpkin. Shouldn't all my effort be counting for something? Well, you won't be able to rule me anymore, because I'm leaving you not for one atom, but four.

That's right. While you were away diffusing, I found some chlorines that I found quite amusing. And we're going to form lead, Cl4, and you won't be hearing from me anymore.

See, over the years, I've grown quite wise. I've learned that love's about compromise. You still have half of your half-lives to live, so go out there. It's your turn to give." Thank you.

[APPLAUSE]

There's a whole book of them on Amazon. So that is first order. First order is pretty exciting because it has nuclear decay. Second order-- not quite as exciting. But we should talk about it anyway.

So second order integrated rate loss-- we're not going to go through a derivation. It's in your book. But here is the equation, if you do the derivation. So now we have 1 over the concentration of A at time t equals rate constant k times t plus 1 over the original concentration of A. And we could plot this one over concentration of t versus time. And if we did that, you would have the opportunity for another clicker question. 10 more seconds.

90s, yeah-- it's kind of hard to come up with clicker questions in this unit, so. But it's fun, for Thanksgiving, we'll have lots of 90s. So we can just look, and this is actually an expression for

a straight line again. So we're plotting on the y-axis one over a concentration of A at all the various different times versus time over here. And so our intercept is going to be 1 over the initial concentration of A. And our slope is going to be what? k, right.

So again, you can measure your concentration as it changes with time, how the concentration changes, plot it, and just determine your rate constant for that particular material. So second order half-life-- we can do another derivation. But in this case, I will just give you the equation.

So half-life equals 1 over k times your original concentration of A. And so this is different from first order. There is a concentration term in the equation. So for second order half-life, it does depend on the starting concentration. So that's really the big difference.

In first order, it doesn't depend on the starting concentration. It just depends on the rate constant or the decay constant, which depends on the material in question. With second order, you do need to know how much you had originally.

So again, how do you know if it's a first or a second order process? And here, you really have to determine it experimentally. So one thing you could do is measure how A changes over time and then plot your data using the equation for first order. And you may see that, yeah, that does not form a straight line when you're plotting with natural log of a concentration of A.

But then if you try plotting it 1 over the concentration of A, you get a beautiful straight line with your data. And so you'd say, that's a second-order process. So again, you're determining these things experimentally, collecting data, plotting the data, determining rate constants, determining the order of the reaction.

Now, this is very exciting. What we're going to talk about is the relationship between the rate constants and equilibrium constants. So I love this. I love when we come back to stuff that we've talked about before and see it in a slightly different way.

So at equilibrium, we talked about how it's a dynamic process. And you have the rate of the forward reaction equal the rate of the reverse reaction. Reactions are still going. They haven't stopped. But the rates are equal in both directions.

So we've talked about how to write an equilibrium constant for reaction. So if we have a reaction of A plus B going to C plus D, we can write our equilibrium constant k and its products over reactants. Unless one of our products or reactants is a solid or a very dilute solution. It's

the solvent. And I heard from your TAs that in the last problem set, some people had forgotten what goes into q or k expressions.

So it's good to review that for this next unit and exam four and the final-- so products over reactants. Now suppose we tell you that it's a second-order process and the rate of the forward reaction here, A plus B, we can write the rate law for that forward reaction being second order, first order in A and first order in B. So the rate constant for the forward direction is k 1 and then times the concentration of A times the concentration of B.

For the reverse reaction, the rate constant is k minus 1. And this is generally true in all the problems. If it's a first step, you have plus 1 k1 on the top, k minus 1 on the bottom. So we have k minus 1 times the concentration of C and D So that's the backward direction.

So at equilibrium, these rates are equal. We just talked about that. We've seen that before. The rate of the forward reactions, so k1 times A times B is equal to k minus 1 times C times D when you're at equilibrium.

So we can rearrange this equation now and say C and D over here over divide by A and B. It's going to be equal to k1 over k minus 1. And we also just saw that C times D over A times B was equal to k. So therefore, our equilibrium constant k equals k 1, the rate constant for direction, over k minus 1, the rate constant for the reversed direction. So here we're relating equilibrium constants and rate constants.

So we thought a lot about what's true if you have a big equilibrium constant. If you have a big equilibrium constant, if you have an equilibrium constant much greater than 1, what's the ratio of products and reactants at equilibrium? Is there more or less products at equilibrium and reactants? More.

So we thought about that, and now we can think about the relationship of the rate constants. So if k is greater than 1, is k 1 greater or less than k minus 1? Greater. And so that would then be the case where you have more products than reactants at equilibrium.

If k is less than 1, a case where there's more reactants than products at equilibrium, then you have k 1 is less than k minus 1. So again, we can think about this in terms of thermodynamics. We can also now think about it in terms of rates.

So one more thing that we need to cover before we end today, and that is about elementary steps and molecularity, which I just love saying that word. So on Monday, we're going to talk

about mechanism of reactions. Most reactions do not occur in one step, and we need to think about mechanisms.

I said it was Wednesday. But it's actually Monday. So it's coming up. It's very exciting. And we're going to talk a lot about elementary steps when we talk about mechanisms. So an elementary step is one of the steps in the reaction.

So reactions usually don't occur in one step. They have many steps, and each step is called an elementary reaction. So we talked about last time that for the overall order of the reaction, you can't just look at the stoichiometry and say what the order of the reaction is. So you can't predict it from stoichiometry for an overall reaction.

But if it's an elementary reaction, if it's a step, that elementary reaction is written exactly as it occurs. So in that case, the order and the rate law can be predicted. So this is you're breaking it down into sort of the smallest unit, the smallest step, this elementary reaction, so you can just look at the stoichiometry for a single step, for an elementary reaction, and project to the order and the rate law.

So elementary reactions occur exactly as written. So that's what we're going to do on Monday. We're going to break down our mechanisms into elementary steps, write out the rate laws, and then figure out what kind of mechanism we might have.

So finally, molecularity-- so molecularity is just the number of things that come together to form a product. And here we have three names-- unimolecular, bimolecular, and termolecular. Unimolecular process, what do you guess? How many reactants are coming together to form product? One.

Bimolecular, what do you guess? Two. Termolecular is a little harder, but just give it a whirl. Three, yes. So bimolecular is very common. And termolecular is not. So I have three molecules to come together. And if you try to think about how you get three things to come together all at the same time, that's kind of rare.

Usually, when there are three things reacting, there are multiple steps involved. But two is good. Now finally, we'll end with a clicker question. Think about which of these would be examples of unimolecular processes. 10 seconds.

So it actually is one and two. So most people got the two. Yes, that's radioactive decay. But

the other, you can have a decomposition. So here we have decomposition into its elements is also a first-order process. Happy Thanksgiving, everybody. See you next Monday.