PROFESSOR: OK, so kinetics we're continuing with today. We talked on Wednesday about first order kinetics and we'll do a brief review of some of that. And we're going to talk about second order kinetics. Today we're going to come back up and talk about chemical equilibrium, which is something I love to do to review things that we've talked about before. And we're going to start in on reaction mechanisms. So, I thought I would mention, some of you have may have seen the activity in the Infinite Corridor, but today is world AIDS day, and today a lot of the compounds that are being used to treat HIV were actually designed based on making inhibitors to enzymes. And so, to design those pharmaceuticals, people had to understand the reaction mechanism of the enzyme, and enzymes, of course, are catalysts in the body.

So, knowledge of what medical individuals needed to know to design these inhibitors to treat HIV are actually a lot from this unit that we're going to be talking about. So, we'll be talking about reaction mechanisms, and we're also going to be talking about enzyme catalysis, which were key points in being able to come up with some of the current treatments against HIV.

All right, so just a little review from last Wednesday. We talked about first order half life. We talked about first order kinetics, we came up with an integrated first order rate law, and we also talked about half life. And you told me last time that an example of first order half life is radioactivity, which we're going to be talking about today.

So, just a little review from last time, you have your first order integrated rate law, and the half life is defined as the time it takes for half of the original material to go away, and half life is abbreviated t 1/2, that's the symbol for half life, so the time for half of the original material to go away. If you plug original material divided by 2 in there, then the original material a to the o for original, drops out and you come up with this equation of the natural log of 1/2 equals minus k t 1/2, and k is, of course, our rate constant. And so, then we can take the natural log of a 1/2 and we get a value. Rearranging that, you get half life equals 0 . 6 9 3 1 over k. And so you told me last time for this plot for first order half life, each half life, half of the original material goes away.

So, one example of a first order half life process is radioactive decay. And the reason why this is a first order process is because the decay of the nucleus is independent of the number of surrounding nuclei that has been decayed. So it's independent of the original starting concentration, and since it's independent, notice that's a blank in your notes, since it's independent, then that makes it a first order process.

So, we can apply first order integrated rate laws to radioactive decay. So here were some of the equations we had last time. We had, this is a different expression of the first order rate law where the material, concentration material of material a, at some particular time equals the original concentration, e to the minus k t, where you have your rate constant and the time that has elapsed, and we also just talked about first order half lifes with this equation here.

So, we can use those same equations, but often you don't see it in terms of concentration of a, you usually see these expressions in terms of either the number of nuclei or a different a, which is a for activity. So instead of concentration, we're talking about the number of nuclei that have decay or capital N.

So, we can write this same expression, but now using N instead of concentration of a, same thing, number of nuclei equal the original number of nuclei, e, to the minus k t, where k is our rate constant, or in this case decay constant, and t is time.

So, with chemical kinetics, we're usually talking about the change in concentration of things over time, but with nuclear kinetics, we're talking about the number of decay events, the number of nuclei that have decayed. And so, here with nuclear kinetics, we measure these events using a Geiger counter. So this can measure radiation, and I'm going to come around and just check the room. And so, the gasket's ionized and then you hear different clicks. See if you can hear the clicks as I come around. So let's just see if we have any problems over here. Oh, maybe a little bit. No, this is fine. There's always a little bit of radioactivity, it's all fine.

So, this is a Geiger counter, which will measure nuclear kinetics, it will measure radioactivity. And my lab has this particular one, because we use x-rays in our experiments. OK, we'll leave this on low just to check things out as we go along.

All right, so we do have a term, A, that we talk about in this unit. Instead of concentration of A, it's activity. And so, activity here, sort of the decay rate, is also called activity, capital A, and so this is equal to the change in the number of nuclei or our decay constant times the number of nuclei. And people will often talk about the activity of particular radioactive compounds.

So, because activity is proportional to the number of nuclei, you can also take this expression and write it as this expression. So you can have either the number of nuclei equal the original number of nuclei, e to the k t, or you can do it in terms of activity -- that the activity at some time is equal to the original activity, e to the minus k t. So, all of these equations can be re-written in this way.

So, let's talk a minute about units. All right, so the activity for units, the new activity is Bq, Becquerel. and that, actually is named after a French person. Henry was his first name, and my French pronunciation is not very good.

This is the current unit. It's equal to one radioactive disintegration per second. The older unit, which you may be familiar with, is called the Curie, and that is 3 . 7 times 10 to the 10 disintegrations per second. Does anyone want to guess, the Curie unit, who that was named after?

STUDENT: Marie Curie?

PROFESSOR: No, it was named after her husband actually, Pierre Curie. And I actually always assume, because Marie is actually more famous than her husband. But she, Marie Curie won two Nobel prizes, so we shouldn't feel too sorry for her. Her husband shared the first Nobel Prize with her in, I think it was 1903, but then in 1906 he was killed in a road accident, run over by something that was crossing the street. So he did not share the second Nobel Prize, because by the time that came around about 1911, he had passed away.

So, at first, we had the Curie, but then that turned out to be a really big number. And so, when you were talking about sort of safe units for workers to be exposed to, if they were being exposed to things 10 to the 10, that really isn't very healthy. So they wanted to have sort of a much smaller unit. And so I guess that Marie Curie at that point talked about how her husband would feel about having the Curie not being the standard unit, but I guess she was OK with it, because if we had kept that same unit, then people would have been using it and it would of had to of been a really, really small number, because it was sort of picked to be set up to something that was too large, and she didn't want her husband's name apparently associated with a sort of an infinitesimally small quantity of something.

So, the Curie was sort of done away with. And Henry Becquerel, who was one of the people who discovered radioactivity and shared that first Nobel Prize, had the unit named after him. And I always ask the freshman chemistry class that as they go through MIT, if they ever discover a unit that is named after a female scientist, to please come back and let me know. This was the one I thought was named after a female scientist, but as it turns out, it was actually Pierre Curie. So, if you hear of any, please let me know for future reference. So, the current unit you'll be using is Bq here for radioactivity.

So, you're not responsible for knowing all the different types of radioactivity. When you're working problems, you can always get this information. I'll just mention that a number of different kinds of radioactivity, some involve a mass change, some do not involve a mass change. So, alpha decay, this isn't actually in your notes, there's a reference to where the table is. You're not responsible for memorizing it, so I didn't put it in the notes. An alpha decay is equivalent to a helium 4 nucleus, so you lose two protons, two neutrons, so that's a big mass change. Whereas say a beta decay involves a loss of electrons, so there's no mass change associated with that. So just to be aware that there are these differences in different types of radiation.

There's also really big differences in terms of half lives of radioactive isotopes, and again, this information would be given to you on a test or a problem-set, so you don't have to memorize it. So, this table is similar to one in your book, and the point here is just how different half lifes can be. So the abbreviation a here is year, d is day. So you see some of these half lifes are in multiple years, some of them are days, so there are big differences in terms of the half life of some of these radioactive isotopes. Some of them stay around for a really, really, really, really long time.

So, I thought I would share with you a poem about half lifes today. And this was written by a former graduate student at MIT, Mala Radhakrishnan, and she is now a professor at Wellesley college right here in Wellesley, Massachusetts.

So, her poem entitled "Days of our half lives," is from her collection of chemistry poetry, "Chemistry for the Couch Potato." And this particular poem involves the uranium 238 decay series. So, here we go.

"Days of our half lives. My dearest love, I writing you to tell you all that I've been through. I've changed my whole identity, but loved, I can not 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 prayed, and finally I had an alpha decay. Two protons, 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 it's large size. But this time my half life was really not very long, because my will to change was quite strong. It took just a month, not even a millennium, to beta decay into protactinium. But you still rejected me right off the bat, protactinium, who's heard of that? So, beta decay, I did much more to become uranium 234. Myself again, but a new isotope, you still weren't satisfied, but I still had hope. Three alpha decays, it was hard, but I stayed on through thorium, through radium, and then radon. I thought I would finally please you, my mass was a healthy 222, but you said, although I like your mass, I do not want to be with a noble gas. You had a point, 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. You shook your head, you were not too keen on my mass number of 214. I had a bad experience with that mass before, an unstable acitone 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 decays don't change a mass number. To bismuth, then polonium, I hoped and I beckoned, my half life was 164 micro seconds.

And then finally I alpha decayed and then I was lead with the prize worthy mass of 210. I've got to admit I was getting quite tired, my patience with you had nearly expired. You were more demanding than any I dated, and much of my energy had already been liberated. But you still weren't happy, but you had a fix, I really like the number of 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, no longer active, but happily stable. It took me billions of years to do, and look how I've changed and all just for you.

And wait, what did you say? You've gotten so old that I'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 any more, because I'm leaving you, not for one atom, but four. That's right, when you were away defusing, I met some chlorines that I found quite amusing. So we're going to form lead c l 4, and you won't be hearing from me any more. See, over the years I've grown quite wise, I've learned that love is about compromise. You still have half of your half lives to live, so now you go out there, it's your turn to give."

And that is "The days of our half lives." So, Mala takes great effort to make sure that all her poetry not only rhymes, but it is chemically correct. So, it's a good way to review material to read "Chemistry from the Couch Potato."

All right, so let's do an example now and think about how things will change over time. So we have an example, we want to know the original activity, and the activity after 17 years of a sample of plutonium. So let's take a look at how we'll do this problem. So first, given the information up there, the first thing we want to do is find the original number of nuclei. So first, capital N o, the original number of nuclei. So, we're given information about grams, so we have 0 . 5 grams. And now if we want to know the number of nuclei, what's the first thing I have to do? Convert from grams to what?

STUDENT: Moles.

PROFESSOR: Moles, right. And here we want to use the molecular mass that's given to us in the form of that isotope. So here, we are given information about 239, and so that's the number we want to use in our conversions. So we can convert that over, but that's going to give us moles, so how do we go from moles to molecules? Avagadro's number, 6.022 times 10 to the 23. This time we're going to talk about it in terms of nuclei per mole, and so that's going to give us 1.3 times 10 to the 21 nuclei.

OK, so now we know the original number of nuclei. The next thing we're going to want to do is find k. And k is our rate constant for decay or our decay constant. So what do we know about k for a first order process? We know the equation for what? For first order half life, right. So that's o . 6 9 3 1 over t 1/2. And in this problem we were given, the half life, and often you will be given the half life or you can look it up, and so we can put that in, so we have 0 . 6 9 3 1 over 7 . 6 times 10 to the 11 seconds. And we can calculate our constant, which is 9 . 1 times 10 to the minus 13 per second.

So now we were asked to find the original activity and the activity after 17 years. So, first we'll find the original activity, and the original activity is going to be equal to our rate constant times our original number of nuclei. So we've just solved for both of these, so we can plug these in, so we had 9 . 1 times 10 the minus 13 per second times the number of nuclei, 1 . 3 times 10 to the 21 nuclei, equals 1 . 2 times 10 to the 9, and what are the units here? It's just like a hum, it's hard to understand.

STUDENT: Nuclei per second.

PROFESSOR: Nuclei per second, which is the same as what? That's equal to something else. Yup, so that's the same as the Becquerel or the Bq, so it's defined as nuclei per second, or number of disintegrations per second.

All right, so let's do the last one. OK, so now after 17 years, so now we can say that the activity at some time is equal to the original activity, e to the minus k t, and we can put in the activity that we just found, which is 1 . 2 times 10 to the 9 Bq, times e to the minus k, which is 9 . 1 times 10 to the minus 13 per second times 17 years, which in seconds is 5 . 4 times 10 to the 8 second. So here, we want to make sure that our units are going to cancel, and this is where people often run into problems. They'll plug in 17 years, and then a rate constant, which was calculated in seconds, and things will not cancel appropriately. So make sure that you get your units consistent so that your seconds are going to cancel.

And so this term, if we do the math out here with the number significant figures, we find that that equals 1.2 times 10 to 9 Bq. That term is insignificant in our problem.

So, the original radioactivity and the activity after 17 years are the same in terms of the significant figures. And so, I choose this problem to emphasize a problem that we have, and that is radioactive waste. It takes a very long time for some compounds to decay. And so you have to think about storing radioactive waste, and think about a container that will outlast that radioactive waste. And how do you know that the container is going to outlast the radioactive waste. You can't really do an experiment because the time involved in doing the experiment, anyone who designs the container won't be alive by the time you're concerned about whether the container is going to be stable or not. So taking radioactivity is an issue. You heard some in the presidential campaign about whether both candidates believe in nuclear energy or not, and I think that both of them said, it needs to be considered, we need to have everything on the table. If we're going to have a real uniform energy policy, we need to think about everything.

So, issues of radioactive waste and how to handle radioactivity safely are going to come back as being current, important topics. And so these may be topics that you will, in your lifetime, have to deal with, either as a scientist trying to come up with new technologies, or as a citizen deciding whether having a radioactive plant in your hometown is a good idea or not. A lot of people are happy about nuclear energy, as long as the power plants are nowhere located near them. But, these are things that you'll have to face, and you probably will be voting on this in the future, if not dealing with it directly.

So that's how you do a problem in this. All right, so let's talk about a medical use of radioactivity. Radioactivity can definitely be our friend, as well as something to be concerned about. And I think I mentioned this in the first day of class, one of the ways that the Chemistry Department has moved to being the number one ranked Chemistry Department of U.S. News and World Report over the years, is a little extra money that came in from the work of -- a patent from Professor Alan Davidson that we were able to do some pretty exciting things with that money over the years. So I always like to mention all the great money-making discoveries that occurred using 511-1 material, and this is another example.

So, he used an isotope of technetium, and it's being used organ scanning, bone scans, it's one of the leading ones for heart imaging. It's also been used recently in breast cancer. It's estimated 7 million uses annually in the U.S. And so, this was patented as cardiolite, and it's really just very simple chemistry. So you're using a d block metal, an isotope of a d block metal, which has your exciting d orbitals. And what did he do, he made a coordination complex with that metal, an isotope of it, and he found ligands, cyanide ligands, those are pretty common ligands. You've seen a lot of coordination complexes with cyanide ligands, and he tried different ligands to get the desired properties of stability and solubility, and that's all it was.

So he used some knowledge of radioactivity, knowledge of inorganic chemistry -- he was an inorganic chemist, he's retired now. And simple coordination chemistry, and made an enormous amount of money for MIT, and particularly, the Chemistry Department, and also, this has saved a lot of lives. So, imaging is something that chemists do a lot of, actually. Not just imaging for cancer or imaging of organs, but also imaging of live cells to try to understand how the cell works when it's healthy.

And so recently, Professor Alice Ting, in the Chemistry Department, received an NIH pioneer award, NIH is National Institutes of Health, and started giving these pioneer awards for people coming up with very innovative ideas, the kind of innovative ideas that most people would not want to fund, because there's a good chance it might not work, but if it did, it would be spectacular. So she received one of these awards for trying to develop technology to image protein-protein interactions in living cells, which is something that people would really, really love to be able to do. And so she is involved in developing technology. So developing of imaging tools is something that a lot of chemists do, it's a very popular area in chemistry. And if it's something that you're interested in, there's definitely a lot of people around that you could think about working with for a UROP position.

OK, so that is first order. And now let's go on and talk about second order integrated rate laws. And we're going to have a little derivation for you, I always like to warn people that it's coming, because all of a sudden equations are coming in and out, and you just want to know where these equations are coming from.

So, as we talked about last time, this is an expression for rate law. You have your rate constant, your concentration of something, a, and it's raised to a coefficient, and here that coefficient is 2, indicating it's a second order process. So if there's nothing up there, that's 1. And then 2, and again, the order of the reaction can be positive, negative, it can be integers, it can be fractions. But this is second order, so we have 2.

Now, as we did with the first order expression, we're going to separate our concentration terms and our time terms. So we're going to bring our concentration term over to one side, another concentration term here, and we're going to have our rate constant and our time term on the other side. And now we're going to integrate, because it is an integrated rate law. So we can integrate from the original concentration of a to the concentration of a at some time, t, and then we'll also integrate from zero time to that time, t, on the other side.

Now, I'm going to take this expression and just bring it up to the top of the page, so that's the exact same expression, nothing has happened. And now we're going to solve that integral. So we can solve that integral, and if you want to look at these -- the back of your textbook has all of these conversions, if you want to look at them. So, we're going to solve that integral, now we have minus parentheses 1 over the concentration of a at some time, t, minus 1 over the original concentration equals minus k t. We can get rid of some of these minus signs. So we're going to bring the concentration of time, t, over on this side, we have our k t, and now we have this other term, the original concentration term is on the other side, and this is expressed in a certain way that gives you the equation for a straight line.

And again, kinetics, you need experimental data for kinetics, and so when you measure your data, you plot your data, and so there's a lot of equations for straight lines that you have, because it's all about trying to plot data, and figure out what the order is experimentally. So, here's an equation for a straight line, and we can plot this, and you can tell me what the intercept of this line is. OK, let's just take 10 more seconds.

Yup, so all of you know how to analyze the equation for a straight line. So, here we have 1 over the original concentration, and then our slope is equal to what here? k. So, you can plot your data as your concentration of a changes with time. You can plot the data, and if the data, if it's plotted as 1 over the concentration of a versus time and it gives you a straight line, that's consistent with it being a second order process.

So, in terms of second order half life, we talked about first order half life, and for any half life, it's just the time it takes for half of the original material to go away. So we can rewrite this and take a to the t, and substitute in the original concentration divided by 2, and then we can have t have a special name t 1/2, so that's the half life. And now we can just simplify this expression. We can bring the 2 up here, and now we can combine our concentration terms on the side. So we take 2, we bring this over, minus 1. And that simplifies 1 over the concentration of the original material here. And now we can solve for it in terms of the half life.

So the half life for a second order process equals 1 over k times the original concentration of the material. So, a second order half life depends on the starting concentration. So that's very different from a first order half life process where concentration term cancels out entirely. So for a first order process, the concentration of the original material does not affect the half life, or for radioactive decay, the original number of nuclei -- it's independent of how many nuclei were around at the time. But for second order process, the starting concentration does matter.

So again, chemistry is experimental. And so what you would be doing in a lab, you would be trying to figure out what the order of the reaction is, and so you could try out your data. You say I don't know if it's first or second order, so for a first order plot, you're going to be plotting the natural log of your concentrations versus time, and if second order, you plot 1 over the concentration versus time. And so you could plot your data and see that oh, look at this, it fits a straight line really well if I plot it as 1 over the concentration. If I plot it as the natural log versus time, the data doesn't fit a straight line at all. So this is not a first order process, this is much more consistent with a second order process. So again, figuring out where something is first order or second order is done experimentally.

All right. Now we're going to talk about kinetics and equilibrium constants. So, I always get very excited, as you know, when we come back to equilibrium constants, so am always very happy at this time in the course when we can relate kinetics and equilibrium constants.

So, at equilibrium, another way to think about what's happening at equilibrium, is that the rate of the forward reaction and the rate of the reverse reaction are equal to each other. So, we can now talk about big letter K, which is our equilibrium constant again, and our little letter k's, which our rate constant. So the equilibrium constant for a chemical reaction a plus b equals c plus d is going to be equal to what, what do I put on the top? Concentration of? c, and concentration of d, right. So our products, and at the bottom we put our concentration of our reactants, or a and b.

Now, we can also think about this reaction in terms of little rate constants. So we have small letter k 1 on top, and small letter k to the minus 1 on the bottom. So, the forward reaction, the rate of forward reaction is going to be equal to k 1 times the concentration of a and the concentration of b. And on the bottom, our rate is going to be equal to the little rate constant, so for the reverse reaction it's the reverse rate constant, k minus 1, and in the reverse direction, our reactants are the products for the forward direction, or c and d.

So, here we have these rates, and at equilibrium, those rates are going to be equal. So at equilibrium, little k 1, a times b is going to be equal to little k minus 1 times c times d. And at equilibrium we had c d over a b is equal to then k 1 over k minus 1, so if we just rearrange this expression and move the rate constants to one side and concentration terms to the other side, this expression is the same as this expression, and we also know what this expression is equal to, which is our big K. So, therefore, our equilibrium constant equals the rate constant for the forward reaction over the rate constant for the reverse direction. And so here is an expression that compares equilibrium constants with rate constants.

So now, let's think about what is true about this. So our equilibrium constant, then, is the ratio or the forward rate over the reverse rate for these elementary reactions. And if we think about rate constants in kinetics terms, if k is greater than 1, if there are more products than reactants at equilibrium, what's true about k 1 and k minus 1? Is k 1 greater than or less than k minus 1? Right. So the forward rate constant is greater than the reverse rate constant. And if K, big equilibrium constant, K is less than 1, if at equilibrium there are more reactants than products, what is true about this relationship? It would be less than. So, you can think about equilibrium constants now in terms of rate constants, which we'll be doing a lot on Wednesday, too.

All right. So let me introduce you to a couple of more terms in the last few minutes. So reactions don't usually occur in one step, but occur in a series of steps. Each step is called an elementary reaction. So, the overall reaction, the order and the rate law, can be derived from the stoichiometry for an overall reaction, you can't use the stoichiometry, but for an elementary reaction you can. So, for an elementary reaction, say one step in the reaction mechanism, that step occurs exactly as written so you can use stoichiometry. And that's going to be handy in coming up with mechanisms.

So, let's just look at one example very briefly. So here we have the decomposition of ozone, which is another environmental issue that you will be faced with in your lifetime. So this is the overall reaction, and you can't use the stoiciomery to figure out the order of the reaction, but if you divide it up into elementary reaction steps, then you can use the stoiciomery to write the rate law for each step of that reaction.

So, the first step here is a unimolecular step. You have one thing going to two things, and molecularity is the number of reactant molecules the come together to form product. So, unimolecular you just have one thing that's forming some kind of product. What do you think it's called if you have two things forming a product? Bimolecular. These are good little one or two point questions on a test, they're not very hard, they should be pretty easy to think about.

So, we have unimolecular, examples would be some kind of decomposition or radioactive decay. Bimolecular, two reactants coming together to form products. And termolecular is three reactants coming together to form a product, and that's rare. And you can remember that it's rare if you think about how you would hold three tennis balls in your hand and have them all come together at the same time to form product, that is a difficult thing to do. Two things coming together is easy, bimolecular is very common. Termolecular not very common, that they'd all come together at the same time to form a product.

All right, so we can write rate laws for each step here. For the first step here, the rate would be equal to a k -- I don't have the k written up here, but there's always going to be a little k over the arrow. So, k times the reactant would be here. For bimolecular, again, assume a k over there. What's that rate going to be equal to? OK, let's just take 10 more seconds since class is almost over. Yup, so it's this one right down here. So we have the rate is equal to k times these two reactants. You can sum up the steps and get the overall reactants. Notice that o is an intermediate, it's formed here, decayed here. It goes away, and so o doesn't appear in the overall expression. So we're going to talk a lot about reaction intermediates next time. And also, remember that you can't prove reaction mechanisms to be correct, they're just consistent with the data that you have.