PROFESSOR: OK, OK, OK. Let's settle down. Weekend is over. Tomorrow, weekly quiz. Today I'll have office hours 3:00 to 4:00. I have to go down to Washington, so I've got to leave a little bit earlier than normal. So I will be available from 3:00 to 4:00

The lecture has started and there's still way too much talking in here. Way too much. You know how much is too much? Any. Any.

So last day, we started talking about oxide glasses, and we reasoned that we could have control of the properties by control of the composition. We started with a network former, which is some oxide that has the capacity for forming covalent bonds through a bridging oxygen. And then we wanted to drop the processing temperature, and we did so by adding modifiers. Intermediates, we haven't talked about and we're going to do that in just a moment.

So if you look in the readings, this is from archival notes that were written by my predecessor, Professor Witt, these are compositions of some typical glasses. I don't expect you know these from memory, but I would expect you, if I gave you the composition, explain to me why the various constituents are there.

So let's try few examples. The first one is soda-lime glass. And you see it contains silica, which is the network former. It contains sodium oxide, calcium oxide, and magnesium oxide. And these are alkaline earth oxides that are ionic, and so these are acting as network modifiers because they're donating oxide anions that go in and break the silicate chains.

And then there's this Al_2O_3 and that's sort of halfway in between, isn't it? Silica is Group 4, or 14, if you want to use the modern notation. Sodium is Group 1. Calcium, magnesium, Group 2. Alumina is Group 3, and it's sort of halfway in between. It's amphoteric. It can either be a former or a modifier.

And in these instances, depending on how much modifier is present, alumina can act as an intermediate. And what's an intermediate do? An intermediate is a covalent oxide. It's a covalent oxide, or an oxide that can act as both covalent and ionic. But in this instance, it's acting covalent oxide with a different coordination number.

And what does that mean? Different coordination number? It coordinates-- remember last day I showed you B_2O_3? Borate glasses? So they have a coordination of three, whereas silicates have four. And what that means is

that there's going to be a mismatch. There's still strong covalent bonds, but they don't fit quite right. And that's going to give even more free volume. And that excess free volume, through covalent bonds, gives you the ability to endure thermal shock.

So if you want to impart thermal shock resistance in a glass, you give it lots of free volume so it can take the rapid change in temperature. So it's a covalent oxide with different coordination number. That is, nearest neighbors, in a covalent sense, from that of the network former.

So you can add a borate or aluminate, what have you. And that'll give you thermal shock resistance. And so alumina here is acting as an intermediate.

Let's go down here. There's borosilicate. borosilicate is the generic term for Pyrex. So Pyrex is a trade name. Pyrex was invented by Corning, and it contains silica as the network former. There's some sodium oxide, potassium oxide-- in rather small amounts. You can see this isn't a heavily modified network, but look at this. 13% B2O3 and 2% alumina. That's the modifier. And what was the hallmark of Pyrex? It had thermal shock resistance. So you could take it out of the oven and put it under cold water and it didn't shatter.

And we have the same analogous behavior for glass ware in the laboratory. For all room temperature and low temperature work in the laboratory, we use Pyrex that has this resistance to chemicals and resistance to heat. This is the big one, here. And that gave birth to functional crockery in the kitchen, where you could work in glass instead of in metal.

And down here we see glass-- let's see, well, here's one. Light flint optical. See, that's 54%. It's down to 54% silica. And look at this-- boatloads of lead oxide. And the lead oxide is acting as a modifier and also changes the index of refraction. It modifies so much that we have almost down to the orthosilicate.

So that the chains are modified to the point where they're almost all terminals. There's very little of this, and most of it is just terminal oxygens. And that means that it's more nearly crystalline, and therefore, you can cut it. And this is the lead crystal. Lead crystal has that high value. So you can see how that comes out.

And this is also taken from the reading. It's a plot of viscosity versus temperature. Only it's a logarithmic plot. And what do you see? Here's pure silica. That's SiO2. And if I want to take it down to the point where, if the viscosity goes down, you have the ability to work with the glass.

So if I want to melt silica, I've got to way, way up here. Over 2,000 Centigrade. So if I want to make bottles, if I want to make cookware, I don't want to run a lehr at this temperature. Lehr. L E H R. It's where you melt glass. Lehr.

I don't want to run a lehr at this temperature. But you can see if I add modifier, the more modifier that I add, the more I break the network. So increasing modifier decreases network connectivity, and that means I can go to a lower temperature and get the same level of fluidity.

So there's a whole bunch of definitions here that I'm not going to go over. You'll have this slide. But basically, it's just different points in processing.

So if you go up here. Strain and annealing. I mean, these are very, very-- you're especially working with solid, whereas softening point, you start getting the glass to flow. And the working point, that's the viscosity that you have to get below. Otherwise, the glass is going to be to resistant to flow. You want to get the glass tacky so that you can put it into an injection mold, shape it, as they do with bottles. They take a blob of glass and boom, they just throw it into a mold and it sprays out. And if you've got the right mass and the right spinning, it makes the wall thickness proper.

But you can imagine, if the glass is really, really viscous, it's not going to flow well enough. If it's too fluid, it'll drip all over. So there's an optimum in there. And this is telling you how to figure out what that optimum is. And you can see that as you change the composition, here's the working value. This is the viscosity that you have to get below which in order to work. And you can see that as you add more and more modifier, you can take the temperature and get it way, way down.

So to work with silica you have to be about around 2,000. With soda-lime you can be down around 800. So that's going to cut your energy costs, isn't it? And it's going to make it easier to recycle. What's the point of recycling if you consume as much energy to recycle as if you started with virgin material? At least with virgin material you can guarantee the quality of the feeds stock. So there's got to be some big saving.

All right. So that gives you a some sense as to what we can do technologically with glasses. I want to show you one last thing with glasses, and then we're going to move on to another topic. You know, new week, new day, new topic.

So I want to go back to this curve. So what am I showing you here? I'm showing you that as we change the cooling rate, we change the amount of quenched-in excess volume. So fast cooling quenches in more of the liquid free volume than slow cooling does. That's why this V excess is small here, whereas V excess is large here for the other one. I'm going to use that in glass strengthening.

So I want to strengthen. Strengthening glasses. We're talking about silicates or borates. Strengthening oxide glasses. Glass is a fantastic material. It's really good in compression, but it's no good in tensions. You know this. If you try to bend glass, it'll break. Why? Not because it doesn't have dislocations. It's got strong covalent bonds. But

you know, suppose you want to strengthen the windshield of your car so that when a stone hits it, it doesn't shatter. What can we do to give it added strength?

So I'm going to show you two ways, and both of them operate under this principle that the yield stress-- this is the stress that will break the glass, and I'm going to say the effective yield stress, what you experience in life-- is equal to the sum of what I'm going to call the natural yield stress, which is the basic property of the glass. Plus, I'm going to increase the surface stress. What I'm going to do is I'm going to modify the surface, and I'm going to put an additive stress at the surface, and that's going to be a compressive stress.

So that means now the effective stress that I need to break the glass is going to be greater than it otherwise would be. So the whole gambit here is surface strengthening. Service strengthening, which means surface modification.

And I'm going to show you two ways to modify the surface to bring the strength of the glass up. The first way is thermal. Thermal treatment. And the thermal treatment is to strengthen the glass. Well, let's see. Let's keep it in the context of the windshield. The technical term for this, the technological term is tempering.

So what I'm going to show you was how we can look at that volume versus temperature curve and understand how we make tempered glass for windshields and so. So I'm going to show you a slab of glass. Here's a slab of glass. And we just got below the softening point-- so T just less than T softening. So now this thing's going to start, it's continuing to become more and more viscous and getting closer and closer to glass transition temperature.

And what we're going to do is we're going to introduce air jets at the surface of the glass. What that's going to do is it's going to cause accelerated cooling at the surface. And the same thing happens on both surfaces, so I'm going to cut this piece of glass in half, and we're just going to look at the upper surface. The same thing happens in a lower surface.

So let's now blow this up. I'm just going to look at the upper-half surface and I'm going to divide it into two zones. This is the first level, most primitive finite element analysis. Finite element analysis.

I'm going to divide it in two, and I'm going to say, this has got two zones. Two cooling zones. Here is the zone of the center, OK? This is the center. And I'm going to call this the inner portion.

And then there's the outer portion. Well, take a look at this curve here. Which is going to have slower cooling? In the center or near the free surface? The slower cooling is in the center and according to this graph, the slow cooling has a smaller residual volume. I've written, V-interior. That's the green line. And then the upper one is a yellow line.

So the upper one where it's high cooling, it's going to have a higher volume. So this is the second piece of finite

element. So I'm going to model this one like so. So this is outer. And the same thing happens on the other side, OK? So it's happening on the bottom as well. But we're just looking at the top because there's symmetry here.

So you see what I've done? This is longer because that graph says it wants to be occupying a larger volume. Problem is the glass can't do this. I can do this with a piece of chalk, but the glass isn't going to look like that. The glass is going to have a flat edge. And how can it have a flat edge?

Because the bottom, here-- this is not to scale, let's make it more to scale-- the top is a narrow zone and the bottom is a big, thick zone, isn't it? So this big, thick zone, which has a small volume, is going to pull on the thin upper zone, which has a large volume, and pull it in. Can you see that? And it's going to cause the introduction of compressive stresses.

So we got to compressive stresses simply using that graph and a little bit of air. So you take that graph, put differential cooling, and now you've introduced compressive stress. And that's all tempered glass is.

So the V-excess of the outer layer is greater than V-excess of the inner layer, or the interior, if you like.

And why? Because the cooling rate, the change of temperature with time of the outer zone, is greater than the cooling rate of the inner or interior. And there it is. That's the beginning. And so now to fracture you have to apply a greater stress then you would have otherwise. So that's good, and that saves a lot of lives.

There's another way. There's another way to surface strengthen, and that's a chemical treatment. And again, what am I trying to do? I'm trying to introduce a compressive stress, but I'm going to use a chemical means. And this one is called ion exchange. And this is used in technology, too.

So now I'm going to take a piece of glass here. This is solid glass and let's put some components in here. So I'm going to put some silica as my network former. I'm going to put some sodium oxide. And I'm going to put some modifier, B2O3. So I got all three here. Former, modifier, intermediate.

And just to put a little skin on the bones here, I want to show what the sodium oxide actually looks like. Sodium oxide goes in as sodium cations, and oxide anions. The oxide anions go in and they break some of the silica chains. But the sodiums don't get involved in that. They just sit around as spectators.

Now what I'm going to do is I'm going to put this, I'm going to soak this in molten salt. Soak in molten salt. This is huge area of my own research. And the molten salt, one example might be I'm going to take potassium chloride. Remember, we talked about making aluminum or magnesium? This is one of the constituents of the melt in which we make electrolytic magnesium. Potassium chloride. And it exists as potassium cations and chloride anions.

Chlorine is green, except we know-- you know, this is the way chemistry books write it, but that's stupid because this is isoelectronic with argon. And it's not green. I know. I've looked at this stuff. It's clear, colorless, and transparent. The chloride ion has to be clear and colorless. It's got a complete shell, but the chemistry books will make it green.

Anyway, here's the potassium ion here. And there's a lot of potassium ion here. There's no potassium ion inside the glass. There's sodium ion in the glass, there's no sodium ion in the molten salt. But these are both media in which ions live.

So can you see this is sort of like the perfume bottle? Things move from high concentration to low concentration. Some sodium wants to leave and enter the melt. And some potassium wants to leave the melt and enter the glass. And where's the potassium going to go? It has to go where there used to be sodium. What's the relative size of potassium ion versus sodium ion? Potassium ion is bigger. So potassium ion goes and occupies a site formerly occupied by sodium and causes compressive stress, because you get all these big ions jamming in there and that's going to lead to compressive stress through ion exchange.

So through ion exchange we can raised the temp. Since r, the radius of potassium is greater than the radius of the sodium, we get a force fit, and this is how we got solution hardening. Hardening is the metallurgical term for raising the strength. Hardening is equal to strength going up. So we get hardening by solution. So this is solution hardening. Solution hardening because the potassium ion is in there.

So we have surface. And this gives a lot of strength. We do the same thing metallurgically if you carburize the surface of a piece of steel. Tool steels, for example, surface carburized. So we get hard surfaces that can cut. You say, well, why don't you just put the carbon in all the way through? Well, then the tool bit will be brittle. So you want something that's got toughness in the center so it can take the impact, but it's got surface hardness so it'll cut. And that's an engineered material. We've got one set of properties at the surface, and we've got another set of properties in the bulk. And it's all brought to you by control of chemistry. And then that's also control of chemistry.

OK. So I mean, I could talk more and more and more. Glasses are just fascinating things. But we've got to get moving. So we're going to move to a new topic. We're going to move to a new topic today.

We're going to start talking about kinetics. Kinetics. And what is kinetics? Kinetics is the topic that we put into 3.091, because it's important, of course, but it's all about the study of reaction rates. It's the study of reaction rates and mechanism.

So why do we study? Well, we study it because I think it belongs here. But first of all, kinetics is related to

productivity and resource utilization. You've got two factories. One produces 200 units per time, the other produces 100 units per time. The one that's producing 100 units per time probably isn't going to be in business that much longer. And it's all about understanding how to get more throughput per unit time, and that leads to competitiveness. So if you're interested in international competitiveness, you've got to know something about kinetics. The two go hand in glove.

Second thing is energy and the environment. A number of you have come to talk to me after class, sent emails because you're interested in energy and the environment. Efficient use of energy involves understanding the kinetics so you can force chemical change with the least amount of energy utilization and do so in a way because its mechanism-- if there's two mechanisms that allow you to get to the same end product, choose the one that has the least toxic impact on the environment. Otherwise, you're going to have to spend money to avoid the effluents, which then gets you back up to number one. Your cost of doing business is higher than the other guy. Guess what? You're creamed in the marketplace.

And lastly, societal. And this is one that excites me, is kinetics leads to productivity, which keeps factories open, which keeps people working. So through understanding kinetics. You go and you look at places in the United States where factories have closed. In many, many instances it was because the technology lagged. If you could just keep things going faster. You've got to make things-- you know how fast you've got to make them go? You've got to make them go so fast that even if the foreign workers are paid zero, you can still beat them in the marketplace. That's your standard. So that's how you design your processes. You design your processes so that you can produce at very, very low cost.

And there's a huge range in reaction rates. You know, you can start the range of rates, rates of reaction. At the one that you have very, very slow. And way over here you have very, very fast, all right? So on the slow end, you have stuff that's sort of cosmic scale. Geological.

And then over here, what do we have? We have explosions. You might say, well, explosions are usually bad, aren't they? Well, no. I can give you an example of where explosion is used to your advantage.

The airbag in the automobile. There is no pump, no mechanical pump fast enough to inflate an airbag on demand. So how do we make those airbags work? And I hope none of us ever has to be present at the deployment of those airbags. But you know, just academically let's talk about how they work.

There's like an explosion that occurs when you're driving. There's an accelerometer and this is a key piece. The accelerometer has to make a decision whether you're applying the brakes just because you've lost focus and you're, you know, whoops! You've had that jerky brake. Or maybe this is one of those holy-mackerel moments, and your jamming on the brakes, and we'd better deploy the airbags.

Once the accelerometer decides that this is one of those holy you-know-what moments, it sends an electric current through a wire, which then raises the temperature to 300 degrees C and causes this reaction to take place. When this reaction takes place, this is a solid, nitrogen is a gas. So the gas has a much, much higher volume than the solid and within milliseconds you get inflation. Well, that's good and that inflates the bag and prevents you from hitting the hard parts of the car.

But you see the other byproduct? That's sodium. And if you look on your Periodic Table, elemental sodium is liquid above 98 degrees Celsius. So now you've got liquid sodium. There's no point preserving the safety of the occupants of the car just to cover them with liquid sodium.

So we better do something about that. So being chemists, what we do is we add potassium nitrate inside the bag, as well. so. That that sodium is mopped up with potassium nitrate, which converts it to sodium oxide, potassium oxide, and a little more nitrogen. [BLOWING SOUND EFFECT] Keep the bag nice and firm.

But now what happens when the Fires show up and they [SOUND EFFECT], you know, they start pouring water on it. This turns into caustic. So now you're going to get covered and wet lye. So that's probably not too good, either.

Just remember, you've been physically saved from smashing your skull on the tempered windshield. So it's so far, so good.

So now what? You want a mechanical, you want a Newtonian death? Or do you want a Coulombic death? I guess that's the question, here.

And so we're going to keep doing some chemistry here and we're going to add silica. And what happens if we add silica to sodium oxide potassium oxide? Well that's a network former, these are network modifiers. We'll make an alkaline silicate glass and that's OK because we put food and beverages in alkaline silicate glasses. So everybody is happy. So that's all the chemistry that goes on inside an airbag. And we've got to understand the kinetics. So I hope I've whet your appetite. OK, that's enough of that. Now let's get to the real stuff.

So let's write a general chemical reaction. The general reaction. What's the formalism if we want to set up the metrics? So I'm going to write just a plain, old equation. This is the classical P-Chem stuff. Little a moles of A, plus little b moles of B go to little c moles of C plus little d moles of D. So this could have been lecture two. Just a straight chemical reaction. Remember we were studying stoichiometry?

So the constituents of the left side of the equation are called the reactants, whereas on the right side of the equation we have the products. And what kinetics gives us, kinetics tells us the rate of conversion. Or the rate of

reaction. I'm using all these terms so you understand their equivalent.

So we can write something like this where the conservation of mass kicks in. So I can't make products any faster than I consume reactants. There's no sources or sinks here. When I lose reactants, I make products.

So I'm going to say, the rate of change of the total mass of the reactants-- this is summation sign-- I'm just saying the rate of change of the sum of all of the reactions must equal the rate of change. So the loss rate of reactants must equal the gain rate of all of the products. That's just simple stoichiometry. Or some people call this conservation of mass or Law of Mass Action, what have you.

And then we count by concentration, usually. Just reminder. This is lowercase c. So this is the concentration of species i goes as the mole number. n is mole number divided by the volume of the reactor. So this would be in moles per meter cubed if we were in SI units. So therefore the rate of change, the ci by dt, is really the rate of change of mole number, isn't it? It's moles of i disappearing, but the volume doesn't change, typically.

And then the last thing is we can use this idea up here that concentration of products can only equal the loss rate of the reactant. So I can write, term by term, the normalized rate loss of the concentration of a divided by its stoichiometric coefficient, for example, would equal the normalized weight gain, or pardon me, the concentration gain of the concentration of d.

So this is just saying a disappears no faster than d appears, mediated by the stoichiometric coefficients. So this is just Law of Mass Action, which is stoichiometry in motion, isn't it? That's all it is.

Now here comes the cool thing kinetic theory. We look at any reaction, I can tell you right now what it looks like. If I applied concentration of i as a function of time, I start off with some value c naught, some initial value, and it just attenuates. We know that's going to happen as we consume the-- it falls and there's some curvature here.

What we're trying to do next is to give some mathematical representation to this. Can we come up with a mathematical formulation of the shape of that curve? And we can, and here's the central tenet kinetic of theory. Kinetic theory says that the reaction rate can be expressed in terms of a driving force. And that driving force is the instant concentration.

OK. These are lofty words. I'll show you what it means with illustration. So that's the overall idea.

So now let's say that the rate of change, the instant rate of change of concentration ci, is proportional to the instant value of the concentration. And you know, the concentration is changing, right? As the concentration decreases, the rate of change decreases. So just this alone, this idea alone would rationalize a curve like that.

As the concentration falls, the rate of change falls, which means the concentration falls, which means-- and raised to some power-- it's not linear, necessarily-- raised to some power. There's a power law at work here.

So now let's do this one more time. I'm going to write it mathematically. But I want you to first see the word, concepts. So let's write it mathematically. That means minus dc_i by dt-- so this is time rate a change of concentration i, the minus means it's falling-- is equal to the concentration of i raised to some power n. This is order reaction. It's not mole number over there. You've got to be pluralistic today. n is going to be used in different ways. So this is called order of reaction. And there's a constant. See up there? It's a proportionality. Here it's an equal sign, thanks to the constant. And this is called the rate constant.

And this what all I need for plant design. Suppose I'm running a chemical plant and I'm taking a plus b and making c plus d and the management says, we want to double the rate of productivity. So you go, I know what to do. We'll increase the concentration. They say, by how much? Well, this allows you, if you know the value of k and n, you want to double this? Then you know what to do here. It's not necessarily double the concentration, Because this is a 1.5 power.

By the way, this doesn't have to be an integer. Could be anything. Could be not necessarily integer and must be determined by experiment. You can't look at an equation and say, oh, that's going to be second order because there's a two in front of something.

So here we are, plant designers. And the management wants to know, how do we make things happen? So I'm going to go back to that equation over there and I'll say that most generally, the rate of change of concentration of a will then go as rate constant times the concentration of a. See, the rate of change goes as something to the power alpha. But it could also be influenced by b. So I'm going to put-- this is the most general form. Then once you make your measurements, a lot of these fall out. I'm even going to put c I'm going to put d. Everything was in that equation.

You might say, well, wait a minute. How can the rate of consumption of a be influenced by the concentration of d? d is a product. I'll give you two examples. One is that d, when I'm making d, d happens to have some catalytic value. So when I start making a convert to d, d catalyzes the reaction, which makes it go faster, which makes more d, which makes the reaction go faster, in which case this is going to have a profound effect.

And unfortunately, there are some other situations where a converts to d and d retards the reaction. And so I start off with pretty decent conversion efficiency, but as I make more and more d, the d chokes the reaction, in which case the value here is going to have negative implications.

So that's why you write it most generally, and then you go and you make some measurements in an experiment,

and you figure out what these are. Some of them might be zeroes, and away you go.

So I'll give you an example of one. Here's one. It's Monday after Halloween, so we'll get something kind of toxic. This was the manufacture of phosgene that was banned by international convention. It was used as one of the toxic gases for trench warfare in World War I. So it's made by the reaction of carbon monoxide and chlorine. $COCl_2$. This is called phosgene.

It's very bad stuff. I used it, actually, in my research. It has really good dehydration properties for salts. If you've got any moisture in potassium chloride, this'll go after it and turn the water into carbon dioxide and HCl. But you've got to be really, really careful with this. Gas leaks lead to a bad day at the lab.

All right, this was banned. It's still use by tyrants throughout the world, and that's why we have international war tribunals.

So here's the kinetics of it. Here's the kinetics of it. dc by dt. So this is the rate of consumption of carbon monoxide determined by experiment goes as the concentration of carbon monoxide and the concentration of chlorine raised to the power 3/2.

So what I've done is mimic here. So in this case, gamma and delta are 0. Gamma equals delta equals 0, and it looks like beta equals 1.5 and alpha equals 1. So I would say that this reaction is first order in carbon monoxide of order 1.5 in chlorine, or overall, of order 2.5. Because, right? This is the order of reaction. This is c to the power 1, isn't it? We don't write the 1. This is great.

So we know, to increase the rate of reaction we increase the concentration. There's another way to increase the rate of reaction. What else can we do to increase the rate of reaction? Increase the temperature. Things go faster at higher temperatures. Again, how? How much? Suppose I said, I want to double the rate of reaction. Do I double the temperature? Do I raise the temperature by 10 degrees? How do I do that?

So to increase rate of reaction, we can increase temperature. But how? And by the way, where is temperature here? I don't see temperature. I don't see temperature in this rate equation. You could say, well, if you increase the temperature you're going to increase the gas volume. But that's piddling effect, right? If I double the temperature, I double the gas volume. It doesn't change the mole number.

The temperatures in here. That's where the temperature. Increase temperature, which then operates on the rate constant. That's the only place left in that formalism.

But what's the quantitative value? Quantitative value was annunciated to us in 1889 by the Swedish chemist Arrhenius. And what Arrhenius found, he found that the rate constant varied with temperature in the following

manner.

Rate constant goes as the exponential of the ratio of minus some quantity call the activation energy e sub a-- I'm going to tell you what that means in a minute-- divided by the ratio of the product of the Boltzmann constant and temperature. And there's a constant of proportionality which we denote A in honor of Arrhenius.

Or another way to write this is A times exponential-- are you familiar with this? Instead of writing e to the something, if there's a messy argument up here you can write it exp. This is the same as this minus ea over the ratio of Boltzmann constant and temperature.

So what's in here? What's in here? Boltzmann constant temperature, we've seen that already. What's the Boltzmann constant temperature product? That's the environment. That's the energy of the environment.

So this is the final environment. And this thing up on top, ea, is a barrier. It's a barrier. Remember we saw the band gap? Same idea. Those ideas go all through physical chemistry. You got thermal energy that allows you to do this 10 trillion times a second. Everybody in this room is doing this 10 trillion times a second. That's what kT is. And then there's a barrier energy. Every once in a while something happens. Sometimes one in a million, sometimes one in a billion. Whatever.

What Arrhenius found was this relationship, which means we could plot the variation of the rate constant. This is a mess, right? This is an exponential-- look, the eye can only see straight lines. What if I show you this? What's that mean? I don't know. Is that first order? Second order? Is that Lagrangian? Is that exponential? I don't know. I know it's a curve. But what's this? I know what that is. And you know what that is. And you can tell goodness of fit.

This is what science is all about. Forget all the other stuff. You know, all that UROP stuff. You're going to work in a lab and discover stuff. Forget that. This is what it's about. You got data. Data are all over the map. Here's the thing-- I need to come up with some f function here versus a g function here that linearize my data. That's all science is about. And how do I get to f and g? Well, there's two ways. One is trial and error. The other way is physical understanding.

And this is what Arrhenius taught us. Arrhenius taught us that the f function for how k varies with temperature, right? The problem, I'm trying to say, k versus t. That's what I'm trying to do. And if I plot k versus t I get a curve. No good. Instead, if I plot some f of k versus g of t, I get a straight line. And this is all science.

So what's f of k? The natural logarithm of k, right? If I've got k equals a exponential, I take the natural log of this, and the natural log of an exponential is just the argument.

And what's in the argument? What's the T function? 1 over T. So if I plot the natural log of k versus the reciprocal

of the absolute temperature, I get a straight line and its slope is minus ea, forgive me, minus ea over k-Boltzmann. Minus ea over k-Boltzmann.

So now it's linearized and I can look at that and within an instant, anybody in this room can look at and say, the data conform or they don't. They don't.

So now let's think about this. We say well, what's the value of this barrier? It's called activation energy. This barrier energy is called activation energy. ea is called the activation energy. And it typically, it varies, but it has values-- just to give you a sense-- about 1 electron volt. 1 electron volt, which you know now is about 100 kilojoules per mole, isn't it? I hear the chorus of yesses. 1 electron volt.

What is thermal energy? What's kT? kT at room temperature, k-Boltzmann at room temperature is about 1/40 of an electron volt.

Now, we are chemical machines. This conversation is occurring because all sorts of chemical processes are at work in me and you. And how's that happening? When all we've got to suck out of the environment is 1/40 of an electron volt and we need on the order one electron volt to drive certain processes. I guess we're all dead. Any ideas? Ay yay, yay.

You guys need-- what's that thing? You've got to call your lifeline or something? Come on. How does anything happen? How do we get--

Why does anything happen in this world? Why should anything happen in a world with an environment of 1/40 of an electron volt?

AUDIENCE: Catalysts.

PROFESSOR: Oh, catalysts. Catalysts. Yeah, yeah. I just went to the catalyst store and I got catalysts. Come on.

AUDIENCE: Potential energy.

PROFESSOR: Oh, potential energy. Jeez, this is good. Who can give me the wackiest answer? Can anybody give me the right answer? How come anything is happening? Over here. Again?

AUDIENCE: Distribution of temperature.

PROFESSOR: Thank you. Thank you. For a moment I thought we were all dead. At some level we were.

So, yeah, it's Maxwell-Boltzmann. It's this, isn't it? And here's room temperature. And here is 1 electron volt. And this is it. And if you use this and you put it back to there, pretty soon you derive the Arrhenius equation. And if you

increase the temperature you know what happens. After you increase the temperature, this. Time to use a hot color or chalk. So now this is T2 greater than T1. That's what's going on. That's what's going on.

So now what is this activation energy? What is the meaning of it? You know, I've told you there's a barrier energy. What does it mean?

Well, you go to the textbook, you see goofy stuff like this. And this is not a slam against the textbook. This is a slam against all chemistry textbooks, because they all write this stupid stuff. You see? a plus b goes c plus d, the energy falls and you have to go over this activated complex. You memorize it, and I ask you to repeat, it and we leave the room and we think, wow, we know physical chemistry. There's nothing here. This is nothing. This is stupid.

Now this is a little bit better. Can you see this? This is the Maxwell-Boltzmann. This is actually a beautiful graph up to a point. See the Maxwell-Boltzmann? Low temperature, high temperature. Only they've turned this thing on its side. See? And there's the energy you need to get over the activated complex. You see what's wrong with this graph? What's wrong with it?

AUDIENCE: The product.

PROFESSOR: Yeah, the product is at a higher level than the reactants. I looked at that and I thought, whoa! I guess you'll activate them, but they won't go anywhere. Anyway, so this is all stupid.

What can we do? What can we do? So I decided to give you a mechanical analogy. So imagine this is the loudspeaker. Can you say the x? People in the back, can you see the x? Give me a thumbs up. Great eyes.

All right. So what do we see here? The center of mass, I've indicated here. All right. So this is in a certain energy state.

Let's get the right graph up there. This is awful.

All right. So this is a plus b. Now this is c plus d. You see, the center of mass fell. It's lower. It's closer to the table than it is here. Can you see when I go like this, the photon goes? Watch this. Yeah, only I can see it. Your eyes don't go to that end of the spectrum. All right. But what's wrong with it? So why does the box not fall over? Why does it not fall over? We agreed that this is a lower energy state, and it is. You're correct. So why does the box manage to stay here and not fall over?

AUDIENCE: [INAUDIBLE PHRASE]

PROFESSOR: Exactly. This is the box at 0 Kelvin. Now we start raising the energy of the box, it starts doing this.

Because above 0 Kelvin, it vibrates. The higher the temperature, the greater the vibration. But we're still in trouble here, you see, because you've only got 1/40 of an electron volt. So now we invoke distribution. I don't know what's happening with any box. Heisenberg tells me that. I don't know what's happening to any box. But if I take Avogadro's number of boxes I'll get this distribution. And some boxes will vibrate very little. And some boxes will vibrate a lot.

And what's the critical level of vibration? It's to get to here. Because once it gets to here it's downhill all the way. And that would be the activation energy. And the fraction of boxes that get to the value of activation energy tip over and then I restore the distribution, because now this one's out of the game and now I distribute that energy over the remaining ones. And as I increase the temperature, the amplitude of the vibration increases, the average increases, the fraction in that red zone increases, and at some temperature it's so, so hot that they actually do this, in which case I have equilibrium. The two states are in equilibrium. So that's it. This is what's going on.

So in three space, you can't go from here to here without going to here. You can try going this way so you-- no, you have to do this. It still has to be mechanically activated so we can show that this is what activation means. So we can plot-- this deserves it's own board-- so we will plot something like this.

And now you'll see this. Sometimes they write this in the books. It's kind of goofy. But they write stuff like this. This is some kind of an energy coordinate. This is an energy coordinate. And this is called a reaction coordinate. OR sometimes they write extent of reaction. Again, some P-Chem term. They usually use Greek C just to make it lofty, but it's meaningless. And then so you write like this-- reactants here, products here, and this is exactly what we're seeing.

What do we see? We see this. Here we have the box sitting like so. And then over here we have the box sitting like so. And right here we have the box up like so. And so now you have, here's the initial energy. This is the energy of the reactants. E of the reactants. This is E of the products. So then this distance here must be delta E of the reaction.

And what's this? That's the activation energy. I have to come up with this; otherwise, I can't make the box fall over. So this is ea to go from here up onto the corner. And now you understand what all this stuff means. So that's here.

And this is the activated complex. What's an activated complex? It's a box on its edge ready to fall over. That's what it is.

All right. I think we're out of time, so let's cut to the end here. What've we got. Oh, just some plots. We'll get to that next day. All right.

So I want to show you a little bit about first-order reactions. This is radiocarbon dating. n equals 1. And strictly speaking, this is not a chemical reaction, but it is first order. So I'll lump it in here. So this is a nuclear reaction.

And what happens in the upper atmosphere? Radioactive carbon produced by cosmic rays, which generate neutrons in the upper atmosphere and then those neutrons attack nitrogen to make carbon 14. That's the radioactive form of carbon. Remember? It's present in one part per trillion, if you look on your Periodic Table for the isotopes.

Now carbon 14 enters the carbon cycle. And so in all of us and in all living organisms the ratio of carbon 14 to carbon 12 is one part per trillion. And carbon 13 is also present. I don't know. What is it? 1 point something percent?

The thing is, the carbon 14 is radioactive. And it decays. Like this. But what happens after somebody dies? Well, they stop exchanging nutrients with the surroundings. They stop breathing, so their carbon level is pegged as it was at the time of death. And now it's a one0way street. It's just carbon decay.

And it turns out you can measure the ratio of carbon 14 to carbon 12 to determine the age, which is given by 5,730 years, which is the inverse of the rate constant.

Now, you can't use this for crime scene investigations, but certainly you can start dating things hundreds of years old, not hundreds of minutes old. So there's a whole bunch of other things that can be used, not just carbon. So this is radiochemical dating. And these are used in trying to nail down art forgeries and all sorts of things.

All right. So here, you can see these. These have all been radiocarbon dated. You know, the Dead Sea Scrolls were radiocarbon dated and they look like they're from about 2,000 years ago. Makes sense. You go out over here. They they found these Indian sandals from Oregon, and then they looked on an electron microscope, and they found something on the sandals that looks a little bit like that. That's a Nike swoosh. I don't know. You people are so--

All right. So now I want to show you the Shroud of Turin. The Shroud of Turin, as you may know, for a long time was reputed to be the burial shroud of Jesus Christ. And this is taken from the *National Geographic* back in the late '80s. Back in the late '80s, they did a major study on it. So this is the artist rendition of how the shroud might have been wrapped around a body.

The question is, what's the date of this? So we can use radiocarbon dating. And so here's the formation of carbon 14. Carbon 14 exchanges with carbon 12 in flax. So it's got one part per trillion. When the flax is harvested the carbon 14 starts to decay. And then we look at the weaving of the shroud and so on. And they had three different labs, they took samples from the shroud. And they concluded that the shroud dates from this period-- 1260 to

1390. And the first time it was mentioned in the literature was around 1354.

So everything seems to make sense that this is not the burial shroud of Jesus Christ. It's something that has importance to certain members of the Roman Church, but it's scientifically not. You know, this stirs up a lot of passion. So people started saying, wait a minute. Wait a minute. There was a fire in 1532 and people repaired the shroud and they were using candlelight and maybe the paraffin and mold and so on covered the fibers. So now, are we looking at the surface effect? How do we know what really happened? The only way to know is to take the whole shroud, put in a big Cuisinart and break open the interior.

Well, in point of fact, what they did was take fibers and look inside. And I think as of the late '90s, the Roman Church says, it's not the burial shroud of Jesus, but it is an object of reverence. And I think it's a good example of how science sometimes comes up against spirituality, and we have to be careful how we handle it. It's a delicate matter.