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3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Session 23

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PROFESSOR: OK, OK. Let's get started.

Going to go right into the lesson. Last day we started looking at kinetics, which was the description of rate and mechanism of chemical reactions. We looked at the general rate law, which shows us that the instant change in concentration of species i goes as the instant concentration. So rate is proportional to concentration. And the order of reaction is shown here as n and proportionality constant is the rate constant k .

So we saw that we can make the rate of reaction increase by increasing the concentration in the reactor. We saw there was a second way to increase the rate of reaction, and that was to raise the temperature. And this is the Arrhenius relationship that shows that the rate constant changes with temperature according to this exponential relationship.

In the denominator, we have the product of the Boltzmann constant and the absolute temperature, which is a measure of the ambient thermal energy that's available to promote reaction. And in the numerator we have a barrier energy, which we call the activation energy. We'll say a little bit more about that today. And the constant of proportionality out here is A , which is in honor of Arrhenius, who first announced the law.

So what I want to do today is to look at some common orders of reactions. So we're going to look at the values of n that are encountered in not insignificant number of reactions. So let's start with the simplest one. The simplest one is first order. First order reactions. That means n equals 1 in this rate law expression. And here's an example of something that we could use. The decomposition of N_2O_5 into NO_2 . And gives us half a mole of oxygen.

And we can write this rate law in terms of the rate of disappearance of N_2O_5 . So I can write minus d by dt of-- I'm going to use square brackets to indicate the concentration-- of N_2O_5 . And this has been measured. You can't predict this from the stoichiometry of the equation. You have to measure this, and on the basis of measurements it's found that the rate of change of N_2O_5 goes as the concentration of N_2O_5 . And there's a constant out here. The rate constant.

So just to make the point, I'm going to put a 1 here. Meaning that n equals 1 and that's why this is a first-order reaction. But this is messy. There's too many characters here. So I'm going to compress this and give myself a nicer font, so I'm going to let the concentration of N_2O_5 , just in this expression, just be c . Lowercase c . That way I can speed this thing up.

So I can rewrite this expression here as $-dc/dt = k \cdot c$. All right.

And so we know what this is going to look like. They all look like this. If we plot concentration versus temperature we expect to have the maximum value of this at time zero. So at time zero I start off with-- if you want c_{star} or c_{max} -- and you know, this thing attenuates.

But I can't look at that and decide whether it's first order or not. The only thing the eye can really tell is a straight line. So what I want to do is I want to modify this thing. I want to map c into some f of c . And I want to map t into some g of t . So that if I plot f versus g , I get a straight line. And then I can take one look at that and go, bingo, this is first order. Or not. Or maybe it's first order and the data are very noisy.

So what we'll do is we're going to integrate that equation. So I'm going to play with this a little bit. So I'm going to transpose. I'll get $-dc/dc = k \cdot dt$.

And then I can integrate this because I know at time 0, t equals 0, c equals some value-- I can call it c_{star} or c_{naught} -- and at any arbitrary time later, I can go down that curve and put some value of time and then I'll end up with some arbitrary value of concentration c . And I know there's some math people in the audience who are probably horrified that the limits and the integrand are both the same. So I'll put a little tilde here that way I don't go to math jail.

So now I'm not integrating c . If I wanted to be a pedant and really make the math instead of me enslaving the math, the math enslaving me, watch this. What I could do is I could make this a carrier variable, s . You know what I'm talking about now, right? But let's get really crazy. This is how bad the math can get. You can do this in a chemistry book.

Let's use some Greek. So I'll make this dx/x . Now I've totally left the class behind, but it's mathematically correct. What we will do is we'll put the t back and put a tilde over it. And now everybody is happy, and heaven forbid, the student might even understand the lesson.

All right. So we do that and what do we get? The integral of dc/c is a natural log of c . This'll be $\ln c = \ln c_{\text{naught}} - kt$. OK, so integrating this thing gives us this expression. And that means if I plot the natural log of c versus time I should get a straight line. And furthermore, the slope is equal to $-k$.

So here's an example that's taken from your book. It happens to be another first-order reaction and it shows the decomposition of cisplatin. This is a compound that's used in certain cancer treatments. And you can cisplatin hydrolyzes to form this monster cation plus a chloride. And it turns out that the rate of decomposition of cisplatin is first order.

Will you look at that curve? That purple line? I don't know what that means. But watch. If I instead plot the natural logarithm of the concentration of cisplatin as a function of time, you get a nice straight line, and furthermore, the value of k is obvious from the slope. So this is an indication of the power of taking the proper order of reaction and then using it in-- if you'll pardon the pun-- straightening things out.

And a couple other things worth noting. I mentioned at the end of last day, radioactive decay. Even though radioactive decay is not a chemical reaction-- it has to do with nuclear phenomena-- and we know chemistry is restricted to the life and times of the electron, we don't go into the nucleus. We simply know there's something in there, there's neutrons, protons, and a whole bunch of other particles.

But chemistry is about the life and times of the electron. Radioactive decay turns out to be first order. It's good to know that because then you can appreciate what goes on.

So for example, you could take something like the decomposition of uranium-238. One of its decompositions gives you thorium-234 plus helium. And it turns out that this is first order, which means that if you were to take a plot of the natural log of the concentration of uranium versus time, you get a straight line. And this slope would be the k , the rate constant.

But it turns out that the nuclear chemists, nuclear engineers, prefer not to talk about the rate of reaction in terms of k . But instead, they like to use the inverse of k , which is the half-life. So instead, express k through half-life.

And the half-life, as the name implies, is the time it takes to decrease the concentration of the species by half. So if I start off here at c_1 and down here I have c_2 equals $1/2 c_1$, then this is the time it takes to cut the concentration in half. So through half-life-- and we can go through this equation here, just put c naught over 2 and do a little bit of manipulation, you'll end up with the natural log of 2 divided by the rate constant, which is 0.693 divided by k . So you can see that there's a direct relationship.

It turns out that the half-life for this reaction is $4 \frac{1}{2}$ billion years. $4 \frac{1}{2}$ billion years. So that means after $4 \frac{1}{2}$ billion years the concentration has gone down to a half, but even then it's probably not safe for the kids to go out and play. So you really need to think about it in this way. So here it is shown in your textbook. Concentration as a function of time. They could have plotted it log linear, then you would have ended up with this. But anyways, they're chemists, so what can you expect.

So here it is. Here it goes down to a half, and then this is a half of a half as a quarter. It's the same time interval. And then half of a quarter is an eighth, and it's the same time interval. So you get the sense. And the most important thing is the half-life is independent of concentration. It doesn't matter what the starting concentration is-- if you know what the half-life is, you know how much time it takes to get to a half. And you know enough math.

What if I said, well, what if I didn't want to go to a half? What if I wanted to go to 10%? Well, you can figure out how to modulate half-life into tenth-life. That's trivial. But the book, being a chemistry book, will show you a table in which they give half-life values for orders of reactions other than 1. And it's stupid because except in the case of first order reactions, the value the half-life is a function of the concentration. So what good is a constant that's variable? I don't know, but I didn't write the book. The only time I care about half-life is in the case of a first order reaction, which is when you have nuclear decay for sure.

All right. So that's enough about first order. Let's go look at second-order reactions.

So here's an example also taken from the book. So second-order reaction, which means that n equals 2 in the rate law expression. n equals 2 in the rate law expression. And the example that they gave was NO_2 . See, look. We went from N_2O_5 to NO_2 . And then we can keep the decomposition going. NO_2 goes to NO plus O_2 .

And again, I'm going to let, in this case, c will equal the concentration of NO_2 . And what you end up with in this case is, if you go through the similar analysis, you get minus dc by dt . It's been measured that the rate of loss of NO_2 goes as the square of its concentration. So this is based on experimental evidence.

It's not because this is a 2. This is not. Please pay attention here. This 2 is not the consequences of the stoichiometry. This 2 was determined experimentally. I could have just written this reaction NO_2 goes to NO plus $1/2 \text{O}_2$. That doesn't make this first order, does it? Experimentally in the laboratory.

All right. So now what we can do is we can integrate this thing. And so we'll get minus the-- let's do it this way. Boards are cheap, so let's jump down to the next one. So now I can then put minus the integral of dc tilde-- cross multiply-- so dc tilde over c tilde squared equals k , the integral dt tilde. And we can integrate this from zero to some time, and this will go from c naught to some concentration. And that will give us 1 over c equals 1 over c naught plus kt .

So this is now the new, improved way of mapping c versus t into f of c versus g of t . So f of c as 1 over c , which means now if I plot 1 over c versus time, I'll get a straight line. In this case, it's got positive slope. It's got positive slope, so that's what it's going to look like. And this is k .

So if I take our data set and I plot it like this, then I can make sense of it. And I think we've got some data here.

So here's the data from this decomposition. And again, what do you see? A line that attenuates. Can you look at that line? Can you tell that line is second order, whereas the other one that looks like this was first order? Of course not. The only way you can tell this to fit it into some linearizing function.

So look at that. What they've done, that's the least squares fit. They plugged it into a least squares fitting equation. You can fit a straight line through anything. It doesn't matter. But what's that mean? I don't know.

So here's the log. This is really important-- look carefully. So somebody took these data and then plotted them as the natural log, which is what you do if it's first order. And look at what happens-- it gets a lot better but it's still not a straight line. But if you were in a hurry, you'd just say, force the fit. You'll get a straight line and you'll assigned the value of k to it and party on. And it's wrong.

So now let's try this. Beta. 1 over c versus time. So what do we get from that? I get two things. First of all, the fact that it's a straight line means that it confirms n equals 2 and the slope of that line is the value of k .

So in point of fact, what I've been doing here is teaching you how to determine the rate of reaction. So let's do it. Let's codify this.

So determination of order of reaction. So in other words, the way the story goes is I give you a data set that looks like this-- pardon me. I give you a data set that looks like this and I say, determine the order of reaction.

So there's two general ways to do this. The first one is called the integral method. And that's what we've been doing up until now. The integral method, it's called the integral method because it's using the integrated form of the rate equation. See? This is the integrative form. This is the integrative form. Hence, the integral method, and it's trial and error. That's what we did. Trial and error. But we don't say trial and error because we're at MIT. So what do we say? We have a lofty way. What's the lofty way of saying trial and error? By inspection. By inspection. Never tell anybody you do things by trial and error. We don't do trial and error. By inspection. It's \$50,000 a year. It's what you get.

OK, so here's what I do. I'm impatient, so I try n equals 1. If I get a straight line on the log plot, good. If not, I try n equals 2. If I got a straight line on $1/c$, good. If not, go to the second way of determining. I give up. Won't waste my time. It's a two strikes and you're out thing.

So what's the second method? The second method is called the differential method. The differential method. And this is fun because it's data fitting and it gets into some nice detail. So what I want to do is to define the rate. What's the rate? The rate is over here. $-dc/dt$, right? You see up in the top left corner the rate law. $-dc/dt$. I'm going to call that positive r .

I'm just compress-- this is like French cooking. I started with this. Look at all those fonts. Then I compressed it down to c , and now I compressed it even more. It's just so much information compressed in that little r there. Poor little r .

All right. So now, let's rewrite the rate law expression. So that's r equals $k c^n$ to the n . There's the rate law expression written very compact.

And now I'm going to take the logarithm of both sides. So taking the log of both sides, I can write natural log of r , the log of a product is the sum of the log. So that's going to be natural log of k plus the log of, da, da, da. $n \log c$. $n \log c$.

And I don't care what kind of logarithms you use. You can make this log base e . You can make it log base 10. If you're feeling like you want solidarity with the Mayans, you can make it log base 5. I don't care. But make them the same. Make them the same. And then what happens? Well, let me show you.

So let's say we've got our data, start off with this data set like so. So this is concentration versus time and we end up with this. It comes down, down, down, attenuates. Remember, what are we trying to do here? We're trying to take this data set and figure out, what is the value of n ? We're trying to determine n .

So what this thing says is. if I make a plot of r versus c so that it's on a log scale, so if I plot $\log r$ versus $\log c$, the slope is going to be n . So how do I take c versus t and construct $\log r$ versus $\log c$? That's what we're going to do.

So here we are and I can start here that at time zero. This is time zero. That's the slope, right? The slope here is the rate. So slope, I'm going to call it r_{naught} . Because that's the time-- it's dc by dt r_{naught} at t equals t_{naught} . But there's no t on here. So what am I going to put? It's when t equals t_{naught} and c equals c_{naught} .

So now I'm going to take some colored chalk and we're going to show you how to construct this. So I've got the slope by taking minus dc by dt here. So I'm going to take this value, r_{naught} , and this value, c_{naught} -- I want to gang them together, I'll bring over here and put them right out here-- so now I've got r_{naught} . Well, actually I should put the abscissa first. So this is going to be c_{naught} r_{naught} .

And now let's do it again. So we'll come down here to some later time. Let's call this t_1 . And at t_1 the concentration has fallen to c_1 , and I take the slope of this. Why am I taking the slope? Because it's dc by dt . That's what the rate is. So here now I've got slope r_1 at c equals c_1 . r versus c . Forget time. Time doesn't belong here. So take those. It's a lower concentration, so it's kind of like a lower energy. So we'll take a lower wavelength here.

So r_1 and c_1 come over here. c_1 , r_1 .

We'll do one more. Three's a charm. Come up to here. This is t_2 . Concentration has fallen to c_2 , and I've got a slope. You see how the slope is getting less and less steep? Because the rate loss says the concentration falls, the rate falls. So this is slope r_2 at c equals c_2 . That's lower energy.

So I'll get the orange. Or maybe this is fuchsia.

So we'll take this one. And this will put these two together and bring them in like so. And this is now c_2 , r_2 . too And what's this thing say? Take the slope. Look, it's a log, log plot. If you've got physical data and you don't get a straight line on a log, log plot, you're incompetent. You're a complete idiot. All right? There it is.

And the slope here is n . And where it intersection, obviously I can't get a negative number, so just allow me to fix this just a wee bit. So there's the axis, and where it hits the axis, this is now $\log k$ isn't it? So I determine the order of reaction.

Good. So now you know how to do it and you'll get some practice if you work the homework.

All right. A couple more things to say and then we're done.

So last thing, we talked about increasing the rate of reaction by increasing the temperature and increasing the concentration. There's one more thing we can do. And what we can do is use a catalyst. Increase rate by use of catalyst.

OK. How does the catalyst work? How does the catalyst work? Well, let's go back to this diagram here. Where we've got, this is called the extent of reaction. Some kind of reaction coordinate. And over here we had some kind of energy coordinate. We had this energy coordinate. Remember, we had this thing? This silly thing here?

So this is the reactions. And this is the product. And we reasoned that the activation energy e_a is sitting here. And we saw with the box, you had to get a box up onto its

ear, otherwise it wouldn't fall over and so on. And there's a finite amount, finite fraction of the Maxwell-Boltzmann distribution. So if we plot energy and the number of particles in the distribution have of given energy, we get something that looks like this. Tails off.

And we said that out here we have the fracture under this line. This is the fraction that has the energy to jump over the activation barrier. So f_a is the-- f is the activated, is the fraction activated. And those are the only ones that can participate in the reaction. These other ones can't surmount the activation barrier.

Now, what the catalyst does is it lowers the activation barrier. Catalyst lowers the activation barrier. It doesn't change the n points. The n points represent the energy state of the reactants and the energy state of the products.

What the catalyst does is it finds a low-energy barrier pathway. A low-energy barrier pathway, which on this curve would mean that if this energy is lower, then the fraction of any distribution that has the requisite amount of energy is much higher. Can you see the area? The blue area is much, much greater than the white area.

So that means that this f_a catalyzed-- I'm just going to write cat here-- f_a catalyzed is much greater than f_a in the absence of a catalyst. And that promotes.

What's an example of it? Well, in an automobile catalyst one of their reactions we're trying to promote is unburned hydrocarbons. There's some unburned gasoline that comes out in the form of carbon monoxide. What we want to do is convert the carbon monoxide to carbon dioxide. And this occurs on the catalyst and I'll show you more of this at the end of the lecture.

But these are both gas molecules and they're zooming through space. And if they're going to react with one another, they really need to somehow move almost on parallel lines so they get close enough to each other for a long enough period of time that they can start thinking about lower energy state. And say, well, gee, if we break this bond and form a new bond, it's going to go to-- you've got to get to know each other, go have a few drinks, and da, da, da.

So it's not happening. In the gas phase it doesn't happen. So what we do instead is we provide a service. This is the catalyst. The catalyst is a solid surface and the CO sits down next to another CO. They sit down and now they're in place long enough in the right orientation to then form CO₂ and then desorb.

So this is how the catalyst assists. We call this-- especially, imagine if it's the other way-- what if this carbon monoxide molecule is turn around so that the two carbons are side by side. That's not going to promote the reaction at all because this thing's got to whip around and so on. This is a. Bad orientation

And what's the Greek idea for orientation? It's stereos. That's what stereophonic sound is. If I close my eyes, the two speakers give me spatial rendition. So this concept here, where things are backwards and they're not the right place. It's called steric hindrance. This is steric hindrance.

One of the functions of a catalyst is to combat steric hindrance and put things in their most favorable orientation to facilitate reaction. So what are characteristics of the catalyst? The catalyst needs to have the following characteristics-- first of all, it

has to have an affinity for the reactants. In this case, the CO. It has to have an affinity for carbon monoxide. Affinity for reactants, so they'll be attracted to the catalyst.

But there's a second piece here. If the catalyst doesn't get rid of the CO₂, can you see that after a very short period of time, the surface of the catalyst will be covered with carbon dioxide and then the reaction starves. It's choked. So it has to have a disaffinity for the products. Disaffinity for the products.

And in the real world, such as in the gas exhaust stream of a car, it's not just carbon monoxide. There's all kinds of other stuff going on in there, and so the third thing that the catalyst needs to have is selectivity. So it doesn't get distracted by other reactions. And selectivity, most important when you have a mixture of all sorts of other species. So that's what the catalyst does.

Now there's one more thing. Just one second. Perfect. Gotcha just in time.

So one more thing here. One more thing. We've shown what happens when you catalyze. So I'm going to put this. This is E_a under the influence of catalysis. OK. This is the E_a of the catalyst.

There are other substances that can retard the reaction. These are called inhibitors. And what's an inhibitor do? It does the complimentary action. So it raises the activation barrier. So this is E_a under the influence of inhibitor.

And what's the value of that? Well, if you buy some antifreeze for use in the automobile cooling system. If you read carefully the label, it's not just ethylene glycol, and water, 50/50 volume percent. There are other additives.

What are those additives? Some of them are called inhibitors.

Oh, I didn't spell this right. No wonder you looked so puzzled. I thought you didn't understand the concept. Inhibitor.

So it inhibits the reaction. What's going on? You've got the iron or aluminum block of the engine, you got the water pump. It's taking heat away from the engine, you're heating everything up, stirring it around. It's a perfect environment for enhancing corrosion. And we don't want the cooling system to act as the corrosion system for the engine. And so we add components to the antifreeze too reduce the rate of corrosion, to lengthen the service lifetime of the vehicle.

And so what does the inhibitor do? It raises the activation barrier for the corrosion reaction and thereby reduces its rate of reaction substantially. So this is inhibited. OK, so this is catalyzed, this is inhibited, and you can see that the fraction of active species over the activation barrier, under the influence of inhibition, is much less than the fraction otherwise. There's a time and a place for all of these wonderful things.

So that's the story of kinetics. That's the story of kinetics, but it's 11:35 and it's time to start a new topic. And now, we can erase. Thanks.

OK. So let's talk about something else. Let's talk about something else. What I want to talk about today is another topic that comes from the general area of rate

phenomena. I want to talk about something else in rate phenomena. We're going to talk about diffusion. And that's from the general class of rate phenomena. That's why it appears with chemical kinetics.

And what do I mean by rate phenomena? Rate phenomena means d by dt is in the room. All right? We're looking at time, domain processes. You know, chemistry, before you came into this class, you probably thought, I know what chemistry is. Chemistry is chemicals reacting. That's what people think.

Isn't that what the ancient Egyptians said? khemia That's where the guys knew how to embalm the dead and so on. It was about chemical reactions. We've been talking about structure, properties, all sorts of things. Well, now we're talking about rates of reaction.

If we want to run a reaction, there's two things that we need to move around to sustain a reaction. So transport of two important quantities. One is matter and the other is energy. We star something for energy. As we just saw, the thing doesn't go. And if we starve it for matter it doesn't go.

So energy in motion is under the general rubric of heat transfer. But we won't talk about heat transfer because we've only got 14 weeks. I'd love to talk about it, but we're out of time. So instead, we will talk about mass transport. And mass transport in solids occurs by diffusion.

And we know what's critical. For example, we know in the case of the Hindenburg, the Hindenburg didn't explode. Why didn't the Hindenburg explode? Because there were 7 million cubic feet of hydrogen, but we couldn't get 7 million cubic feet of oxygen to the site. Because of the limitations of mass transport, 2/3 of the people walked off of that vessel. It was on fire, and many of them died because they panicked and they jumped to their deaths. Very few people were actually affected by the fire. So it's a good example of mass transport, negating the rate of what otherwise could have been an explosive reaction.

So I'm going to look at a simple example today. And what I want to do is look at the doping of semiconductors. You know, we've studied semiconductors.

Dave, could we cut to the document camera, please?

So what I've got here is I'm going to show you a silicon wafer. And the silicon wafer has got some features on it. So it's already been doped. Oh, that's pretty, isn't it? So cute.

All right. So what we've got here, remember this is the 8-inch diameter single crystal. So this was cut from a single piece of silicon 8 inches in diameter, about 2 meters long. How did they make a single crystal? They immersed the tiny single crystal into the melt and gradually pulled the single crystal out. Sort of the way you can grow rock mountain candy. And if you're really careful, the entire giant, 2 meter length, 8 inches in diameter, is one single crystal. And then we take this and we cut it with a diamond saw into wafers, Each of them about a millimeter in thickness.

And, of course, the width of the saw turns into dust So your yield [SNAPS] right off the bat is about 50%. Because [SAW SOUND] it's all gone. [SAW SOUND] it's all gone.

And now what we're going to do, is we want to dope it. So how do I get the boron in here? We say, why don't we add the boron to the melt, but what if I want to make pn-junctions? So I want to get some boron and some phosphorous. If I add the boron and the phosphorous, it then goes nuts. I need to have p-type against n-type.

So how do I get it in here? That's we're going to talk about. We're going to talk about how we make those features. See those features? Because if you're really good, you start with those features and you cut them up and then you end up with this, which is this. This is a Pentium chip. The amount of material science, physical chemistry in that device is absolutely phenomenal. What lies underneath this piece of gold is absolutely phenomenal. It's what powers the information age. And it all starts with this stuff here. It's that simple.

So how do we get the boron in?

Dave, let's leave this up. It's a pretty image. It might soothe the natives, so let's just leave it up.

By the way, that spider network is all the gold wires that are addressing. It doesn't do you any good to have a gazillion features there but you can't get information in and out. So if you've got a gazillion features, you need a gazillion leads to take information in and out. That's very, very thin gold. How do you do that? Not with a paint brush. It's all with this stuff. That's why I teach you this instead some of the other stuff.

OK. So now we're going to dope. We're going to dope the silicon with boron. Number one point to remember-- we're going to dope the silicon in the solid state. We do not add boron to molten silicon. We're going to add boron to the silicon in the solid state.

So I'm going to draw this wafer. Only it's not to scale. It's going to look more like a hockey puck than a thin wafer. Anyways, imagine it's this. OK? So this is the silicon wafer, the silicon wafer on edge. And this is where all the features were that I showed you.

So we're going to do is we're going to try to introduce boron. We want to get boron into the silicon, we're going to bring it in from the surface. So this is a silicon wafer, which means it's a single crystal. It's a single crystal. And we could use Laue methods to figure out which is the face. Is that cut on the 0 1 1? Is it cut on a 1 1 1? And so on.

So now we're going to dope with boron. How do we do it? We decompose diborane. We introduce diborane, it's a gas. B_2H_6 . And we flow diborane over the surface at some constant concentration. And what happens is that the diborane decomposes. B_2H_6 on silicon. And I'm going to write silicon with an x. What's the x mean? Crystalline. Single crystal. Make sure no one is thinking this is being performed in the liquid phase.

And this diborane decomposes to elemental boron plus hydrogen gas. So hydrogen is a gas, and the boron goes into the silicon. Boron goes into the silicon where it goes on to the silicon sites.

I could just write a rate constant for this. We just studied kinetics. I don't know. What is it? Second order?

You know, it doesn't have to be integral order, by the way. It could be of order 1.5. Nothing is saying it has to be integral order.

OK. So now what I want to do is I want to ask, what happens as the boron goes in? So that's the next question. As it diffuses in. So what I'm going to do is I'm going to draw this little cartoon here. So I want to look at here's the surface of the silicon. So I've got a gas phase here and I've got boron going into the silicon crystal.

So I'm going to now get a little bit quantitative, if you'll permit. And so it's going to look like this. And put it right underneath here. So this is x . this is depth from the surface of the silicon. So this is the free surface of the silicon. And I start off with some concentration surface value, c_s . Meaning concentration at the surface. And that's fixed. So c_s fixed by B_2H_6 concentration in the gas phase.

So that's fixed. Now, question is, what does it look like? The advance of the boron? So this is now the concentration of boron in silicon. This is the silicon crystal here.

So what does it look like? Well, one possibility is it goes in like this as a front. See if I wait, goes in farther and farther and farther. That doesn't happen. Sorry. Take that off. You know what happens? Same thing we've been looking at all day.

So now what's the question? Question is, what's the functionality of this? Is this 1 over c ? Is this $\log c$? Is this some other function of c ? I want to map this into some f of c versus g of x so I can get a straight line. Why do I want a straight line? Because I want to be quantitative. Because you are in charge of designing a fab line and they want to know what the residence time of a silicon wafer is supposed to be at billion dollars multiples. You know, the units are in billions of dollars. So you don't want to make the fab line any bigger than it needs to be, the residence time any longer.

This is only way you're going to be able to design it. You have to understand this because the design specification is going to be dope to a certain concentration of a certain depth. So how long does it take to get boron in? You can tell me. Set the concentration here and wait 5 minutes, 10 minutes, 30 minutes.

Two companies. One takes 30 minutes to process the wafer, the other takes 10 minutes to process the wafer. Guess which company is going to be in business two years from now? It's not going to be the one that takes a long time. Hint.

So we need to know what the rules are here. And the mathematical formulation was set by Adolf Fick. Adolf Fick, 1855, answered the question, what is the form of that line? He's an interesting guy. He was at the University of Zurich. And it's sort of like the Balmer story. Remember J.J. Balmer was the school teacher in Switzerland. This guy was in Switzerland, too. Something going on there in Switzerland in the late eighteenth hundreds.

So remember J.J. Balmer? He fit not his own data, he fit the data of Angstrom. Angstrom made the measurements, Balmer fit the data. Well, same thing here. Fick did not make the measurements. He looked at some data that had been taken back in 1833 by Thomas Graham. Thomas Graham had been making measurements back in the 1830s of gases diffusing through porous membranes. Or just say, through

membranes. Obviously, if they weren't porous they wouldn't be diffusing. Redundancy. Department of Redundancy. This is diffusing through membranes.

So what happened was that he modeled it. And here's what he came up with. He came up with-- oh, by the way. I didn't mention what he was. He was a physiologist. He was a medical doctor. He just poured through the scientific literature for amusement, evidently.

OK. So this is what Fick gave us as the model for the data. He gave us what we know as Fick's First Law, Fick's First Law of Diffusion. And we'll just call it FFL, Fick's First Law of Diffusion. And we'll write Fick's First Law J_i , which is the flux. This is the unit of measure of mass transport, the flux, which obviously is the mass flow rate. We said this is mass transport, so this is the mass flow rate of species i , OK? And we're going to say in the x -direction because things diffuse in all directions, right? If I open a perfume bottle here, the diffusion will take place in all directions. So I'm going to make this one dimension.

So the flux is a mass flow rate of i in the x -direction. J_i in the x -direction. Remember we said the Chemical Rate Law? We said the Chemical Rate Law was that the rate of progress of a chemical reaction goes as the concentration. Well, Fick studied Graham's data and he said, the flux doesn't go as the concentration. It goes as the gradient in the concentration. That's how you linearize those data.

So you take the concentration gradient, which is dc by dx . OK. So that's the concentration gradient. Gradient in concentration of i in the x -direction. You could write this as-- make this vector-- but we're not going to do that. It would make it one-dimensional here. And the constant of proportionality is D_i , which is called the diffusivity or the diffusion coefficient. And puts the minus sign. Why?

Well, you know things move from high concentration to low concentration, right? So I open the perfume bottle, the odor gets-- the odor, pardon me-- the fragrance gets stronger as you get closer to the bottle. Things move from high concentration to low concentration. So if I gave you this concentration profile-- what's profile mean? Profile means-- this is a concentration profile-- if I draw someone like this, this is head on, right? And if I do the right view like this, this is the profile. Profile. Side view. This is profile.

Concentration profile, obviously, the concentration is higher to the left. So things are moving from left to right. But look at the slope. The slope is a negative number. So if the slope is a negative number, but I want to get a positive flux, I need to have the minus sign in here. Diffusivity is a physical constant. It has to be a positive number. So this is Fick's First Law.

I'll just give you the units and then we'll stop.

So what are the units? Well, the units in flux are in SI units kilograms per second. And we're going in one direction, and so as we're trying to diffuse into this piece of silicon, we have to normalize it per unit area. So it's kilograms per meter squared per second. You know that concentration is kilograms per cubic meter. d by dx is 1 over meter, which means then that the diffusion coefficient or the diffusivity has units of length squared per unit time. This is the units of the diffusion coefficient. And we'll get back to business next day.

David, may we cut to the slides again, please? OK. So I talked to you about-- oh, yeah. There's all this. You see they give you a half-life? Crazy. Forget it. OK. There's the book talking about activated catalyst, da, da, da.

This is Fick's First Law. This is the paper from 1855. Go ahead. "On the Influence of Diffusion" by Dr. Adolph Fick. So the number one catalyst in the world, number one application is automotive catalysts for exhaust. So gasoline is octane. C_8H_{18} , which we burn in air. We burn it in air, we make hydrocarbons. Pardon me, we burn hydrocarbons, which obviously means the carbon goes to CO_2 , ideally, and the hydrogen goes to H_2O .

But sometimes you get incomplete combustion. I already showed you that. Maybe we stop it CO. But remember, air is 4/5 nitrogen. So when you burn hydrocarbons you also, at these high temperatures, mix nitrogen and oxygen and make NO_x . And this was actually the precursor to smog.

So what we want to do is to eliminate these imperfect combustions. So we want to convert the unburned hydrocarbons. There's actually some of the CH compounds, volatile, then don't get burned. We want to burn those to H_2O in water-- pardon me, H_2O in CO_2 . The unburned CO has to go to CO_2 .

You might say, but isn't CO_2 a greenhouse gas? Yeah, it is. But you know, given the choice of carbon monoxide and carbon dioxide, my advice is go with carbon dioxide. Carbon monoxide will kill you at about 200 parts per million. And then NO_x , we want to convert that to carbon dioxide.

So GM alone tried over 1,500 catalysts. Why GM? Why not the auto industry? Because the U.S. Government, in its wisdom back in the 1970s, invoked the Sherman Antitrust Act and forbid the automobile industry to collaborate in the search for a catalyst. And since they didn't understand the science of catalysis it was trial and error. By inspection. And it's a huge space, trying things.

But they eventually found, after 1,500 tests, platinum-palladium works for hydrocarbons and CO, and rhodium works for NO_x . It's almost as though mother nature said, I'll give you a catalyst and it's going to be the most expensive part of the Periodic Table. You buy this stuff at the jewelry store, you see.

Furthermore, this is an oxidation reaction. This is an oxidation reaction. This is a reduction reaction. So if I told you I want you in the same place at the same time on a vehicle moving 80 miles an hour to conduct simultaneous oxidation and reduction reactions with no intervention, you'd say impossible. They did it. They did it. This is the power of selectivity of the catalyst.

So this is an old diagram from GM literature. Now we have fuel injectors, here, but fuel goes into the engine, out to the exhaust. There's an oxygen sensor, which I'll show you next day. Oxygen sensor measures what composition of the output gas is, sends it to an electronic control module, which then goes back into the carburetor. And the catalytic converter is right here.

And Dave, if you show the document camera.

This is the monolith. This is a piece of ceramic because platinum and rhodium and all of these other elements are so expensive.

See, this thing's having a hard time. So we'll cheat a little bit. We'll put this here and then it'll focus.

All right. So what you're looking at, these are long channels. And just to give you a scale, this is about a half of a millimeter. This is about a half a millimeter square and they go all the way down for a length of about eight inches. And then the walls, the interior walls, are coated with a very, very thin layer of platinum, palladium, and rhodium.

Because these are expensive metals. And it's a surface effect. So you get no value if you have an inch deep of platinum. The only stuff that works is the free surface. What you'd really like is a monolayer. But a monolayer of platinum has no mechanical strength. So you put the platinum, palladium, and rhodium down on a catalyst support. and this stuff is made of a ceramic, it's magnesia, alumina silica that's been extruded like pasta, and then fired. The technology is absolutely phenomenal. Goes into this.

And then to get the platinum-palladium-rhodium they have a very thin acid wash. chloroplatinic, chlororhodic acid, wash, little bit of surface tension, holds just a little bit of water, fire, out comes the metal. Just thick enough. If it's too thick, dilute the concentration of the acid. But use that precious metal sparingly.

Platinum hit \$2,000 an ounce last year. \$2,000 an ounce. You steal a car, throw the car away, and get the catalytic converter.

So anyway, that's underneath. That's what's going on underneath the car. And actually, I'm holding for you the elements of clean air, the catalytic converter. But the catalytic converter can't work unless we control the air to fuel ratio, which we have to do with an oxygen sensor. I'll show you next day. And you've got to feed it into a CPU. If you don't have a CPU, it can't make rapid feedback to keep adjusting the air-to-fuel ratio.

All right, Dave. Let's cut to slides and we'll get out of here.

So I'll show you what else is in here. OK, there's that. So there's the old thing. There's the engine, da, da, da. Exhaust, the control module. And look, in the old days they actually had-- they look like little ball bearings-- cost of these things was phenomenal.

So last thing, we had to go to unleaded gas. Unleaded gas was brought in because the lead would be broken down into elemental lead because lead is volatile as an oxide. The lead alloys with the platinum. Turns it into a lead platinum alloy. Lead has no catalytic value. Because if it did, we would use lead and not platinum.

OK. We'll see you on Friday.

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