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3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Session 24

PROFESSOR: OK. OK, settle down. Settle down. Let's get started.

So last day we started talking about diffusion. Diffusion is a solid-state mass transport by random atomic motion. I made the first point last day and today I'll make the second point. We'll see why it's random atomic motion. We reasoned that we could describe the ingress of material. Here I'm showing a concentration profile. A profile is nothing more than a plot of something as a function of position.

So, this is looking at, for example, the doping of a wafer. This is the free surface at x equals 0. As we go to the right, it represents depth. And we fix the concentration at the surface and the material tails off to zero deep inside the specimen. Fick in 1855 annunciated the law of diffusion, shown here, that says that the rate of ingress expressed by the flux is proportional to the instant gradient in concentration. And the constant proportionality is the diffusion coefficient. This is where all the material science lies. It's inside the D. That's what we're going to talk about more today.

And so we see things tail off and what we want to do is figure out what the mathematics are that'll allow us to render this thing into a functional representation. Because all we know right now is that we've got something tailing off. Ok?

And so this is the gradient multiplied by the diffusion coefficient and you can see that the red line represents the flux. The gradient is maximum at the surface, so the flux is maximum at the surface. And as we move farther and farther into the piece, the gradient in concentration becomes less steep, which means the absolute magnitude of the flux becomes less steep, and we go deep inside where there is no doping yet. The variation of concentration is constantly 0, so the slope is zero, which means the flux is zero. So the two sort of track, one and the other. And we recognize these are negative slopes since the minus sign is here. Even though we have a negative slope, we have a positive ingress.

And then the other thing that we realized was that the diffusion coefficient has a temperature dependence. And the temperature dependence looks like this. It's an exponential of some kind of a characteristic energy divided by the product of -- this is the gas constant, this is not the Rydberg constant. The gas constant is simply the Boltzmann constant per mole. So if you take the Boltzmann constant, multiply it by the Avogadro number, you get this. But if you see something times T, you know it's got to be either gas constant or Boltzmann constant. This two-letter character string has to have something akin to a Boltzmann constant, otherwise you don't end up with an energy term. And this in the top is a barrier energy. It's a barrier energy to diffusion and out here we have the pre-exponential. Unfortunately we didn't give it the letter F in honor of Fick, it's just D naught. And so there it is.

So if we take this equation and we plot it, natural log of d versus 1 over T, that'll linearize the equation, and we end up with something that gives us a straight line. And the slope is minus Q over R, where this Q is some kind of a barrier energy. And the R is the gas constant or the Boltzmann constant. So this is the gas constant. It's on your table of constants. It's got a value in SI units of 8.314 joules per mole Kelvin, OK? Just the Boltzmann times Avogadro number.

So now I want to invite you to join me in some pattern recognition. If I give you the temperature dependence of a quantity that looks like this , in other words, the logarithm of that physical parameter versus 1 over T, gives you a straight line. You know from the work that we did on chemical kinetics, this is the representation of something that is an activated process. Remember the box that would fall on its side, and it had to go up on its corner? So we had some physical sense of what activation is.

Now this has a log, something versus 1 over T dependence. This represents some kind of an activation energy. An activation energy. But what's the activated process that's going on here? So that's where I want to take you into the atomistics.

So here's a cartoon taken from one of the readings. And it shows a set of atoms here and the atom next to the vacancy wants to move into the vacancy. And you can see the artist's rendition is showing that in order to get from the current position into the vacant position, it's got to squeeze through this narrow channel. And it takes energy to move through that channel. And there's an activation barrier associated with that motion. Can you see when the atom is sitting right at the saddle point? The system is highly activated because it's pushing out against those atoms. And then finally it falls into the new slot and the energy drops. So the activation energy is associated with moving through this saddle point.

So what really happens here, I'll tell you right now. First of all, we have to recognize that the system is depicted there, because it's a freeze frame, but we know that above 0 Kelvin, everything is in motion. So the only way we can rationalize what's going on is to, first of all, recognize that we have a pulsating lattice. We have a pulsating lattice. Everything's vibrating. And what's the heartbeat? What's the idle speed? I've told you this before. Everything that's going on in this room has an idle speed, a heartbeat, of 10 trillion times a second. That's the Debye frequency, OK? The idle speed or the heartbeat. The heartbeat is called the Debye frequency. Here's frequency, lowercase nu, in honor of Peter Debye. And it's on the order of about 10 to the thirteenth per second. 10 to the thirteenth Hertz. That's 10 trillion. So 10 trillion times a second atoms are going like this. Pulsating. All right?

So what has to happen for that operation to occur? Well, I've got an atom here, vacancy next door, but because it's close packed the atoms on either side close in. There's no way this can squeeze through. But, imagine, 10 trillion times a second. If I'm lucky enough to see the moment when the atom above pulsates up, the atom below pulsates down, a channel can open up and then this thing can squirt through. Now, that doesn't happen every time. If it did, history would have ended. At 10 trillion times a second, it's all over for everybody. Right?

So what happens? What's the frequency at which we will get this unique combination? It turns out that frequency, noted gamma, is called the jump frequency. That's the jump frequency. And the jump frequency is on the order of about 10 to the eighth Hertz. 10 to the eighth Hertz, which is about 100 million. So if you take the ratio of the Debye frequency to the jump frequency, you see you get a value of about one try in about 10 to the fifth is successful. One try in about 10 to the fifth is successful. And that explains what's going on here.

So, what now does that mean in terms of Q? What's the breakdown of Q? Well, clearly, Q, the activation energy for diffusion, must involve both the energy to form the vacancy -- I'm going to call it delta Hv, and that's the energy for vacancy formation -- if you don't have vacancies, you cannot have motion -- plus the delta H sub m which is the energy for atom migration. So you have to form the vacancies and then you've got to squeeze through those saddle points. So that's how we get a sense of it. And I think I've got another slide.

OK, so they're I've simply put the markings on for you so you can see the atoms above and below jumping in the right direction. That allows the atom on the left to squirt to the right.

Now, this is also related to energetics. It's related to energetics because the energy to form a vacancy and the energy to squeeze through those saddle points must be related to the binding energy. And what else is related to binding energy? Melting point. So, this is an elegant plot that simply shows that the energy -- these are all FCC metals: lead, aluminum, silver, gold, copper, and iron. They're all FCC on this chart here. Iron has both BCC and FCC, but this is comparing apples to apples. And you can see that there's lead melts at 327, aluminum at 660, silver 980, all the way up. Iron 1535. And you can see that the activation energy for -- that's this Q-value -- the activation energy for diffusion scales with melting point. Again, an indication that this analysis makes sense.

And then, here's the other one, the interstitial. If you have interstitial diffusion you've got plenty of interstitials, so you don't have to pay the penalty to create the interstitial, but it's much, much more difficult to squeeze through the saddle point.

So, it turns out that activation energy for diffusion by interstitial means is still fairly highly activated. So this is in the case of substitutional systems, all right? This is for substitutional. Substitutional atoms. What do I mean by that? An atom that sits on a lattice site. If an atom sits on a lattice site, it has to jump to another lattice site, which means there needs to be a vacant lattice site.

On the other hand, if we're talking about interstitial special atoms -- not substitutional atoms, interstitial atoms -- the assumption is that there's plenty of interstitial sites. There are very few systems that I can think of where the interstitial sites are so heavily occupied that this assumption is invalid. So in that case, you don't have to pay for vacancy formation. It's simply equal to the enthalpy, which we know is analogous to the energy for a condensed system of atom migration. Atom migration gives you the whole story and it goes back to the same picture, and so on.

Now, I said it's random walks, so let's look at another one. So, this is an interesting example. This is self-diffusion in cobalt. Cobalt has a number of isotopes. One of them is 59 and one of them is 60. 60 is a radioisotope. Cobalt 60 is a radioisotope and it's used in a variety of technical endeavors. And so what we've got here is a sandwich of cobalt 59 -- cobalt 60 and cobalt 59. So even though cobalt 60 has radioactivity and it's got a different number of neutrons in the nucleus, chemically it is identical to cobalt 59, just as carbon 14 is chemically identical to carbon 12.

So there's no concentration gradient. Fick's Law says it's supposed to go by concentration gradient. The concentration gradient is zero across that piece. And yet if you wait for long enough, you will start to see -- the dark atoms here are meant to represent cobalt 60 in the sandwich -- after some period of time, the cobalt 60's will move outward. And if you wait long enough, the cobalt 60 concentration will be uniform throughout the specimen.

So what's going on? There's no chemical concentration gradient, and yet over time, the cobalt 60 spreads out. And the answer is this is happening by random walk. We've got the pulsating lattice. Pulsating lattice. 10 trillion times a second those atoms are vibrating and there's going to be some vacancy. All of a sudden an atom falls into a vacancy.

And the mathematics of this -- look at this, this is no accident -- this curve here represents something that looks like a Gaussian distribution. At any given time, the amount of cobalt 60 that's veered from the center band can be portrayed by the Gaussian distribution, the bell curve. And what's the physical model for the bell curve? It's the drunken sailor. Or I guess I have to be PC. I'm not going to just pick on sailors. Maybe it's the drunken cougar, the soccer mom that went out drinking.

OK, so what happens with the drunken cougar, she comes to the door, and she starts to walk, all right? And then she walks one way or the other way, until she finally falls. And if you go through the number of steps that it'll take before the drunken sailor falls, you get this distribution. It's an old physics problem. The drunken sailor problem. And it's a normal distribution. And that normal distribution tells you that everything's going about by random jumping. Random jumping, according to this, all right? So that's why we say that diffusion is a random walk problem.

Before I turn this off, I want you to take a look carefully. What's wrong with this textbook cartoon? Any ideas? It's a substitutional system, right? It's cobalt and cobalt.

This is absolutely impossible. What's wrong with it? There are no vacancies. There are no vacancies. It's impossible. There's no vacancies to jump into. This thing is jam-packed, so it's physically unrealistic from a thermodynamic standpoint. There has to be some finite population of vacancies. Given this system, there's no way that the black atom could jump into the neighboring site, because you'd have to have the entire system open up, and the chances of that happening are vanishingly small. So it just shows you, just because something costs 150 bucks and is pressed between two hard covers doesn't mean it's full of truth, OK? Be careful here when you look at this.

So, again, the artist needed to be guided. We need to put a few of these things out, just to give symbolic recognition to the fact that we need to have some vacancies. OK. All right, let's keep going. Let's keep going.

Here is some data. Here is some data. Various data. This is diffusion. This is the logarithm of the diffusion coefficient versus 1 over T. So let's look at the top. This is hydrogen in iron. So temperature increases from right to left. So, go up, up, up, up, up. And roughly 900 degrees Centigrade, iron changes from BCC to FCC. And you know from our previous unit, the number of nearest neighbors in FCC is greater, so there's less void fraction, right? So that means that it's much more difficult to move. And you can see, first of all, the order of magnitude drop in the diffusion coefficient, and also, it's subtle, but the slope is steeper, because the activation energy for diffusion is steeper in a closer-packed system.

This is carbon in iron. Same thing. Relatively gentle slope at the same temperature, there's a phase change to FCC and it takes much, much more energy per unit increase in temperature to get the comparable increase in the value of diffusion coefficient. This is iron, self-diffusion in iron. So this would be radio tracer iron in iron. Very much lower. You see these values are up around 10 to the minus 5, 10 to the minus 6. This is down to 10 to the minus 11, 10 to the minus 12 centimeters squared per second. Iron diffusion changes at the transition temperature. Now iron going through FCC iron.

Here's the last one. Look at this one. This is carbon in graphite. So how does carbon -- suppose I had some carbon 14 in graphite. What's the bonding in graphite? Silence. It's covalent. It's sp2 hybridized. It's really strong bonds. The activation energy -- you know, forget just jumping through that saddle point -- you've got to break those covalent bonds. It's very, very high energy to get carbon to move through graphite. And so you see very, very low values and very, very steep temperature dependence.

Now, there's another way to think about this. Again, this is now looking at the atomistics. So this is the same material trying to indicate that if you use Fick's Law, moving in from the surface into the bulk, we have a certain front. So this is some isoconcentration line. So we could take this value off of the graph arbitrarily. So they're saying c greater than c i. Because it trails off to zero, right? It's asymptotic. There's no sharp cut-off here. It trails off. So what they're doing in that graph is arbitrarily saying, let's call this ci.

And where's the front at concentration ci, given a constant value of cs at the surface? And you can see that there's a near-constant rate of advance through the bulk. But along the grain boundary you go much, much farther in the same amount of time. Why? Because the atoms in the grain boundary are not bounded the same way as the atoms in the bulk. There's this gap, this misalignment. And so, it's easier to make that jump, and you can see you get much, much more advancement along the grain boundary. And this is a crack. And this material covers the surface. You get surface diffusion. Surface diffusion is very important in many processes, and it's very fast, because on a surface, you've got no atoms on the top. It's almost liquid-like, isn't it? You've got atoms to the bottom, but you've got no atoms to the top, so you can move unconstrained.

Go back to this one. Imagine here. Imagine if you didn't have any atoms on the top, how easy it would be to make that jump. All right, let's go and see what the data are. Nothing like data. And I got data for you. Let's look. Click, click, click. All right.

Here's the data. This is all for the diffusion of silver. So I'm going to use this value, this schematic, and I'm going to give you the value for silver diffusion in the bulk, silver diffusion in the grain boundary, and silver diffusion along the surface.

So these are the data. So this is log diffusion coefficient versus 1 over T. Only, I hate this graph, because somebody got really wimpy. You know, it bothers them. You see, when you plot something like this, you end up with, if 1 over T increases from left to right, this really means that high temperature is over here, right? 1 over T increases this way, which means temperature is increasing this way. So somebody, some weenie, got all nervous here and put the numbers backwards, you see? That way, the high temperature is over here, but it looks stupid, because when I see an activation plot, I want a negative slope. It's non-physical to have a positive slope. So I condemned this and I turned it around.

So now let's look at it the right way. So this is log d versus 1 over T, and this is the bulk, lattice or bulk. This is grain boundary and this is surface diffusion, all in solid silver. OK, look at this. First of all -- I'm going to jump from here -- one, two, three, four. Four orders of magnitude faster diffusion along a grain boundary, which makes sense, because it's less constrained.

And now let's go from grain boundary at constant temperature up to surface. One, two, three. Three orders of magnitude along the surface. So you can see the effects. And there's the melting point of silver, right here. So at the melting point of silver, the diffusion coefficient is about 10 to the minus 8 centimeters squared per second, which is the diffusion coefficient of virtually every metal at its melting point. So I happen to know that number. 10 to the minus 8 centimeters squared per second. Not that I know it as a function of temperature, but I know it can't be any faster than that.

So I said, this is near liquid-like behavior, what's the next thing to look for? Let's get some data from real liquids and see if this hunch is correct. What's the number here? 10 to the minus 5 to 10 to the minus 4 centimeters squared per second. This is diffusion in molten ferrous alloys. This is manganese in molten iron. 10 to the minus 5, 10 to the minus 4. Bingo. It really does behave like a liquid, in terms of diffusion. Surface diffusion is very fast, very fast. And it's all explained by this simple model of atom jumping.

And I continued it. Here's data from glasses. We studied glasses. So here's a suite of different glasses. Log k. This is permeability, which is related to diffusion coefficient. There's a gas constant in there, but forget about it. So this is essentially log of the diffusion coefficient versus 1 over T. We've got a family of lines. And what's the difference here? This is pure fused silica up here. SiO2. There's borosilicate, there's soda lime, and there's lead borate. So what's happening? We're adding more and more modifier as we go from top to bottom. And as we add modifier, we break the length of the silicate network, which means it packs tighter and tighter, and as you get tighter and tighter packing, the diffusion coefficient gets lower and lower.

So train your eye. Let's pick 200 degrees Centigrade, right here. So at constant temperature, the more modifier you put in, the lower the diffusion coefficient because things are more tightly packed. It's like walking down the infinite corridor in the middle of the hour, versus walking down on the hour. On the hour, there's too many people. It's tighter packing. And if you're the least bit civilized, you're going to have to move a little bit slower, whereas, if you walk down the infinite at around now, no problem. It's liquid-like behavior.

And now this is the isotherm at 300 hundred degrees C. This is from some old Corning literature. Corning used to make glass, at one time. And this is the logarithm of diffusivity. And this is now the set of silica B203 and P205, and these are all network formers, right? They all form covalent bonds. So the more silicate, borate, phosphate you put in, the more stretched out becomes the network.

And sure enough, look up here. See they didn't have names for their glasses like the Malibu or the Corvette or something. They called their glasses by four-digit numbers. So someone would say, oh, this customer needs, oh, I'd sell them a 7040. All right? Because it has a certain mix of properties. So forget about what those numbers are, just know that this axis indicates that as you move up, up, up, up, up, the higher diffusivity is associated with a much more open structure. So, again, a link between atomistic behavior and atomistic structure. It's all there.

OK. So let's leave that up there while we go a little bit forward.

OK, so now, so we've been down buried at the atomistic level. Now let's jump up to the continuum level. We'll go back to Fick's first law. And I want to do something a little more quantitative. So I want to look at diffusion across a permeable membrane. So this is gas through a membrane. Gas through a membrane. And the membrane is shown here. This is the walls of the membrane. Membrane has thickness L. Membrane of thickness L. In fact, we'll give it a name. Let's call it membrane. All right, so here's the membrane of thickness L, and I'm going to put gas on the left at P1, and it's a constant P1. So we keep -- we've got a ballast here, so even though something starts diffusing, the amount that we lose doesn't affect the constant pressure over here.

And on the right side, I'm going to put a second pressure, P2. And just for argument's sake, I'm going to say that P2 is less than P1. So that means we're going to end up with mass transport from left to right. And so, I want to ask, what's this going to look like if we use Fick's Law? And so beneath I'll make a plot, a concentration profile, from x equals 0 to x equals L. And I can morph this into concentration.

We know the gas law is PV equals nRT. This is the gas law. P is pressure. P is pressure. V you know is volume. But I'm going to write all these out, because some of these letters are used so many times that we don't know, is this the Rydberg constant? No, it's the gas constant that you've seen on the first board. It's the Boltzmann constant times the Avogadro number. T is absolute temperature, temperature in Kelvins. And n is not the quantum number, it's mole number. Mole number. PV equals nRT. And we know that concentration of i is mole number of i over V. Both of those appear in here. So if you take what's underneath there, and I'll expose it in a second, you'll convince yourself that Ci equals Pi divided by RT. And that's how you get that permeability thing to turn around as well.

OK, so, I started with gas pressure, but I'm now going to write this in terms of concentration. So I'm going to morph P1 into C1 and over here, P2 into C2. And I want to plot the profile. So what's the profile look like? I'm going to plot the profile at steady state. At steady state. At steady state, after I've waited a while, I have a straight-line profile across here, at steady state. It's pinned at the two ends. It's pinned at the two ends and varies continuously across here.

And you can see from Fick's Law, that if you have a situation in which the gradient is invariant across the piece, the gradient is -- dc by dx is the same here, as it is here, as it is here, as it is here. dc by dx is invariant, right? It doesn't change. This is a straight line. Well, if dc by dx is invariant, and d is a constant, then J is invariant, which just means no sources are sinks. All of the material that goes in, must come out. This means that J is not a function of time. J is invariant. J is not a function of time. I come back here ten minutes later, I have the same profile. That's what steady state means. That's what study state means.

OK, and then, of course, if I wanted to be a little bit pedantic, I could say, in certain systems, the diffusion coefficient is a function of concentration. So, when the diffusion coefficient is a function of concentration, then even at steady state, you might have some bowing of the profile, but that's a little bit more advanced.

OK. So, I can describe everything that's going on here. If I wanted to know how much material leaves from inside over a certain period of time, then I can simply say that total material lost is given by Fick's first law when you have steady state. It's simply going to equal the product of the flux, which is mass per unit area per unit time times the area times the time.

And that's sort of analogous to Faraday's Law, right? If I wanted to look at how much electrical charge I get for a certain period of time with current passing, I could say that the total charge is the product of the current times the time. You know this relationship. Well, can you see that J times A is analogous to the current? It's the mass current. It's mass flow rate. Mass flow rate per unit area times area gives me something that's analogous to the current, and the time is the time, this is the total material lost, this is the total electrical charge. These two are the comparable equations.

OK. Now, I want to go to the more sophisticated question, and that is, what happens before steady state? Before steady state is achieved? Suppose at time zero, the membrane has no gas in it. And at time zero, I inflate the left side. And just to keep things simple, I'm going to set c2 equals 0. It's a linear equation. You can always add it, but I just want to keep it simpler for the analysis. So, suppose at t equals 0, we inflate to c1 on the left side of the empty membrane. There's nothing in the membrane. So, let's see what happens.

First, I'm going to solve the problem graphically. Because we know what's going to happen. I'm going to have to do the mathematics. So, here's what we expect. This is going from 0 to L. And we've got nothing in the membrane on both sides, so that's good. And then, at time zero, I inflate to c1. There's nothing in here.

So, what do I have? Well, I know if I wait long enough, it's eventually going to look like this. Because that's the steady state solution. I've put here c2 equals 0, for simplicity, but we can change it. It's a linear equation. We can just add. So, what happens at time 0 plus? I start getting diffusion in from left to right, following Fick's Law. So it's going to look like this, isn't it? This is the approach to steady state. Some books will call it nonsteady state or unsteady. Unsteady to me means unsteady, so I refuse to use those terms. I call this the transient. That's the literary term. The transient. We're talking about the approach to steady state. And in some systems, you never get to steady state. But that's OK.

So here's what it's going to look like at some very, very short time afterwards. It's going to look like that, only somewhat modified for this geometry. So it's going to look like this, isn't it? It's pinned at c1, and it's pinned at 0, and it varies continuously. So this is at time t 1. What happens at time t 2? At time t 2, it advances a little bit farther.

But in all instances, the slope and the shape is given by this, Fick's first law. So this is at time t 2. And let's do one more. Three's a charm. So, let's take a green one. All right, so here's at t 3, still pinned at c 1 and still pinned at 0. So this is at t3. And then finally, this is steady state.

So if we park at any place -- let's park at x1. Watch here. Can you see that the slope at t1 is gentle? The slope at t2 is steeper than t1. The slope at t3 is steeper than t2, and this is the highest. So, we go from nothing, to gradual, gradual, gradual, until we finally reach steady state, and we stop. And then at that point, we just continue to have to mass flowing through. And look, the concentration is zero, but the flux is not zero, because the flux isn't related to the concentration. It's related to the concentration gradient. Zero concentration, but non-zero concentration gradient. In fact, just for grins and chuckles, I could plot the ascent of this. I could plot time at x equals x1. I could plot J. And what's J? At time zero, it's zero. Then it's small, then it's larger, larger, larger asymptotically. And this is J of steady state. And this is t1, t2, t3. That's the approach to steady state. And you might say, well, this is kind of a professor's pedantry. It's not! This is doping of semiconductors. You don't run processes at equilibrium. You run them far from equilibrium. So in the transient mode, doping, outgassing, drying, what have you.

So, now I want to give you the shape of the concentration profile. So how do I do that? OK, so the shape of the transient profile is not given by Fick's Law. The Fick's Law just gives me the gradient. In other words, here's what I want. I want C as a function of x at any given time. That's what I want. I want to be able to plot the profile. So, profile is C of x, but C of x varies with time. So, I need C of x at different times. What gives me that? What gives me that is Fick's second law. Go to FSL, Fick's second law.

Now, Fick's second law, I'm just going to put it up here. I'm going to show you the solution. I don't expect you to solve it. I would, you were all required to have differential equations as a pre-req, but you don't. So, I'm just going to put it up here so that you see it. It's a partial differential equation, and it looks like this. And it's really beautiful. It's got a beautiful symmetry and the fonts look great, so that's why we put it up here.

So, this is the partial in time goes as the double derivative in space, because we need a two-variable function, right? We want x and t. And this assumes that the diffusion coefficient is not a function of concentration. If it is, the equation is messier. This assumes a constant diffusion coefficient. So, this, as you can see, is a partial differential equation, which is a bummer, because it's hard to solve, all right?

But, it's linear. It's a linear partial differential equation, which means the solutions are additive. We know this already from LCAOMO. So, I can handle, because I can solve it once and then I can give you ways to patch it, to make it useful.

So, the solution. First of all, how do I specify this fully? Every time you differentiate -- I'm going to give you some math here, real math that you can use. When you differentiate, you throw away information, right? The derivative of a constant is zero. So, what was the value of the constant? It's gone. You lost it. So you have to bring it back. So when I double derivative this, I need two pieces of spacial information. And when I take a derivative with respect to time, I need one piece of temporal information. That's math. All the other lemmas and postulates, forget them. This is how you use it, all right?

So, I need two pieces of spatial information and one piece of temporal information. So these specify our boundary conditions, right? So, what are our boundary conditions. So, I will need the concentration of all x at time 0. That's this. The answer to this question.

And what we're going to do is say that it's a constant. I don't know what the constant is, it could be zero, it could be any arbitrary number, but I'm going to give you the solution for the situation in which the initial concentration is a constant. So, you could look at this and say, well, what happens if it's a non-zero constant? You ready for linearity? Watch this. This is how cool linearity is.

You see this set of solutions? This is the set of solutions for C equals 0. What if C equals some non-zero value? I just shift the origin down to here to the non-zero value and everything sits there. That's what superposition gives you. That whole set of solutions just gets jacked up by the value of C naught. If C naught is 0, this slams down onto the x-axis. That's real math. You're the master. The math is the slave. Never let math enslave you. I won't. I refuse.

So that's how you make C equals C naught work. And then you have to peg the concentration at the surface. I can give you examples where that's not the situation, where you have a variable concentration at the surface. The solution I'm going to give you won't work for those. So, x equals 0 is the surface. So, at x equals 0 at all time, I have some fixed value, which I'm going to just call C surface.

And I need a third boundary condition. And the third boundary condition is a mathematical trick. We're going to say that this only works at short times. It's called the short time. And at short times, I'm going to say that -- from the perspective of the diffusion experiment -- at very, very short times, this sample appears to be infinitely long. Because the amount of material that goes in doesn't hit the other side.

So, at very, very short times, we can pretend that it's semi-infinite. And so then we can write that the concentration -- this is the short time, which means infinite size, and you'll see that the two are related -- that the concentration at infinity, then, doesn't change from the initial value. The concentration at infinity for all time must equal the initial value C naught.

And so if you put these three boundary conditions into that equation, you end up with this. This is the thing. You get C minus Cs over C naught minus Cs. This is surface concentration. This is initial concentration. This is C. It varies by this amount. Error function of x over 2 times the square root of Dt. So, you tell me the time and I can tell you the relationship between concentration and position.

Now I've got to tell you what the error function is. Here's the error function. This is this problem before. This is the solution I'm going to show you. Here's Cs. Here's C naught. The most general case. C naught could be zero. And this curve here is given by this equation, OK? And this is an example of doping, isn't it? This is how doping would work. And this is the case where C s is greater than C naught. If we turn it around and we make the surface concentration less than the initial concentration, we'll get the complementary situation. The complementary situation looks like this. So in this case, C naught is up here, Cs is down here, and we end up with this. So now matter is going out, because Cs is less than C naught.

So this is -- what do you want to call it -- this is effusion, this is some kind of a drying process, outgassing. And this is doping. And what's the shape of this curve? The shape of this curve. ERF. That's what math is. You find a mathematical function that templates for the curve. And ERF, I'm going to show you, is related to random walk statistics. So, it's physically validated. It's the best fit. I mean, heck, if you find anything that is pinned at two ends and has curvature, you'll get a reasonable fit, but what's the right fit?

The right fit is this. The error function looks like this. Here's the error function. Error function. I'm going to plot ERF of z as a function of z. And it goes from 0 to 1. It looks like this. All right? And here's an error function table. Those are exact values. And it turns out that ERF is pretty much linear up to about point 6. Up to about point 6. ERF of point 6 not to less than about 1% is point 6. And then as you go farther and farther out, and eventually, ERF of infinity equals 1. But you don't even need tables for 0 up to point 6. And you can push it, go to point 6, 5, if you want. Yeah, let's do it. Let's push harder. 6, 5. It's linear. You don't need tables. Right? And so ERF of 0 equals 0. Oh, let me give you the function.

You know how you can define sine? Sine is that integral of something over 1 minus blah, blah, blah? We've got a definition for this one, too. It's cool. It's cool.

Here's what the error function looks like. ERF of z equals the integral from 0 to z of e to the minus u squared du. You might say, why is he showing us all of this? Because he wants to torment you, that's why. No, it's because I'm trying to teach you something.

What's e to the minus u squared? Actually, I think I can squeeze it in right there. What's e to the minus u squared du? This function here, that's the bell curve, isn't it? e to the minus u squared. That's this thing. It's symmetric, right? It's a minus u squared, so it doesn't matter if u is positive or negative. And e to the 0 was 1, and then back and forth. And so what this is doing, is it's integrating from zero out to some value. That's all. That's the random walk. This is the drunken sailor. How far does the drunken sailor go? That's the shape of this curve, the integral. And we'd like it to be so that if you integrate from zero to infinity, the area will be one. It turns out that this area here is root pi over 2. So, therefore, to normalize, we put 2 over root pi. That's how you get the error function. All right? So, the integral from zero to zero is zero, and the integral from 0 to 1 is going to be, whatever it is, point 8, 4, et cetera, et cetera.

So, that's it. That's it. Now we have the functional relationship to describe any of these curves. And you'll get some practice in doing that. And it's a lot of fun. Because now you can talk about how long it's going to take to dope something, and so on. Outgassing.

And now I'm going to show you something really cool, and I'm not kidding you. This has served me well. I've been here 30 some odd years, and I've been in consulting situations where I can, in my head, figure out order of magnitude of what it's going to take to run a diffusion problem. Because you've got, up here, C minus Cs over C naught minus Cs equals ERF error function of x over 2 roots of Dt. So, this runs from 0 to 1. The right side. When I went to school, the left side of the equation had to do the same thing as the right side of the equation. So if the right side of the equation runs from 0 to 1, the left side of the equation runs from 0 to 1. So, let's pick a -- are you ready -- average value from 0 to 1. What would you pick? I'd pick point 5.

Now, I don't have to go to the error function tables because point 5 is less than point 6. So ERF of x over 2 root Dt is essentially equal to x over 2 roots of Dt. So, now I've got one half equals one half x over root Dt, from which I can say that x is approximately equal to the square root of Dt. And I can be sitting in a meeting and someone says, gee, I don't know how long it's going to take. This thing's going to go down about 100 microns. And how long is it going to take?

So, I pick a number, like, OK, if this is 100 microns, and this thing here is 10 to the minus 8, now you just take the square root of that, and tell them, oh, it's going to take so many minutes, and they go, huh? How did you get that? It's right there. And I'm not trying to tell them a number for three significant figures. They just want to know is it going to take a minute, an hour, a day, or are we out of business? And you can make that calculation with this. This is so powerful.

And everything I told you about diffusion applies to conductive heat transport. You can do the same thing for heat transfer, figure out how long it's going to take for a wave to go in. This is really powerful stuff. Anyway. Let's move on. Well, there's our pal.

OK, so I was going to give you the last element today. The last element. Remember, we talked about clean air. So, I'm showing you the catalytic converter. That's this thing here, coated with platinum, rhodium, and so on. And I'm showing you the electronic control module. That's the CPU. It's a little bit toned down from a Pentium, but it certainly started from one of these units. So, we've studied all of this. Right? OK.

And, so now, I want to talk about this piece here, the oxygen sensor. why do we need an oxygen sensor? Remember, the last day I told you that to get rid of NO, the NOx, you have to reduce, And to get rid of CO and unburned hydrocarbons, you have to oxidize. Well, you have to pick. You can't have two different atmospheres in the same place at the same time. Turns out there's a lucky sweet spot. Can you see that the conversion efficiency is high for both reduction and oxidation reactions if you peg the air-to-fuel ratio at 14.6. So you can't just set the carburetor or the fuel injectors at some arbitrary ratio, because as you change humidity, as you change temperature -- what happens when the temperature goes down? How much oxygen is there in the air? It's still 20%, but PV equals nRT. You ever try barbecuing when it's -- I mean, I don't know, maybe you're not from the Northeast. But if you want to barbecue when it's 0 Fahrenheit? Do you think you get a hotter fire or a colder fire? How much oxygen is there per unit volume in cold air versus warm air? Think about it. It'll be on the next exam. I'm just kidding.

OK. So, anyway, here's the sweet spot that gives you both oxidation and reduction. And so we need a feedback loop. That feedback loop is provided by the oxygen sensor. Dave, would you mind cutting to the document camera? So this is an oxygen sensor that's used on automobiles. Here's the plug. This goes into the pin set. And the oxygen sensor is inside this housing. This housing, you can see -- OK, what I'm going to show you is what's going on inside here. This has got all kinds of protective stuff on it so that it doesn't get dented during installation and so on. But it sits inside the exhaust train. It sits inside the exhaust train.

Now, may we go back to the slides, please? Every car that's running a catalytic converter has to have one of those in order to control, right here, to make sure the air-to-fuel ratio is optimum. Otherwise, the catalytic converter is either not doing a good job on NOx, or it's not doing a good job on hydrocarbons and whatever the other thing is.

Anyway, so here's what it looks like. So, this is what's inside. It's a closed, one-end tube made of zirconia. Zirconium oxide. And zirconium oxide conducts oxide ions. And there are platinum electrodes on the front and the back. And what I showed you was from this side. And this is the exhaust gas going along here, and this is the edge of your exhaust train. And two wires coming off of that sensor go to the CPU. The CPU measures voltage and then from there, it regulates the air-to-fuel mix to the engine, to the exhaust gas, and around and around and around we go, so that when exhaust gas gets to the catalytic convert, it is optimally being converted.

So, we want to get fast response. We don't want slow response. And it's a solid-state sensor and solid-state diffusion is slow, but that's we have to rely upon. So we add a dopant. We add a dopant to zirconia to stabilize its crystal structure and create more oxygen vacancies to get faster diffusion and a shorter response time. So what we add is calcia, one of the candidates, and it creates oxygen vacancies, and these oxygen vacancies allow us to get more rapid response time. So, these oxygen vacancies compensate for the charge imbalance, thanks to the addition of calcia. So, it's an engineered material. Without this it doesn't work, all right?

And so, now what I've shown you is that on the basis of this oxygen sensor, we can monitor the exhaust gas flow so as to optimize the conversion here in the catalytic converter and do so by sending information to the CPU on the car. And the number one consumer of CPU's is the automobile industry, because every car has at least one, if not multiple, CPU's. So this is a good example of how understanding the lessons of solid state chemistry can allow us to build fuel efficient automobiles that have minimum toxic emissions to the environment.

All right, we'll see you on Monday.

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