

MITOCW | MIT3_091F18_lec35_300k

As I mentioned last Friday, there is one more topic that I want to cover.

And that is the topic of diffusion.

And so today, I'm going to talk about diffusion, which will be in the context of what diffusion depends on and how do we describe it.

And in particular, there's two laws, Fick's first law and Fick's second law, that I want to talk about.

And I want to talk about how this looks in the context of some of the chemistry that we've learned, some of the things that we've learned.

So diffusion, this is kind of a standard picture people show for diffusion, although really, this is probably mostly convection, which is the movement.

It's not diffusion.

But diffusion kind of has taken on this broader meaning.

And so what do we mean by diffusion?

Well, diffusion comes from the Latin word diffundere.

And that means to spread out.

But in this class, we're going to start by thinking about it as a particular movement down a concentration gradient.

And that is what's happening here.

You see there's a very concentrated droplet of dye that you put in there.

And then it's less concentrated out here.

You probably don't have any.

So the concentration of the dye out there is zero.

And in here it's very high.

And so it wants to go down a concentration gradient.

So that's movement down a concentration gradient.

OK.

How do we describe this movement?

And it really goes back to experiments that Robert Brown did.

And this is the original paper that he wrote way back in the early 1800s.

I love the title of this paper, "A Brief Account of Microscopical Observations Made Specifically in the Months of June, July, and August 1827 on the Particles Contained in the Pollen and Plants and on the General Existence of Active Molecules in Organic and Inorganic Bodies." What a nice, detailed title.

That was Brown.

So he started with pollen.

And he looked at it.

And it looked like this.

[MUSIC PLAYING]

Oh, that's very loud.

There wasn't supposed to be music.

So that's what he saw, except this isn't what he saw.

This is what Koshu Endo randomly posted online and I'm showing you.

But if you look at pollen in a microscope, and you're Robert Brown back in the early 1800s, you'd see this.

So he thought, aha, OK, there's life.

This is must have to do with biology.

And things are alive.

And so they move.

And it must be something like that.

And so he put other things in.

And they did the same thing, they jiggled around.

And then he said, well, OK, what about if I put something that was once alive but is not alive anymore.

And it did the same thing.

He said, OK, wait a second.

Maybe there's something to do with having ever been alive, the spirit of the particles.

And he said, OK, the ultimate spirit, I'm going to break some glass-- which is what he did, I love that.

I like breaking glass too.

And so he broke the glass.

And he took little pieces of glass and put it under his microscope.

They did the same thing.

They all did the same thing.

So they were really perplexed.

What was going on?

This is the microscopic basis.

This is now called Brownian motion.

It's random motion due to thermal energy and collisions.

And it's the connection of this microscopic random motion due to thermal energy and macroscopic observables that led to a big advance in our understanding of diffusion.

And so the question of how far took 80 years.

So one of the first questions, you say, how far do these things go.

How far are they going?

They're randomly moving around.

I got that.

I see it in the microscope.

How far do they go?

So how far?

Well, that was a question that you can answer if you can get the mean squared displacement.

I don't know.

I say tomato.

And so displacement, it's OK, mean squared displacement.

And it really came from Einstein in 1905.

Actually, this is what Einstein did for his dissertation, his Ph.D. work was on this topic.

It was on understanding how to go from these kind of microscopic random fluctuations to some macroscopic observables.

And so, the mean squared displacement, well, that's just the average of some measurement of some distance the particles go.

So if you go back to the dye, there it is.

But now it's in atom form or molecule form.

And it's diffusing around, diffusing around.

And OK, you say, well, how far did it go.

That would be the circle.

And that's something that Einstein tackled in his Ph.D.

and found that the mean squared displacement is-- well, let's just say it's equal to 6 times some constant times time.

This is in three dimensions.

If you're in two dimensions, it's 4.

If you're in one dimension, it's 2.

But the main point isn't that.

The main point is that the mean squared displacement is a function of some constant times time.

And so if you just wait long enough and you know this constant, then you can figure out how far things diffuse.

That was pretty cool.

That was pretty cool.

But you see, now, what we're going to be more interested in in this class is not how far but how fast.

We're interested in how fast.

And again, these are questions that Brown couldn't answer.

Brown observed these things and wrote about them.

And that's why it's called Brownian motion.

But it was later that people said, well, let's try to think about how to write this down and come up with theories that explain it.

And so for how fast, now we have the flux.

So we have the flux or the diffusion flux J .

And what we want is a way of describing how much.

So it's an amount of something, the amount of the substance per area.

You're going to normalize it.

So you say, I'm going to take this sheet.

And I'm going to say, how much of it is crossing this sheet area per time.

So amount of a substance per area per time, that's the flux.

So it could be grams.

The amount could be grams, mass, kilograms, micrograms, nanograms.

It could be number of atoms, moles.

That's also an amount, moles.

So we just say amount, it's general.

Grams, moles, et cetera, n number of atoms.

That's what moles tells us.

Grams, et cetera-- The time could also be-- well, the area could be centimeter squared, meters squared.

That's an area.

And then the time is usually seconds.

Usually, it doesn't have to be.

And so this is what Fick's law gives us.

So this was first established.

How do you get a dependence of this flux?

How do you get a dependence of this flux?

And again, we've got this constant in there.

And Fick's first law is all about that.

Fick's first law says that this flux is proportional to-- and I'm just going to write it like this for now-- concentration gradient.

So that's C divided by the change in X. C is concentration here.

We'll draw an arrow.

Concentration is C.

Now, we could use brackets.

Bracket A, concentration of A, mass per liter, something like that.

I'll use the letter C, ΔC over ΔX .

So that's the concentration gradient.

Oh, by the way this wasn't as far.

It didn't take as long as Einstein.

But this was 1855.

OK, good.

So Fick came along maybe 30 years later.

And he said, well, I want to know how fast things are going.

I want to understand how to describe the flux of these randomly moving things.

And I notice that it depends on the concentration difference.

And in particular, I like it when diffusion is positive.

So J is equal to minus D times dc/dx .

And that is Fick's first law.

Gesundheit.

And D is a constant.

D is this constant again.

So D is the diffusion constant.

We'll talk about this, diffusion constant.

There's the concentration gradient.

And we got a minus sign.

Notice, movement down a concentration gradient.

But if I didn't have a minus sign, then I wouldn't have a positive flux.

Then the droplet wouldn't spread out.

That wouldn't be good.

So we're going from high concentration to low concentration.

When I've got a bigger change in the concentration, I've got faster diffusion.

That's what Fick's first law tells us.

OK, good.

Very importantly, Fick's first law means it's steady state.

Notice, there is no t here.

There's no time.

For that, we have to wait for the second law.

So steady state diffusion, and that means not a function of time.

The kinds of problems where Fick's first law matters is-- and I know some of you have probably seen Fick's first law.

I get that.

But in a little bit, we're going to connect it to crystals.

But the kind of diffusion where the first law matters is the kind where you're holding concentrations equal.

Let's say you're holding a concentration gradient, and it's not changing.

And so you're wondering, well, if I hold a concentration at one thing here and at another thing here, how fast do things diffuse.

That's what Fick's law tells us.

And so let's do an example.

Here's my example.

I found these gloves, because I was looking for copolymers.

Here's a copolymer that doesn't have the nitrile groups.

Remember, the nitrile groups last Friday that were so important when we were doing our polymer design.

This doesn't have it.

This is butyl rubber.

OK, fine.

So there's the copolymer.

It's copolymerized with these two groups.

But now, it's got those groups, because it gave me the right flexibility and some of the other factors that I want in the glove.

But is it strong enough chemically?

And that's a very important question.

We talked about this last Friday that these chemical groups change the mechanical properties.

They also use the chemical resilience.

And so here I have it.

I have a toxin.

This is why we wear gloves, because we don't want to get methyl chloride into our skin.

Methyl chloride is toxic at 50 parts per million.

Keep it out.

Be very careful.

So I don't know.

I look up online and say, well, OK, butyl rubber.

These feel comfortable.

But how are they?

OK, with methyl chloride, which is a toxin, it's a molecule, it has a diffusion constant of 1×10^{-6} centimeters squared per second.

The gloves are 0.04 centimeters thick.

And I'm working with paint remover.

I'm working with paint room.

The concentration of paint remover is a gram per centimeter cubed.

Am I safe?

How much am I going to be exposed to this?

At my skin, I'm starting out with zero.

What's the flux through the glove?

Can I stay safe?

Well, first of all, one thing that we can do is we can look at-- just to make sure we understand.

So there's the diffusion constant.

Why does it have those units?

You can see this.

The units of J are an amount-- this is what we already said-- divided by an area times a time.

So if the units of C are an amount-- OK, I stayed with grams-- over a volume, then you can see right away that diffusion must be area over time.

It has to be.

If it's not, then the units don't work.

I've got concentration over a length.

This is a $1 D$. I'm going across some membrane maybe or some area.

This is a membrane, the glove.

And so you can think about this for yourself.

The units have to be area over time.

Is it area over time?

Centimeters squared per second.

They were, OK.

So that worked.

Now, another thing is, before we do the math, why does this happen anyway?

Why is there diffusion?

And it's actually quite straightforward to understand, even when you go all the way back to Brown's experiments with pollen.

You say, well, things are moving randomly.

Why is there now a direction?

Why is there now a direction?

How is that possible?

How can there be a direction if it's all random?

How can there be a concentration gradient?

And then you can get that, because if you have some high concentration-- Let's suppose that this is a high concentration, and this is a low concentration.

And you've got the Brownian stuff going on.

It's all in something.

There's Brownian motion.

Whatever containers these are, whatever is in whatever, it's got Brownian motion.

And so that means that, because it's random, it's equally likely to go that way as it is to go that way.

But see, at the high concentration, I've got more particles.

You can see that, because I drew bigger, longer arrows, so it's obvious, more particles, because it's more concentration.

There's just a lot more of them.

So there's more going across.

If I tried to draw a boundary here or boundaries inside here, and I look at those as my areas.

There's a high concentration.

There's a lot of stuff going randomly back and forth across them.

Down here, you can do the same thing.

But there's a lower concentration, so there's less stuff going back and forth across those barriers.

And now I bring them together.

I bring them together.

I bring the methyl chloride to the glove, to my hand.

Or I bring something with a high concentration next to something with a low concentration.

And I keep the concentrations of the endpoints fixed.

I hold these fixed.

Fick's law tells me now how this happens.

And you know that if I bring them together now, well, look, this was going just a little bit back and forth.

And this was going a lot bit back and forth.

And so there's going to be a net diffusion that way.

Right there at the edge, you can see it.

More goes to the right than goes to the left.

And so this starts to create a diffusion gradient.

That'll create a diffusion gradient.

So that's why it works.

That's why concentration gradients cause diffusion.

And Fick's first law tells us how.

OK, well, if we go to the question-- so let's see-- so the J -- so now I've got my glove.

And so the J is equal minus 1.1×10^{-6} centimeters squared per second times-- and this is going to be-- OK, I started with what?

I started with 1 gram right per centimeter cubed.

And on the skin I've got 0.

So it's going to be time 0 minus 1 gram per centimeter cubed.

And that's going to be divided by the distance 0.04 centimeters.

And this goes to something like 2.5 times 10 to the minus 5 grams per centimeter squared second.

That's the flux.

That's what Fick's law tells us, because my skin is good enough.

My body is good enough that any time a toxin, a methyl chloride molecule touches it, the skin just takes it away and poisons me.

But that's important.

It's not good, but it's important, because it keeps this concentration fixed.

Otherwise, this would build up.

And it would be changing.

So you can't use Fick's law.

No.

Fick's law applies when these two concentrations are fixed, and there's not a time dependence.

Instead, there's a rate.

There's a flux that you're after, J.

And so now you say, well, can I handle this.

Can I handle this?

Work it out, 50 parts per million.

I should have used the nitrile.

Should have used the nitrile copolymer.

Go back and make new polymers.

Maybe you need much, much better chemical resilience, which might lower this diffusion constant.

This is serious stuff.

This is serious stuff.

And it's so serious that I want to talk about eggs.

The rubber glove stops this toxin.

Well, it slowed it down.

Did it slow down enough?

Use Fick's first law.

But you can make membranes that are actually very selective.

It's the coolest thing.

You make a membrane that only allows water to go through but not salt. That's a selective membrane.

And that's called osmosis when you can allow one fluid to go through.

It's semi-permeable, permeable to one type of fluid but not another.

And the egg is such a great example, I had to show you this video.

I made this years ago in another class, because I wanted to show it.

This is what you can do with eggs.

They're so cool.

Here's a video.

So you soak them in vinegar.

OK, it's even got directions and everything.

We don't need any volume.

And there they are.

OK, you soak them in vinegar.

Now, the vinegar dissolves the calcium carbonate.

You know this.

You've done these reactions.

So there you go.

You soak them in vinegar.

Leave it overnight, I'd say, is probably best.

Then you peel off the vinegar.

And look, there's a membrane.

The egg has a really cool membrane.

This isn't cooked.

This is just a raw egg.

But now I add a bunch of syrup.

Now, this is almost pure sugar.

So the concentration gradient is enormous, because the liquid inside the egg doesn't have any sugar in it.

But outside, the liquid has huge amounts of sugar in it.

So the water inside the egg wants to diffuse out.

Eight hours, well, it's kind of enough.

18 hours, you pick that membrane up.

It's a really cool membrane, the egg membrane.

It's a semi-permeable membrane.

And it's hard to see here.

But you see, all the water is kind of gone.

It's totally deflated but completely stable, because the membrane's that strong.

The water inside has left.

And then if you get some green dye and you put it back into some green water, then you can make green eggs.

And you can make green ham that way.

And that's osmosis.

But it's semi permeable.

You've got to give the credit right.

You got to give the credit right in these things.

This was years ago when I thought I had a career in that direction.

So the egg is just such a cool membrane to play with.

And I thought, most of us can access an egg.

If you want to play with a really cool semi-permeable membrane, that is cool.

And you really will see Fick's first law at play.

You will see it, and you will feel it.

Now, there's one thing I want to comment on about all this stuff.

And we are not going to learn the details of entropy in this class.

That is really something for a thermodynamics class.

But I got to just correct something, because it's in your textbook, because a lot of this diffusion stuff, and in fact dissolution-- remember we talked about salt dissolving?

We did whole lectures on this, the dissolution.

Remember, these all have to do with the total energy of the system.

But we really focus in this class on one part of that, on one part, which is called the enthalpy, the bonding, the potential of the bonding.

But there's a whole other part that's related to the entropy.

And we're not going to go into this in detail, like I said.

You won't be tested on this.

But I got to bring it up.

So entropy can be really important.

Why does something dissolve?

It may be dominated by entropy.

It may be dominated by entropy.

That goes into the total energy still.

So we still have our happy place, lower energy better.

But as you learn more about what that energy entails, you've got to start including entropy in the future.

So Averill says, "...for now, we can state that entropy is a thermodynamic property of all substances that is proportional to their degree disorder." No!

That's not true.

That is not true.

So I have a question.

So you see this all the time.

Entropy, higher entropy, more disorder.

My room is messy, it's got a high entropy.

So which of these has a higher entropy?

Which one of these has a higher entropy, and which is lower?

This is a very simple grid.

They've got the same exact number.

How many think that the one on the right is-- it's the smoother one, right?

How many think that this is the lower entropy system?

I've set this up.

I've set this up, because you know that's not.

But why?

The reason is the real reason for what entropy.

It is not simply, because in this-- these are computerized experiments.

So we told a computer to pick randomly a place on a grid a certain number of times and then fill it in.

But in this case, you restricted it.

You said, no.

I can't have any two squares next to each other.

And in this case, you simply did it randomly.

So this looks smoother.

This looks less disordered.

But this has a higher entropy.

Why?

Because you have fewer options.

And that is what entropy is about.

Entropy is about the number of possibilities that you have.

Now, that might look more disordered, it might not.

But under the hood of entropy is possibilities.

It's number of states, of accessible states.

A salt atom in the crystal has very few possibilities.

If it were a perfect crystal, one, it's got to be in the lattice.

But once it goes into the liquid, it's got many more possibilities.

It's those numbers of states that matter.

That's why its entropy goes way, way up.

It's the number of possibilities, the number of possible states.

OK, good.

That was my aside on entropy.

Now, we talked about Fick's first law.

We talked about diffusion.

We looked at drops.

And we made sure the gloves we choose are going to be safe.

What about solids?

What about solids?

Well, things diffuse around in solids too.

Here's a red atom that is going to diffuse.

Watch this super high-tech video.

How does it do it?

A vacancy comes in.

Look at that vacancy, moving around, moving around, bam!

That atom moved, it moved, self-diffusion.

It moved.

It's an atom of the same type that was able to move in the lattice because a vacancy diffused through right.

And so there's the beginning.

And there's the end.

You see it moved over by one position.

But now we're all thinking.

We're all thinking, and we're going back to our days of, well, OK, hold on.

What really happened?

So here's the vacancy on one side.

Here, it went over to this side.

There's the atom going through.

So the vacancy moved that way.

The atom moved that way.

But as you know, that atom had to experience some barrier.

So it had to get over some activation.

It had to get over some activation.

And that really helps us answer a question that has been burning in our minds this whole lecture, which is, what else does flux depend on.

We saw the concentration gradient thing.

We looked at it in very simple terms.

We understood it.

But what about D itself?

Well, when you see something that's an activated process, there's only one person that ever comes to mind, right?

First name S , last name A . And it's Svante, because you know that if it's an activated process, then there's some pre-exponential factor times the activation energy divided by $k_B T$ if it's for a single atom.

Or if it's a mole, you use R .

There's your activation energy right there.

But so now, we can start connecting this.

So one thing you know about that diffusion constant is it will have a temperature dependence.

And you also know now that if you plot the log of it versus $1/T$, you will get that.

Oh, we're back.

We're in our happy place with this.

It's Svante.

So this is an activated process for an atom diffusing.

These kind of atoms diffusing through their own lattice, remember, these have high barriers.

This might be kind of hard to do, but it's still going to happen.

It's still going to happen.

You might also get something like this.

And this goes back to our discussions of defects in crystals.

You might get an interstitial diffusion.

So this is diffusion.

This is the topic that we're covering.

But now we can relate the equation that governs diffusion, the D , to the crystal and to the chemistry, because what is the barrier that that feels when it goes through.

So remember, an interstitial, like carbon and iron to make steel.

That would be an interstitial defect or an interstitial atom that you've added to the system, to the iron lattice.

And how does it move?

Well, that's absolutely critical, because it tells you how to make it.

And we'll get to an example of that.

So if I look now at these plots-- and these are plots I think I showed you back when we talked about interstitial defects.

You can really connect it to what we've learned.

So just to start, these are the log diffusion coefficients.

So that's the diffusion coefficient that we're talking about right there.

Versus $1,000$ over T -- so it's 1 over T scaled by $1,000$.

And these are those beautiful Svante Arrhenius dependencies.

And these are experimental measurements.

And look, here's hydrogen in BCC iron.

Here's hydrogen in FCC iron.

Now, notice, at the same temperature, there's a huge difference.

And then, I have FCC up here, and then I've got BCC over there.

Why?

Well, those are the stable phases at those temperatures.

But notice that when they're at the same temperature, there's a huge difference.

Why?

Because you know from the crystal structure that there's more room.

So the activation barrier will be lower in BCC.

Those voids are bigger.

There's more space.

It's not as well packed.

We've covered that.

And look at this.

So there's hydrogen, it's really small.

There's iron, iron in BCC Fe compared to hydrogen in BCC Fe.

Look at those orders of magnitude.

So there's an iron atom diffusing in its own solid.

And here's hydrogen atoms.

You can see there's carbon and so forth.

So this is the picture that comes back.

If we want to think about diffusion in solids, we can connect it to the packing and crystal structures, because we know that these atoms, these interstitial atoms are going to diffuse through the interstitial space.

What is the interstitial space?

Well here, as just an example, I showed just BCC and FCC.

Here they are.

Here's is an octahedral site.

This is BCC down here.

So notice, the shaded in atoms are the lattice sites, BCC, at the corners and in the middle.

And now, you see, the red atom is in the middle.

Gesundheit.

Let's say the red atom was here.

And it's moving to there.

And now it's in the middle.

So it might take that path as it diffuses.

It's going to find the voids.

Diffusing atoms find the voids.

And so if you have something that's trying to diffuse, it's going to want to find these voids.

This is an octahedral site, because this is an octahedron.

And you can have one of those in an FCC crystals as well.

You can have an octahedral site.

So in FCC, you've got lattice sites in the face but not in the center.

And so its octahedral site is here.

You've got tetrahedral sites.

Those are other voids in the crystals.

We touched on this a little bit when we talked about defects in crystals.

But now I want to relate it to diffusion, because how a crystal has voids is critical to D , how something diffuses in it, whether that something is something in the crystal itself or something you've added to it.

And how it has voids depends on the bonding, the chemistry, and the crystal structure.

So you could answer questions like this.

These are some just fairly straightforward questions that you could answer.

What if I had carbon-- this is what I just showed you-- in alpha or gamma iron?

Well, so I'll just write the answer.

It's alpha iron, because it's an open-- I don't need to calculate stuff.

Which one is BCC, which one is FCC?

And it's alpha, because it's an open BCC structure.

And so the diffusion barriers are going to be lower.

Iron in alpha iron at 500 or 900?

Well, now I've got a temperature question.

I know D is going to be higher, so 900 degrees C because of influence of temperature.

Iron or hydrogen in alpha iron.

It's like what we just talked about.

So this would be particle size.

H is smaller.

These are conceptual questions.

What's the fourth one?

Silicon vacancy in silicon or helium in silicon.

Well, for a vacancy to move, you need those kind of same atoms move.

And if a same moving through those sites, that's harder.

That's harder than if a small interstitial like hydrogen is moving through those voids.

That's why, when you look at this, iron is orders and orders of magnitude slower.

The D is orders and orders of magnitude slower than carbon or hydrogen. And so that's going to be He, because the vacancy diffusion is so much slower.

And then five, Mg, this is a good one, because hydrogen in platinum or hydrogen in magnesium.

Well, magnesium has a larger atomic radius.

And you look it up.

And you say, they've got the same close-packed crystal structures.

But one of them has a larger radius.

What does that mean?

Well, it says something about the voids as well.

The voids are going to be larger.

Remember, this is happening through the voids.

This is happening through the voids.

This is how batteries are engineered.

This is why we have a revolution in batteries.

So this is a couple of years old.

There so many great review articles on battery technologies.

This is the cathode.

By the way, what is a battery?

Well, a lithium battery is basically two sponges.

And one of them is usually carbon.

And when you're running your battery, lithium ions are going in.

And the carbon is so strong and able to hold those lithium in and not break down.

So we often use carbon on the anode side.

And then when we charge it up, we push them back over to where?

Where they came from.

That's the cathode, which is a lithium compound.

But it has to be a material that can hold lithium in it, hopefully at very high concentration, but also be OK to lose it and not completely collapse.

And so you've got lithium ion phosphate, those are these ones.

You've got manganates.

You've got cobalts, cobalt oxide materials.

There are so many battery materials.

They all work the same way.

If it's a lithium battery, the lithium is going to leave some crystal that has lithium in it.

But the crystal has to stay.

So it's like a sponge that loses something from it but stays intact.

And that's something goes over to the anode.

It gets soaked up there.

And you can recharge, discharge, recharge, as you're just pushing these lithiums back and forth.

Oh, but you're pushing them back and forth.

You are diffusing them.

That's what you're doing.

You are diffusing them through whatever structure you're putting them into.

So if it's the cathode, and you're trying to get the lithium to come back in or to go back out, then you can imagine that the barriers and the dimensionality itself are crucial.

What is an activation energy for a lithium atom in a given material?

And does it take a 1 D path?

It turns out these can be extremely efficient.

Look at those.

They're practically holes, they're lines in the lithium ion phosphate.

It's a really nice cathode material, because you've got these channels.

These high conduction channels, these highways.

But then you say, well, but maybe I need 3D voids.

Maybe it shouldn't have channels.

It should have voids, so it can choose more paths.

Maybe we have planes.

Maybe it's a layered structure where they have these 2D planes they can travel through.

What's the best?

Well, it's not trivial, because it's one of these, as usual, constrained optimization problems, where, when you make the pathway faster, you might need to have more voids where you'll lose material.

Or maybe you make the material unstable.

So you want it to have a really high density.

The lithium diffusion and a battery material is related to the charge time.

So here's another paper from a few years ago.

If you plot materials-- now, here's the specific power.

And so that's how much power, watts per weight.

Here's the watt hours.

So that's the energy per weight.

And this is the charge rate.

This is the charge rate.

And notice, so you want it to be very, very fast-charging.

And these are good materials.

There's the lead-acid battery that's still in your car.

These are nickel metal hydrides and so forth, other technologies.

Here are the lithium ion batteries.

This is what's in your cell phone.

Notice something, as I get up to faster charge rates, more open voids in material, I lose energy density.

I go this way.

I don't want to go that way.

I want to go this way.

Constrained optimization, these are the things.

What goes into solving these problems is calculating diffusion barriers and energy densities and all the other things that matter.

But if you want to target fast charging, you've got to know the diffusion barriers.

One of the number one challenges in battery design is to keep that high while continuing to push up that way.

Polymers, you could imagine that a polymer is slower.

It makes sense, right?

Because it's harder-- as we talked about when we talked about polymers, it's harder to make crystalline polymers, to keep a polymer from having some amorphous region.

After all, you've got these 100,000-unit long strands of spaghetti.

So it kind of makes sense that the diffusion is going to be lower in a polymer than in one of these crystals, like an olivine, lithium ion phosphate.

So that makes sense.

But polymers would be great, because they're lighter.

And they can be flexible.

And so we like polymer batteries a lot.

We want them for many applications.

So these are the kinds of tradeoffs that you think about.

And D is right there in the center, because none of us want a battery that takes two days to charge.

And now we get to the next part, which I'll just introduce, which is, now we're going to think about time.

And I want to set this problem up.

And then we'll solve it on Wednesday and then and then finish.

But I want to set it up, because the next thing that's related to diffusion is time.

And I want to give you an example of how that's so important with something called case hardening.

So if you buy a gear-- and you do buy gears all the time.

Whether you like it or not or know it or not, lots of stuff has gears in it.

And you look at the gear closely, it would look different on the outside.

If you do a cross-section, most gears are going to look different on the outside.

And the reason has to do with exactly what we just talked about.

If this is a piece of iron, pure iron, it's going to be too soft.

So you're now turning this.

And it's got to have mechanical integrity.

And so you've got to make it harder.

But the thing is, if you put it in and it's pure iron, it's too soft.

But now if you make it this really ultra-high strength, carbon-infused steel, it gets too brittle.

It gets too brittle.

And so you need a balance.

And one of the ways to balance the mechanical strength of something like a gear or many, many other materials is to harden just the outside.

That's cold case hardening.

The case, it's the case.

How do you do it?

Well, you get carbon.

Remember, carbon going into the iron makes it a lot harder, but it also makes it more brittle.

So if you made the whole gear the same amount of carbon infused in iron, is going to be too brittle.

If you don't put any on, it's not mechanically strong enough.

So what you do is you very, very delicately expose this piece of iron to carbon.

You harden it, but just on the outside.

Now, how does the carbon get in?

Diffusion.

It gets into the material through diffusion.

So then the question at your gear-making plant that you have to know is, what temperature and how long should I expose this gear to how much carbon.

You've got concentration.

You've got temperature.

And you've got time.

And if you know that, you can actually process this material in just the way you want.

And you have to know those parameters.

And that is Fick's second law.

So these are steel pipes.

And they are going to be case hardened.

So what's happening?

You've got an iron with a certain amount of carbon content.

But now, I need to add more carbon but just the right amount to the exterior of those steel pipes.

How long should I do it?

And that is Fick's second law, which I'll write down.

So how do we figure that out?

Well, we use the time dependent version of Fick's law.

And Fick's second law says that the change in concentration with time is equal to the diffusion constant times the second derivative of the concentration with position.

That's Fick's second law.

And so this is non-steady state, which means-- and we're not going to derive this.

But I do want you to know that this is the Fick's second equation and how you might apply it, which is why we'll do a problem with it.

But it's non-steady state.

And that means that the concentration that you're going to get is going to be a function of position and time.

It's going to be a function of both.

So now, I can answer the question.

Remember before, I had to keep the concentrations fixed to apply Fick's first law.

Now I can answer the question.

Well, OK, if I have certain parameters, what is the concentration going to be.

What is the concentration going to be at some time and some place?

And that's exactly the question I have to answer.

How much carbon am I going to have at what position in the case hardening?

In what position of the pipe exterior, how much carbon am I going to have at what time?

How long should I leave it in the oven?

That's the question I'm trying to answer.

And by the way, what temperature?

And so the thing that Fick's second law helps us understand is, if I start with some C_S that's the starting concentration, and I have a starting concentration C_0 , and I expose at the surface some higher concentration-- remember, before, I kept these fixed.

I kept these fixed.

And I got a flux.

Now, I'm going to be able to get this.

So this line here is time equals 0.

But now I can actually get this profile.

Time 2, time 3, that's the position through some surface.

So this is what Fick's second law tells us.

It tells us these profiles, the concentration in the material.

And it just simply is a time-dependent version of diffusion.

OK, what we're going to do is we're going to pick up with this.

We'll do this example of case hardening.

We'll do a few more comments on the class.

I'll tell you a little bit about the final.

And please bring your laptops on Wednesday for the last 15 minutes.

We'll reserve for you to do evaluations.