NARRATOR:

PROFESSOR: So gas exchange. So this is the last lecture on how does stuff get into and out of the ocean. And then after the midterm, we'll deal a lot more with what goes on within the ocean in terms of internal cycling and dynamics. And so what we're interested in is, for soluble gases, there's going to be fluxes in and out of across the RC interface, and we're interested in these fluxes, which we're going to call of f.

Typically, the way this is formulated or discussed is in terms of two components. It's going to be the flux is going to equal a kinetic component times a thermodynamic component. And if any of you have had transport theory, like diffusion, thermal conductivity, this should look very familiar. It's basically, almost everything in this formulation has been stolen from physical chemistry and chemical engineering adapted. And there's a lot of crossover between the chemical engineering and the environmental communities in terms of gas exchange.

The kinetic component is going to depend on things like properties of the water and turbulence. So this kinetic component we're going to try to set up so that lots of the kinetic component are independent of the particular gas. And we'll also show you how to reference gas one to, say, gas two. The thermodynamic component is going to depend specifically on individual gases, and is essentially a measure of things like the solubility of the gas, the atmospheric and ocean concentrations.

Oh, do you want me to move? I can move. Well, I can't anymore. I was just going to move the tip for you guys right there. And this is pretty standard, this separation into a kinetic component and a thermodynamic component. So we're going to-- first we're going to talk about solubilities and the thermodynamic component. So you need to know a little bit about the composition of the air, and there's some notes or a table in the notes.

Most of the atmosphere is nitrogen. It's about 78%. Next comes oxygen, which is 21% And then everything else, argon is 1%, and then everything else, if you look at this well, it actually looks like it already adds up to 100%. Everything else in the atmosphere is small. It's either in parts per billion or parts per trillion.

STUDENT: Parts by volume?

PROFESSOR: Well, yeah, I'll get there in a second. The way these are usually reported are as partial pressures. So you guys all remember PV equals nRT? The partial pressure is the pressure that a gas would exert, independent of the other gases all by itself at that particular concentration or molar ratio and temperature. You'll see it traded back and forth, whether it's reported as parts per million or mole fraction, because the pressure that a gas exerts depends upon how many moles are there, not on its molecular weight.

So PV n is either the mole fraction or it's the partial pressure relative to the total pressure. For most gases, you can assume ideal behavior. That is that you can actually use PV equals nRT without any corrections. For some gases, example, CO2. You actually need to look at the fugacity. It's a fairly minor correction, but it's basically deviation from the ideal gas law associated with the fact that CO2 is interacting with the other gases.

Also, almost all the air-sea gas exchange measurements are reported for dry air. So they've actually dried the air and removed the water vapor. So it would be PPM, parts per million relative to dry air, not the total pressure. And so when you go back and apply total pressure, you just have to make sure you know what's-- you just need to keep track of what's been done with the water vapor because it can be several percent, particularly in the tropics.

Usually, we're going to formulate our equation in terms of not the partial pressure, but the concentration that would be in-- I'm trying to see what the convention is. It would be the concentration in the air-sea surface that would be in equilibrium with the atmosphere. So if you have, say, a partial pressure of some gas C we want to find out right at the air-sea surface what would be the concentration that would be in solubility equilibrium with that partial pressure.

So rather than working in partial pressure in one side and concentration in the other, we're going to convert partial pressure into a corresponding solubility equilibrium concentration. Now, there's a couple ways of doing that, and I will warn you that the literature is not consistent. If you remember from physical chemistry [INAUDIBLE] one form of Henry's law, it's basically relating the partial pressure of a gas to a solubility concentration as a function of an equilibrium constant, temperature in the ideal gas constant.

You'll also see things often recorded like this, which is technically the Bunsen solubility law, where this k equilibrium is now actually a Bunsen solubility coefficient. But in the literature, people are very sloppy, and sometimes you see it. Sometimes you see Bunsen solubility law written as Henry's law. So they go back and forth, and you just have to be very aware. Sometimes this is also written as a beta. You just need to be aware of where the beta is coming from and what they're talking about.

STUDENT: And units will help with that.

PROFESSOR: Yes. Wel, units.

STUDENT: Well if you use them.

PROFESSOR: Yeah, if they use them. Yeah.

STUDENT: You mean pressure of your gas C in those last questions, not pressure gas A?

PROFESSOR: Oh, this is supposed to be-- yeah, sorry. It's pressure of-- if the atmospheric pressure of C. So I guess I could put a little C here if you wanted. It is the pressure of C, but it's the-- yeah, sorry. I didn't match those very well. It's the atmospheric pressure of those of compound C. Yes, that's a good point. It's not total pressure. It's the partial pressure of that particular gas. Thanks.

Units. The modern standard for gas exchange literature is, gases are reported in micromoles per kilogram. Unfortunately, you will see all sorts of things. The most confusing, particularly if you go back in the older literature, is that oxygen, which is ubiquitous not just for gas exchange, but for hydrography and for biology, was often reported as milliliters per liter. And you say milliliters of what?

It's actually milliliters at STP, standard temperature and pressure. And there's a conversion in the notes, but it's essentially 1 milliliter per liter equals about 43.6 micromoles per kilogram. And since we're assuming ideal gas behavior and it's at standard temperature and pressure, this-- you're using. But so you'll often see the older literature oxygen values that are about a factor of 50 lower than if you had them in micromoles per kilogram.

So what determines this Bunsen coefficient or the Henry's law coefficient? Well, there's essentially three things. You've got a gas that you're trying to stick into water. So we've got all these water molecules that are happily bound to each other. Remember they're all sitting there undergoing their lovely little hydrogen-- have all their little hydrogen bonds. They're quite happy. You gotta put a hole in the water in order to put a gas in.

And so the first thing is going to be the energy to create a cavity. And that's going to just depend upon the solvent. It's just basically, you gotta break the water, break those hydrogen bonds and make room to stick your gas in. The second thing is the energy to keep the solute in the cavity. And that's going to depend upon the solute.

For example, a big solute might bounce around more slowly so it stays in the cavity more easily. A smaller solute has a much harder time and has a higher diffusion rate, and it's going to bounce out quite quickly. And then the third component is the solute-solvent interaction, which of course, depends upon both the solute and the solvent. And this is things like, we know that water is polar, unless it's 400 degrees and 5,000 bars.

Water is going to be polar, and so polar gas molecules are going to be more soluble than non-polar gas molecules, because it's easier. You gain energy back from the solute-solvent interaction, and it helps if things are polar. Now, there's some examples in the notes. We're going to do a fair amount of stuff looking at noble gases. So the noble gases are helium up to xenon. Yeah.

And a lot of the gas exchange work has focused on those, because those are the geochemical things that you want to know. But they don't have other physical and biological sources and sinks. And so you can isolate using the noble gases, what's going on with gas exchange. And then you can apply them to your molecule of interest, whether it's dimethyl sulfide, or CO2, or oxygen, or something like that.

So a couple of rules about solubility. If we were to plot now the Bunsen solubility against temperature, what we would see is that helium would be down here, and xenon would be up here. So there's a couple things. One is, solubility-- sorry-- increases as you decrease temperature. And that makes sense. Colder water is going to hold more gas. If anybody's ever played with a soda can or a soda bottle, if it's warm, you open it up, it spills all over the place.

Well, that's because a lot of the CO2 in the carbonated water has degassed and is sitting over the lid, where if you cool it down, put it in the refrigerator, more of that gas goes into the water and you have less pressure-- a smaller pressure then built up underneath the cap. The other thing is that there tends to be a relationship in this case for the noble gases, where the larger gases are more soluble.

And if you want details on that, there's more. There's a nice figure in your notes, and tables and the references to go look up coefficients. I should warn you that often these betas, just like what we saw for, say, temperature and salinity, where you're given an equation, a very complicated polynomial. That's also the way that these are calculated for seawater because of salinity effects and temperature effects, as you will usually be some long polynomial as a function of temperature and salinity that will give you an exact value. But there are tables and curves you can pick up.

The other thing is that salinity-- salinity works to disrupt some of these solute-solvent interactions because of all the large ion charges bouncing around and all of the-- basically, yeah, because of all the high ionic strength. It disrupts some of the solute-solvent interactions, which actually help make the gas more soluble. And so as you increase salinity, you decrease solubility. And this is often written as-- I'm not going to test you on spelling on this one because I never--

It's the [INAUDIBLE] relation, which basically says if you had your Bunsen coefficient for fresh water and your Bunsen coefficient for whatever salinity, those are related, and you can actually calculate them as a function of salinity. This is an approximation. In reality, we're going to use the full polynomials. But it basically says that if salinity goes up, solubility goes down. And it's a fairly substantial effect. It's order of 20%, 30%.

STUDENT: Does that also hold for nonpolar gases that [INAUDIBLE] be for solubility [INAUDIBLE]?

PROFESSOR: Well, even like the noble gases can have small inducible polarity.

STUDENT: Something like methane?

PROFESSOR: Oh, yeah, methane, as well. But even like xenon has a salting out effect because it can be inducibly polar, which is why you can actually make some-- you can actually do some stuff with noble gases. So that's all we're going to cover on solubility. Any questions on that? If anybody wants, we got one of the world's experts on this of stuff here, Bill Jenkins. And he you can go talk to him, and have coffee and spend the afternoon.

Great. So we'll go back to our simple flux model for the flux. We're going to start to delve into what we're going to call the kinetic component. It's often approximated by this coefficient, little k. And sorry, this is just notational. Gas exchanges notational help. These come from so many different fields. The [INAUDIBLE] relation uses a little k with an S. k is just what is typically used for the kinetic component in gas exchange, and I think I've kept it straight in the notes.

But usually, it's going to be formulated as something like a kinetic component times the concentration in the water. So I'm going to use C is the concentration in the bulk water. And C0 is the atmospheric equilibrium concentration. So C0 is a fictional quantity. It would be what the water right at the very surface that's just touching the gas would have as a concentration. You don't actually measure C0. What you do is you measure the atmospheric partial pressure, and then you compute C0. So C0 would be that Bunsen coefficient times the pressure in the atmosphere.

So this is kind of going back to, remember, the kinetic component and the thermodynamic component. This is going to be the kinetic component. This is going to be the thermodynamic component. So the thermodynamic component, you go out and you make measurements [INAUDIBLE]. And you make measurements of the partial pressure in the atmosphere.

Now, one confusing thing is often, the way people make concentration measurements in the water is they take a bottle-- a blob. A blob-- a blob of water, a parcel of water. And then the way they instead of making concentration measurements, they may take this and actually compute its own partial pressure-- seawater partial pressure. So sometimes you'll see this instead of being written as k, C minus C0, you might see it as k, P minus P0, where or PSW minus PA.

Just for some gases it's instead of-- it's easier to make partial pressure measurements for the seawater, rather than to make concentration measurements. Just depends upon what the easiest chemical technique is. Everybody set with that? OK. So there are several models of gas exchange, and these are really simple conceptual models to give you some framework in which to interpret observations.

The first one is called the stagnant film model. And the stagnant film model is going to try to simplify everything by saying that if we were to plot depth, and we're going to plot concentration. So we're going to start off with at C0. We're going to say that the atmosphere is well mixed. And for most of the gases we're going to be talking about in this class, it's a pretty good assumption that most of the resistance to gas exchange is on the water side, not on the air side, because they're what are called sparingly soluble gases, so things like CO2, O2, N2, the noble gases.

They're soluble in seawater, but they're not significant. It's not significantly soluble in seawater. So you can basically make the assumption that the atmosphere, the transport is so quick that the atmosphere is a well-mixed box. So this C0, you make an atmospheric measurement, and then you can say, OK, I'm going to know what the concentration and equilibrium is right at the surface.

For the stagnant film model, it's just like what it says. Stagnant film where the only processes going on are diffusion, molecular diffusion. So we have that relationship. Remember, we have flux, right? The flux across this stagnant film is going to be constant. We're going to assume there's no chemical reactions, no biological reactions. There's a very small film.

So if you have molecular diffusion going on, and you have no sources and sinks, and you have a constant flux, can anybody tell me what the profile is going to look through that stagnant film layer? You may have molecular diffusion. Straight line. Good guess. Well, or good knowledge.

[LAUGHING]

Across that stagnant film, there's actually going to be a straight line. And then there's going to be-- we're going to assume that there's some bulk concentration, C, and that the Oceanside is actually well mixed, as well. So all the turbulence that's going on down here keeps this infinitely well mixed. There's this stagnant film layer and then an infinitely well mixed atmosphere.

The reason why this is a straight line, if you remember, from Fickian diffusion, Fickian diffusion or molecular diffusion says that the flux is simply equal to a diffusion coefficient times the gradient. Well, if the flux is fixed and the diffusivity is fixed, you have a constant flux. Otherwise, you'd be draining or adding gas in and out of the stagnant film layer. But the only way for that to occur is if you have a constant gradient and a constant gradient [INAUDIBLE].

Where the stagnant film comes in is we're going to say that this stagnant film has a thickness delta z. So we're going to approximate the Fickian diffusion as flux equals minus D, delta C, over delta z. So we're just turning the little d DC and Dz into delta C and delta z. Then we're going to say, well, we have minus D, delta z. And then the delta C is just the C minus C0.

So these things we can measure. We know D. We can look that up in a table. It's a diffusivity. So we could rearrange this equation. If we could estimate f from some measurements, we could then turn around and calculate delta z. It's like, well, I'm not really interested in delta C or delta z per se. But if I had a set of gases for which I could measure the fluxes and then compute delta z, I could then use that delta z for other gases for which I couldn't make flux measurements. That make sense?

And often-- oh, yeah, let's do one thing-- the diffusivities, the units on those are length squared over time. So meters squared per second, for example, is a typical diffusivity. It depends upon temperature, and the solute and the solvent. So you actually need to know what gas it is and whether it's in water. Water has different diffusivities than magma or methanol. And you also know the temperature.

D tends to increase with increasing temperature. So if warmer waters, diffusion tends to occur faster. And also, as molecular weight goes up, diffusivity goes down. So bigger molecules tend to diffuse slower. Now, for the noble gases, there's nice sets of relationships. As soon as you get a molecule that is not spherical, then it's not just molecular weight. It's also its polarity and its actual shape.

But these can be-- these are recorded, have been measured in the lab. They've been measured in the lab for fresh water. They've been measured in the lab as a function of salinity and temperature. So let's show an example of how you might do this. So we're going to talk about radon. Everybody remembers from Bill Martin's lecture on radioactive isotopes and radionuclides. Everybody remembers that radon 222 is a daughter of what?

STUDENT: Radium 226.

PROFESSOR: Right. Radon 222 is the daughter of radium 226, or yeah, radium 226. And so this is a gas. This is not a gas. And so, because the radium is always decaying to radon 222, we can look at the imbalance between how much radon you would expect to see based on how much radium is there versus how much is actually there. Remember, we would expect the activity of radon 222 to equal the activity of radium 226, unless there's some process that's removing the radium.

This is the secular equilibrium that Bill talked about quite a bit. So if you were to look in the field, what you'll often see is that in the deep water, this would be depth and this would be, say, 100 meters. What you might see is that the activity of radon 222 is low in the surface, and then tends to increase at depth, and this dashed line is the activity of 226.

And so deep in the water column, they are in secular equilibrium with each other. And right up near the surface in the mixed layer, there tends to be a deficit of radon. And that's simply because radon has been lifting out the top. Now, everybody have that? Can I switch? You guys studied at MIT? OK. So what we want to do is set up a mass balance for radon 222, and we're going to do it over the mixed layer.

So remember the little diagram I had, where that's radon 222, and this is the radon 226. We're going to approximate and say that there's going to be some mixed layer depth h. And we're just going to look at the mixed layer, and we're going to assume that everything is well mixed within that mixed layer. If you had to do the calculation for real, you could integrate over that and find out averages and all that. But typically, things are pretty well mixed in the mixed layer, and for first order, that's a good assumption.

So we're going to say we want to know the first look at the production terms. The production term of radon 222 is simply going to be the mixed layer depth times the activity of 226. So radioactive decay is producing radon, and if we know the radium activity, that gives us the production rate of radon. There's going to be two loss terms. One is simply going to be the mixed layer depth times the activity of 222.

The second one is going to be a flux term, which is going to depend upon a piston velocity, which I'll get to in a minute, times a delta concentration. Remember, that was the flux form that we showed previously. So from the stagnant film model, this is going to be-- this term stays the same. We're going to assume that the atmosphere has no radon 222.

And that's not a bad assumption. The half life for radon is about four days. And so over the open [INAUDIBLE], the amount of radon in the atmosphere is really small. That's not true over land because you have outgassing of-- you have uranium-rich soils and rocks, have a lot of radium, and you get a lot of radon out. Fills up your basement, fills up your shower. So we're going to assume that the sea-atmosphere for radon goes to zero.

And we're also going to assume a stagnant film. So then what we would need to know is simply the diffusion rate of radon over the stagnant film depth-- remember that's the piston velocity-- times the concentration of radon 222. Now, usually, this is formulated in terms of [INAUDIBLE]

--constant number of molecules that are there. Yep. Oh, did I drop out?

STUDENT: We lost them too.

PROFESSOR: We can't hear you either, so we'll give it a second. The answers to the midterm are--

[LAUGHING]

STUDENT: I think she said she heard that.

STUDENT: Do we have you back? I'm out.

PROFESSOR: OK, cool. How far back did you miss?

STUDENT: I'm below the word loss.

PROFESSOR: OK. So what I was saying was that there's two components to the loss term. There's going to be radioactive decay for radon, and then there's going to be gas exchange. And the gas exchange is going to depend upon the concentration difference across the interface and a piston velocity. We're going to assume that the concentration of radon-- so this would be for radon-- is going to be zero. And so all you need to know is the concentration of radon in the water because that's going to drive gas exchange across the interface.

So all I did was then expand this lost term, so this would still be loss. It's going to equal the radioactive loss term, and we're going to replace this k by the stagnant film model. So we have the diffusivity of radon. We have the thickness of the stagnant film. So this is that stagnant film. And then we need a concentration.

And the way we're going to get that concentration is we're going to go back and remember what the definition of activity is, because usually, these are measured and reported in activities. So we want n, and n is just going to be the activity over the decay constant. So then this would be the activity of radon over lambda for radon. So if we assume steady state, which for when they first went out and started to do these experiments in the '60s, they weren't able to make the experiments long enough to see what actually was changing over time, so that's something [INAUDIBLE].

Steady state is that production equals loss. And I won't go through, but what you can find if you notes, well, is you can rearrange the equation for delta z, because everything else in here is known. H is known from your measurements. The activity of 226 is known, the activity of 222, diffusion coefficients, lambdas, et cetera. And so you can rearrange and find delta z as some function of the activities of 222 and the activities of 226.

And what they found was that the delta zs tended to be in the tens of microns for stagnant films. And you can go through the whole calculation in the notes, and I would recommend it because it's a pretty useful, both in terms of remembering secular equilibrium and radioactive decay, and also gas exchange.

STUDENT: Can I ask a quick question?

PROFESSOR: Sure.

STUDENT: What's system velocity?

PROFESSOR: Ah. Good question. I should have covered that. I'm going to slide this up a little bit. Do you guys have everything? Remember I wrote f equals k delta C at the very beginning? And this k can also be it's the D over delta delta z for the stagnant film model. I think I wrote it as kC minus C0, but that's the same thing. If you look at the units D has units of meters squared per second, length squared time because it's a molecular diffusivity.

Z has units of 1 over m, or 1 over length. So this term k, or capital D over delta z, has units of meters per second. And it's often called a transfer velocity. I actually like transfer velocity because it so hearkens back to transport theory, transport phenomenon. But for reasons that escape me, it's also called a piston velocity. And I think the idea was that you can imagine that as this piston sitting at the bottom of the bottom of the mixed layer, pushing up, pushing the gas from the mixed layer into the atmosphere, or similarly, pushing gas from the atmosphere down into the ocean.

It's really terrible. It's really terrible nomenclature, but it has leaked into the notation. But essentially, this is the kinetic. It's the kinetic. The stagnant film model is not the best model. Oh, and I should say these are order of tens-- k is typically tens of centimeters per hour. And that's just also a historical thing that ks are often reported at centimeters per hour rather than meters per second. And that's just so the units look more closer to 1.

So the stagnant film model is a really good pedagogical tool and useful for the initial interpretation. But what was found was it's actually not a very good model for open ocean conditions. If you think about it, you've got this little-- you're supposed to have this little stagnant film that just sits there, and nothing happens to it. Well, if anybody's gone out to the open ocean, particularly when the wind picks up, it's hard to imagine a little constant film that stays there indefinitely.

So a new model or a competing model, if you like, is the film replacement model. And the argument for the film replacement is that let's say you have some stagnant film sitting up at the surface. So it would be if you were to do this in cartoon, you might have some stagnant film that then stays there for some length of time, but then some eddy comes along and pulls that film off. And you'd have no stagnant for a while, and then a new stagnant film would develop.

So that film basically gets wholesale replaced every so often. And so then the problem becomes, you're going to have, say, a diffusional flux into that film over time, and then whatever gas has built up, it's one, and then maybe you got lots of gas that's built up. All of that gas gets transported down into the interior when that film gets replaced or overturned. And then you start off with no gas, and then it would build up with time. This would be time in this direction.

So then we no longer have a steady state problem, and we need to look at the flux into the film as a function of time. So f as a function of time into a infinite slab. So we'll assume that the film is thick enough that we can treat it as an infinite slab. It's going to equal, again, the concentration difference, where this is the concentration difference from the atmosphere to the bulk fluid. Same thing that we've been approximating before.

And it's going to depend upon diffusivity in the water. Except now it's going to depend-- instead of being depending upon linearly on diffusivity, it's going to depend upon the square root of diffusivity. It's going to depend on pi, which is just a constant, and time. And that says that when you bring this-- when you bring this parcel up, what you'll notice is that this equation is actually unstable. At zero time, it says you have this infinite flux.

And that says that right when you bring it up, you're exposing water that has had-- that essentially has zero perturbation to the gas concentration right at the surface. So you're exposing it across just that molecular layer of the atmosphere spirit to the water. And so you have this very, very rapid rate for a very short period of time. But as time progresses-- the square root should be all the way down, by the way.

As time progresses, this term gets smaller. And it basically says as this film-- as time progresses, this film fills up with gas, and so the flux gets less and less, because this film starts to become equilibrated with the atmosphere. That make sense? And the only way to increase the flux is then to rip that film off, put it down, and then bring up a new film from a new, uncontaminated film.

What we actually want to know is the mean flux over some time theta. That's going to be the mean life. The mean life of the film. And that's just going to be-- the mean flux is going to be 1 over theta. I'm just going to integrate from zero to theta, integrate the flux. And that just has a very similar form, except now instead of having t, I have theta in the denominator.

And so what we've done is, instead of having-- remember in stagnant film, we had the transfer velocity. Piston velocity was equal to D over delta z. And the film replacement model, it's now 2 over the square root of diffusivity times pi times theta. Now, there's a very useful non-dimensional coefficient that we use a lot, which is the Schmidt number. And the Schmidt number, SH equals the viscosity of water over the diffusivity of a gas.

So this is the viscosity of water, and diffusivity of a gas. Now, the nice thing about this is that this gives you some information about relative transport. If the viscosity of the-- if the viscosity of the fluid were to go up, you'd expect turbulence to be damped, so it gives some measure of turbulence. And if the diffusivity of the gas goes up, you'd expect the gas to be more effectively transported.

The Schmidt number looks a lot like you've got a D term. We can then, instead of just computing D, we'll actually report these ks in terms of Schmidt numbers. And remember at the beginning, I was saying one of the things we want to do is how to go from compute k or one gas, and then go to a second gas. That was one of the goals. We're going to try to compute gas exchange with things we can measure, and then we're going to apply those to other gases.

The way we're going to relate them is through the Schmidt numbers. So we have for the stagnant film model, we're going to say we have some-- we're going to have k is proportional to D to the one half. That's what this says up here. Well, and this is proportional. Well, that's also proportional to Schmidt number to the minus one half, because D is in the denominator of the Schmitt number.

So one of the things you will see a lot-- and did we put it on the top set? I can't remember if we made it switch Schmidt numbers.

STUDENT: I haven't done the last question. [INAUDIBLE]

PROFESSOR: OK. Is that the generalized forms of the flux equation for the replacement model is k0. So this might be some piston velocity you measure, say, with radon or some other noble gas. Would then be, you'd have a Schmidt number correction. So you'd have the Schmidt number that you originally made the reference measurement with for k0, and then the new Schmidt number, where this is the Schmidt number for whatever gas that you're interested in.

So this would be the flux you're trying to compute for new gas times the concentration gradient.

STUDENT: Is that with your subscripts, the words in parentheses.

PROFESSOR: That's a these are both Schmidt numbers, and that's just supposed to be a Zero. So it's the same k0, Schmidt number zero. So if I had made a measurement with radon, I would plug in the piston velocity for radon, the Schmidt number for radon-- oh, excuse me-- and then minus 0.5 for the replacement of the model. And that's simply because the piston velocity is proportional to Schmidt number to the minus one half.

Have I lost you guys? How you guys doing up at MIT? Yeah? Riveting stuff, huh?

STUDENT: Yeah.

PROFESSOR: Sometimes you'll see this written as-- people will say, well, I don't know whether it's whether I believe the stagnant film model or some other model, and they will write it as same general form. Schmidt number over Schmidt number reference to the minus n, where n might be the exponent that they're actually trying to find from their experiment.

STUDENT: I'm sorry. Because for the standard film model, it's going to be one thing.

PROFESSOR: Yeah. If we were to go back, remember, k-- k was proportional to diffusivity for the stagnant film model. So if we come down here, that would say that k for stagnant film model would be proportional to 1 over the Schmidt number, so Schmidt number to the minus 1. So if the stagnant film model were dominant, then n would be 1, where for the film replacement model, it's 0.5.

STUDENT: That's good. Just a quick clarification. For the equations up there, the 2 pi theta not z, right? You were pointing out.

STUDENT: Yeah. Oh, that's 2, right?

PROFESSOR: That's a 2. Yeah.

STUDENT: I thought it was.

PROFESSOR: Yeah, I tried to cross my Zs. So yeah, I usually am pretty good about that. Makes up for some of my poor handwriting.

STUDENT: So this is the flux from the atmosphere to the bulk.

PROFESSOR: Oh.

STUDENT: [INAUDIBLE] the atmosphere.

PROFESSOR: Yeah, it just depends upon the concentration gradient, whether it's going to be from the atmospheric to water, from the water to the atmosphere. So now, I've told you how I have computed a k0. We went through an example with radon. We've now gone through how to transfer from gas to gas, and there's actually a table of Schmidt numbers for seawater in your notes that you can look at. It's basically 1 over-- you can think of it as 1 over diffusivity.

So just invert everything we said about diffusivities in terms of sensitivity to temperature and molecular weight. But what does k-- what else does k depend upon? It depends upon the solute, but it also depends upon other environmental conditions. And there's a fairly long-running debate in the literature about the values of k and how to measure them. And I don't know whether-- I don't know whether it's actually getting resolved or not with time or whether we're just headed into some more confusion.

So we had flux equals k, Schmidt number, Schmidt number, zero to some exponent delta C. There's a couple of things that we think increase k or k0. Would be wind speed. So higher wind leads to more gas exchange. Well, that makes sense. Higher wind leads to a lot more turbulence. It leads to wave breaking, bubbles, all sorts of things like that. So that kinetically makes some intuitive sense.

The second thing that people have tried to do, so people have spent a lot of time trying to build models or empirical models relating k0 to wind speed. The theory on this is somewhat weak. It's, how does wind speed then affect turbulence [INAUDIBLE]. But you can make empirical measurements. You could go out and make radon measurements, for example, in high wind speed conditions, and then go out a few weeks later or season later and make them under low wind conditions, and then look at the radon deficit and look at how k differs under those two conditions, and then try to basically map that out.

You could look at bubbles. And the bubbles are usually approximated by white cap coverage. And it makes sense that bubbles should increase gas exchange. If you think about it, you're taking gases out of the air and you're sucking them down into the water. Some of that gas is dissolving before that bubble reaches back to the surface. And that would be a net flux into the water. Similarly, you can also think of bubbles as increasing the surface area between the water and the air.

And by increasing the surface area, if you had something that was supersaturated in the water, you could diffuse gas into those bubbles, and some of those bubbles are going to make it back up to the surface. When they make it back up to the surface, they're going to lose gas to the atmosphere because they're going to pop. So those both would increase the-- those both would increase the transfer velocity.

It should increase with fetch. Does everybody know what fetch is? Fetch is basically the distance the wind is blowing over. The fetch is basically, if the wind is blowing from one side to the other, the fetch is the distance across the lake. And if you looked at the lake, if you were on the-- if you were on the-- say the wind was blowing this side. If you looked at the waves, the waves would be really small on one side of the lake, and then they might be really big on the other side of the lake.

And that's just because it takes a while for the wind-- for the momentum and the wind to be transferred into the water and to build up a wave state. And since turbulence, you think the same thing might be true for turbulence. It might depend upon the wave state and how long the wind has been acting on the water. Most of the time in the open ocean, fetch isn't into problem. But sometimes you'll also see it as wave state.

So if the wind suddenly just kicked up in speed, the turbulence might not have caught up to it yet. And one way to do that would be to look at the wave states. If you go out and look at the gas exchange measurements-- and there's an example in the book. And this is where things get rather contentious in the literature. If you plot piston velocity or transfer velocity as a function of wind speed, the data kind of looks like this.

And depending on how you interpret the data, whose data you decide to keep, whose data you decide to throw out, you can pass a number of different lines through that curve. Some of the curves, there's a classic curve by Liss and Merlivat. Liss and Merlivat. And you can tell that this field isn't as mature as other fields because the relationships are still-- we still talk about individual people's curves rather than saying, this is so-and-so's law. This is just somebody's estimate.

So Liss and Merlivat said, well, we view it kind of goes like this. There's actually three broken lines. So it'd be three-- the right place for that-- three discrete lines that are joined together. There's a better word for that.

STUDENT: Is U wind speed?

PROFESSOR: Oh, yes. U is wind speed. Thanks. And it's usually referenced. You'll often see it as U10, which is the wind speed at 10 meters, because wind varies at the height above the surface. And so you try to reference it for a common height. Liss and Merlivat is basically three discrete lines, so they're basically linear in each region. And it's piecewise linear. That is important. Piecewise linear.

Another famous one that goes through the same cloud is the Weinkauf relationship, which is k is proportional to the square of the wind speed. So it's a quadratic relationship. Now, from there, it gets really ugly. Weinkauf also now has a cubic. You have other people who are arguing it's actually linear with wind speed. And in some ways, the data isn't strong enough yet to partition between those.

The problem is, obviously, the quadratic and the cubic, when you get to very, very high wind speed, the piston velocity keeps on shooting up. We don't have a lot of data at very high wind speed. It's very hard to go out and make gas exchange measurements in a hurricane, both technically, and also because you just don't know where the hurricane is going to be. You basically have to position yourself ahead of a hurricane, and know where it was in advance and all that.

There are attempts to resolve that with some other measurements, which I'll talk about in a moment. But I do want to touch on one other thing that comes up a lot in exams and general exams, and things like that, which is the-- yeah, and, and, and-- which is the gas exchange residence time. So remember back we had that little model where we had some thickness h, which was the mixed layer.

Well, you could think that gas exchange is going to try to push supersaturated waters towards equilibrium. Similarly, it's going to try to push undersaturated waters to equilibrium. And you can approximate that as a time scale. So this would be a time scale for equilibration that's going to be proportional to h. The deeper the mixed layer, the bigger volume you're looking at, the longer you would expect it to take to come into equilibrium, because your flux doesn't depend upon mixed layer depth.

So your flux doesn't know how big the mixed layer is. So if you have a 10-meter mixed layer, the equilibration is going to go very fast. If you have 1,000-meter mixed layer, it's going to go very slow. And your piston velocity, your transfer velocity, if you think about that, that has units of meters. This has units of meters per second. And so you're left with something that is in time. And typically, typical values are tens of days for most gases.

So it's going to take a few weeks to a month or so for other things to start equilibrating. And technically, it's the 1 over e. It's the 1 over e-folding time. So if you started with a concentration difference, after one e-folding time, you'd be down to 1 over e the original perturbation, and then 2 e-folding times, you'd be 1 over e squared, et cetera.

STUDENT: I don't understand the term folding time.

PROFESSOR: So DC, Dts. Let's say you had some perturbation is equal to, say, minus kC. If you solve that, remember DC over C equals minus k Dt. And so it actually looks like radioactive decay. It's going to be C at any time is going to equal C0, e to the minus kt. And so when time-- when you get to 1 over e-folding depth, this is going to be-- this value would be 1, and so then it would be C equals C0 over 1 over e. And that's just called unfolding.

It's just conventional notation. It's called 1 over e, but it equals the time. There are some caveats to the residence time. I went slow today. Oh, no, that clock's fast. It's 55. I went slow today. There's a couple of caveats to the residence time. For CO2, remember, most of the CO2 in water is in what-- most of the inorganic carbon in seawater is in what form? Bicarbonate. So most of the dissolved organic carbon is in bicarbonate.

And so if you want to equilibrate the CO2 system, let's say you had 14 CO2. So you had radioisotope CO2 diffusing into the water. It's got to fill not only the dissolved CO2 gas. It's also got to fill H2CO3 star, bicarbonate, and carbonate ions. So there's actually a correction that t is going to equal h over k, just like what we wrote, times the total amount of CO2 in the water, the total DIC dissolved ionic carbon, over CO2 aqueous.

And this latter factor is somewhere between 100 to 200. So the gas exchange timescale for C 14 is going to be about 100 to 200 times longer than a normal gas, because CO2 has this huge reservoir of other compounds that aren't actually gases. Remember, the hydrated form the bicarbonate and the carbonate ion, they are not gases, so they cannot exchange across the air-sea interface. But in terms of a residence time, or in terms of equilibration time, you have to fill up. You have to put C14 and plug it into all of these other reservoirs, fill up all those other reservoirs before you came to equilibrium.

So that means that t for C14 is about 10 years. Now, the last little tidbit I want to get to, there's a section in the notes on-- there's a long section in the notes on methods, and you can read that. And your problem set actually goes through one of the examples of one of the methods. But the last thing I want to touch on is what happens for CO2 gas. That's not C14. So you have regular gases [INAUDIBLE] approximately weeks to months.

You have 14 CO2, which its t is approximately 10 years. It turns out for CO2 gas, t is intermediate between those two. It's about one year. And it has to do with the fact that as you add CO2 to the water, what are you doing? What are you doing? You're increasing total CO2 or DIC. But what else are you doing as you add CO2 to water? You change it. You change its pH.

So you are actually decreasing the pH. And one way of thinking about that is you're actually shifting the acid-base equilibrium from bicarbonate to CO2 aqueous, or H2CO3 star. And so that actually speeds up the equilibration because you're actually filling up more CO2 aqueous, so you're coming into equilibrium with the atmosphere faster. And so you get an intermediate time scale between the 10 years you would expect. If the pH didn't change in seawater, CO2 would have the same equilibration time as 14 CO2. This is because pH changes.

We're out of time. There's some discussion in the notes that are on the web page about all sorts of fun, different ways that people have measured CO2, or excuse me, have measured gas exchange. Read those through. Oh, yeah. What I said was that the notes have discussion of the different methods that have been used to measure gas exchange, and you should read those. But for problem sets and stuff, I think some of these equations, the stagnant film model, the film replacement model, and the residence time are more useful and might be more amenable to being an exam question, for example.

STUDENT: Yeah, I was just going to ask, does that mean in areas where surface water pH is lower than [INAUDIBLE]

PROFESSOR: Well, but the pH isn't going to affect-- it's the change in pH as you equilibrate, because this is the time scale to reach equilibrium.

STUDENT: But if you've already used up your alkalinity, [INAUDIBLE].

PROFESSOR: Well, it does change. There's something called the-- it's called the Revelle factor, and it actually changes. It actually changes slower in low-pH environments. Yeah, we will get to the Revelle factor later in the semester. Great. Good to see some of you in--

STUDENT: Question.

PROFESSOR: Yeah.

STUDENT: It has to do with [INAUDIBLE].

PROFESSOR: Oh, hang on. One more time.

STUDENT: What does it have to do with it being carbon-14. And what do you-- why is it [INAUDIBLE]. I don't understand what that has to do with being carbon-14.

PROFESSOR: Ah. The difference is, if you're just adding an isotope, this would be the equilibration time if the pH in seawater were fixed or buffered by something else, but that's not true. But it is true if you're adding an isotope of CO2 because you're not actually changing-- you're adding so little of this that you're not actually changing the seawater pH of the seawater chemistry, Where if you add CO2 gas, you actually are changing the seawater chemistry.

And then it speeds up because you're basically getting-- if you add CO2, you're making it more acidic and you're actually increasing the aqueous CO2 concentration faster. And so you're equilibrating with the atmosphere faster. Does that help? It is a tough concept. We should probably go over it. We'll go over this again in recitation on Monday.