[SQUEAKING]

[RUSTLING]

[CLICKING]

PROFESSOR: OK. So we are going to spend today mostly on the Clausius-Clapeyron equation. And remember we're still in chapter seven of the text. OK. Good.

So what is the CC equation? The CC equation is the following. We have a phase diagram here. I'm going to draw a little close-up section of a phase diagram, and this is very generic.

And all right. So let's say we have alpha. I like to use colors. Let's make alpha kind of teal, and let's say we have beta. And beta is going to be kind of purple. And we have a coexistence line between them.

And at any point on that line, we have a slope. Right? We have rise over run. So here's a little dP, and here's a little dT.

OK. What makes these phases stable? Well, over here, mu of alpha is less than mu of beta. Right? That's the definition we developed last time. And over here, mu of beta is less than mu of alpha.

But on the coexistence line-- right? Last time, we developed the conditions for two-phase equilibrium. So on that coexistence line, mu of alpha, which is, of course, a function of temperature and pressure, equals mu of beta, which is a function of temperature and pressure. So if I take a little jog, I take a little jog from here. Let's see. We'll start running out of colors pretty soon.

Let's take a little jog. Let's walk a little bit. If I'm going to stay on the line, I need d mu of alpha, which is, of course, a function of temperature and pressure, to be equal to d mu of beta as a function of temperature and pressure. Right? I want you to think about this line as a mountain ridge, and you're walking along the mountain ridge.

And you want to stay on the ridge because if you fall off the ridge, you fall very far. It hurts. And the ridge is a curvy line. And so if you want to stay on the ridge, you just can't walk in any direction for as long as you like.

If you want to stay on the ridge, you can't walk in x and y as much as you like, north, west, east, and south. You need to stay on the ridge. So you only have one degree of freedom, right? If you walk a little bit north, you've got to adjust a little bit west or east to stay on the ridge.

That's pretty intuitive if you're on a mountain ridge. You don't have to go through all that thinking and think about multivariable calculus. You just don't want to fall off the ridge, but that's what's going on here. We want to stay on the co-existence line. This is the condition to stay on the line.

All right? The potentials are equal. And so if I take a little step, I've got to take a step such that the changes of these chemical potentials are also equal so that I stay on the ridge. OK. Questions on this concept because we're going to start evaluating this condition now. So it's going to get kind of mathy.

All right. So let's evaluate that condition. That's the condition for the line. All right. So d mu alpha, we know what this is.

Who wants to give me an expression for d mu of alpha? It's something times dT plus something times dP.

STUDENT: Minus S dT plus V dP.

PROFESSOR: Right. You may recall that chemical potential is molar Gibbs free energy. So we're seeing the same differential form here as we did a couple of weeks ago now, when we developed a differential form for d Gibbs. Right?

So the only thing I've done here is I'm expressing the molar Gibbs free energy as chemical potential. And I'm adding the phase labels because now I have a heterogeneous system. Multiple phases, so I have to keep track of the phase labels.

So thank you for that. I didn't see which rectangle answered that question, but thank you for that. And likewise, we have for beta-- OK. So this is true for alpha and beta phase. And I want the d mu of alpha to be equal to d mu of beta. So I'm going to combine these three lines.

All right. I'm going to plug in for d mu alpha. I'm going to plug in for d mu beta. I'm going to see what I get. And so what I get is what? d mu alpha equals minus S alpha dT plus V alpha dP. And that's going to be equal to minus S beta dT plus v beta dP.

I'm going to collect terms. Collect terms, and I get S of alpha minus S of beta dT equals v of alpha minus v of beta dP. And this here, this is a transformation quantity. I hope everyone watched the three D's of thermodynamics.

And if you did, I hope you found it useful. So this is the transformation quantity. This is delta S, and this is delta v. As we go between phases beta to alpha, these are transformation quantities. And we're going to then divide through.

Divide through, and we're going to get an expression for the slope. dP dT equals delta S over delta v. Right? That's pretty useful. So now we have an expression for the local slope of that coexistence line as a function of these transformation quantities.

And we have something else. For an isothermal equilibrium transformation, we know that delta S equals delta H over T. So I can re-express this as dP dT equals delta H over T delta v. So these are equivalent, and these are called the Clausius relation or equation.

OK. So that's what these are. These are very famous. And so it's a differential equation. It's a differential equation for this line, right?

It's not an equation for the line. But it's giving the slope of the line as a function of temperature and pressure, where temperature and pressure parameterized these transformation quantities, delta S and delta T.

OK. So this is in general true for any two-phase coexistence line. We're going to analyze it now for the case of vapor pressure because the equation simplifies for vapor pressure. And it's also a very useful result which is used in lots of different fields.

But before I move on to a specific case, this should be a good time for questions on the general case.

STUDENT: Can you explain when you said that for the isothermal equilibrium transformation why you specified that case?

PROFESSOR: Sure. I think that was [INAUDIBLE] but anyway. Thank you. So when we are having an isothermal transformation, at equilibrium, if alpha and beta can transform to each other at equilibrium, that's almost the meaning of coexistence. So then delta G has to be 0. That, again, was our requirement for equilibrium at constant temperature and pressure.

That's the Gibbs free energy of two phases is equal, or, in other words, the chemical potentials are equal. So delta G equals delta H minus TS. Right? That's just from the definition.

And if it's isothermal, this is delta H minus T delta S because T here is a fixed number for an isothermal transformation. So this has to equal 0 if phases alpha and beta are in equilibrium.

So this is useful. And I mentioned this in the last class that the fact that delta H minus T delta S is 0 for two-phase equilibrium. It's used, for instance, in databases for transformations.

You might see temperature, and you might see delta S. We might see delta H, and you might see delta S, or you might see a pair of numbers. But you might not see all three because having all three is redundant because you have to have this condition satisfied.

And you can check that. If you open the textbook and you go to phase transformations for the elements, there's a bunch of data here. And if you like to, you can go and check in, for example, silver here.

Silver melts from FCC to liquid at 1235 Kelvin. I know you can't read the numbers, but I'm just pointing out the structure of the database. And there's delta S for the transformation and the delta H of the transformation. And you can confirm that delta H minus T times delta S is going to be 0 for every single set of these.

So De Hoff is nice, and he gives you extra information. Right? But he could, for example, block out the temperature of the transformation and not list the melting temperature. And you say, what on Earth? It's a table of melting temperatures, and he doesn't list the melting temperature? What is he doing? Right?

Well, you can solve for the transformation temperature from delta S and delta H under the condition and the delta G is 0. Now, I don't know if that answers your question. If it's off base, please try again. [CHUCKLES]

STUDENT: No That was helpful. Thank you.

PROFESSOR: OK. Thank you. All right, so let's move on. Right. So let's use the Clausius-Clapeyron equation. Using the CC equation, vapor pressure. All right. So this is a very useful case, and let's just remember what we're doing here.

All right. So I have temperature here. I have pressure here. That's a typical way that vapor pressure curves are plotted. And there's a typical curve, and here's solid, for instance. And here is vapor.

I used green for both. That's not very creative. Let me point out that everything we're about to do also applies if that's liquid.

So it's a vapor pressure over a condensed phase. It doesn't have to be over the solid phase. It could also be over liquid.

So here, vapor condenses. Right? On that side of the curve, vapor condenses. And here, solid sublimes, or liquid evaporates, as the case may be.

All right. So that's the meaning of this phase diagram. OK. So on the coexistence line, vapor is saturated. That's an important word. You need to be able to interpret that word when you see it in all sorts of problems. It's saturated-- that's a really important concept-- at its saturation vapor pressure.

So these terms, saturation and saturation vapor pressure, you're going to encounter these all over the place, even on your weather forecast. And it's nice to be able to connect it back to the thermodynamics. OK. So we're on the curve.

Let's say if excess vapor pressure is added, what will happen? Imagine you have a system. You have these two phases in a box, and you turn up the vapor pressure. What will spontaneously happen?

STUDENT: The vapor will condense to decrease the vapor pressure.

PROFESSOR: Thank you. Will spontaneously condense to-- and I put this in quotes-- try to re-approach, right? To try to re-approach P sat. Likewise, if vapor pressure is reduced-- let's say you hook it up to a vacuum pump-- what will happen?

Let's do it.

STUDENT: Solid will will evaporate.

PROFESSOR: Solid will. Thank you. I'm going to use the case of the solid, but you're right. Spontaneously sublime to-- again, in air quotes-- try to re-approach saturation vapor pressure.

OK. So it seems that when you're on this coexistence line, if you try to change the intensive parameters of the system, if you try to change the pressure, say, the system will respond to try to counteract your change. It will try to resist whatever you're trying to do.

If you try to increase the pressure, it's got a way to try to pull it back down. If you try to decrease the pressure, it's got a way to try to push it back up. All right? So it has a way to resist you.

What's the principle behind that? And it's a French guy. Who remembers? There's a general principle which explains this.

STUDENT: Le Chatelier's.

PROFESSOR: Right. This is a really nice example of Le Chatelier's principal-- that is nature reacts in such a way to counteract any external impulses, or, in other words, it's stubborn. It will resist you by any means possible.

So in this case, you're on the coexistence line. It has a means of resistance, which is this phase transformation. And it will use that phase transformation to try to resist the changes which you imposed. All right. So I hope that's a little bit intuitive.

Let's do some math around that. All right. So let's calculate the saturation vapor pressure. How do we do that? We have a differential equation, right?

So how do we get an equation from a differential equation? Right? I have to solve it. So we do it by integrating the CC equation.

And as we'll see, normally, in general, you can't do this because you might not have closed-form expressions for everything that you need. But we're going to make some approximations. So in general, we have this. dP delta v equals dT delta H over T. Right?

If we're going to integrate this thing, in general, we need what? We need delta H as a function of T and P. And we need delta v as a function of T and P. Right?

In general, we're going to need these things. And even if these equations of state exist, there's no guarantee that they're separable or that we know how to solve the equation. Right? This is why we use computers.

So in general, these transformation quantities can be-- right? As we saw last time, in general, I'd say this is pressure. This is temperature.

Let's say there is a standard T0 P0, like standard temperature and pressure conditions. Right? Standard state. And someone gives us the transformation quantities there, right? And we actually need them over here.

Right? And some other P and T. Right. So in general, we can integrate. So, for instance, calculating delta H as a function of T and P. dH Equals cP dT minus plus v1 minus T alpha P.

So delta H at T and P equals delta H at, say, T0 and P0, some standard data which I found maybe in a database, plus from T0 to T d delta H at fixed pressure plus from P0 to P d delta H at fixed temperature, which equals delta H T0 T0 plus T0 over T dT prime, dummy variable, delta cP.

So there's my capacity differences. So here's where that data comes in. P0 to P d P prime, dummy variable, and, again, a transformation quantity, v1 minus T alpha. These are transformation quantities.

Right. These characterize the change as you move between phases. Right. So I'm just laying this out in general. Very rare that you actually have to do calculations like this. Let me lay out how to calculate delta v.

Calculating delta v, right? That's the other part of the integrand, delta v. So we have dV equals v alpha dT minus v beta dP. That's the general form.

So delta v at some temperature and pressure equals delta v at a standard temperature and pressure plus from standard temperature to my desired temperature, d delta v at fixed pressure, plus from standard pressure, my pressure of interest, d delta v at fixed temperature equals delta v at T0 P0 plus T0 T d dummy variable delta v alpha plus P0 to P, dummy variable, delta minus v beta. And again, these are transformation quantities. They're the differences between phases.

Transformation quantities. All right. So why am I telling you this? Right?

I can hear a line from "Hamilton" in my background. Why am I telling you this? I'm telling you this because, in general, you need a lot of data to do these calculations.

You need to know the heat capacities of all the phases and their differences. You need to know the thermal expansion coefficients of all their phases and their differences. For this calculation, you need to tell the volume of all the phases.

And here we are calculating delta v's. You need to know the volume of all the phases. Right? And if you don't know the volume of all the phases at all temperature and pressure, you have to know it at some temperature and pressure. Then you need the thermal expansion coefficient of all the phases. And you need the isothermal compressibility of all the phases. Right?

So, again, you can see why CALPHAD or computer calculation and phase diagrams is so powerful because it integrates all this stuff for you automatically. Right? So, in general, this requires knowing-- writing is getting sloppy here-- this requires knowing cP as a function of temperature and pressure, v as a function of temperature and pressure, alpha as a function of temperature and pressure, and beta as a function of temperature and pressure for both phases.

So let's get phase labels here, right? There's a lot of information that we need to tabulate for both phases, kappa equals a, alpha, and beta. Right? However, for vaporization of a condensed phase over a limited temperature range, we can simplify using three assumptions.

One, we're going to say delta H is approximately equal to a constant. That's probably the worst approximation. We don't know if it's good or not. We're just going to go with it.

If delta H is a constant, I don't need to do all that heat capacity integrating and so forth. Right? It's just a number. OK. Two, volume of the gas is going to be much, much greater than volume of the solid or volume of the liquid. Right?

If I assume the volume of the gas, molar volume, is much, much greater than the solid or the liquid, then delta volume is approximately equal to what? Delta volume is the transformation quantity.

I am vaporizing. So delta volume is approximately equal to it.

STUDENT: The volume of the gas?

PROFESSOR: Right. Exactly. Right? Delta v equals volume gas minus volume solid, right? And if the volume of gas is so much bigger, we can say it's basically equal to the volume of the vapor.

When typical condensed phases sublime or evaporate, you have factors of 20,000 or more increase in volume, molar volume. So that means you're making an error one part in 20,000. It's a pretty good approximation.

So I would say that this is a good approximation. This one here is kind of an eh approximation. It's OK. It's not bad. And the third approximation is that the gas behaves ideally.

So we can use the ideal gas equation of state. And unless you're at high pressures, that's also a pretty good approximation. So what we're going to see next is how these three approximations-- well, what I'm going to do, I'm just going to outline the way that this goes forward because on the P sat you need to use this a little bit. So I want you to explore a little bit.

But if the volume of the gas equals RT over P, that's PV equals nRT. And that's approximately equal to delta v, and delta H is constant. All right?

Let's remember what I'm trying to do here. Here, I have dP delta v equals dT delta H over P. So let's see.

dP delta v equals dT delta H over T, right? OK? And so what? We have dP RT over P equals dT delta H over T.

All right, so this is a constant now. dH is our constant. That's our approximation. We have temperature and temperature, so it's separable. I can take this temperature over here.

So I'm going to have dT over T squared on the right-hand side with a constant factor. On the left-hand side, I'm going to have dP over P with a constant factor. So this is now a separable and easy differential equation to solve.

And as you can see already, you're going to get logarithms from the dP over P term. OK. So I'm going to leave it here for you to finish this calculation. And you'll use the result in the P sat.

And this is very well described in the textbook. So you can step through. It's a nice calculation to finish. I'm going to move on to Gibbs phase rule. So we're going to leave this here.

Questions on saturation vapor pressure? This is a good time for them. I will note that we're going to return to the concept of saturation vapor pressure on Wednesday, when we're going to do an extended example.

So this isn't the last you'll see saturation vapor pressure. And it will come back with a vengeance in a couple of weeks from now, when we do multi-phase, multi-component reacting systems.

STUDENT: I just have a quick question. So in order to assume dP over dT equals delta H over T delta V, we said that it had to be isothermal?

PROFESSOR: Yes. I'm sorry. You're referring back to delta [INAUDIBLE] equals delta H minus T delta S?

STUDENT: Yeah. And then we said when we wrote the second form of the Clausius-Clapeyron equation that it had to be isothermal for that?

PROFESSOR: Correct. Right.

STUDENT: So then why is dT not 0?

PROFESSOR: So good question. This is a consistent point of confusion. And again, I won't put you on the spot and ask you whether you've watched and spent time thinking about the three D's of thermodynamics video. I don't mean to suggest that's a panacea, but this is a very confusing point.

These are transformation quantities. These are functions of temperature and pressure at any given temperature and pressure that they're numbers. So, for instance, delta S, delta V, delta H, delta v-- at any given temperature and pressure, they're numbers.

They characterize the change in state variables as you move between phases. Being functions of temperature and pressure, they depend on temperature and pressure. So I want you to think of these capital D deltas as the distances between these surfaces. And I'm sort of drawing surfaces here, but I drew it in the last lecture, and it's really well illustrated in the textbook.

So each of these quantities-- delta S, delta V-- is the distance between, let's say, the surface S for phase vapor and S for phase solid, as drawn in the last lecture. And since they're functions of temperature and pressure, they vary with temperature and pressure.

So, for example, you have volume. Wow. That's a really fat pen. That's not helpful. Let me find a page where I have some white space. There. I have white space on this page.

Let me grab a pen that's not too worn not yet. So let's say I have volume of phase alpha. That, of course, depends on temperature and pressure. Volume of phase beta-- that, of course, depends on pressure and temperature. And so I might have a transformation quantity, the change in volume as I transform from alpha to beta.

This equals volume of beta temperature and pressure minus volume of alpha temperature and pressure. And so this explicitly depends on temperature and pressure. Right. That means that even though I can consider an isothermal transformation between alpha and beta, I can also ask how that quantity varies, let's say, with temperature.

Right? That's the slope of that surface for varying temperature with fixed pressure. And I'm hesitating to launch into redrawing all those surfaces that I did the last time because if I do it quickly, it'll be too messy to be useful. And if I take my time, I'll be repeating myself, and we'll run out of time with today's lecture.

Another way to think about it is that at any given temperature and pressure, a fixed temperature and a fixed pressure, I have these equilibrium conditions between the two phases. And now I'm going to take a little trip. I'm going to go from one temperature and pressure to another temperature and pressure. And Clausius-Clapeyron is about making sure that I stay on that equilibrium condition.

OK. I don't know if that was helpful. Let's move on and then, as time allows, come back to that question at the end of the lecture. But again, transformation quantities are super important. Gibbs phase rule, we're going to go over this a little bit quickly.

Gibbs phase rule is the answer to the following question. How many phases can coexist at equilibrium? How many phases can coexist at equilibrium? So Gibbs phase rule is a linear algebra problem.

It's like this. Number of degrees of freedom equals number of variables minus number of independent constraints. So hopefully, this is familiar from linear algebra. So let's count variables.

I just have to go through this in order for it to make any sense. All right. So let's see. For phase alpha, I have a temperature and a pressure. Sorry. That was drawn for phase beta.

I apologize for temperature. Temperature and pressure for alpha. Temperature and pressure for phase gamma and so forth. For each of PH phases, I have two variables. That's what I need to set up.

I need to suggest an array of pha phases and two variables. So in this approach, the number of variables in my system equals 2 times pha. And I use pha because the textbook uses P, whereas every other page of the textbook P means pressure.

So I don't like what they do, so I use pha. All right. OK. Now let's do a number of degrees of freedom, number of variables, number of independent constraints, number of constraints. Number of constraints, I'm not going to write this out because it's very well presented in the text. But my constraints are my equilibrium conditions such as T of alpha equals T of beta equals T of gamma equals T of all the other phases.

And, for example, P of alpha equals P of beta equals P of gamma equals and so forth. So I have my variables, and I have my constraints. The variables come from counting. The constraints come from the equilibrium conditions, which we've already derived. And then we skip straight to the answer.

The answer is that my number of degree of freedom equals 2 times phases minus 3 times phases minus 1 equals 3 minus the number of phases. This is Gibbs phase rule for unary systems. Right? So this is skipping straight to the answer.

It's more thoroughly developed in the text. What does this mean? That's what I want to get to. That's why I'm rushing ahead.

A one-phase region, phase equals 1. The degree of freedom equals 2. For example, the TP plane-- all right? So this is getting back to what we know to be true, which is that in a unary phase diagram, in general, I'm going to draw the one for water here because it's pretty familiar.

See, this is temperature. This is pressure. This is liquid, solid, and the vapor.

In general, in a unary phase diagram, I can stick in one phase region. And I can wander around randomly in temperature and pressure and remain in that one phase region. That's the meaning of having two degrees of freedom.

I can wander at random in temperature and pressure independently while remaining in my one-phase region. Now, it's considered two-phase region. Two-phase region, pha equals 2. So what's my degrees of freedom? Anybody?

STUDENT: 1.

PROFESSOR: 1, right? So what does that mean? If I am in a two-phase region, let's say, on that coexistence line, I can move along the line and maintain my two-phase coexistence condition.

That's one degree of freedom, right? If I move in temperature, the move IN pressure is prescribed. I can't move independently in both pressure and temperature. And it's prescribed by the Clausius-Clapeyron equation. We just derived that.

So that's one degree of freedom. It's a line, right? This is a coexistence line. And finally, a three-phase region, number of phases equals 3. So my degrees of freedom equals 0.

What's a geometrical object with 0 degrees of freedom?

STUDENT: A point.

PROFESSOR: Point. So we have in unary phase diagrams so-called triple points. These are points where three phases can exist at equilibrium, can coexist in equilibrium. However, there are special points.

If I change temperature or pressure away from those points, I fall out of that three-phase coexistence condition. So, for example, my triple point here of water is-- gosh-- what is it? It's like 10 torr and right around 273 C. I forget exactly the number.

If I'm in any temperature and pressure other than that special triple point, I cannot have all three phases coexisting at equilibrium. And it comes out of this relatively simple linear algebra approach. And four-phase region, not allowed.

So from thinking about the number of independent variables in a unary system, that is pressure and temperature, and deriving the conditions for equilibrium, which you'll recall came from entropy max condition, in thinking about those things, we have arrived at a pretty strict set of rules. And they're fully consistent with everything we know nature does.

So I think that's kind of cool. It's an example of the deductive power of thermodynamics. You start with these abstract principles and some math. And you get very practical real-world predictions that are borne out.

What happens? How do I get a four-phase region? Does anyone know?

There are four-phase equilibria in nature. They're allowed, but they're not allowed in unary systems. How do I get a four-phase coexistence?

Right. It happens if I somehow increase my number of variables faster than I increase my independent constraints. And that's what happens when you add multiple components to a system.

So we're going to revisit Gibbs phase rule when we do multi-component systems, except if multi-component. OK. So this is the end of our treatment of unary phase diagrams.

In terms of new material, on Wednesday, we're going to study saturation vapor pressure in some detail. I hope this does give you a little bit of a flavor of the pace of this class. There's no way that I can cover all the material and work examples in lecture. And so we rely also on the textbooks, on the readings, so please do keep up.