[SQUEAKING]

[RUSTLING]

[CLICKING]

RAFAEL JARAMILLO: Right, OK, let's get going. We're going to talk about unary phase transformation today. So we talked about this. We started on this road a little bit last time. So we're going to now really dive in.

I think I was asked to use the fat pen. So I'm going to do that. So first, phase transformation, a phase transformation is when a material transforms from one phase to another. Sounds pretty straightforward. In this case, because it's unary, there's no change in composition. By definition, there can't be. There's only one component.

But we'll see that more generally, phase transformations come in lots of different flavors, including transformations that are associated with composition changes. And this is the first one we're going to encounter. So we're going to start, as we often do, with water. It's a very familiar substance and the phase diagram of water. So here's temperature. Here's pressure. And let's see.

At low pressure and high temperature, we should have the gas phase. At low temperature and high pressure, we should have liquid phase. Sorry. Solid phase. And kind of in the middle, we should have the liquid phase. And there's this phase boundary that separates them. And we'll just take that solid to liquid transformation as an example.

And imagine heating up across the solid to liquid boundary. And we'll ask what is this process? What actually happens? So what happens, we break bonds. We break bonds. We do something to the enthalpy. Do we increase it or decrease it?

AUDIENCE: Increase.

RAFAEL JARAMILLO: Increase. Bonds are low energy states. So to break them, you need to put energy in and pull those molecules apart from each other. So you're going to increase the enthalpy. We need to increase disorder. And we go from a ordered crystal to a liquid. And so we increase entropy.

That's what happens across that phase transformation. Let's talk about it a little more quantitatively here. So let's see, I'm going to draw two plots, one on top of the other. This is when having the graph paper really comes in handy. Even with the graph paper, I can't draw a straight line. Oh well.

So what I'm going to plot here is the reversible heat. I'm going to heat the solid and melt it. I'm going to plot reversible heat. And on the first plot, I'm going to draw a temperature. On the second plot, I'm going to draw entropy. And so let's see, let's start over here in the solid phase. And we're going to be heating the system.

And what's going on? We're going to be heating the system. And at some point, we reached the melting point. So let's say that this is the melting point. So let me draw some lines here. So this is like-- we're adding heat. We're heating the solid. And at some point, we reach the melting point.

What does entropy versus heat look like in this region? What does entropy versus heat look like? Let's see, this is region one, give you a moment to think about it, region one, heating the solid. And I want you to recall that ds equals dq reversible over t. So what does entropy versus heat look like?

AUDIENCE: [INAUDIBLE] plus or maybe constant.

RAFAEL JARAMILLO: I'm sorry, I didn't hear what the first thing. You said, perhaps constant. But there was another answer in there too.

AUDIENCE: Perhaps very having a very small, kind of similar to [INAUDIBLE] slope that is plateauing.

RAFAEL JARAMILLO: Would it be a positive slope or a negative slope.

AUDIENCE: A positive slope.

RAFAEL JARAMILLO: Positive slope, good because you can see ds dq is strictly positive. It's one of a temperature. All right, and is it going to be curving as a positive curvature or a negative curvature?

AUDIENCE: Just have a positive curvature.

RAFAEL JARAMILLO: So it's going to have a negative curvature because you can see the slope is 1 over t. So as t increases, it's going to-- slope is going to decrease. So let's draw that a little bit exaggerated, decreasing slope. OK, good. All right, now, we've reached the melting point. And I'm going to keep heating.

I'm going to keep adding heat. What happens to the temperature as I continue to add heat energy to the system?

AUDIENCE: It stays constant.

RAFAEL JARAMILLO: Stays constant. It stays constant as long as I'm in the solid plus liquid coexistence region. That's right. Good, so that hopefully you know from experience that at unary phase transformations, the temperature is constant as long as you have two phases present. And you know that from boiling water on the stovetop.

So so the temperature stays constant. But what happens to the entropy? Does the entropy stay constant as well?

AUDIENCE: I'd say so for breaking bonds for transitioning to the liquid phase, it would increase.

RAFAEL JARAMILLO: Whomever that was, I had a little bit of a hard time hearing you. Can you try again?

AUDIENCE: I'd say, since we're breaking into [INAUDIBLE] bonds and transitioning to the liquid phase with a lot more disorder, it would increase.

RAFAEL JARAMILLO: Good, that's good intuition. You're thinking you're increasing disorder, so entropy has to increase. That's right. And the math bears you out. ds equals dq over t. So as long as there's dq, we have ds. The slope is fixed. So we're going to increase there our entropy, literally with the added heat. Now, all right, great. We have melted all the solid. And let's keep on heating the system, what's going to happen now?

AUDIENCE: So it would kind of look similar to when we were in phase one, but I think the slope would increase.

RAFAEL JARAMILLO: Thank you, So let's see. So let's say we're going to have-- we're going to have increase. We're going to be back in this kind of a regime. I don't know what the temperature dependence of the heat capacity is. But it tends-- the heat capacity tends to increase with increasing temperature. You might know that from some experience recently.

So I draw that with a slightly decreasing negative curvature. But it's kind of neither here nor there. And down here, the entropy continues to increase. But it's going to continue to increase at a slowing rate. So let me use a different color here. And so let's make this really explicit, this slope, that slope is 1 over cp of the solid phase.

And its-- I drew it as weakly temperature dependent. I drew some curvature there. And this slope is 1 over cp of the liquid phase. And so these heat capacities can be temperature dependent. So there's some curvature there. Good, so phase one was heating the solid phase. Phase two is melting. Melting solid at the melting point. And phase three was-- step three, I should say, liquid. OK, so that's good. Now, let's draw another plot, which is let's draw now-- before I had q as my control parameter.

You're burning fuel. And that's the control parameter. But now, I want a parametrically plot, or before 2 dependent parameters, s versus t. So I'll start you off here, s versus t it's like this until we reach the melting point. Now, so this is phase one. What does s versus t look like in phase two?

AUDIENCE: I think it's still a line.

RAFAEL JARAMILLO: Yeah, it's a line. But with what slope?

AUDIENCE: I think still a positive slope, but not curving.

RAFAEL JARAMILLO: Well, in phase two, is entropy changing? You're adding heat energy to the system. So entropy is changing. In phase two, is temperature changing?

AUDIENCE: It's also heat added in some substance to get the temperature to increase.

[INTERPOSING VOICES]

AUDIENCE: Sorry.

RAFAEL JARAMILLO: Go ahead, please.

AUDIENCE: Would it just be like a straight line up--

RAFAEL JARAMILLO: There you go.

AUDIENCE: Temperature isn't changing.

RAFAEL JARAMILLO: That's right. In phase two, we're adding heat energy. So we are increasing the entropy of the system. And as I think correctly pointed out, we're increasing disorder. We're melting the solid. So we definitely want that increasing entropy. But the temperature is locked at the equilibrium melting point. So we just have a vertical line up. And then at some point, at some-- it's after some amount of heat, we have melted all the solid. And we are-- so this was phase two. And we are back in the single phase region.

So this is the parametric plot of entropy versus temperature. And there's an important quantity here. The quantity is delta s solid to liquid, entropy of melting. So this is the quantity you're going to find in the databases. In fact, you'll find it in the appendix of the textbook.

The entropy-- or if you like, the enthalpy, or heat of melting delta h solid to liquid equals reversible solid to liquid equals t melting delta s solid to liquid. So the enthalpy of melting is another thing which you'll find in the databases.

Or maybe you'll find the melting point. You see that there's one equation here that relates enthalpy, melting point, and entropy. So often, the databases, including the textbook, may not give you all three numbers because from any two, you can determine the third. So if you ever go to a database, and this will happen to you, I promise you, in your professional life, where you're looking for, let's say, enthalpy. And the database doesn't list it. It lists entropy, and heat, and equilibrium transformation temperature, you'll be momentarily annoyed. And then you'll say, oh yeah, I'll just calculate the enthalpy change from the entropy change and the melting temperature.

That's happened to me more times than I care to think about. OK, good. So these parametric plots happen a lot in thermo. I hope you're getting used to them. You have one on the exam, not quite that, but a parametric plot. All right, so let's have some facts about phase transformations. The higher temperature phase always has higher entropy.

So if you have a transformation from a low temperature to a high temperature phase, high temperature phase always has higher entropy. Let's see how that works out. Let's consider now a generic solid solid transformation, alpha to beta. Consider alpha to beta. And they coexist at some temperature. That's the transformation temperature.

So at that temperature, heating converts alpha. Heating converts alpha to beta. That's the definition of beta being the high temperature phase. So that means that as we convert alpha to beta, dn of alpha equals minus dn of beta is less than zero. We're transforming moles of alpha into moles of beta.

We also know that heating increases the entropy because ds equals dq reversible at the temperature that this is happening, which is t alpha beta, which is greater than zero. We also know that the entropy is extensive. So s equals n of alpha, s of alpha plus n of beta s of beta. And here, I'm going to do-- right around here, it's useful to start using different notation for extensive versus molar quantities.

So I'm going to put a dash here. This is consistent with the textbook. Quantities like s of alpha or s of beta, so forth, are molar entropies. That is entropies per mole, which are intensive properties. Quantities with a dash are total entropies and are extensive.

So we're going to use that from here on out. It's consistent with the textbook. Previously in the class, I think it's been-- it would have been more confusing than worth it to introduce this notation. But from this point forward, it becomes worth it. So questions. This is a good time for questions on what this means, because we'll be using this notation a whole heck of a lot.

OK, well, I'll let you come back.

AUDIENCE: Yeah, I have a question. The line where it says heating converts alpha to beta, is that talking about molar quantities?

RAFAEL JARAMILLO: Well, here, it's just a phase label. So it's not really molar quantities. But here, what we're saying is that we're converting moles of alpha into moles of beta. So n of alpha is the number of moles of alpha. And n of beta equals the moles of beta. And so this equation is conservation of mass. And I'm only saying that I'm going I'm transforming from alpha to beta. That's why that's less than zero.

I don't know if that's helpful. Ask me again. Let me make the conclusion here. And then ask me again if that's so-- so all these facts that I'm heating, that beta is a high temperature phase, that heating increases entropy, and entropy is extensive, these require-- I wrote r three times, require that s of beta is greater than s of alpha.

Hopefully that's intuitive. If I'm converting from alpha and beta and I'm increasing the entropy, then beta has to have more entropy than alpha. That's all there is to it, really. And what this means is what does this actually mean? I had two phase system. Beta is a high temperature phase.

Let's use a nice blue for the low temperature phase. And I have a phase boundary between them. The phase boundary is moving. The phase boundary's on the move. The beta phase is expanding at the expense of the alpha phase. So entropy is increasing. All right, so let's talk about building unary phase diagrams. We've talked a little bit about what happens when the phase is transformed. How do we build the diagrams?

And I'll remind you that the reading for this is chapter 7. So first, I want to talk about the role of chemical potential. Why do I want to talk about that? Role of chemical potential, well, let's remember that the change-- now, I'm going to use this extensive thing. The change in the total Gibbs free energy of a system equals minus sdt plus vdp plus-- let's see, what do I want to use-- I'll use k. u component-- well, no, this is a phase label because it's unary.

So I've got some temperature. I've got some pressure. And I've got the potential to transform between phases. k is a phase label. OK, good. So at fixed temperature, at fixed temperature and pressure, I get to ignore 2/3 of the right hand side of the equation. That's why those are the natural variables. At fixed temperature and pressure, equilibrium condition is dg equals-- it becomes really rather simple.

So let's talk about what that means in reality. Here's phase alpha. Some two phases, here's phase beta. And they're going to have a phase boundary between them. And alpha phase has chemical potential mu of alpha. And beta phase has a chemical potential mu of beta. And this phase boundary is open, so mask and flow. So that means that a molecule is free to jump from beta to alpha.

So let's imagine this is a dn of beta. And this is a dn of alpha. And we require mass conservation. It means that dn of alpha equals minus dn of beta. So what happens if the chemical potential of beta is less than the chemical potential of alpha?

What happens if the chemical potential is beta less than the chemical potential of alpha? Let me write that down. If mu beta is less than mu alpha then what will happen?

AUDIENCE: Alpha start going to beta.

RAFAEL JARAMILLO: The mass will flow from alpha to beta to decrease Gibbs, right? So there's going to be a little bit of a downhill flow. There's a driving force for the mass to flow from alpha to beta to lower the overall Gibbs energy. Similarly, if mu of alpha is less than mu of beta, then mass will flow from beta to alpha to decrease Gibbs.

So what's the one and only scenario in which the system undergoes no spontaneous change, where the two phases coexist without any net flow of molecules from one phase to the other?

AUDIENCE: The mu of alpha equals mu beta.

RAFAEL JARAMILLO: Right, transition for phase coexistence is mu alpha equals mu beta. That's right. So if and only if the chemical potentials are equal, then there's no driving force for a molecule of beta to hop into alpha. And there's no driving force for a molecule of alpha to hop into beta.

Those transformations will happen spontaneously on a microscopic level. But on a macroscopic level, they'll balance out. There'll be no net flux from one phase into the other. And so observing the system, we'll see that these two phases are in equilibrium. They're coexisting. And one is not spontaneously transforming into the other. That's the meaning of phase coexistence.

So this is yet another example of what I call Gibbs free energy price shopping. Nature molecules, at fixed temperature and pressure, they go price shopping for Gibbs-- lowest Gibbs free energy. Whatever is the lowest, that's what they're buying. That's what they choose.

Risking some extreme amount of anthropomorphization here. But I find that helpful to think about. All right, so that's the role of chemical potential. It tells molecules where to go to reach equilibrium. What is chemical potential?

What is this mysterious thing that's so important? Well, first of all, just a reminder, chemical potential is the partial of Gibbs by mole number at fixed temperature and pressure. In other words, it's the molar Gibbs free energy. So if you have a system for which Gibbs free energy at t and p and 1 mole equals mu, then the Gibbs free energy for t, p, and some arbitrary number of moles equals n times mu.

So that's what chemical potential is. We've done some calculations of how it varies. You're going to do a lot more. Let's talk-- have we done calculate-- yeah, we have. Determining phase equilibrium. That is how do we draw phase diagrams. How do we do it? It's a three-step process.

Step A, at each pressure and temperature, calculate mu for all possible phases. k is a phase label. So we're going to calculate this thing, mu, and we'll say equilibrium at a given temperature and pressure is the phase with lowest mu.

And as we've seen a couple of minutes ago, if multiple phases have the same mu, then they can coexist. So that's the conceptual way to build unary phase diagrams. And I'll tell you, this is how CALPHAD software does it. So soon, you're going to be playing with CALPHAD software. If you haven't downloaded and installed ThermoCalc student version, please do so.

And what that software does, and really, the software helps you gain an intuition for this. What the software does is it calculates mu of k for all the phases that it knows about. And then it goes Gibbs free energy price shopping. It looks for the lowest one. And it makes a map of the lowest ones. And where two phases coexist with the same chemical potential, it draws a coexistence line or coexistence point.

So I find it helpful to think of these in three dimensions. And unfortunately, this means I'm going to have to draw in three dimensions. So I'm going to try here to draw a couple of chemical potential surfaces. I think even the process of watching the struggle to draw these will be instructive. Of course, there are better pictures in a textbook.

So let's see. Mu of t and p is the surface, right? It's a function of two variables. It's a surface over the tp plane. And each phase has its own surface. OK, so let's see. Let's try to draw that. Let's draw-- all right, so let's draw the first surface. I'm going to draw some phase here. It's going to have-- running out of purple. Don't like running out of purple.

All right, let's make this look really nice and three dimensional. All right, t, p, and g. And then let's draw another phase. Let's draw a blue phase. So let's call this phase alpha. And let's call this phase beta. So these-- I'm just drawing sections of surfaces. These are functions, right?

This is mu as a function of pressure and temperature for phase beta. And this is mu as a function of temperature and pressure for phase alpha. OK now, let's think about a given temperature and pressure point. Grab another color. Let's think about pressure and temperature point down here. And let's-- if I draw a vertical line, I cut that surface.

And then I cut that surface. Whenever I cut it, I draw a little thing there. All right, so at this t and p-- this pen is totally dead-- at this point, I'm drawing with fading pink. Let me just toss that marker on to the floor so I'm not tempted again. At that point, what's the equilibrium phase, alpha or beta?

AUDIENCE: Alpha the equilibrium phase because it has the lower Gibbs energy.

RAFAEL JARAMILLO: Thank you. That's right. So you imagine a number of these manifolds, these surfaces. And the computer, you don't normally have to do this, the computer does it for you. It calculates Gibbs free energy for each point. That's a function, calculates Gibbs free energy as a function of t and p. And at any given point, you can look at this and say, oh, alpha is the equilibrium phase because it has the lower Gibbs free energy.

Another thing to point out here is there is a distance, a vertical distance between those two surfaces. It's the change of Gibbs free energy from alpha to beta. And that thing is a function of temperature and pressure. So I want you to imagine that this is a surface with some curvature. This is a surface with some curvature. And as I move my pointer around on the xy plane, the vertical distance between those surfaces will change. In general, it's temperature and pressure dependent.

So this is, again, a fancier version of that transformation quantity, which we saw in the first 10 minutes of lecture with entropy. With entropy, we had this transformation quantity. This transformation quantity was a delta entropy at a given temperature. And it's assumed here, this is all at some given pressure. So here's a delta s as I transform, in this case, from the solid to the liquid phase.

This is in water. Well now, I have, again, a transformation quantity. I have a delta g. I say transform from the alpha to the beta phase of some unknown material. This is very generic. This will apply to many, many different materials. And now, we've made it explicit that transformation quantity, its distance, is both temperature and pressure dependent.

In about a week and a half, we'll see it's also composition dependent. And then I no longer have any chance of being able to draw this. But the concepts remain the same. OK, I want-- I'm going to stay here for a minute, even though I'm worried about time. But this is such a critical concept. I want you to-- I want to refer you to a little mini-lecture that I recorded called the three D's of thermodynamics.

This is about delta, delta, and delta. It is confusing when you first see it. We have all these change quantities. And so I hope that little mini-lecture helps clarify this point a little bit. I also want to share a page from the textbook, a page from the textbook, which, of course, does very beautiful drawing. This is-- they're drawing this as mu, the same thing as g for urinary system, molar Gibss free energy for-- let's see, they're drawing this here for a liquid phase.

And then they drive separately-- sorry, they're drawing this here for a solid phase. And they're separately drawing this here for a liquid phase. And then when they put the two drawings together, you'll see that there are points where those two surfaces touch. Two surfaces intersect along a line. That's just a geometric effect. So what we're seeing here is that there is a line of phase coexistence, where solid and liquid coexist.

And that's what we saw at the very beginning when we started with the phase diagram of water. There's a line of phase coexistance. Those lines are where these surfaces intersect. So I didn't try to draw this on my graph paper. But it's the same concept as what I did try to draw. So let me go back to the camera. And why don't I finish up. And then hopefully we'll have some time for questions.

All right, so how do you actually calculate this thing? Calculating delta mu for, let's say in this case, a change of t and p. All right, this thing is a function of t and p. So it's going to vary as we vary t and p for a given phase. Let's see, all right, so we know something. We know that the d mu equals minus s dt plus vdp. That's molar Gibbs free energy.

So that means that the change in mu is initial to final d mu. That's just fundamental theorem of calculus. And now, I have to plug something in. So now, I'm going to have-- well now, I better draw some coordinates. Let's see. Here is temperature. Here's pressure. Let's say here's my initial point. Here's my final point.

And my actual process that I'm trying to engineer might be this. But we're talking state variables here. So I can take any path that I like. And so naturally, I want to integrate first along one fixed, variable, and then along the other fixed variable. So let's make that explicit.

We have initial, then final. Let's see, I did dp first. I did dp first. v, and this is a function of t and p. And then I'm going to go from my initial to final dt. And here, I have minus s, which is itself a function of t and p. So I'm integrating the change. The fixed temperature, and then I integrate this change for fixed pressure.

And so this is it as far as the calculus is concerned. This implicitly assumes that we know the equations of state, there's plural equations of state, v as a function of t, p and s as a function of t, p. So formally, it's all well and good. It's relatively easy to write down.

In practice, you're probably going to be making some approximations. Or the computer is going to be doing a numerical integration based on database values, or so forth. Right now, we're at the level of concepts. All right, let's go one step further.

In general, we don't know v t, p and s t, p. But we can calculate from standard values. Let's say s0 and v0, standard values, standard conditions.

So for instance, we know that ds equals t, p over t dt minus v alpha dp. And we know that dv equals v alpha dt minus v beta dp. And so if we have data, we can take standard values and integrate the change in s and v as we vary temperature and pressure. And this highlights that s of t and p and v of t and p, they're also surfaces over the tp plane.

So your mind has to think about all these surface in multi-dimensional space, the surfaces of the state functions. They might be entropy. They might be Gibbs free energy. They might be volume. Depends on what you're trying to calculate. In principle, you could do the calculus if given the equations of state. In practice, it's a computer going to be doing it for you.

One last-- one last line in this vein. And we'll be done. So let's talk about calculating delta mu for a change of phase at fixed. So we just talked about how to do it for varying t and p. Now, let's talk about change of phase. So delta mu is the same thing as delta molar Gibbs free energy equals delta h minus t delta s. For isothermal process, t is fixed. So we have delta h minus t delta s.

At phase coexistence, at phase coexistence, delta mu equals 0. We figured that out about 40 minutes ago. That for two phases to be coexisting in equilibrium, they have to have the same chemical potential. So that means at phase coexistence, delta h equals t delta s. Another-- we were here again about 40 minutes ago. This is a very, very useful expression.

And these values, these are tabulated. So turn to the back of the book and you'll see tables of these data. Away from phase coexistence, away from phase coexistence, we can evaluate delta h and delta s, again, from standard data h0 and s0 and the differential forms, which in this case, are dh equals cp dt plus v1 minus temperature alpha dp. And ds equals cp over t dt minus v alpha dp.

Again, these are surfaces. These are state function surfaces over the tp plane. So it's exactly 10:55. And I got through what I wanted to get through. The main thing I want to leave you with is this visual. All of these state functions are surfaces over the temperature pressure plane. They each have their own local curvature as a function of temperature and pressure.

When comparing phases, we compare vertical distances between surfaces. What's the difference between alpha and beta at this temperature pressure point? When calculating changes as a function of temperature and pressure in a given phase, we consider moving along these surfaces. And the calculus that we've established so far to this point in the class gives us everything we need to do those calculations.