[SQUEAKING]

[RUSTLING]

[CLICKING]

RAFAEL JARAMILLO: Let's get right into it. We are-- I'm going to overview here thermodynamics of binary phase diagrams. That's what we're working on. So we've done notation and bookkeeping, notation and bookkeeping. We've talked about solution modeling. And we've talked about spinodal systems in some detail-- spinodal systems.

And this is spontaneous unmixing, so phase separation, when both phases are in the same-- so this is-- we haven't made too much of this yet. But it's been underlying our talk about the spinodal, which is that-- this red pen is dying. Life is too short to keep dying sharpies on your desk.

So spinodal systems are spontaneously unmixed when both phases are in the same structure. We haven't made a lot of this yet, but it's been an important point that all the spinodal systems, it's the same structure. You have a chromium-rich bcc and an iron-rich bcc, or an ethanol-rich liquid and dodecane-rich liquid, or so forth and so on. But the structure is the same.

And so this is our story thus far. And what we're going to do is we're going to now generalize this to analyze what happens when you have phase separation between two phases that have different structures. And so when you had two phases that had the same structure, you only need one solution model. You only need one solution model to analyze the free energy, to analyze the free energy composition plots.

So today we're going to start introducing more complexity, which is having multiple solution models. And more generally, the pure components-- What do I mean? Pure components may be in different structures. Let me illustrate this with a simple example. Let's do silicon germanium. It's one of my favorites. Does anyone remember, who has a higher melting point, silicon or germanium? Give you a hint.

STUDENT: Is it germanium?

RAFAEL JARAMILLO: No, it's silicon. Lead is very soft, very soft. We know that lead melts. We saw it run off the roof of the Notre Dame a couple of years ago in Paris-- then tin, then germanium, then silicon. Carbon, it doesn't even melt. It's [INAUDIBLE] at 3,700 kelvin. So as you go up here, you have stronger and stronger covalent bonds, meaning higher and higher melting points. So silicon has a high melting point than germanium. Thank you, mousepad.

All right, so here's what we're going to have is we're going to have a lens diagram, which looks like this. Here's the melting point of germanium. And here's the melting point of silicon. And, of course, this is a two-phase region. As we saw in the last lecture, this is a fully miscible system with a fully miscible liquid, and a fully miscible diamond-structured solid-- sometimes just use alpha for the ground state solid structure-- so fully miscible system.

So if you're below the melting point of germanium, you only need one solution model to analyze this whole phase diagram. That is the solution model for diamond-structured silicon germanium. And if you're above the melting point of silicon, you also only need one solution model to analyze the whole system. That is the liquid-phase solution model.

But if you are in between these two temperatures, you need two different models because the endpoints are at two different structures. So if you have a temperature, which is intermediate, we need two different solution models to analyze the system. So let's look what that looks like. So for temperature less than the melting point of germanium, we can draw a free energy composition diagram.

And let's just say it looks something like this. This is going to be x. And let's just say it looks like this. For some , temperature, low temperature it's fully miscible. All the solutions, solid solutions, are stable. So we have that positive curvature. And I'm going to label that alpha because that is the alpha-phase solution model. Here.

For temperature greater than the melting point of silicon, I'm again going to have a relatively simple looking for energy composition diagram. The liquid is fully miscilbe. So we expected downwards curving for energy composition diagram. And I'm going to label that liquid.

But things get a little bit more interesting when we are in between. When we were in between and we have different reference states, that is the pure components are in different structures-- I'm just going to go ahead and draw it and we could talk about why it is. So let's see.

This is the silicon axis, the x silicon axis. So when I'm on the left-hand side of this free energy composition diagram, what is my composition? What is my system made out of when I'm along this axis? This is the silicon opposition axis.

STUDENT: From the left it's germanium and on the right it's silicon.

RAFAEL JARAMILLO: Right, OK, good. So left is germanium, right is silicon. So what is the reference state of germanium in this temperature range? That is, what state do you find pure germanium at this temperature? And it's unstated that the pressure is 1 atmosphere unless stated otherwise. So what is the reference state? What is my state here of germanium? Or I should say, what's the phase of germanium in this temperature range?

STUDENT: Liquid.

RAFAEL JARAMILLO: Liquid. So my liquid-phase solution model is going to start from zero because the free energy of turning pure germanium into a liquid is zero. It already is a liquid. However, this is going to zoom up above zero for pure silicon. Pure silicon is solid alpha. So the solid alpha solution model starts at zero. And that is going to zoom up above the zero axis for germanium.

What is that telling us? That's telling us that if you have pure germanium, you have to input free energy to turn it into a solid. Or if you have pure silicon, you have to input free energy to turn it into a liquid because those are not equilibrium states.

So we're going to read the equilibrium states of the pure components from the solution model that intercepts zero on a free energy and mixing plot. And what do I have here? I have a common tangent. And I expect to have a common tangent because I have a two-phase regime. For these temperatures, I have a two-phase region. So we're going to be analyzing this in quite a bit of detail.

Let's consider the process. All right, let's consider the process of actually making a solid solution at some intermediate temperature. And this is not going to be the process that you would use in the real world. This is going to be thermodynamics where we can take any process we like and imagine a reversible process and calculate changes in state functions.

So what I'm going to first do, so I have-- what are my starting-- what are my starting materials? Again, liquid. So I have here a beaker, a beaker of liquid germanium. That is not so clear. Here's a beaker of liquid germanium. And I have, let's say, a crucible of solid silicon. That's my starting point.

I'm at this high temperature. My pure components are liquid germanium and solid silicon. And let's imagine a process that converts this starting system into an alpha-phase solid solution. So here's my process. First, I'm going to convert the germanium from liquid to alpha phase.

Maybe you can do this in reality. But you can definitely do this in your mind. You can definitely do this when you do a calculation. So in your mind, you're going to take some pair of atomic tweezers. And you're going to pick up each and every atom. And you're going to force it into the diamond-cubic structure and hold them there.

This is called a reference state change. reference date change, it's sort of the topic of today's lectures. And the second thing I'm going to do is I'm going to mix solid silicon and solid germanium in the alpha structure. I'm going to mix them. This is described by solution model, which we have already spent some time with.

All right, so we have two steps here, two conceptual steps. The second step we spent time with you're at least somewhat familiar with. The first step is new. Reference state change, this is new. And if I want to do this, if I have liquid germanium, and I imagine a process that converts it from liquid to alpha phase, is it going to go up in Gibbs free energy or down in Gibbs free energy?

STUDENT: Up in Gibbs free energy.

RAFAEL JARAMILLO: Up, I think you said up. Let's say you said up because up is right. At this temperature, the germanium is liquid. So nature is telling you, I am happiest as a liquid. My Gibbs free energy is lowest when I'm a liquid. That's the reference state. That's what equilibrium is in nature.

So if you're going to force it into a different state that you don't find at equilibrium, by definition you're going up in Gibbs free energy because at fixed temperature and pressure, equilibrium is a state of lowest Gibbs free energy. So thank you for that.

And if you look at our free energy composition diagram here, for pure germanium, we're going to imagine there's an intercept of this curve. And we'll be drawing these more and more. This is a gamma [INAUDIBLE] alpha. This was a liquid.

And on this plot, which is a plot with units of joules per moles, a Gibbs free energy plot, there's some Gibbs free energy you need to put in. You need to pay some Gibbs free energy to convert the system from liquid into alpha phase. And, again, with a few exceptions, this is not how you actually do it in the lab or the factory. But it is the way you analyze it and get the right answer. So let's talk about how much free energy is required to effect these reference state changes.

STUDENT: I have think quick question actually, if that's all.

RAFAEL JARAMILLO: Yeah.

STUDENT: So is the reason that the Gibbs free energy goes up, is that because of-- that the delta S is changing?

RAFAEL JARAMILLO: Well, delta G equals delta H minus T delta S for isothermal processes. This is sort of-- I want to bring you a question all the way back to the baby book. The whole class is about balancing delta H and delta S.

And so, in general, you don't know. If you have some transformation that raises Gibbs free energy, it could be an enthalpy-driven thing, or an entropy-driven thing, or both. In general, you don't know. Now, in this case, if we take liquid germanium and we're turning it into solid germanium, what do you think the change in entropy is?

STUDENT: I think it would decrease just because it's a solid.

RAFAEL JARAMILLO: So let's write that down. Delta H liquid to alpha, and delta S liquid to alpha. So delta H liquid to alpha-- delta S, sorry, delta S is less than zero. That's what you just said, that the entropy decreases. And that's exactly right. The liquids are more mixed up. They're more disordered. They have higher entropy. Let's just finish the argument. What about delta H? Is delta H bigger than zero or smaller than zero?

STUDENT: Is it like an exothermic reaction, going from liquid to some sort of solid?

RAFAEL JARAMILLO: It's good thinking. So remember, high-temperature phases are higher enthalpy phases. The liquid is the higher temperature phase. The solid is the lower temperature phase. So it's exothermic. Another way to thinking of this is there are heats of crystallization. There are heats of crystallization Or heats of condensation if it's-- maybe you're thinking about climate systems. And I'm looking at the window thinking about climate systems and thinking about phase changes in water.

But, yeah, you're exactly right. It's going from a high-temperature phase to a low-temperature phase. So it's necessarily lowering the enthalpy and also lowering the entropy. So we have this thing which is negative, and this thing which is negative, so this thing which is positive. So you don't necessarily know whether delta G will be positive or negative if this is all the information you're given.

But in this case, I'm telling you the temperature is above the melting point of germanium. So you know that the Gibbs free energy, change has to be positive because if it were negative, this wouldn't be the reference state. But let's analyze this graphically a little bit, is where we're heading. Does that address your question? I didn't see you ask that, but--

STUDENT: Yeah, that makes sense, thank you.

RAFAEL JARAMILLO: I love the questions and interruptions. It's hard to really have a back and forth over zoom. I know that, but the more the better. So let's talk about the temperature dependence-- temperature dependence of the free energy of the pure components.

Everything that we learned from unary phase diagrams we're going to need here. We're going to need to use all that stuff in order to build up binary phase diagrams. So let's draw that for germanium and silicon. This now is going to be temperature. And this is going to be Gibbs free energy. And this is going to be for pure germanium-- pure germanium.

I'm going to draw the Gibbs free energy versus temperature curves for the two phases in question here, alpha and liquid. OK, first off, let's recall, Gibbs free energy versus temperature, is this-- have a positive slope or does it have a negative slope?

STUDENT: A negative slope.

RAFAEL JARAMILLO: A negative slope. And the curvature is negative as well. So let's draw the Gibbs energy for alpha phase. Let's just say it looks like that. All right, now I want to draw it for liquid phase. How should the Gibbs free energy for liquid phase look?

By the way, let's just mark-- let's mark the melting point here. It's kind of a hint. How should the Gibbs free energy per mole of the liquid phase look?

STUDENT: Should it also be negatively sloped and cross through the alpha phase?

RAFAEL JARAMILLO: Cross through, perfect. So it's going to more or less look like this, except there's going to be some important features. It has to cross the alpha phase where they coexist. Where those phases can coexist, their Gibbs free energy has to be equal. We know that from the unary phase diagram module. So it's got to cross that. At high temperature, does it lie below or above the solid?

STUDENT: Below the [INAUDIBLE].

STUDENT: Below.

RAFAEL JARAMILLO: Right, great. So here we have it. How's that? That looks good. This is completely consistent with what we know about the phase diagram. At high temperature, the liquid phase is the equilibrium phase. It has lower Gibbs free energy. At low temperature, the solid phase is the equilibrium phase. It has lower Gibbs free energy.

At the coexisting temperature, they cross. And they have the same Gibbs free energy. And now we can see graphically the measure of what we need to pay to transform germanium from liquid to solid. And we can see that this measure flips sign once you cross through the coexistence point.

So this is the energy you need to pay for that reference state change. Let me draw something similar for pure silicon, which will basically look the same except I'll put the melting point higher. That's make believe because I haven't really labeled the axes, but.

Liquid, alpha, and we have, again, a measure delta G-- this is silicon-- liquid to alpha. And it's sign flips as we go through the melting point. So there's a reason why we spent time on these sorts of plots. I know we plotted S and we plotted H. Now we're plotting G.

There's a reason we spent time on these sorts of plots back when we were doing unary phase diagrams. It's because you need to have these in the back of your mind as you're building binary phase diagrams. You need to understand this stuff is the data input that goes into binary phase diagrams.

Or as I've mentioned before, if you look at a binary phase diagram, the unary phase diagrams are kind of hidden here. That is an isobaric slice of the unary phase diagram of germanium. And that is an isobaric slice of the unary phase diagram of silicon. So this stuff comes-- this stuff is essential.

OK, so how do we account for this? How do we account for this? Accounting for delta G of some component k-- now I'm going to make this a little more general-- any transformation between any two phases alpha to beta. And that, of course, is a function of temperature that is temperature dependent. And as we've just written down, this is delta H, alpha to beta. And that thing is temperature dependent minus T delta S alpha to beta. And that thing, of course, is also temperature dependent. It does both, maybe temperature dependent.

All right, at the alpha/beta coexistence temp, at their equilibrium coexistence temp, we'll call that T alpha, beta, at that temp, delta G equals zero because they're in equilibrium. Often, we will make an assumption.

And I want you to recall back to some problem sets and such where we did this. If the transformation heat capacity, that is the difference in heat capacity between the two phases, can be ignored, then delta H and delta S are approximately temp independent.

So, again, this is stuff from unary phase diagrams we're recalling. In the case that the heat capacity difference is negligible, then you have approximately temperature independence of those things. And when that is the case, your expression for the temperature dependence of the Gibbs free energy simplifies. And you should convince yourself. Work this on the side after class-- a few lines of algebra, five minutes of your time. All right, so that is a simplification.

This thing is linear in T. And what do you need? What data do you need to evaluate this? You need transition temp and the entropy of the transformation. And that's the sort of data that-- as a reminder, that's the sort of data you get in databases. So here's, for instance, phase transformations of the elements. Here's a bunch of phase transformations of pure materials.

And normally you get these triples. You get a temperature-- I know it's blurry, but I'm looking at the book, Appendix C. There's a temperature of the transformation, a delta S of the transformation, and a delta H of the transformation. So this is the data that you find in databases.

OK, so let's keep moving. We're talking about two-phase equilibrium. We're talking about coexistence, solving for two-phase coexistence. Let's make this specific. Let's go back to the case of silicon germanium where we know we have two phase coexistence in between the melting temps.

And so we're going to use our two-phase coexistence conditions from previous. What's that? Chemical potentials are equal. Chemical potential of silicon and the alpha phase equals the chemical potential of silicon in the liquid phase. And that's going to become the following. The chemical potential of silicon in its reference state-- what's the reference state of silicon, somebody, at this temperature, below the melting point of silicon?

STUDENT: Solid.

RAFAEL JARAMILLO: Solid, thank you. So the chemical potential of silicon in its reference state, which is a solid, plus the mixing term in the solid phase-- that, that's that. Now we're going to do the right-hand side. The right-hand side, we have chemical potential of silicon in its reference state, which is solid. Now we need to pay some free energy. We need to get silicon from solid to liquid. And then we need to mix in the liquid phase.

So mu silicon zero equals reference state, reference state for pure silicon, which here is alpha-- delta mu silicon alpha mixed. What's that? Solution model for alpha phase solid solution. Delta mu silicon mixed in the liquid, that comes from a solution model for liquid phase solution. And delta mu silicon alpha to liquid, that's called a reference state change.

So you're all going to be great accountants when you're done with this class because that's what we're doing here. It's just accounting, accounting, accounting. Let's do the same thing for the germanium. The other equilibrium condition is that the chemical potential of germanium in the alpha phase is the chemical potential of germanium in liquid phase. So this is a two-phase equilibrium condition that we've derived very recently.

And for this case, you end up with chemical potential of germanium in its reference state. Its reference state is the liquid. So we need to pay some free energy to get germanium from liquid to the alpha phase. And then we're going to mix germanium in the alpha phase. And that is going to be equal to chemical potential of germanium in its reference state, which is liquid. And so now all we need to do is make the liquid solution. So, again, we have the liquid stuff and the solid stuff.

So I'll be really explicit here, mu germanium zero equals reference state of pure germanium, which here is the liquid phase. Delta mu germanium mix in the liquid comes from the solution model for liquid-phase solution. Delta mu germanium mix alpha comes from the solution model for alpha-phase solid solution. And delta mu germanium liquid to alpha is a reference state change.

So we're really, we're bringing out all the stuff that we've done to this point in the semester. Everything we've done is needed here. We need to be able to calculate the temperature dependence. We need to be able to identify our reference state. So we need to be able to read unary phase diagrams.

We need to be able to analyze solution models, solution models. And you're going to have different solution models for different phases. So we need to analyze solution models. We need to be able to calculate Gibbs free energy changes for pure materials going through transformations.

And in order to do that, we need to calculate temperature dependence of enthalpy change transformations and entropy transformations. And in order to do that, we need data for temperature dependence of heat capacity. So it's like, it's all coming together in this process of making binary phase diagrams.

So I want to say one final thing, and then pause, and have a brief discussion about the p-set and take questions. So if both solutions-- we have two solution models here, alpha and liquid. If both solutions behave ideally-- which is not realistic, but it's a nice model.

If both solutions behave ideally and if the heat capacity difference is approximately zero for both pure components-- so a lot of ifs here-- then the coexistence conditions-- phase coexistence conditions being mu k alpha equals mu k-- well, let me make this not liquid. Let me make it beta so it's a little more general. That's coexistence conditions-- can be solved explicitly.

And you have closed-form equations, functions for the resulting phase diagram. So the math there is a little bit complicated. We're not going to do it in this class, but section 10.2.1, figure 10.22. So DeHoff does this. It's kind of interesting-- figure 10.22.

So if those conditions are met, then you can have different types. All different phase diagrams that can emerge. And this is an example of the different types of binary phase diagrams that you can get. And so these are all two-phase systems. It's alpha and liquid, alpha and liquid, alpha and liquid, alpha and liquid. It could have been called alpha and beta. It doesn't matter. And you can get different shapes, different types of lens diagrams there.

But that's not very general. It doesn't look like what nature provides us. In all other cases, we use computers. So in all other cases, we let the computer do the work for us because it becomes unrealistic to do it ourselves. And so we use the computer to evaluate these equilibrium conditions, or it's saying the same thing to say we use a computer to evaluate the common tangent conditions and draw the phase diagrams for us.

So in the days and weeks ahead, we're going to be using CALPHAD more and more. We're going to be using Thermo-Calc more and more. We're going to use some other software that we wrote to play with these free energy composition diagrams. We'll have a guest lecture by Professor Greg Olson who has made a very successful career, built largely from data-driven predictions of high-performance materials using CALPHAD tools. So that's where we're heading.