

**RAFAEL
JARAMILLO:**

So today, we're going to continue working on the thermodynamics of binary phase diagrams. And just as a reminder of where we're going, PSET 7 is due Friday. And that's a very lightweight PSET, reflecting the holidays. PSET 8 is a much bigger problem set, and is going to involve using several different pieces of software that we're going to spend the next week learning and exploring.

So I'll just get into it. But if you have any questions about the timeline of the class for the next week or so, please speak up.

And we have settled into DeHoff, chapter 10, which is really the most substantial chapter in the textbook. And there's a reason for that. It combines everything that we've learned, and it's the most substantial unit of this class.

So we are in a holding pattern in DeHoff chapter 10 for at least several lectures.

OK, so we're going to learn about the taut rope construction. And we're going to do that with the example of a lens diagram that we've already seen. That is, the silicon germanium system.

So I'm going to start by drawing the phase diagram of the silicon germanium system. Who has a high melting point, silicon or germanium?

STUDENT:

Silicon?

**RAFAEL
JARAMILLO:**

Silicon has a higher melting point. It's more strongly covalently bonded, because it's a smaller atom. And it's higher up on the periodic table in that column. So it has a higher melting point. So let's draw the lens diagram here, and there we have it.

There is the melting point of silicon. And here is the melting point of germanium. And I'm going to mark some temperatures. We're going to have T1, I'm going to have T2, goes right through a nice tie line there. I'm going to have T3, nice tie line there.

And I'm going to have T4. And so this, of course, is the lens, has tie lines everywhere. I'm going to just draw a couple.

And a low temperature, we have solid phase, which we know is a diamond cubic crystal structure. And high temperature, we have liquid phase.

All right, and what we're going to do is I'm going to draw the three energy composition diagrams at four different temperatures. One, two, three, and four. So let's start with T1.

So at T1, this is ΔG mix. At T1, would somebody like to tell me what my solution model for the alpha phase should look like? I'm going to-- what should my solution model for the alpha phase look like for T1? Its low temperature?

STUDENT:

Should it be negative at all points?

RAFAEL Negative at all points, and curved upwards. Because this is a fully miscible system. This is a solid solution that's stable at all compositions. That's what the phase diagram tells us. So there is a solution model for T1.

JARAMILLO:

All right, now, the slightly harder question here-- what should my solution model for the liquid phase look like at T1? This is new. This, you know, but this next question I asked, this is new.

I'll tell you, because it's new. It's going to look something like that. Why is that? This is a model for the free energy of a phase, which is never stable. We can still model it, though. You see, I'm not drawing it across the full composition range. This model shoots up to some high value at the two y axes.

Why? Because it takes free energy to turn germanium or silicon from alpha into liquid at this temperature. So we have to imagine this shooting up to some high value. But we can draw it, and we can think about it. That's T1.

All right, what about T2? T2 is-- we've seen this, T2, we've seen. So what is this going to look like at T2?

For pure germanium, what is the reference state at T2?

STUDENT: Liquid?

RAFAEL Liquid. So my liquid solution model has zero free energy for pure germanium. What is my reference state for silicon at T2? Right here?

JARAMILLO:

STUDENT: The alpha phase?

RAFAEL The alpha phase. Next time, yeah, so there we go. And that's going to go up. So I have alpha phase. I have liquid phase. And I have now a common tangent.

JARAMILLO:

I have a common tangent, which is what we expect. Because we have here a tie line connecting two compositions. Now, I'm going to draw here for T3.

T3 is qualitatively similar, but the liquid phase has become more stable over more of the range. The alpha phase has become less stable.

So again, alpha, liquid, a common tangent. And lastly, somebody who has not spoken yet today, what is my free energy composition diagram at temperature of T4 that is up here. What is the only stable phase at high temperature?

STUDENT: Liquid.

STUDENT: The liquid.

RAFAEL Liquid. So what will the liquid solution model look like?

JARAMILLO:

STUDENT: Would it look like the plot for T1, except the curves are reversed now?

RAFAEL Exactly right. This is a case where the alpha phase is fully miscible, and stable everywhere. And here's a solution that's never stable. Now, we've just flip-flopped.

JARAMILLO:

The liquid phase is fully miscible, stable everywhere. And the alpha phase is unstable everywhere. Alpha-- great.

OK, now we're going to talk about the taut rope construction. So what I'm going to do is, I'm going to use green, and I'm going to imagine you're going to imagine putting a rope and anchoring the rope here and here. And imagine the rope is initially floppy-- you have a floppy string.

And it comes out this side. And I'm going to grab hold of the two ends of the string, and I'm going to pull it taut. What we'll see is the taut rope will now trace the alpha. It will trace the alpha solution.

All right, that was kind of silly. What happens in this case? If I do that in this case, the taut rope traces the liquid solution until the point of common tangency. And then, it becomes a straight line until it traces the alpha solution.

You can see that geometrically, right? If these were objects and you had a string and you pulled it taut, it would trace the solution, where the solution is stable, then it would trace the common tangent. And then it would trace the solution where the solution is stable.

What if you did it here? Pull the rope taut, it's going to trace the solution while it's stable, and then it will do the common tangent and then it will come up and trace that solution.

And similarly here, it's going to tell you that the liquid phase is stable everywhere. So this taut rope construction, which you can have this very visual sense of, gives you the phase diagram. At any given temperature, you do the taut rope, you pull the rope taut, and wherever the taut rope goes, that's your phase diagram.

So that's neat, right? That comes from two things. It comes from the fact that positive curvature implies a stable solution. We know that from previously.

And it comes from the fact that the common tangent condition defines the two phase region. So those two pieces of geometry, put together, give you the taut rope construction.

Any questions on that before we move on?

STUDENT: Do you always place the rope at the bottom part? Like below everything?

RAFAEL JARAMILLO: Yeah, loose rope, taut rope. Yes, you always put it-- imagine it hanging well below, and then pulling up. And it's always anchored at 0.

Imagine having little eye bolts. Imagine this thing is a geometrical object-- I wish I had a model of this. I've never seen a model. But something with balsa wood would be fun to play with.

And imagine you have eye bolts here, and you have a string and you put the string through the eye bolts, and then you pull up. Yeah.

Any other questions on this? This is meant to help. It's not meant to hurt. The taut rope construction is meant to illustrate how to find the free energy-- the minimum free energy configuration. That is, how to find equilibrium.

All right, let's move on. We're going to do more and more taut rope. It's not the last you'll see of it.

We're going to talk about eutectic reactions now. Eutectic reaction. So here's what a eutectic reaction is-- it's a liquid that transforms into two solids. A liquid transforming into solid one, and solid two. We'll visualize this.

Let me just define eutectic point, and we'll look at some phase diagrams. A eutectic point is a local minimum of the liquidus at temperature T_{eutectic} .

Do folks know what the liquidus is? I haven't defined that yet. Let me pull up the slides. And while I do-- while it loads, I'm going to define it. The liquidus is the locus of points on a binary-- on a binary phase diagram, above which, only liquid phase is stable. That's the liquidus.

All right, let's look at some phase diagrams. OK, so here is aluminum silicon. This is eutectic phase diagram. This is a very typical geometry. Your eye will pick out eutectics right away, because eutectics have this gull-wing shape.

This is the liquidus. This purple line here that I'm laser pointing out, is the liquidus. It is the locus of points above which only liquid phase is stable. And in the eutectic system, you have a local minimum to that.

It's also known as melting point suppression. So right there is the eutectic point. This phase diagram has a narrow region of FCC. Almost no solubility here of aluminum and silicon. So the solid solution of aluminum and silicon here in the diamond structure is too narrow to view on this phase diagram.

And huge regions here of solid-solid, solid-liquid, and solid-liquid coexistence. And that point there is a eutectic reaction. Because when you cool through that point, you transform from one liquid phase, into two solid phases.

This up here is a single phase region. It's a liquid. And this down here is a two-phase region. You see all the tie lines, which thermocol draws in green.

So at minimum there, that minimum of the liquidus, is the liquidus eutectic temperature. It's also known as an invariant point. It's called an invariant point.

And here's a nice example. This is an example of a system with multiple eutectics, don't have to just have one. So here is the magnesium nickel system. Nice, clean phase diagram, but it has multiple eutectics. So here's the eutectic between magnesium and this magnesium to nickel solid phase.

And here is a eutectic between-- well, we'll come to intermediate phases, we'll get there. But there's a solid phase here, that melts congruently. And the eutectic between that phase and pure nickel.

So anywhere you see a local minimum of the liquidus, you have a eutectic reaction. At this reaction, you have a transformation from liquid to these two phases. And at this reaction, you have a transformation of liquid to these two phases.

So you'll see, each of those eutectic points had this general form-- transformation from a liquid of high temperature into two solids at low temperature.

All right, what is Gibbs phase rule tell us? Gibbs phase rule tells us that degrees of freedom in such a thing is C minus phase plus 2. And so that's 2 what? Minus 3 plus 2. So that's 1.

So I have 1 degree of freedom at a eutectic point. And that's weird, because it's a point. It's a point, like a triple point, it's a point. A point should have 0 degrees of freedom.

What's with 1 degree of freedom? Does anyone have a guess as to where that degree of freedom is in the phase diagram?

What's a geometrical object with 1 degree of freedom? What do we call that?

STUDENT: A line.

RAFAEL A line-- it becomes a line in TP and composition, higher dimensional space.

JARAMILLO:

So in this class, we don't worry about pressure dependence of binary phase diagrams. That's an advanced topic. But since we're learning fundamentals, I want you to be confident that Gibbs phase rule holds. And I'll show you a binary phase diagram projected, drawn in three dimensions, just for fun.

So here is-- see, this is why we don't draw these very often, because they're a horror to look at. But this is a binary phase diagram now where pressure is this vertical axis, and temperature is into the board. Temperature is like into the board, here. And composition is here.

And this is taken from a textbook, from Gaskell. And they conveniently step through. They're giving you these isobaric sections here. So here's an isobaric section at one pressure, and you see there's a eutectic point-- a eutectic point between the liquid and alpha and beta phase. And they draw this at very high temperature. They also show the lens here between the liquid and the vapor. This must be a low pressure.

And then, as we reduce the pressure, I'm going to pump the system down, you see the liquid phase is shrinking. And the vapor phase is taking over. But you still see that eutectic point. It's still the same reaction-- alpha and beta transforming into liquid.

So I'm going to flip backwards-- see, alpha and beta transforming into liquid. There is that same point, it's a point on the line-- alpha and beta transforming to liquid. But if I go to a sufficiently low pressure, I lose it. Now it's gone-- I no longer have alpha and beta transforming into liquid.

So it was a line, it was a line that had 1 degree of freedom, as promised.

I also need to tell you what a eutectoid is. A eutectoid reaction. A eutectoid reaction is a third solid that transforms into two solids. So this is the low temp, and this is the high temperature.

So I'm going to show you an example of a eutectoid. Before I do that, I'll ask-- how would that this is the high temperature equilibrium state, and this is the low temperature equilibrium state? How would you know that? Or how would you guess that?

You know very little here-- you just know that high temperature, it's one phase, one solution phase, and a low temperature is two different phases. In general, two different solutions. How might you guess?

STUDENT: This is more what we're doing in 3.023, but it reminds me of an oxidation and reduction reaction, where at lower temperature it would reduce.

RAFAEL That makes sense. It's not quite that, though. And we'll get there in this class, as well. The reason is, this is more mixed up. If you have two solid solutions, and you take all those components, and you mix them into one solid solution, you necessarily have a higher entropy of mixing in this case-- in this case.

And you can convince yourself of that by drawing your own free energy composition diagrams. So in general, high entropy things are favored at higher temperature. This is something that you know.

It's a little bit more apparent here. I have a liquid solution and two solid solutions. So here, you might say, oh, yeah, the liquid is higher entropy. That makes sense, that it's the high temperature phase. But it holds even here.

So let's look at some eutectoid reactions here.

OK, so here is brass, copper, zinc. And who sees a eutectoid reaction? You're looking for that typical, gull-wing shape. But in this case, the liquid-- well, how come I don't have this laser pointer here? In this case, the liquid has no eutectics. It doesn't have anywhere that gull-wing shape.

But there is a eutectoid somewhere in the reaction, in the system. Who sees it?

STUDENT: Is it the delta phase?

RAFAEL Yeah, delta. This delta phase is just a little solid solution, little delta phase. And it has a little minimum here.

JARAMILLO: There's a little gull-wing shape. Your eye should start being able to pick these out. These are little gull-wing shapes.

And so this is a reaction-- you cool down the high temperature phase of the delta solid solution. And when you cool through that point, you go into a two-phase region. What two phases coexist in this region, now, below 555 degrees?

Samuel, are you willing to--

STUDENT: Gamma and epsilon.

RAFAEL Gamma and epsilon, right. So see how we're reading this phase diagram? The single solution, the single phase regions are labeled alpha, beta, gamma, delta, beta, epsilon, eta. And the unlabeled regions, you infer, are two-phase region. So when it cools down from the one-phase delta, I go into a two-phase region, gamma and epsilon.

Fantastic, thank you.

Just for fun, what happens when I heat up delta, and I go through this point? What is this region? What two phases coexist in this region?

STUDENT: Would that be gamma in liquid?

RAFAEL Gamma in liquid. So this is a funny system. I have gamma and epsilon, heat up, heat up, heat up, gamma and epsilon heat up, heat up. Sudden transformation, everything mixes spontaneously into a new crystal structure, delta .

Heat up, heat up, heat up, heat up, heat up, heat up-- oh, suddenly, I have spontaneous un-mixing again. But in this case, it's into two phases, back to the gamma solid crystal structure, and some liquid. And as I heat up further, the liquid phase fraction increases, increases, increases, hit the liquidus, and now I have one liquid solution. Right.

There you have it. One solid phase, two solid phases.

All right, so let's draw free energy composition diagrams for eutectic systems.

And for those who are interested in this, and I hope you all are, on the supplemental videos section of the course, there is a video-- a demo. A demo that we made-- we made it for this course, and also for the ed-ex course, of the indium gallium system. So that's a eutectic system, indium gallium, you have melting points depression.

It's very important in microelectronics. And I can tell you why liquid indium gallium is very important for microelectronics another time. But we have a nice little demo where you see two systems, which are solid at room temperature, liquefy when you mix them. So there's melting point suppression.

So go check out the demo, if you like.

So let's draw a free energy composition here for-- we're going to start with the temperature below the eutectic point. I'm afraid I'm going to fail my spelling test here. Is that spelled correctly, anybody?

Two immiscible solid phases, liquid, unstable. OK, below the eutectic point, I'm below the liquidus, the liquid is unstable. I have two immiscible solid phases. So I'm going to draw a free energy composition diagram. This is now general, this is not particular to any one system.

All right, so first, let's have an alpha phase. Let's have a beta phase. And let's have a liquid phase. Now we know, from the start of this lecture, when we were looking at the lens diagram, the liquid phase here is just something that is like that. It's everywhere unstable, so it's never going to factor into the taut rope construction.

This is 0, this is ΔG_{mix} . And let me draw my taut rope. My taut rope is going to be pulled like this, and then it's going to become a straight line. Sorry, I didn't quite hit my common tangent point there, but I think you can get the point.

There, so there is my free energy composition diagram for this system below the eutectic point. Here are my points of common tangency. So in this region, I have an alpha solid solution. In this region, I have alpha and beta two-phase. And this region, I have beta solid solution.

Beautiful. Let's move on. At the eutectic point, liquid becomes stable. So what does that look like?

Here's my 0. What color did I use? Alpha was green, so let's draw alpha. Beta was blue. So let's draw-- beta was blue-- let's draw beta. I'm going to cheat a little bit here.

Here's my taut rope in this case. All right, so here's my taut rope. But now, the liquid phase is just barely stable. So now, I have a unique point of a common tangent that's common to three phases. Right at that eutectic point-- here's liquid, alpha, beta.

Here are my points of common tangency. So again, on the left hand side, I have an alpha solid solution. This here is alpha and liquid. This here is liquid and beta. And this is a beta solid solution.

Let me finish this sequence here with a free energy composition above the eutectic point. This is a liquid one-phase solution, stable over a finite composition range. What does that look like?

So I'm going to, again, have a little alpha region. Alpha. Going to have a little beta region-- beta. But now, the liquid has become very stable. So my liquid is going to come down like that. Sorry, it should have had some more curvature here, but I didn't. But anyway, here's liquid-- let me draw this a little more curved.

Here's my liquid phase. And where are my common tangents? Now, I'm going to have a couple of them. Here's one. And here's one.

Cool, so now I have a more interesting system. Over here on the left hand side, I have an alpha solid solution, in that little region. Then, in between these two, I have alpha and liquid. So here's my taut rope coming down here.

And then, you see my taut rope gets pushed around. It's like a plunger-- the plunger liquid phase came down and pushed the rope. Liquid phase came down and pushed the rope down. So in between these two points of common tangency, I have a liquid solution.

Then, my taut rope comes up here. And in this region, I have liquid and beta. And finally, over here on the right hand side, I have a beta solid solution.

So let me flip back a little bit and step through those one more time, and remind us what our phase diagram will look like. So here is a little itty-bitty schematic, eutectic phase diagram.

So at temperatures below the eutectic, I am going to be where? I'm going to be somewhere like here. You see I have an alpha phase solid solution, and a two-phase region. And then a beta phase solid solution. Alpha, two-phase region, beta.

All right, let's flip up. Now, I'm at the eutectic. Draw this again. I'm not going to be able to reproduce the same drawing every time, but that's fine. So here, I'm at the eutectic. So here, I have-- again, an alpha phase solution in equilibrium with liquid. Which then is in equilibrium with beta, right there at the eutectic point. And I see the two conditions of common tangency.

And then, at the highest temperature that I've drawn, I'll move down here--

Here, let's say I'm there at this temperature. So I have an alpha phase solid solution. Then I have a two-phase region, between alpha and liquid. And then a liquid solution. And then, a two-phase region between liquid and beta. And then, a beta solid solution.

So just as we did in the last lecture before the break, we are seeing the phase diagram emerge, flipbook style. As we draw these energy composition diagrams at individual temperatures, we're seeing the phase diagram be painted through a series of tie lines.

I have one more thing I want to share with you today, but I'll pause now and take questions on this. Let me finish drawing my taut rope here, taut rope comes down, curls around, taut rope goes up, and then taut rope finishes.

You see how this liquid phase can be seen as having pushed-- plunged the taut rope construction down? Let's do this flipbook style again. All right, liquid was unstable, and it came down, it's touching the rope. And then, it pushes the rope down.

Imagine the rope is elastic. That's a case of an intermediate phase. And we'll cover that in more detail shortly. But you see what's happened here is an intermediate phase, meaning I have one phase that stable on the left hand side of the diagram, a different phase, which is stable on the right hand side of the diagram. And intermediate to those, I've got a third phase, which is a solution phase, which is stable.

And intermediate phases have this feature on them for energy composition diagrams. We've got a phase, which is very unstable on one side of the diagram, very unstable on the other side. But stable in the middle.

And the textbook has more drawings that are like this, or illustrating this energy composition diagrams, almost flipbook style, in how they generate phase diagrams. And we're certainly going to be doing a lot of that on the next piece, on problem set eight.

All right, there's one more thing I want to share with you, which gets to often a point of confusion around using CALPHAD software, which is the following. Do we like to plot ΔG of mixing, or the total Gibbs free energy? As you've found already, we analyzed ΔG of mixing in lecture, because we start by learning solution models. And there's a good reason for that.

However, most thermodynamics software, including Thermo-Calc, prefers to plot total Gibbs free energy. And so you need to go back and forth. Fortunately, it doesn't matter. It doesn't change the resulting phase diagram.

And let me just draw that schematically. Here's a system for which I'm going to plot-- now, I'll draw this for a two-page region. Here's a free energy of mixing for-- here's an alpha phase, and here's a beta phase. And I have a common tangent construction. And my phase system is what, alpha solid solution, two-phase region, beta solid solution.

Here's alpha, here's beta. And now, for the exact same system, at the exact same temperature, this is what the Gibbs free energy looks like-- the total Gibbs free energy now, not the Gibbs free energy of mixing. The total Gibbs free energy for this exact same system at this exact same temperature, often looks like this.

Now, we're going to plot total Gibbs. Well, this is the Gibbs free energy for component one in its pure state. And at some other number, this is the Gibbs free energy of component two in its pure state.

And it dropped us down so I can cheat a little bit in my drawing. I'm going to draw a dashed line connecting those two. And my total Gibbs free energy versus composition diagram will look like this.

The important point, and of course, I cheated a little bit, because I did the drawing so that it would work out, is that whether you got ΔG of mix, or the total Gibbs free energy does not change the resulting common tangent construction, specifically, it doesn't change the compositions that are at equilibrium at this temperature. It's the same two compositions.

What is this line? This straight line connecting the two reference states? Line connecting G_1^{naught} and G_2^{naught} . That's just-- well, we know what that is, we've written that down before when we were solution modeling. That's $x_1 G_1^{\text{naught}}$, plus $x_2 G_2^{\text{naught}}$. And sometimes, we prefer $x_1 \mu_1^{\text{naught}}$ plus $x_2 \mu_2^{\text{naught}}$.

This straight line offset, because you offset here by the straight line, doesn't change the face of those [AUDIO OUT].

And you can work this out for yourself. You could prove to yourself that if these two points satisfy the common tangent condition, then these two points do, as well. Or you could just believe me.

So this hopefully addresses a point, which often does trip people up when they're starting to use the CALPHAD software. And that's where I'd like to leave it for the day.

So on Friday, we're going to continue in this vein, we're going to look at more free energy composition diagrams. We're going to move on from eutectic reactions, we're going to look at peritectic reactions. And on the problem set that's going to go out on Friday, we're going to be using a new piece of software, which is an aid for visualizing these free energy composition diagrams, and for visualizing how the free energy composition diagrams give rise to the overall phase diagrams.

And so we will start on all that, and be doing that for at least another week or so. And that's all I have to say.