[SQUEAKING]

[RUSTLING]

[CLICKING]

PROFESSOR: All right. So good morning, again, everybody. What are we doing today? What did we do last time? We worked on solution models. And we were working on new tactics and things like that.

So we're continuing to sort of gently dip our, first, our toes and our ankles into the deep end of the pool of the class, which is binary phase diagrams and free energy composition diagram. So we're getting deeper into the pool now. So what I want to start with is some basic results for the equilibrium condition for multi-component and heterogeneous systems, including Gibbs phase rule. And then, we'll walk through a number of slides showing you binary phase diagrams. How they look. Some interpretation of them.

The reading for today includes reading in both the Hoff and Callister. And I hope that people are able to do both because there's a lot of foundational context that isn't really appropriate for a Blackboard or whiteboard lecture, but you have to be familiar with. Just how phase diagrams look, and how they present differently in different resources. And how they're used. So we'll try to give you some of that today as well.

But we'll start with something a little bit more specific. Equilibrium and multi-component heterogeneous systems. OK, so we actually haven't done this yet. We've done equilibrium in multi-component homogeneous systems. That was reacting gas systems.

And then, we've studied solution models. Those are some models of phases, which are multiple components. But we've studied them in isolation, that is, a model of a single phase, a given phase. And so it hasn't been heterogeneous yet. Heterogeneous means more than one phase.

But now, we're going to start putting it all together. So let's draw a general picture of this and derive the equilibrium condition for this. I'm gonna need new Sharpies. Add that to my shopping list. Maybe this one is a little better.

OK. So we have-- that's a phase. In general, let's have a phase alpha. And it has temperature alpha, pressure alpha, and x1 alpha, x2 alpha. And although in this class we're only going to deal with binary systems, that is, two components. Right now, what we'll derive is more general. So you can imagine having more than two components.

And then, we're going to have phase beta. And this, in general, is at some temperature, some pressure, and it has some composition. Which of these pens is better? This pen is better.

Life is too short to keep faded Sharpies on your desk. OK. So the overall system is isolated. Overall system is isolated. And so we're going to use our isolation conditions that we remember from some time ago.

And here's what we're going to ask ourselves. What is condition for equilibrium between alpha and beta if the phase boundary is open so material can flip back and forth? Non-rigid, so this phase can grow or shrink. And this phase can grow or shrink. Right? And thermally conductive. Or sometimes that's known as a thermal. But we'll just say thermally conductive. So what is our condition for equilibrium in this situation?

So we're going to do something like what we did a couple of weeks ago now. For the total system, for the system as a whole, we can write the full differential of entropy. So we're going to sum now over phases. Sum over phases. And we know what this is. This is just from the combined statement here, so phase label J.

And of course, each phase we have to sum over components. Sum over components. Mu, K, J. T, J, dN, K, J. This is very similar to what we've done before. dS equals 0 at equilibrium leads to the equilibrium conditions. And I'm not going to write this out because you've seen it before, more or less. That is thermal equilibrium, mechanical equilibrium, and chemical equilibrium. Right? OK. Thermal, mechanical, and chemical.

All right. So let's see what the implications of this are. We're going to start with Gibbs phase rule. So we did Gibbs phase rule before. We did it rather briefly for the unary systems. We're going to revise it now.

Revised for multi-component systems. Right. And as before, we're going to use this Ph to mean phases. So Ph phases and C components. As before, I'm not using capital p for phases as the book does because capital P means pressure.

So this is a problem in linear algebra. We count our number of variables. The number of variables, let's see, for phase alpha, we have temperature of alpha, pressure of alpha, x1 of alpha, x2 of alpha, and all the way up to Xc minus 1 of alpha.

I'm not including the mole fraction of component C because it's determined by the mole fractions from 1 to C minus 1. Right? You don't have C independent mole fractions. You have C minus 1 independent mole fractions because they have to sum to 1.

OK, that's for phase alpha. Here's for phase beta. T beta, P beta, x1 beta, x2 beta, so forth and so on, Xc minus 1 beta. And we can repeat this for each of Ph phases. So we have this many lines of variables. And for each phase, we have 2 plus C minus 1 variables per phase.

See what we're doing is we're counting the intensive variables that control-- that describe the system. So the number vars equals number of phases times 2 plus C minus 1. All right, so let's just number of phases times C plus 1. So that's a number of variables that describe the system.

And now, we're going to apply our number of constraints at equilibrium. Number of constraints at equilibrium. So the equilibrium conditions we found in two slides ago, so they're as follows. Temperature of alpha equals temperature of beta equals, ba, ba, ba. Right? For as many phases as you have, you keep going. Pressure of alpha equals pressure of beta equals, ba, ba, ba. And you keep going.

Then, chemical potential of component 1 in phase alpha equals chemical potential of component 1 in phase beta equals, so forth. Then, of course, chemical potential in component 2 in phase alpha equals chemical potential in component 2 and phase beta. And you have to carry this all the way down to the chemical potential of component C in phase alpha equals the chemical potential of component C in phase beta and so forth and so on.

So we have C plus 2 rows of equations-- temperature, pressure, and all the components. And how many independent equations per row do we have? So this is going from temperature alpha equals temperature beta equals ba, ba, ba, all the way up to the temperature of the final phase. How many independent equations do we have, let's say, in this one row?

STUDENT: Minus 1?

PROFESSOR: Yeah. Right. This equals that. That equals that. That equals that. That equals that, and so forth. And then, the final one equals the first one. And you can just count the equal signs, right? The number of equal signs you're going to have is going to be Ph minus 1. Right? Good.

So that means we have our number of constraints equals C plus 2 times Ph minus 1. OK. So now, we have constraints, and we have variables. So again, this is a linear algebra thing. The number of degrees of freedom DoF equals variables minus constraints. And this comes out to be C plus 2 minus number of phases. And this is a rather well-known result. This is Gibbs phase rule for multi-component systems.

That's Gibbs phase rule for multi-component systems. And what is that in words? Somebody, what are we doing here? What does that tell us in words? What does that mean? Degree of freedom is the number of thermodynamic variables that can be independently varied while maintaining equilibrium between Ph faces in a system of C components.

So an example that you're familiar with already was from unary systems. We had temperature, and we had pressure. And we had several saturation vapor pressures, for example, which kind of looked like that, a P sat. You remember that? That was a coexistence curve between vapor and solid phases in the unary system. This is unary.

How many degrees of freedom does a line have?

STUDENT: One?

PROFESSOR: One. You can move along T, left or right, but once you've decided how far to move along T, you can't arbitrarily vary P. You've got to tow the line. So basically, you can move along the line in this direction or that direction. That's your degree of freedom.

This is a condition for two-phase equilibrium. Right? This was degree of freedom equals how many components in unary? 1 plus 2 minus 2. Two phases, one component, right? So this is 1. The line here has one degree of freedom.

So if you start here, and you go over here, you vary temperature and pressure in some random way. And you end up over here. You no longer can maintain two-phase equilibrium. Right? You'll be in a one-phase region. And the entire system will vaporize. That's what that means in the context you're more familiar with.

So now, let's see what that means in this new context. Case of binary system. Binary system C equals 2. So if we have one phase, degree of freedom equals 3. So for example, what are three things which I can all independently vary while staying in the same phase? What are my three independent parameters for solutions at fixed temperature and pressure?

STUDENT: Volume?

PROFESSOR: Well, no, temperature and pressure, right? Those are my independent parameters for a fixed temperature and pressure system, so temperature and pressure. And let's say composition of component 1.

I can vary any of these. And I can vary them all three. And I can vary them at random. And I'll still be in a one-phase equilibrium. That's what that means.

What about two-phase? Degree of freedom equals 2. So here, I can vary two parameters, but then third will co-vary deterministically if I'm to stay in two-phase region. And we're going to see this emerge in the next couple of lectures with two-phase regions in tie lines and so forth.

All right. So for example, free to vary T and P, but then x1, x2, of course, follows my x1 must follow. OK, so that's an example.

Three-phase, right? Degree of freedom equals 1. And four-phase degree of freedom equals 0. So before, we couldn't have four-phase equilibrium with unary systems. That wasn't allowed. Now, we can. And we see that in nature.

And here, before we had three-phase regions. Those were called triple points. And they were points in unary phase diagrams. They couldn't vary. Now, three-phase regions are lines in temperature, pressure, composition space, right? In this three dimensional space, these three-phase regions are our lines.

So I'm done on the board for now. I'm going to switch the slides and walk through some examples of binary phase diagrams. And hopefully, illustrate some of this stuff. So let's see some examples of binary phase diagrams.

Here's one that I think I pulled from Callister, right? And we talked about sugar water before in the class. And so this is a very simple binary phase diagram. We have the x-axis being composition here in weight percent. Normally, we like to stick with atomic percent, but this is in weight percent.

And the y-axis here in temperature, they even have Fahrenheit. And we have this concept of a solubility limit. So if you start with pure water, here in the left-hand side, and you start adding sugar, at some point, you reach saturation. And if you add any more sugar, that sugar will precipitate as solid pure sugar at the bottom of the beaker.

So this over here is a two-phase region. And we understand that you can't actually have a uniform material with any of these compositions. What's actually happening when you have an overall system composition in this region is you have the coexistence of saturated sugar water and pure solid sugar. So that's what we understand this to mean.

Why does this solubility limit curve go up and to the right? Why does it not go up into the left?

STUDENT: Does it relate to the density?

PROFESSOR: It actually doesn't relate to the density. This means that, let's say imagine this 65% weight percent composition, which would be super saturated at lower temperature. If we raise the temperature, now, we can actually achieve that solubility.

Why would the solution phase be more favorable at higher temperature than lower temperature?

STUDENT: Because it has higher entropy, so--

PROFESSOR: It's an entropy effect. That's right. We remember Gibbs is h minus ts. So as we raise the temperature, entropy becomes more and more important and becomes a stronger driving force.

So solutions are more mixed up. They have higher entropy than two-phase regions with a segregated pure solute. And so that's why you see solubility regions typically expanding, getting wider, as you raise the temperature. All right.

So let's talk about some other systems. Some definition here. Isomorphous system, so now, we're getting away from sugar water. We're going more towards solids that are more in line with the core of DMSE. Isomorphous systems means systems for which both pure components have the same crystal structure. So that's the definition.

So an example we like in DMSE is silicon-germanium because silicon-germanium is an isomorphous system. And it's one that DMSE has played a major role in developing. So silicon and germanium both have this diamond cubic crystal structure. Silicon-germanium alloys have a pretty important role in microprocessors.

And let's see what the phase diagram looks like. So this is a phase diagram of silicon-germanium. So now, what do we see? At low temperature, that is-- what's the axis here. Low temperature means below roughly 1,000 C, below 940 C. That counts as low temperature when you're dealing with covalently bonded solids, like silicon and germanium.

You have the diamond structure throughout. So you have diamond throughout this entire region. It's fully miscible, right? Germanium is fully miscible in silicon. Silicon is fully miscible in germanium. And we have only one phase field labeled alpha solid solution.

In high temperature, we have fully miscible liquids. That's maybe not too surprising, although, we saw even last lecture an example of liquids which did not mix. But at high temperature, we have fully miscible liquids. At low temperature, we have full miscible solids.

And the intermediate region gives us this lens-like shape. So this is called the lens diagram. In general, any phase diagram that has this kind of appearance with a two-phase region separating two fully miscible regions can be called a lens diagram because it looks like a lens.

So what happens if I prepare a system with 30 weight percent silicon at 1,200 degrees C? What happens at equilibrium for that system? Does anybody know?

STUDENT: Is it a phase transformation?

PROFESSOR: You're going to have-- yeah, you could call it a phase transformation. If you wait long enough, what is your final phase composition going to be? What will you find in your system if you wait long enough for the transformation or the spontaneous process to complete?

I have an overall composition of 30 weight percent silicon, and the temperature is 1,200 degrees C.

STUDENT: Is it a combination of the alpha and liquid phases like in the shaded region?

PROFESSOR: Yeah. Right. So the shaded region is a two-phase region. It's a combination of alpha and liquid. In fact, it's written right there-- alpha and liquid.

And to find out what compositions those phrases have, you use the lever rule. And you apply the concept of tie lines. So we have a liquid solution at this composition. It's about 16 weight percent. And a solid solution at this composition it's about 45%. So it's a two-phase system with a germanium-rich liquid and a silicon-richer solid. Phase separation, phase segregation. That's right.

You should be familiar with this because it takes just a little bit of flipping through the textbooks and looking at different pictures, which we're going to continue to do for the next 20 minutes. But this is something which you just have to familiarize yourself with how to read these binary phase diagrams. Here's another point. The y-axis here tells you something about pure germanium. The y-axis here tells you something about pure germanium because it's 0 weight percent silicon. All right.

So what does it tell you about pure germanium? What can you learn about pure germanium from just this y-axis alone?

STUDENT: It has a melting temperature of about 940?

PROFESSOR: Right. You learn its melting temperature. This is a little slice of the pure germanium phase diagram. What's unsaid here is the pressure. Pressure is almost never reported in binary phase diagrams. And unless it's reported otherwise, you can assume one atmosphere.

OK. So at one atmosphere, as you take pure germanium, and you heat it up, you're in the alpha, alpha, alpha, alpha, alpha liquid. So in between, it melted. Good.

What's the melting temperature of silicon? Maybe somebody who hasn't contributed yet today.

STUDENT: 1,412 degrees Celsius.

PROFESSOR: Thanks. Yeah, 1,412. That's right. So if you take pure silicon, you can see it's in alpha, and now, it's in liquid. So it melted. 1,412. So these binary phase diagrams contain unary phase diagrams. They contain isobaric slices through unary phase diagrams along the y-axis. If you like, you can imagine the unary diagram just coming out of the board. OK?

Let's see what else. Here's a binary phase diagram. We've seen this one already. So this is an isomorphous system, but it has a miscibility gap. This is not a system which is fully miscible. This is a system, which is miscible at high temperature, but immiscible at low temperature.

So we've started to see that the last time. This is called the spinodal system. And as you start at high temperature, and you start cooling down, you have separation into an ethanol-rich phase and the dodecane-rich phase.

So for instance, let's imagine that I'm at 4 degrees Celsius, and I have an overall system composition of 0.6 mole fraction of ethanol. What should you expect to find at equilibrium? Let me ask this. Should you expect to find a uniform solution with 0.6 mole fraction of ethanol? The class isn't sure.

But somebody guess. Let's take a wild guess. What would I expect to find it equilibrium? Overall, in the system composition, this is what I prepare, 0.6 mole fraction ethanol, 4 degrees C. I shake up the beaker, and then I wait for a long time. What will I find at equilibrium?

STUDENT: It would spontaneously unmix.

PROFESSOR: It would spontaneously unmix. Thank you. And it would unmix into what? What would I find at the end of this process? I love that-- spontaneous unmixing. That's exactly right. What would be the final product when the changes stop happening?

Part of this is stuff that you're working on in this p-sat, which isn't due for four days, so I'm sort of putting the class on the spot. But you imagine the tie line drawn to connect the edges of a two-phase region. So what you have is an ethanol-rich phase with 85% ethanol and a dodecane-rich phase with, whatever this is, 33% of dodecane. And those are the two phases that you'll find coexisting at equilibrium.

Here's a slightly more complicated spinodal system. Now, instead of a spinodal system with a liquid spinodal phase, we now have a solid. So there's a little bit more going on here. This purplish region is a solid solution between aluminum and zinc.

Now, often in phase diagrams, the parent or the peer material will be indicated in parentheses. What that tells you is that this solution region has the structure of pure aluminum. Reading by phase diagrams is often an exercise in being a little frustrated in how the people who made the diagrams are very concise. In other words, there's a lot of shorthand.

And you'll encounter binary phase diagrams drawn in many different ways and with many different types of shorthand. If I could wave a magic wand and change all the binary phase diagrams in the world into a uniform presentation, I would do so, but I don't have that magic wand. And so, instead, my job is to get you familiar with being a little bit annoyed that you're not getting all the information you need. Because many of you will see this next in industry. You'll go straight from O to O to actually needing to read these things on the job. So that's why I'm showing you these different presentations because it's the sort of thing you're going to find out there.

So aluminum here, doesn't mean that this whole region is pure aluminum. It's, obviously, not because this is a binary phase diagram. What it does mean is that this whole solution region here has the structure of aluminum, which happens to be FCC.

So we have an aluminum-rich FCC solid solution here. And here is a spinodal. At below 353 degrees C, this solution will spontaneously unmix into a zinc-rich FCC and then aluminum-rich FCC. So this little dome here is a spinodal system.

There's more going on here, of course. There's more to read. We see that zinc over here, zinc over here is octagonal [INAUDIBLE]. You can dissolve a little bit of aluminum and HCP zinc, but not too much before its phase segregates. The liquids are fully miscible. If you go up above the melting point of aluminum, which you can read here is 660 degrees C, then zinc and aluminum mix completely.

On these phase diagrams, which are this is as produced by ASM, and this is the Society for Metallurgy, so you're going to see a lot of these phase diagrams in your careers because ASM is a major source of data. They indicate solution regions with this nice purplish color. And they indicate two-phase regions with white fill. So they don't say two-phase region. They don't tell you what two phases are coexisting.

How do you tell what coexist? So look where my cursor is. What two phases coexist for systems with this overall composition as my cursor is? You want to draw a tie line. So what two phases coexist at this overall system composition?

STUDENT: Aluminum-rich FCC and a liquid.

PROFESSOR: Aluminum-rich FCC and liquid. Great. OK? Here's another example.

Somebody who hasn't contributed yet today, please. What phases coexist when I have an overall system composition that's indicated by the cursor there?

STUDENT: Is it zinc-rich FCC and HCP?

PROFESSOR: That's right. You're going to have-- here, I'll indicate a little more. You're going to have a zinc-rich FCC with this composition coexisting with HCP with a little bit of aluminum dissolved in it.

So you have this composition coexisting with this composition. That's how you read those two phase regions. Good. So you have here, what? This is kind of interesting because if you cool down just a little bit more, let's imagine cooling down to this temperature.

So when I am at the slightly higher temperature, my system at equilibrium is zinc-rich FCC and the HCP with a little aluminum. But if it cool down, suddenly my system composition and equilibrium is now aluminum-rich FCC and HCP with a little aluminum.

These phase diagrams get very rich and complicated, as you can imagine. We're just learning the basics here of how to read them. Let's move on.

Here's another example. This has something called intermediate phases. So we have this chromium titanium system. The chromium titanium system contains a lot of things which we're going to learn about. It contains a spinodal looking thing. It's got this BCC region, which is fully miscible in this little narrow temperature range. At 1,400 degrees C, looks like, this system is fully miscible as a solid in the BCC structure. And you see here they've indicated that with parentheses tie chromium, fully miscible as BCC.

But when I cool down, I have spontaneous unmixing. And here, I don't just have spontaneous unmixing into chromium-rich BCC and titanium-rich BCC. This system gives me intermediate phases, which we'll cover in a couple of weeks. So it gets a little bit complicated.

I notice that my annotations haven't disappeared. So let me clear those. Here we go. OK.

This system also has an interesting phenomenon of liquid melting point suppression. So this is indicative of new tactic-like behavior. We haven't gotten there yet. When you see the melting point of the solution is actually lower than the melting point of either of the pure components. That's very common behavior.

We could probably stare at this for another hour and continue to be learning. Let me move on. Now, not me move on. Let me sit here for another minute and collect any questions or curiosities that have come up. Is there anything about this that you're just burning to have answered? Understanding that this is kind of complicated. And we'll be spending the next couple of weeks on diagrams like this.

STUDENT: So what happens when there's like a tie line that goes through multiple phases? Is it just telling you about what's happening on the left and right or?

PROFESSOR: Yeah, they're complicated. So what on earth is going on here? This is what's going on. Are you talking about this tie line here?

STUDENT: Yes.

PROFESSOR: Let's look at all the tie lines in this diagram. Let's start there. At 686 degrees, they've drawn a tie line in between titanium and its HCP phase, which has a tiny little sliver of chromium solubility. You can just see that little purple region.

And this ti-chrom 2 room temperature polymorph RT, room temperature polymorph. And so this two-phase region down here below the tie line that's drawn is a two-phase region between titanium room temperature polymorph and this ti-chrom room temperature polymorph.

Now, when I go above, what happened? I went above this kind of funny looking minimum. Now, this two-phase region is between ti-chrom in the BCC structure and this ti-chromium 2 room temperature polymorph. Whereas this two-phase region is in between titanium-rich HCP and this ti-chrom BCC.

You could identify similar sorts of funny business over here when you look at this point, which is the lowest temperature that the high temperature 1 polymorph is stable at. So you have a phase transformation here between a room temperature polymorph and a high temperature polymorph. And it looks like there's two high temperature polymorphs. There's a ti-chrom 2 HT2. So there's several solid state transformations here. Ti-chrom 2 room temperature, if you heat up, it transforms to ti-chrom 2 high temperature 1. And it continues to transform to ti-chrom 2 high temperature 2.

I can't tell you what those crystal structures are. I don't know the titanium chromium system very well. But we know how to find out. We go look up [INAUDIBLE]. We learn what they're all about.

And this is not purely academic because these are structural alloys. And different crystal structures have different mechanical properties. So you might care very how much of your finished part is ti-chrom 2 high temperature 2, ti-chrom 2 high temperature 1, and ti-chrom 2 room temperature. Right? That might be a really important thing for you.

So there's this funny tie line here that starts off at 1,271. Jogs down a little bit to 1,269. That indicates the transformation in between the high temperature 1 and high temperature 2 polymorphs of titanium and chromium 2.

Yeah, it gets complicated. It gets complicated in a hurry. So these diagrams are drawn minimally because I think if they were drawn with all the features, it would be like unreadable. But you do need to learn how to read them.

Let me move on, show you some examples. Here's another example. We have a lot of spinodal examples in polymer systems. This is an example of a polymer blend PFB and FABT. This is a polymer blend that's used to make solar cells.

And this is, I think, AFM data-- Atomic Force Microscopy-- showing you that when you prepare a fully mixed system, in this case a thin film, and you anneal it, that is, you try to drive it towards equilibrium with time and temperature, you start to see pattern formation. That's the word for this. This is called pattern information.

What starts off featureless develops features. And these patterns, which happen over nanometer length scales, often have real functional implications. So for example, this is a report of the efficiency of a solar cell based on this stuff.

The efficiency only gets out of the basement once they start getting the pattern formation. And there are reasons for that which go beyond the scope of this class, but the point is that by changing the morphology, by changing the phase fraction and driving from the single phase to this two-phase situation, you can affect the performance of something like a solar cell. So it becomes important.

There are countless examples for why this pattern formation-- controlling it-- is important for technology. Most of those examples-- there are probably more examples in structural metals than there are in other fields. But as we saw in the last lecture, it extends even to cosmology.

OK. It's 10:55. I'll walk quickly through. Let's see, brass is nice. I like brass maybe because I used to play French horn when I was in middle school. So this is brass. This is complicated.

We're going to start stepping through diagrams like this. We're not ready for it yet, not quite. But here's brass with copper zinc. So copper-rich FCC is called brass. Over here is zinc. We've seen zinc already. We saw it a couple of slides ago. It's HCP.

And in between, you have all these intermediate phases. Let's look how-- here's a simplified view. Copper in parentheses, meaning this is a solution with a crystal structure of pure copper. This A here is an alpha. Here's zinc. Here's a zinc solid solution.

Coming back to Gibbs phase rule, here is a single phase region with three degrees of freedom. I can vary pressure, temperature, and composition while still staying in this brass phase. Right? Temperature and composition are x and y in the plot. You have to imagine pressure coming out of the board. OK, three phases.

Here's a two-phase region. So this is a two-phase region. This is a region of coexistence between alpha and beta. And they only have two degrees of freedom because the composition of the phases is fixed by the end points of the tie line.

We're not going to fully take time to think about that now, but I wanted to point it out. Here's a three-phase region-- alpha, beta, and liquid, only one degree of freedom. So this defines a line through the temperature pressure composition space. I don't have a four-phase region here.

OK, We're two minutes over, so I'm going to end before I entertain you with pressure dependent ternary phase diagrams, which mercifully, is not covered in 3020.