[SQUEAKING]

[RUSTLING]

[CLICKING]

PROFESSOR: All right, so it is Friday, and we are where? Problem set is due today-- problems that will go out later today. And we're going to continue today with binary phase diagrams. We're still very much firmly in DeHoff chapter 10. And today, we're going to talk about peritectic systems and intermediate phases and start spending more time with the software. OK, so let's talk about peritectic reactions.

OK, so eutectic reaction we defined earlier, and now we're going to do peritectic. And this is a peritectic reaction. So I'll define it formally, and then I'll show you some examples, just as we did for the eutectic case.

So a peritectic reaction is a liquid and a solid at high temp transforming into a solid. That is our peritectic reaction. So as before, we have the Gibbs phase rule gives us c minus Ph plus 2 equals 1. So just as with the eutectic case, this is a line in T P composition space.

As for eutectic-- as for eutectic case. And by the way, speaking of eutectics, I hope some people were able to check out that video demo of the indium gallium system. And as with eutectoids, we have peritectoid, which is kind of like a peritectic, but not quite. And this is a peritectoid solid 1 plus solid 2 going to solid 3.

So let's see some examples because I know this is kind of dry. So here's the copper-zinc system. We have, again, brass-- and so we've seen this system before. I like to come back to systems that you've seen, just from familiarity. So we have pure copper and solid solution of copper with zinc here. That's the alpha phase. And then we have several other solid phases. So there's a beta phase and the gamma phase, delta phase, epsilon phase, and then there's pure zinc, which is eta.

And what I want to highlight now are these transformations. So I'm going to flip back and forth here. This region here is bounded by the liquids, the delta phase, and two isoforms here, one at 697 and one at 594. And you could see that this region here is what? Somebody told me, please-- what is the phase composition in this region that I'm working?

AUDIENCE: They'll turn in liquid?

PROFESSOR: Delta on liquid, right. Two-phase region-- delta on liquid. And you see, you can cool down and enter this epsilon solid solution. So right there is a peritectic. So just as your eye can start to pick out eutectics with this [INAUDIBLE] shape, your eye can start to pick out peritectics. It looks like a beam balancing on a triangle. There's a triangle, and there's a beam. And visually, I can start to pick these out. So there's a peritectic. Here's another one.

So right here is beta on liquid two-phase region. This little sliver is beta on liquid two-phase region. And then down here is a gamma. And so there we have, again, a little beam balancing on a triangle. And there we have another peritectic. And there's another one there. And I picked out five peritectic points here. And just so that you've seen it, these are sometimes called invariant points, same as with eutectic. It refers to the fact that although they are, in fact, lines, on a binary phase diagram at fixed pressure, they appear as points. So they occur at only one given composition and temperature as long as you're at 1 atmosphere.

So peritectoids-- here, I have chosen the copper tin system now. The copper tin system is definitely complicated. I'll start with these peritectic points here, for instance, is copper and liquid. Two-phase region here-- copper solid solution and liquid. And if you cool down, you enter this nice, purple solid solution, which is labeled as-- it's got this funny label-- high temperature phase of copper 0.85 tin 0.15. So that's a peritectic. Here's another peritectic point here. Here's a nice, typical peritectic. Here's the beam balancing on a little point. So up here, we have a coexistence between a solid and the liquid. And down here, we have a solid solution phase. Those are peritectics.

But we also have peritectoid, and I don't want to dwell on this for too long because they're less common. But if you look, I zoomed way in here. And if you look in this little triangle region here, this little triangle region is a two-phase region where we have coexistence between this phase, which is copper 3 tin high temperature, and this phase here, which is copper 3 tin room temperature. In this little triangle region, at equilibrium, the system will phase separate into solid 1 plus solid 2. And if we cool down right into this tiny little sliver, then we enter a single-phase region, which is copper 10 tin 3 high temperature.

So for every one of these transformations that we can find in a phase diagram, there is often a type-- there's a label, eutectic, peritectic, eutectoid, peritectoid. We have others that we haven't discussed. I think that's all I have to say on peritectics and peritectoids. Consider it a series of labels to characterize common visual motifs in these phase diagrams. There are pretty substantial implications of these types of transformations for materials processing, but that really goes beyond the scope of 020 and veers into kinetics and, of course, materials processing, which you take later on.

Questions on peritectics, please, before we move on?

I'll move back to the board. We're going to now talk about another feature of binary phase diagrams, and that is intermediate phases. Intermediate phases so an intermediate phase is a phase that is stable for some intermediate composition, but not for pure components. So it's a phase that does not exist in the pure component case, and it is structurally distinct from reference space.

So let's show an example-- chromium iron. So here is chromium iron. And this is generated using Thermo-Calc. And chromium iron is a kind of a fun system. It has this weird-looking thing, which will come to. But what I want to focus on now is this intermediate phase. So you see, there is something that looks like a spinodal. This whole region here is BCC. This whole region here is a BCC solid solution. And it looks as if chromium iron are fully miscible in BCC, except that miscibility is interrupted. And there is this teardrop shape here, intermediate phase, which, unlike BCC, it is structurally distinct.

And-- how come I can't get my laser pointer here-- so we have BCC, and then this region here is a two-phase BCC and sigma coexistence. This is a sigma solid solution, intermediate phase, and then if we keep on moving to the right, we have a sigma and BCC two-phase region again. And if we drop sufficiently low temperature, sigma is no longer stable, and we have a very typical spinodal pattern, which is chromium-rich BCC and iron-rich BCC coexisting in this wide two-phase region.

And these are, indeed, very distinct structures. So BCC, body centered cubic, is a structure that you know. It has only one site. There's only one type of site in a BCC lattice, and has eight-fold coordination, whereas this intermediate sigma phase-- I had to look this up-- this is a structurally very complicated material. There are five inequivalent crystallographic sites. And they have different combinations of 12, 15, 14, 12, and 14. So yeah, this is kind of a complicated thing, and this structure does not form for pure chromium, and does not form for pure iron. But it does form for this chromium iron solution.

As you might guess from the coordination numbers, do you think this is a more closely packed structure than BCC or less closely packed? Well, I'll ask what is the coordination number for a close-packed either FCC or HCP? Who remembers this? Nobody remembers this from Structure or even from 3.091, the coordination number for a closely packed lattice?

AUDIENCE: Is it 12?

PROFESSOR: 12, right. So this crystal structure here has coordinations which are 12 and higher. And, as you might guess, the way it does that is it has atoms of two different sizes. You can't get coordination number higher than 12 if you only have one type of atom. But you can find ways to pack in more atoms if you have atoms at three different sizes. And you might guess that this phase becomes more stable at higher pressure. It seems more dense, and you'd be right. So you might guess that the range of stability of this solution might be expanded as you increase the pressure. But right now, we're just sticking at 1 atmosphere.

So let's go back to the board. So how did the free energy composition diagram look? So, for example, chromium iron is a case of a spinodal interrupted by an intermediate.

So let's draw a free energy composition diagram for this. So we know what a spinodal free-energy composition looks like. Let's draw it in a region of phase separation we have here. OK, that's a typical solution model for a system that undergoes spinodal decomposition.

But now let's say that I'm at a temperature for which the sigma phase is stable for intermediate compositions. Could somebody please tell me, qualitatively, how I should draw this sigma phase solution model? So this is the BCC phase model. How should the sigma phase model look?

We know it's going to be stable for some intermediate competition. So somewhere in the middle of this diagram, we want that sigma model to be a stable solid solution. And we know that we need this BCC phase to be stable on the left-hand side of the diagram and we need this BCC phase to be stable on the right side of the diagram as well, and that there's going to be regions of two-phase coexistence. So we need some common tangents. You think about the taut rope construction. How should I draw a sigma?

AUDIENCE: Would it be a parabola that's like a U-shape?

PROFESSOR: Yeah, it's like a plunger. Imagine the taut rope. I'm going to I'm going to risk really messing up here. Imagine the taut rope like this. Don't worry, I ordered more sharpies. They were delivered to my office. So we will be back in business. Imagine that this is a-- man, I really messed up. Imagine this is the taut rope. I should have drawn this more straight. Imagine that there was no sigma phase. In that case, I would have the taut rope like this-- single-phase, spinodal decomposition, single-phase. Does that make sense? Did I draw that decently?

And now I'm going to introduce a sigma phase, and the sigma phase is going to be like a plunger that comes down. And it pushed my taut rope into in a new configuration. So now my rope got pushed down, around. So this phase came down and pushed the taut rope, and now I have what I want to have, which is I have solid solution BCC, two-phase region, solid solution sigma, two-phase region, solid solution BCC. Thank you for that.

So you can see how introducing the intermediate phase disrupts the spinodal. And so we're going to spend some time now in Thermo-Calc. So what I want to do is I want to share my Thermo-Calc screen. OK, can you see Thermo-Calc? Is it open?

AUDIENCE: Yep, we can see.

PROFESSOR: OK, wonderful. So what I'm going to do is I'm going to generate the iron chromium phase diagram. And by the way, this stands in as a bit of a tutorial on using Thermo-Calc. And there are also tutorial videos on Thermo-Calc available on the course website that I shot previously. So if you find yourself stuck on just how to navigate this software, there are resources available.

So what I did is I clicked on Phase Diagram because that's a good template to start with. All right, here I am. So I was able to define the system-- system definer. You see this project window here? I'm going to keep iron demo database, and I'm going to click on chromium and iron. And so the generic project has the system definition, an equilibrium calculator, and a plot renderer. And the equilibrium calculator is configured to calculate the phase diagram at 1 atmosphere as a function of temperature and composition.

So the first thing I'm going to do is just run this and generate a phase diagram. And I did save a version of this project with everything already computed, sort of like on a cooking show. I've got the cake baked in the other oven. But I want to at least step through some of this in front of you so that those of you who have not seen Thermo-Calc used in certain ways will feel a little more comfortable with it because we're going to be using it a fair amount on the upcoming problem set.

And so what it's doing is it is solving the common tangent construction. It's solving the taut rope construction, which is also called the convex hull construction. If we were getting into the numerics of this, it would be the convex hull-- solving for that convex hull solution for the system. And although the iron chromium phase diagram is already known, Thermo-Calc does everything from scratch.

So here we go. Here is the iron chromium system. Just as promised, it has this intermediate phase. Now you've probably discovered that sometimes mousing over is effective and sometimes it's ineffective. Right now, it's telling me I'm in BCC A2, if folks can see that-- BCC A2. So it's a BCC phase that Thermo-Calc has labeled as A2 for some reason. And it's this wide rating of solubility. And here is another solid solution. And for some reason, Thermo-Calc says insufficient information, but that's not true because all I need to do is mouse over the two-phase region. And it tells me this is BCC A2 plus sigma. And that's what I was expecting to see. This is a BCC and sigma two-phase region, and here is also the BCC and sigma two-phase region. And down here is a BCC and BCC region of spinodal decomposition.

There's one more thing which I want to highlight, which is kind of interesting. For pure iron, pure iron transforms from FCC at low temperature-- from BCC at low temperature into FCC and intermediate temperatures and back to BCC at high temperatures. Iron is a funny creature in that way-- BCC, FCC, BCC.

And we've reminded a number of times in this class that if you look along the y-axis of binary phase diagrams for pure components, you're looking at a slice of a unary phase diagram. So I want to show you-- quickly, I'm just going to switch over to PowerPoint-- how we are, in fact, looking at a slice of the unary phase diagram.

So here's the unary phase diagram of iron. Unaries are able to plot temperature and pressure now on one two-dimensional sheet because we have no composition variable. And if we focus here at 1 atmosphere-- that is, 1 bar-- we see alpha iron BCC, gamma iron FCC, delta iron back to BCC. So BCC, FCC, BCC, liquid-- BCC, FCC, BCC, liquid. So iron is a funny creature that way and, of course, that has implications for steel making.

And anyway, back to the binary, you can see that behavior by tracing pure iron along the right-hand side of the binary phase diagram. OK, questions on that? I want you to be able to look at binary phase diagrams and read off some information about the energy systems. For instance, chromium appears to melt at around nearly 2,200 Kelvin. You can just read up the y-axis and say BCC, BCC, only one structure of chromium, until it melts-- becomes a liquid. So you can get a lot of information from these.

But I wanted to show you for energy composition diagrams. So what I'm going to do is I'm going to ask Thermo-Calc to plot for me, for energy composition diagrams at three different temperatures, in this region where it's just a simple spinodal, in this region where there's an intermediate phase, and this region, right above the end of that intermediate phase region. So I'm going to plot 700 Kelvin, 900 Kelvin, and 1,114 Kelvin, right there above the end of that region.

And so I want to show you how to do that. First, I'm going to rename these modules, just to make things visually simpler. You don't have to do this, but you can do this. So this is Phase Diagram Calc. That's the calculation of the phase diagram. And I'm going to rename this Phase Diagram Plot.

So now I want to create a new successor to the system definer. It's going to be an equilibrium calculator. I want to calculate the equilibrium of this system. I'm going to rename this. I'm going to call this 700 K Calc. I'm going to calculate some properties of this system at 700 Kelvin. Over here, to my setup window, I'm going to make this a one-axis calculation. So I'm going to be at 700 Kelvin, I want to plot mole fraction, and I want my access to be mole fraction from 0 to 1. So what I've just done is I've set this up to calculate the equilibrium properties of the system at 700 Kelvin as a function of mole fraction iron for iron going from 0 to 1.

And, by the way, while I'm at it, I'll go over here to the phase diagram calculator and change this into mole fraction so that I can deal with mole fraction instead of mass percent.

So this calculator here is going to calculate properties of the system at 700 degrees. Now I want to plot that when it's done. So I open up a plot renderer, and I'm going to call that plot renderer 700 K Plot. Again, you don't have to name these things. I can name them Apple and Banana. But it helps me keep it clear. So the 700 Kelvin plot, I'm going to have the x-axis be composition mole fraction iron. On the y-axis, I want free energy, Gibbs energy per mole for all phases. So I go back up here. I'm going to perform the tree. And it's going to do all the calculations in this tree.

And again, if I apologize once, I'll apologize 100 times for turning these parts of lectures into software tutorials. I don't like being subject to the whims of software and waiting for software to run, but I think this is important, not only because we ask you to do these things on P Set 8, but because it really is quite an important job function for people that are designing and making materials for a living, which is where many of you are headed.

And I will also mention that one of the originators of this approach to designing materials is Professor Greg Olson, who will be giving a guest lecture in this class next week, talking about some of his experiences in industry using CALPHAD software to design really cool real-world things.

All right, with that justification, it should be finishing-- wonderful. So now I have two plots. I have the phase diagram plot, which for some reason is still in mass percent, probably because I still have it plotted as mass percent.

And then we have the 700 K plot. This is a plot of free energy, has the function of mole fraction of iron at 700 degrees for all phases plotted. And so you're a little bit familiar with these sorts of plots now from P Set 6, I believe. This is the free energy of chromium-rich BCC, and then the data kind of flatlines.

And the data flatlines not because this suddenly becomes composition independent, but simply because the software-- the database doesn't have data for this region. And so it extrapolates. It does a weird thing. The programmers decided to make it flat. This flat region is not real data. And you could say the same down here. This is iron-rich BCC. There's a solution model. It looks real. It's got some curvature to it. It looks as we expect for, let's say, a regular solution model. And then that flatlines.

So what's going on? What do we actually expect here, between these two regions of the solution model? I'm moving my mouse--

AUDIENCE: A common tangent?

PROFESSOR: A common tangent. So one funny feature of Thermo-Calc is if, instead of plotting all phases, you plot system, it will stop plotting the different phases with different colors, and it will just plot the free energy of the system as a whole, as one line. And so although you lose the common tangent construction-- it becomes a little bit not obvious where the tangent starts and stops-- you do now get an accurate plot showing the free energy of the system as a function of composition. So this is a straight line right there. That's your common tangent. And we can flip back and forth between these views, between all phases or system.

Another funny feature, or you might call it a bug, in Thermo-Calc is that if, instead of plotting per mole, you plot for no normalization-- the actual numbers don't change, but the way that it extrapolates to regions of no data does change. So the actual data has not changed. This is still the solution model for chromium-rich BCC. This is still the solution model for iron-rich BCC. And it's the same data.

But for some reason now, when you plot no normalization instead of per mole, it decides to add the zero point and makes a big straight line. And these crossing straight lines-- they're not real data. You should not pay any attention to them. I won't make excuses for Thermo-Calc. It's the way it is.

So getting back to the actual thermodynamics, at 700 degrees Kelvin, we expect a spinodal-like system of phase separation between chromium-rich and iron-rich BCC. And that is just what we see.

Now let's do it at 900 Kelvin, where we have an intermediate phase. So equilibrium calculator-- I'm going to rename this. I'm going to call it 900 K Calc. And I'm going to make this calculation at 900 Kelvin, one axis, and again, I want my axis to be iron composition. I'm going to change my composition unit to mole fraction. And I'm going to make sure I can plot the results. So I'll call this plot renderer the 900 K Plot. And I'm going to plot composition and mole fraction on the x-axis, and the y-axis, again, I'm going to plot Gibbs energy per mole for all phases. Let's see what happens.

Looks like the point density is a little low. Instead of plotting 50 points, let's plot 100 points across the axis. I have to start this again. That looks a little better, a little smoother.

So here I have a solution model. Point density is a little low-- lack of data. In intermediate phase, lack of data and another solution model. And if I plot this for the system instead of all phases, you now see the solution model is connected with tie lines. And looking back at the phase diagram for 900 Kelvin, solid solution two phase-region, intermediate phase solid solution, two-phase region, solid solution.

I was going to finish this and plot it at 1,114 Kelvin, where you can just see that it becomes a single solid solution almost across the entire composition range. I'll do that in a minute if time allows. But I want to pause and ask for questions, either on the thermodynamics or on the software.

OK, I want to show you one more neat thing before I come back to this at 1,400 Kelvin. I mentioned, I think in the last lecture, what happens if you were to imagine the nonexistence of a particular phase? I think it was a liquid. I said imagine that we could turn the liquid phase off, remove it from consideration. How would the phase diagram change? Now I'll ask you, imagine if the sigma phase didn't exist. How would this phase diagram change? What would you think would happen?

AUDIENCE: Would you just get regular BCC-BCC separation, like for the lower section?

PROFESSOR: Right. Let's see that. I want to show you how you can do that. Go up to My Project and go to the System Define. The system definer, we chose the atoms-- chromium and iron. But there's a bunch more information here. Species-- chromium and iron. There's also phases and phase concentration. And these are the phases over which the system calculates equilibrium. Each one of these phases is a solution model for which Thermo-Calc has at least some data. So here is kind of like the guts that we've been playing with, the solution models. And I'm just going to uncheck sigma.

So now what the system is going to do is everything it did before, except it's not going to include the sigma phase. So you can kind of play God in going to perform the tree. So we're solving the taut rope construction here for a world in which the chromium iron system does not have a sigma phase. And so Shane gets that this would look like a BCC region of phase separation, or I'll just call it a BCC spinodal.

So let's see. It might take a little bit of time. Oh, look, there it goes. Look at that. So here is the phase diagram of iron chromium in an alternate universe in which the sigma phase does not exist. And so you see we have a spinodal. We didn't get rid of the FCC phase. We didn't get rid of the liquid. But we did get rid of that sigma phase. And what do we think the free energy composition diagrams look like? They look a little more boring. Let's have a look. 700 K? There's a two-phase region phase separation. 900 K-- same thing. Well, the point density is a little poor, but common tangent phase separation.

So on the problem set eight that goes out later today, we have a number of tasks for you. About half the tasks are here in Thermo-Calc and involve not the iron chromium system but a different system, where we ask you to generate these plots, generate data, then extract the data. Then we ask you to analyze data in a data analysis software of your choice-- Excel or MATLAB or Mathematica or what have you. And then the final part of the problem set is you're going to then simulate the free energy composition diagram and the resulting phase diagrams using a phase diagram simulation tool which we've built for this class. and that I'm going to introduce on Monday.

So if you look at the problem set, the first part you could start on this afternoon. The second part, I advise that you could wait and start on after Monday when we introduce the phase diagram explorer. But what it's going to boil down is going into Thermo-Calc, looking at a phase diagram, then reverse engineering the phase diagram, understanding what models are underlying the phase diagram, what data do I need to populate those models, and then how do I simulate those models in another piece of software. And by the time we're done with us next week and this next problem set you will all be experts at not just reading phase diagrams, but understanding how they're constructed.

So that is almost everything I wanted to get through today. I did not have time to talk about more general free energy composition diagrams for intermediate phases, mainly because the software is too slow to load. It's not going to be terribly important for this P Set. So I'm not too concerned about it.

But if you want to know what you're missing, I was going to walk through-- where is it? There's a nice schematic in DeHoff of intermediate phases. And the free energy composition diagrams, the intermediate phases in general produced, and I reproduce the picture right here in DeHoff-- so DeHoff Figure 10.19. A general binary phase diagram with an intermediate phase. And here's, flipbook style, the way that the free energy composition diagram evolves to give you these intermediate phase diagrams. So just further views of the type of phenomenon which we saw about half an hour ago.