

[SQUEAKING]

[RUSTLING]

[CLICKING]

**RAFAEL
JARAMILLO:**

So what I wanted to do today is reverse engineer the iron chromium system. We started playing with the iron chromium system last time, and so it's a nice place to pick up. So I've got Thermo-Calc here open, and I suppose you can probably see it. And what I'm going to do is I'm going to start by loading the iron chromium system. So I think Thermo-Calc should run a little faster today than it did on Friday. Knock on wood--

[KNOCKING SOUND]

--because I already have the thing running. So I'm going to take chromium. I'm going to take iron. You see how I'm in the Fe demo? Iron demo database. And when I hit perform tree, it's going to do its generic thing which is after it defines a system, it calculates the phase diagram. And then it's going to plot the phase diagram.

And I'm going to then take us to where we left off on Friday, which is I'm going to create a simplified version of this phase diagram where I turn off all but the BCC and the liquid phases, and then recompute the phase diagram. So has anyone had any trouble running Thermo-Calc? Good.

Today is the last today which I'm going to spend running software in front of you in lecture. So for better or worse, I want you to learn how the software works and to be familiar with it, and so we're spending a little more time. On Wednesday, as a reminder, we are going to have a guest lecture from Professor Olsen, who's going to tell you about how this sort of software is used in the real world and has led to some really nice developments throughout his career. And then on Friday, we're going to be on to new material. Back on the board, as it were.

So what it's doing is it's calculating the Gibbs free energy as a function of composition and phase. That is, it's drawing those free energy composition diagrams. And then it is doing the taut rope construction-- or if you like the inverse, hull construction-- and finding all the tie lines, and coming up with the phase diagram. OK. Well, that's nice, but I'm going to simplify this.

I'm going to reveal the hidden spinodal. So I'm going to go to phases and phase constitution. I'm going to turn off sigma. And then I'm going to turn off this austenite phase, this FCC phase of iron, just to make it really simple. And I'm going to recompute.

So while I'm waiting for this, I'm actually going to jump ahead a little bit. Save some time. So what we're going to see is we're going to see a simplified version of the phase diagram. And we're going to talk about modeling it. Modeling the simplified iron chromium.

This lecture is all about modeling, right? What it means to build a model. So let's draw the phase diagram that you're going to see when Thermo-Calc finishes being slow. And I want to draw-- call your attention to some salient points.

So the first thing you're going to see is we're going to have iron and you're going to have chromium. And we have a spinodal region. And then we're going to have a lens like two phase region, something like that. So this here is alpha or BCC structure. This here is liquid.

All right, we're going to have a spinodal. And that happens at around 910 Kelvin and right around the middle of the composition range. Then we're going to have our melting point. Chromium melts at T_{melt} of chromium equals 2,180 Kelvin. That's the melting point of chromium. And we're going to have iron melts at T_{melt} iron around 1,810 Kelvin. So that's what we hope to see.

Let me go back to Thermo-Calc. Good, there we go. You guys see that? We're going to make some changes here. I'm going to plot as function of mole fraction. And I would like to plot things-- well, right now it has iron as the independent axis. I drew it as chromium, but you can imagine how that looks. And I'm going to-- what am I going to do? What am I going to do? I'll recompute.

Working hard. That was an entry. It said, working hard. All right, so my question for you is-- while this is working. See, it has to recompute because the x mole fraction of iron is actually a different set of numbers than a mass percent of iron. And although it could just apply a linear transformation, it doesn't know how to do that. So it recomputes the whole thing.

OK, we're going to switch back to the board and talk about building the model. So now we're going to talk about building a model. What is needed to model this phase diagram? What does that even mean? What does that even mean?

So we're going to start by building a model for pure iron. Let's start by building a model for pure iron-- Fe. And so what does pure iron need to do? Pure iron needs to melt at 1,810 Kelvin. Right? That's how pure iron should behave. So we need our model to capture that. We need our model to capture melting at 1,810 Kelvin. All right, so what do we need for that? What do we need for that?

Needs to melt at T_{m} iron. So what that means is that the Gibbs free energy of iron in the alpha phase as a function of temperature, and the Gibbs free energy in the liquid phase for iron as a function of temperature, these curves cross at T_{melt} . Or I should say, T_{melt} of iron. So if we have plot at Gibbs free energy, Gibbs temperature-- and here, I have the melting point-- in general, have something like that for the alpha phase and that for the liquid phase where they crossed at the melting point.

And we know that Gibbs equals H minus TS . And we know how to model the temperature dependence of these. Or not even model, we know how to calculate the temperature dependence of these. All right, so what we're going to end up doing is we're going to model the temp dependence of H and S , and the transformation quantities.

That is, the change in enthalpy on melting at the melting point, the change in entropy on melting at the melting point. And that, of course, is equal to the change in entropy on melting at the melting point divided by the melting point. Right, so I have the enthalpy change, the entropy change, and the melting point temperature. And if you give me any two, I'll tell you the third via this equation. Let's take these one at a time. Enthalpy and entropy-- what do I need to build those models? What data do I need?

I'm going to draw this fairly generically. Here's temperature, here's enthalpy, right? This is modeling H of T for pure iron. That's what we're doing. We're modeling H of T for pure iron. So I'm going to draw the melting point right in the middle. T melt-- I guess I'll keep the iron label-- T melt of iron. And let's say that it looks as follows. Let's say it looks like this. OK, what happens at the melting point of the enthalpy? How should this curve look?

AUDIENCE: It should jump upwards.

RAFAEL JARAMILLO: Thanks, That's right. There's an enthalpy of melting, right? A specific heat of melting. And then it continues on its way. So this here, this here is the alpha phase. And we know that in principle, I can imagine the enthalpy of the alpha phase being a function and continuous. In practice, this might be increasingly hard to measure or to calculate. And here's the liquid phase. And I can, of course, imagine this being as a function that continues but becomes increasingly inaccessible.

And let's mark some features on this. So first of all, I want to start by marking 25 degrees C. Why would I want to mark 25 degrees C? That there is H of the alpha phase for pure iron at 298, right? At 298 Kelvin. That is the enthalpy in the standard state-- 298 Kelvin, 1 atmosphere. Come back to that in a second.

All right, so that's a data point. That's good. What about the slope? The slope of this curve, dH_{α}/dT , at fixed pressure equals the heat capacity of the alpha phase. Which is, of course, temperature independent in general. That's the slope.

Likewise, the slope up here. Right? Slope dH_{liquid}/dT at fixed pressure equals the heat capacity in the liquid phase. That's that slope. And we have the transformation quantity. So that jump in enthalpy is the transformation entropy-- transformation enthalpy. $\Delta H_{\alpha \rightarrow \text{liquid}}$ at the melting point.

OK, so now we have on this plot, all of the data that we need to build this model. We need a reference point. We need heat capacities that we can integrate. And we need to know what the transformation quantities are.

So for instance, if I asked you what is the enthalpy at this temperature for iron? You would start here at the reference data. You would integrate the heat capacity up until the melting point. Then you would add the transformation quantity. And then you would continue integrating the enthalpy up until the desired temperature.

Now something I want to point out. The enthalpy in the standard state, this is set to 0 for elements by convention. There's no such thing as a 0 of energy in the universe, so we can always set zeros of entropy wherever we like. And so by convention, we set it to 0 for elements at 298 Kelvin at 1 atmosphere. So it doesn't really matter at this point here. It'll end up being 0.

And this is a preview of something to come later, so don't worry too much about this statement. But if the pure component is a compound-- let's say that my pure component is silicon oxide and I'm making a phase diagram for a glassy system, for instance. Then we use the standard enthalpy of formation.

Again, don't worry too much about this. We're going to come back to reacting heterogeneous systems in about a week and a half or two weeks, and we'll use this more and more. All right, so now I have a model for the enthalpy. Good. Let's model the entropy. And this is going to be similar.

Again, I'm modeling entropy, ST , for pure iron. Let me go a little bit faster here. So likewise, I'm going to have a melting point. I'm going to have, let's say, 25 degrees C. And I'm going to have some function.

This pen is dying. Right, so entropy goes like that. And then there's going to be a transformation entropy. And then entropy will continue to go like that. And I have alpha phase, and I have liquid phase. And in general, this function continues. In general, this function continues. And as before, I have a transformation entropy. Transformation entropy. I have a standard entropy. Standard entropy.

Entropy in the standard state. And I have my slopes. Slope dS_{α}/dT at fixed pressure equals C_p_{α}/T . You know that. And similarly, we have slope dS_{liquid}/dT p equals C_p_{liquid}/T .

All right. And so here, again, we have a picture of all the data that we need to model entropy as a function of temperature for pure iron. A reference value, the heat capacity data which gives me the slope-- and that is how to integrate this curve-- and transformation quantities. And as before, if I needed to find the entropy at that temperature, I would start here. I would integrate up. I would transform. I would continue integrating up, and I would find my value.

So let me summarize this. The data, right? Hold on. Sorry. With this enthalpy model and this entropy model, I now have fully established the model, or at least the types of data that I need to model this system. All right, that's an important point.

What data do I need? Data needed to model pure iron. What sorts of data do I need? Well, I need standard state data. Standard state data, that is S°_{298} and $\Delta H^{\circ}_{\text{form } 298}$. Which, again, for an element, it doesn't have to form. It's already been formed, so that's 0.

I need heat capacity data, right? Heat capacity. So I need C_p of the alpha phase as a function of temperature, and I need C_p as the liquid phase as a function of temperature.

And I need transformation data. Transformation. So I need $\Delta H_{\alpha \rightarrow \text{liquid}}$ at T of melting. And I need $\Delta S_{\text{transformation } \alpha \rightarrow \text{liquid}}$ at T melting. Or alternatively, I just need the melting point. I need two of those three.

So this is the type of data that I need. All right, this-- dead pen. These three numbers here, this is a triple with two are independent. So I need two of those. What about the heat capacity data? Heat capacity data. This can be modeled as polynomials.

So for example, I can have this model. $C_p_{\alpha} \text{ temperature} = a + bT + c \text{ over } T^2$. Right? And I'm also going to have $C_p_{\text{liquid}} \text{ temperature} = a + bT + c \text{ over } T^2$. It's just a polynomial.

But I need to be careful because these are different phases. So in general, these coefficients are not the same. So I'll label them a_{α} , b_{α} , c_{α} , a_{liquid} , b_{liquid} , c_{liquid} . Right. And again, if I-- let's say I'm given the enthalpy of transformation and the melting temperature, I can simply calculate the entropy of transformation.

OK. So how do I get this data? How do I get this data? So let's go back to Thermo-Calc. So here's Thermo-Calc. And what I'm going to do is get Thermo-Calc to give us some of this stuff.

So the first thing I'm going to do is I'm going to rename some of these objects. So this, I'm going to call the phase diagram calculator. This is just to maintain sanity. You don't need to do this. Phase diagram plot. And then I'm going to create a new equilibrium calculator. And this is going to calculate the quantities of pure iron for me as a function of temperature. I'm going to rename it. I'm going to rename it pure iron calc.

So what I'm going to do here is I'm going to make this mole fraction, and I'm going to make it pure iron. And I'm going to calculate the properties along one axis, and that axis will be temperature. So I'm calculating the properties of pure iron mole fraction $x_{\text{Fe}} = 1$ along one axis, and that axis is temperature. And this will calculate all the thermodynamic properties for me.

I'm going to create a plot here so I can plot and view some of these properties. So let me call this pure iron plot. And I'll start by plotting on the x-axis temperature and the y-axis Gibbs energy. And we'll do this for all phases. We'll perform the tree. So now the system has already calculated the phase diagram, and so that's not changing. But I added this new calculator here, which is calculating some properties of pure iron, and it finished.

So look-- this is the Gibbs free energy of pure iron as a function of temperature. And it's plotted for all phases, meaning the blue data is for the BCC phase, and the red data is for the liquid phase. These are two different curves. The difference is the kink there is a little subtle. It's not very obvious. But these two curves do intersect at the melting point, as they should.

Let's calculate and plot-- let's plot enthalpy instead. Enthalpy. I'll plot for all phases. Perform. Ah ha. Cool. This is now enthalpy of iron as a function of temperature with the two different phases marked in two different colors.

I have a point to make here, which is this looks real. This looks real. This looks real. This looks real. And then it gets zeroed, right? The 0 is not real. That's simply the program representing to you the fact that it doesn't have any more data beyond that point. So it doesn't know what the enthalpy of solid iron is at temperatures in which the liquid is stable.

So here's the enthalpy of solid iron. Here's the transformation quantity. All right? And there's the enthalpy of liquid iron. That's neat. OK, how do I estimate the transformation enthalpy? That is, the enthalpy of melting iron from this plot. Does anybody know how I would do that easily and quickly?

AUDIENCE: Enthalpy over temperature?

RAFAEL I'm sorry, One more time.

JARAMILLO:

AUDIENCE: Like, heat over temperature, which is like enthalpy here?

RAFAEL Well, the y-axis is already enthalpy. So how do I measure the transformation enthalpy?

JARAMILLO:

AUDIENCE: Oh, like the-- we go to the temperature at the melting point and take the two values?

RAFAEL Yeah. So I'm just going to mouse over it, right? Your boss is hovering over you and you need an answer quickly.

JARAMILLO: Here we go. You see? Can you guys see how I mouse over? It's giving me the value at the cursor. Folks can see that?

So I'm going to say 72,416 minus 58,445. That's it. That's my estimate of the transformation enthalpy. And I'll say maybe that's good to two digits. So I'm not going to carry five digits of significant figures, I'll carry two digits. So if someone asks you for the transformation enthalpy from this data from this plot-- they ask you, you were in a hurry-- you just mouse over, or take a ruler, or any other method of doing this, and estimate the value.

Cool. All right, what about entropy? Entropy. All right, there's the entropy plotted for system. I'll plot for all phases just so it'll colorize those two different phases. Great. Similarly, the entropy increases with temperature. It jumps up when you melt, and it continues increasing with temperature.

And as before, if you wanted to calculate the transformation entropy-- sorry. I didn't mean calculate. If you wanted to estimate the transformation entropy, just mouse over. It's 99 minus 92. So let's say the entropy of melting iron is 7. And I'm going to look that up. Everybody, appendix C-- phase transformation for the elements. Iron BCC to liquid, delta S of transformation-- 7.6. Not bad, right? So we're in the ballpark.

Let's say I want to get the heat capacity. This I'm going to have to work a little bit harder because Thermo-Calc unfortunately does not output heat capacity data. It does output enthalpy, however. So I'm going to show you how I'm going to estimate the heat capacity.

I'm going to grab this enthalpy data. I'm going to grab it as follows. I'm going to create a new successor from the pure iron calculator. It's going to be called the table renderer. I'm going to rename this. I'm going to call it pure iron table. And I'm going to ask the table to be enthalpy of the system as a function of temperature.

There we have it. Those are the numbers. Now I'm going to right click. I'm going to Save As. And I've already gone through this exercise. But as you can see, iron enthalpy. OK? So I Saved As, I'm going to save over iron enthalpy dot text. So now I have that data on my hard drive.

Now I'm going to go over into a data analysis software of my choice. This case, it's going to be MATLAB. So now I'm in MATLAB. If you don't use MATLAB, that's fine. You can use Excel, or Mathematica, or Igor, or any program you like. Python-- whatever you're comfortable with. Import Data-- and I'm going to import chromium enthalpy dot text.

OK, I don't know whether this shows the Import window, whether Zoom is sharing the Import window. In fact, probably isn't. So never mind that. I'm going to import an object-- chromium enthalpy. Great. And now I have in my workspace, an object called chromium enthalpy. Can you see that?

OK, let me dock this. That's right. OK, so I have an object called chromium enthalpy. Let's see how it looks. Plot chromium enthalpy. Let me dock this plot so that you guys can see it. There we go. You see this? You see the plot? It doesn't look so good because the data is not ordered by temperature.

So let's plot it with a point line style instead so we don't have to see that jump. That looks much better. OK, so now we have chromium enthalpy. All right, what am I going to do now? What should I do now? What should I do now? I'm going to fit it.

So it's going to bring up a curve fitting utility. Give it just a second. OK, so here's MATLAB's curve fitting utility. Lots of programs have something like this. And you see what I'm doing here? I've got the data, and I'm going to fit it to second order polynomial.

And for now, I'm going to just fit-- well, it doesn't make sense to fit both phases because we don't expect both phases to fit to one model because they're different phases. So I'm going to stick with just the low temperature phase. And that means that I'm fitting the enthalpy as a function of temperature for-- I'm doing chromium here, aren't I? Not iron. Same applies. I'm fitting enthalpy versus temperature for the low temperature phase.

OK. So this fits pretty well with the second order, right? It fits pretty well through a second order polynomial. I don't see a need to go to a higher order polynomial. What if I instead wanted to fit the liquid phase? Let me exclude all of the low temperature phase data. Would you recommend fitting this data to a first order polynomial or a second order polynomial?

AUDIENCE: First order, because it's a line.

RAFAEL JARAMILLO: Yeah. This looks like the quadratic term is really superfluous here. So quadratic term is really not needed. And you can actually see this in the fitting results in the value assumed for the quadratic term, which is close to 0, and the uncertainty in the quadratic term, which is large. So I think that the liquid phase in this particular material is better fit to enthalpy versus temperature being a straight line. And what is the slope of that line, by the way? What's the slope of enthalpy versus temperature? The slope of enthalpy versus temperature?

AUDIENCE: Heat capacity at pressure.

RAFAEL JARAMILLO: Yeah, it's the heat capacity. So what is this fitting routine telling me? It's telling me that the heat capacity of liquid iron is 50. That sounds about right. Let me look back in my table here. And you can look up the data, obviously, online. You don't need to have the book handy. Although having the book handy is handy.

And let's see. Does it have the heat capacity of liquid iron? Well unfortunately, it doesn't have the heat capacity of elements of high temperature. But you'll find numbers between 45 and 50 are typical of liquid metals. Great. OK. Now I want to make a note here about this procedure. And then we'll move on to modeling the solutions.

So what have I just done? I've modeled the temperature dependence of H. That's what I've done, right? I've modeled it as follows. $H = p_1 T + p_2$, right? And I want to model the heat capacity as $C_p = a + bT$. So by inspection, I see that twice times my polynomial-- my quadratic coefficient is b. And my linear coefficient-- that is, the slope-- is a. This is as in MATLAB. And this is my heat capacity model.

But what I want is this. Right? I want this. That's the heat capacity data. So what's the derivative of this polynomial? It's $2 p_1$. $C_p = 2 p_1 T + p_2$, right? And I want to model the heat capacity as $C_p = a + bT$. So by inspection, I see that twice times my polynomial-- my quadratic coefficient is b. And my linear coefficient-- that is, the slope-- is a. This is as in MATLAB. And this is my heat capacity model.

Again, we're gaining a little proficiency here with modeling, and data analysis, and flipping back and forth between software, and so forth. All right, so let's say that I've done building my model for pure iron. I do that for all the phases of iron, and I grab the transformation quantities. And then I'm going to build my model for chromium. All right, kind of similar procedure. And then I need to build my solution models.

So let's start with the spinodal phase. And let's model a simple regular with one adjustable parameter, right? $\Delta H_{mix} = A_0 x_1 x_2$. One adjustable parameter. You know that.

All right, so now we're going to grab that data from Thermo-Calc. How do we do that? Let us now calculate the properties of the system now at a fixed temperature as a function of composition. Mole fraction iron from 0 to 1 at a fixed temperature. What temperature?

This over here is a solid solution region. Let's plot it in the solid solution region. Let's plot it at 1,000 Kelvin. That's a nice round number. So I'm going to plot at 1,000 Kelvin, the thermodynamics of this system as a function of iron composition. I'll call this 1,000 K calculator.

And then I want to be able to plot that. So I'll call that-- call that slow is what I'm going to call that. I'll call that 1,000 K plot. And what I'm going to want to plot is the enthalpy, right? I want to fit a simple regular solution model, which means I need the enthalpy as a function of composition.

Huh, neat. You see that? Now how would I go about fitting my simple regular model to this data? Somebody, how would I go about fitting my simple regular model to this data?

I'm going to do it by eye. It's quicker. I could export it and fit it in MATLAB. I'm going to do it by eye. This is x_{Fe} . Right around 50/50 is kind of a special point. The data kind of looks like that. This is enthalpy. The straight line connecting those two endpoints is what?

$x_{Fe} = 0$. I'm going to read that off. That's about 24.8 joules-- kilojoules per mole. We read that off the plot. Sorry-- H_0 of chromium. I'm going to read that off. That was about 19.5 kilojoules per mole. And H at $x_{chromium}$ equals one half was about 29 kilojoules per mole.

And I can see just geometrically that this height here, this is 0.5^2 times A_0 . OK, that's simply $x_1 x_2 A_0$ where x_1 and x_2 are both 0.5. So I can just read right off the plot that A_0 for the BCC phase is about 28 kilojoules per mole. You can get all that simply from mousing over the plot and pulling these numbers out to two or three digits.

All right. Alternatively, you could-- alternatively, you could export data and fit it. You could do that. You could do that. All right. And you're going to likewise build model for liquid phase. Right? We build a model for the BCC phase-- BCC phase. We're going to likewise build a model for the liquid phase.

All right. Now we have a model for pure chromium. We have a model for pure iron. We have a model for the liquid phase solution. We have a model for the solid phase solution. What do I do next? At each temperature, we draw free energy composition diagram and find common tangents, if any. If there are any.

All right, so I have two phases. I have alpha, which is x of chromium $\mu_{chromium}^0$ in the alpha phase, plus x of iron μ_{iron}^0 in the alpha phase, plus the solution model-- the alpha phase. I have the liquid phase. This is x chromium $\mu_{chromium}^0$ in liquid phase, plus x iron μ_{iron}^0 in liquid phase, plus the solution model. These terms, these are the pure component models.

And those, of course, include reference state changes because we've built in to those models the fact that these materials melt. Right? Or maybe there's other state changes for the pure materials. We built that in. And these are the solution models. So this is it. From this, you get the phase diagram.

So to pull way back, we have pure component models. We have solution models. Those feed into the free energy composition diagrams. And those result in the phase diagrams.

This is thermodynamics, right? This is what we're trying to work on this semester. So this problem set, which is out and is due Friday, was going to include all three aspects-- building the models, plotting the models, and solving the phase diagrams using this web based app. But instead, because the web based app is funky, we're going to limit it to just that first part.

And with the remaining minutes, I'd like to try to show you what you're missing because I was able to get this web based version to play a little bit nicely. So I want to show an animation of how this process works. So never mind all this data entry screen you're going to see in a minute because you won't be using it.

But I'm going to simulate a two lens system, which is like the one you were asked to do in the p set with two lens system. It's loading. It's loading. So this is a screen where you would enter all the parameters for a model that you've built. And here-- can you see this? Can you see these two plots?

What this program is going to do, it's plotting the Gibbs free energy as a function of composition for three phases now. Three phases. In the last 15 minutes, we've been working on a two phase model. Now we have a three phase model-- liquid, alpha, and beta.

And it's going to show you the free energy composition diagrams at a series of temperatures. And at each temperature, it's going to determine if there are any common tangents. And if there are, it's going to draw that as a tie line on the phase diagram. And we have this animated so that effectively, it sweeps the temperature and paints the phase diagram.

So the red arrow down here indicates the temperature. And right now, we are in an alpha phase region. But you're going to see the beta phase is starting to become more and more competitive. And at some point, it develops a common tangent with the alpha phase when component one transforms to beta.

There. It's actually happening now. The common tangent is so teeny tiny, you can't really see it very clearly. We have it marked in red, and we have these gray lines indicating its extent. And you see what's happening is that two phase region is being painted across the phase diagram.

Now, believe it or not, we're in the beta phase. This whole system is stable as a beta phase solid solution at all compositions. The alpha phase is now no longer stable for any composition. And liquid is now about to become relevant.

What's going to melt first is the stuff on the left. The green line is going to become the favorable phase for the stuff on the left right around now. And we're going to get another series of common tangents that sweep across the phase diagram as the system melts from left to right.

And there you have it. That thing on the bottom, we don't have such a high temperature point density. I think we're stepping in every 20 Kelvin steps. So the density of tie lines isn't as high as you might like for a published phase diagram. But nevertheless, you can see this is a two lens system-- three phases, two lenses.

OK. That's where I wanted to get to for today. I'm going to stop recording, and I'm happy to take questions.