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3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Exam B Problem 7

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Hi there. I'm Brian. We're going to be doing problem number 7 of the 2009 final examination. So the way I like to approach these problems is to identify what I think is important to know before attempting them. Things that you should review that will help you successfully navigate the problem. I call this the what I need, W I N. So for this particular problem, which I think of as the phase diagram problem, you need three things critically in order to successfully complete it.

Number one you need to have a general understanding of what a phase diagram is, how to read it, how to write it, how to interpret the information it gives you. You can find a lot of this in chapter 9 of Shackleford. Along the same lines you should probably know how to go in between binary and unary phase diagrams. How they are related at least. In this problem it's not absolutely necessary to know this. But in similar problems we might ask, this is critical to understand how these two are interrelated.

The second thing you should know is some language like critical point and triple point. Where these are and what they mean on the phase diagram. And the third thing is the phase coexistence. So what does that actually mean? How do you find it on the phase diagram?

So with these three particular points, I'd review them and then I would recommend attempting the problem afterwards.

So we're going to start the problem. We're going to start over here. I'm actually going to start this from a reverse direction. And review really quick what a binary phase diagram is. because this is actually the phase diagram which you will see most often as you progress in your career as a scientist or an engineer. This is something you'll see a lot of the time. It'll have either one element and another element. Or one compound and another compound along the axis. And it shows the different phases which exist at certain temperatures and compositions. So in general it's important to sort of understand what a phase is. So a phase, is a chemically and a structurally homogeneous material given certain state conditions.

So a phase diagram depicts picks all these phases. It's the master plot of phases that are in equilibrium given a particular set of state conditions. When I say state conditions I'm actually referring to things like temperature, pressure, I even sometimes consider composition to be one of those state conditions. So in a binary phase diagram, what we're looking at is the temperature versus the composition.

So if you have some composition of silicon and germanium at some temperature, you know exactly what phase it should be at thermodynamically. It doesn't actually

mean it will be, but it should be. So that's what a binary phase diagram looks like. So this is something you'll see a lot and this is something you probably will become used to seeing a lot as you go on in your years. We're going to come back to this in a second.

But first, for now, we're going to actually attempt the problem that's given. And then I'll tie both of those together for you. So let's go over and let's actually look at the problem now. We'll go back to that in a second. We're asked to draw a unary phase diagram for silicon. And we're given some critical information. Specifically on the problem we're given the triple point, we're given the critical point, and we're asked to draw this. Not to scale, of course, but what it should generally look like.

So the first thing I do is label my axes. Pressure, temperature. And then we're given certain data. So I'm just going to throw it down right in the beginning. We're given pressure and temperature for triple point. We're given pressure and temperature for the critical point. So I'm going to put those points down right now. Because I know that's part of the answer.

So let me first put down the triple point. We're told the triple point occurs at 0.15 atm. And we're told that that is at a temperature of 1415 celsius. So temperatures are going to be in celsius and our pressures are going to be in atmospheres. So we're going to go up to find this point. In fact I'm going to give it a different color. That is our triple point.

I'm next going to plot the critical point here. We're told that that occurs at a pressure of 6,600. So not to scale of course. But that's going to be somewhere all the way up here. Now we're told that that is at a temperature of 4880. So here's a point here. So we've just put two points down. But that's not enough to complete the problem. It doesn't actually answer all the questions.

The problem actually also asks us to provide the normal boiling point and the normal melting point of silicon. So you're not actually given those temperatures because you've got to be clever. And all the students in our class are given a periodic table during the exam. So I would encourage you to have a periodic table with this type of data. So if you look at the periodic table for silicon you can then find your melting point and you can find your boiling point.

So this data, a normal melting point and a normal boiling point will occur at 1 atmosphere. Let me just put 1 atmosphere on the pressure here. Again not to scale. So anything that occurs at this particular pressure, this isobaric line, is going to be normal. So our normal melting point occurs at 1414, which is right next to 1415. There we go. And our normal boiling point occurs at 3265. These are approximate numbers. So we'll put that here.

And now if you've seen a unary phase diagram before, which I hope you have during your studying, you'll know that it looks somewhat like a y shape. So one thing we're going to do now is we're going to connect these dots. We know that at very high temperatures we're going to have what's a gas, basically. And at very low temperatures we're going to have something like a solid. And we have some liquid in the middle. And the way we're going to delineate these phases is to connect these dots.

And this is what our unary phase diagram is going to look like. So in order to complete this problem-- it was actually not too bad of a problem-- all you have to do is label some particular aspects of this graph. So number 1, we have a solid region, we have a gas region. That implies this must be the liquid region. I'll put an L there.

You're asked to identify 1, 2 and 3 component regions. Or three 1-phase regions, 2-phase regions. So number 1, you could have chosen for a 1-phase region, you can choose a point here in the gas, a point here in the liquid, or a point here in the solid. I'll just choose one in the gas. So something here, let's call that *i*, for answering part *i*. You could have chosen a point along any of these lines for a 2-phase equilibrium. Which implies that at that point, so at that specific pressure and at that specific temperature, you have both phases of equilibrium.

Let me just choose one and explain it. So let's choose something here. Between 0.15 and 1. So let's choose this point. There we are. So at this point, at whatever pressure we're at and whatever temperature we're at here, we have both liquid and gas in equilibrium. They both coexist. You're not tending towards one or the other. They're both there. So that's part B, the 2-phase coexistence area. So we put that here. *i i*.

And the third part is the 3-phase coexistence, which is-- almost you can pull it out of the name-- the triple point. At the triple point-- and there's only one of these-- you have all three, gas, liquid and solid coexisting together. So we've already sort of made that. That was our blue dot. 1, 2, 3. That's that point right there. So not to scale. But this is the answer. This is full credit.

One thing that's really interesting to note is that on this particular answer we have a negative slope on our solid-liquid coexistence line. Now you've probably seen this before in your studying and it occurred with water. Most materials actually will have a positive slope. If you think about it it's sort of counterintuitive. What this implies is that if I'm at a constant temperature and as I raise my pressure I'm going to go from the solid to the liquid. Intuitively, we would think that the solid is more densely packed and therefore as we increase the pressure we're going to tend towards a solid. That's not the case in water and in this problem is not the case with the data we're given for silicon.

In this case as we raise the pressure we're actually turning into a liquid. It's kind of counterintuitive. Another way of actually saying that is the liquid phase at this particular temperature is more dense than the solid phase. And you see that with water, which is why ice floats on top of water. So that is our unary diagram. That is the full credit on this problem.

I do want to tie it in really quick though, with what a binary diagram is. Because this is a very important concept to get and a potential problem. So we're going to go back over to binary phase diagram over here. And so what we're looking at on this binary phase diagram is actually, it's the temperature versus the composition at a specific pressure. Now for a binary phase diagram you're going to assume-- unless you're told otherwise-- that it occurs at 1 atm, 1 atmosphere.

If I want to go between the binary and the unary that we just looked at, you need to add your third axis. So if we had a third axis-- let me draw that here. This is going to be our *z*-axis. There's the *z*. We know that if we put a pressure along this axis, we're going to be able to extract what we had for our unary diagram.

So let me do that for you. I'm going to call this the pressure axis. Going back in and out of the board. And actually this is at 1 atm. Which implies at some point farther back we have the origin. You can just do this lightly so it doesn't get too confusing. We have an origin for our pressure. So at this point we have 0 pressure. We don't work with negative pressures. 0 pressure. Which implies-- let me just draw the Cartesian form of this-- so we have composition, we have temperature, we have pressure. That's our x, y, z.

Now what happens is that as we increase pressure what happens to, for example, this point? Now what is this point? This point is the point where we go from the solid to the liquid. That's the melting point. What happens to the melting point as we increase or decrease our pressure? Well that information is given on our unary phase diagram. Let's go back really quickly.

As we increase our pressure we can see that what's going to happen with our point is it's going to go up. So what basically we have to do is we need to take-- you have to think three-dimensionally-- and take this graph and you're going to take it and spin it and put it on to one of those planes there. So we're going to get an idea. This is something that I would challenge you, the listener, to do and think about and do on your paper after you've completed this problem successfully.

I'm going to draw it right now. And I'm going to let you look at it and think about it, what it means. So let me do that. Let's take a look now. This is our temperature axis. Here's t. Here's p. Remember unary was p versus t, so you've got to do a little flipping. But let me just draw it now. It kind of goes up to the words. But you get the idea. This is-- if you do a little flipping and I challenge you to do that, some three-dimensional thinking-- this is the unary phase plot that we gave for our answer. And the point I'm trying to make is that you can go in between your unary and your binary diagrams by understanding that. For example, binary diagram is at a constant pressure and your unary diagram, unary means that it has one material, one composition.

So in this particular problem I've created germanium to be our b element. And we're operating here with pure silicon. So you can go in between if you have the grasp of that concept. So I would challenge you to think about that. If you've gotten the problem right and you understand this concept, I think you're good to go on phase diagrams.

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