[SQUEAKING]

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RAFAEL JARAMILLO: All right. Good morning, 020. Today is the last lecture of technical content of the semester. So that's kind of exciting. And it's the last time we're going to use this little piece of graph paper, which is not particularly exciting. But, anyway, next week, we're going to change gears a little bit and do our second social and personal hour on Monday. And I'll send around reading for that shortly.

And on Wednesday, we're going to do a Zoom game show. So I hope we have a good attendance for that because we're going to try to make it as fun as we can over Zoom. It won't be as much fun as in person. But, still. Anyway, that's next week. Today, we're going to work an example which pulls together some concepts which we've been using the last couple of lectures.

So this is what we're going to work on today-- reacting systems that have gases and condensed phases. So we spent a couple lectures in the middle of the term on reacting systems with just gases. And then in the last couple of lectures, we've talked about oxidation, which are reacting systems with oxygen gas and in condensed phases. That is metals and oxides.

So we're going to just generalize that a little bit. I shouldn't say generalize because we're going to work a specific example. We're going to move away from oxides and do an example problem which I really think ties together a lot of concepts. And it's a silicon-carbide problem. And before I move in here, this is not-- everything we're going to do today is not necessarily particular to silicon carbide. It's particularly the silicon carbide and the details of course. But the approach is general for a lot of materials.

So what I'm going to do is show you the phase diagram of silicon carbide and briefly talk about why anyone would care about silicon carbide. And then we'll start working on that problem. So let's see. Here we go. The formation of silicon carbide. OK, before I label the solid phases, somebody, how many solid phases are there in this diagram?

You should be able to read a diagram like this by now.

AUDIENCE: Three?

RAFAEL JARAMILLO: Three solid phases. Silicon is a line compound here, which is sort of giving you a hint, silicon carbide. So silicon, silicon carbide, and carbon. So three solid phases. Thank you. And one liquid phase. And, all right, so here's a peritectic reaction, right? This is a peritectic reaction. Has that t-shaped. It's liquid, silicon, carbon-containing melt in graphite reacting to form silicon carbide.

So silicon carbide forms out of a peritectic. Silicon of course melts at 1,414 C. Carbon doesn't melt actually. It's sublimes. And it's way off the scales of 4,000 degrees or something like that. And silicon carbide decomposes. It doesn't melt. It decomposes. It's very high temperature. So you can see the silicon carbide here is a refractory material. It's a refractory ceramic material.

So it's a very hard. It's conundrum. That's the mineral. It's also known as moissanite. So it is a wide-bandgap semiconductor and an abrasive. And I learned a couple of things about it. I knew it's an abrasive. A lot of times, if you go and buy grinding wheels and such, or high-performance mechanical abrasives, or ultra-hard components used for brake pads and things like that, it'll be silicon-carbide containing. That I knew.

Silicon carbide is a wide-bandgap semiconductor. And it may be the future of power electronics. So it's important in my area of expertise for that reason. I also learned today that it was the first ever LED, was made with silicon carbide. It's about 110 years ago. And it was noticed that silicon carbide can be made into an LED. Of course it's not it's not the LED wide-bandgap material of choice.

Does anyone know what wide-bandgap semiconductor is providing most of the light quite possibly in the room you're sitting right now? Nobody knows. It's a Nobel Prize a couple of years ago. Gallium nitride. So another wide-bandgap compound semiconductor, not a refractory material. It falls apart more easily than silicon carbide. But, anyway, there's lots of exciting reasons to know about-- you should know about silicon carbide. And I think you should care about it, too, because it's important for a number of reasons. And it's got an interesting history.

Enough about that. Let's talk about a problem. I'm going to give you a problem. This is like a word problem you might find on a test or something like that. Place pieces of silicon carbide and carbon-- and for now, I'll label that graphite but just keep in mind it's carbon-- into a vacuum oven.

A vacuum oven is an oven that can operate under vacuum. They're all over campus, if you don't know already. And now I'm going to do it. I'm going to put them in the oven. And I'm going to pull vacuum. That means evacuate the oven. And we're going to pull this vacuum to approximately 0 pascals. So there's no absolute vacuum. But on this scale, your gauge is reading 0.

We're going to seal it. Pull vacuum. Seal. And then heat to 1,700 C. You observe two things. Silicon carbide and carbon are both still present.

You also observe that the pressure is 4.0 pascals. So let me draw this visualization here of the experiment. And what you observe is a vacuum oven. It's got a nice, insulated walls, nice vacuum seal. A lot of money for a vacuum furnace that can grow to 1,700 C. But there's a number of them on campus.

And, OK, so here's silicon carbide. It's a chunk of silicon carbide sitting there in the vacuum furnace. And a chunk of graphite should be gray, right? Why not? Graphite, a chunk of graphite. Yeah. And you've got some gauges on there. Often, gauges and block diagrams are indicated like that. So you've got a gauge saying that pressure equals 4.0 pascal. And you've got another gauge reading the temperature equals 1,700 degrees C.

This is the problem statement. Are there any questions about the problem statement? I haven't asked the question yet. This is a setup. Will somebody express this observation in thermodynamics language for me? What does this observation mean?

AUDIENCE: There are multiple phases.

RAFAEL JARAMILLO: Right. And the phases are?

AUDIENCE: Silicon carbide, and carbon.

RAFAEL JARAMILLO:	Oh, right. I'm sorry. Yes. That's right. The phases are in--
AUDIENCE:	(WHISPERS) Equilibrium.
RAFAEL JARAMILLO:	Someone just whispered.
AUDIENCE:	Equilibrium?
RAFAEL JARAMILLO:	Equilibrium, right? The phases are in equilibrium. You heat it up. And you observe that they're present. This is a class in equilibrium thermodynamics. You can infer from context that these things are both present. So they are coexisting in equilibrium, right? Multiple condensed phases coexisting in equilibrium. What's the third phase that's present? You can't unsee it. This is important. You need to be able to interpret these observations in thermodynamics language if you're going to solve thermodynamics problem.
	So we've got two condensed phases in equilibrium. There's a third phase. Would somebody tell me what is the third phase?
AUDIENCE:	Gas phase.
RAFAEL JARAMILLO:	Gas. Right. There's gas. There's a gas phase there. You can't see it with your eyes. But it's there. Your pressure gauge tells you it's there. There's some pressure. There's some gas pressure. Good. Thank you. All right, here's a question. Question, what is the Gibbs free energy of formation of silicon carbide at 1,700 degrees C.
	That is silicon in its solid phase plus carbon in its graphite phase going to silicon carbide. And I'm asking for a delta formation. And I'm going to give you some reference data. You need a little bit more information to answer that question. Reference data.
	You know or you measure that the saturation vapor pressures at 1,700 degrees C are-- this is the data you have. P silicon saturation, 1,700 degrees C equals 4.4 pascals. And P carbon saturation at 1,700 degrees C, what do you think it is? Is it larger than silicon? Or is it smaller than silicon? The saturation vapor pressure of carbon.
	You might ask yourself, which is more volatile? I'll give you a hint. What are the saturation vapor pressures of these refractory materials? Are they higher than that of silicon? Or are they lower than that of silicon?
	Think about what you know about bonding. Think about what you know about refractory materials. Ask yourselves, what's more volatile?
AUDIENCE:	So would the saturation vapor pressure of carbon be 0, then?
RAFAEL JARAMILLO:	The saturation vapor pressure of nothing-- there's no component or compound for which the saturation vapor pressure is 0, right? Think back to the unary phase diagrams. It's always finite. It's something. It exists. But how does it compare to that of silicon?
AUDIENCE:	It would be much smaller than that.

RAFAEL JARAMILLO: Much smaller. Right. Exactly. Much, much less than P sat of silicon. That's right. And this should be something that you just intuitively understand, which is that more strongly bound compounds, refractory compounds are less volatile and therefore have lower vapor pressures. They also have lower melting points, right?

You know that carbon is very strongly covalently bonded to itself. Silicon is strongly but less so covalently bonded to itself. Germanium is even more volatile. It falls apart more easily. And by the time you get to tin and lead, you have really high vapor pressure, low melting point materials. So periodic table knowledge there.

All right, both of these are about below 10 to the minus 5 pascals. So you have these two materials that have very, very low saturation vapor pressure and one that has a reasonable saturation vapor pressure. That's the reference data. OK, here's the problem statement. What is the Gibbs free energy of formation of silicon carbide?

So what I'm going to do is I'm going to start by-- I'm not going to start by asking how do you solve this problem. I'm going to start just by writing down an expression for the thing we want to solve for, just manipulating terms, trying to think out loud here on the page. So let's see. Delta formation of silicon carbide-- well, just by definition you know what that is.

It's the Gibbs free energy of silicon carbide minus the Gibbs free energy of silicon in its reference state and its pure state minus the Gibbs free energy of carbon and its reference statement because it's-- and the stoichiometry's really easy. 1 mole of silicon and 1 mole of carbon forms 1 mole of silicon carbide. So this expression is very, very easy.

All right, well, for 1 mole of silicon carbide, G. so carbide equals-- this is just partial molar properties. So this we know. And it's just the chemical potential of silicon plus the chemical potential of carbon-- right? This we know-- in silicon carbide, in silicon carbide.

So it's just partial molar properties and stuff we know. And I'm just going to plug this in. And what we get is the free energy of Information of silicon carbide expressed in terms of the chemical potentials. So it's the chemical potential of silicon and silicon carbide plus the chemical potential of carbon and silicon carbide minus the chemical potential of silicon in its reference state minus the chemical potential of carbon in its reference state.

I'm going to do one more thing. I'm just going to rearrange. I'm going to say it's silicone and silicon carbide minus silicon in its reference state and the chemical potential of carbon and silicon carbide minus chemical potential of carbon in its reference state. So I have the free energy of formation expressed in terms of differences in chemical potential.

And you can see how this is similar to solution modeling, right? I have delta mus. This is a delta mu. This is a delta mu. It's just the stoichiometry is fixed. And so we don't have to worry about composition variables anymore. We just have one of these and one of these. All right, and I'm going to I'm going to tackle these one at a time. So I'm going to tackle this one first. So I'll just label it 1. And I'm going to tackle this one second. I'm going to label it 2. So if we can find equations for these quantities, then we know our answer.

So I'm going to take these one at a time. And then I'm going to start asking you folks some questions. So look alert. Let's take 1 first. 1. Here, what I want to do-- sorry. One of the things I want to do with this working an example thing is I want to split back and forth between equations and word problems, word problems and equations.

You have to be nimble. And you have to know the material well enough to do that. You know by now that's an important skill. So how does the chemical potential of carbon differ from its pure reference state?

All right, this sentence is this expression, all right? This expression is the difference in chemical potential for carbon in between this compound and its reference state. That's what that expresses, right? That's also what this expresses. How does the chemical potential of carbon differ from its pure reference state? So I'll ask you. Somebody, please volunteer and answer. How does the chemical potential of carbon differ from its pure reference state?

And while you're thinking about that, I will just return to my observation.

AUDIENCE: So I guess this is kind of like the P sat where they're in equilibrium. It's in equilibrium with the pure phase.

RAFAEL JARAMILLO: So, OK. Good. And so-- sorry, I'm talking over you, And so, Priya, your answer is?

AUDIENCE: It should be the same.

RAFAEL JARAMILLO: Right. Right. And that was you, right? You're hidden. But, yeah. So, OK.

AUDIENCE: Yeah. Sorry.

RAFAEL JARAMILLO: It doesn't. It doesn't It doesn't differ. Why? As pointed out, pure carbon is in equilibrium with silicon carbide. That's an observation. What that means is that the chemical potential of carbon and silicon carbide is the same as the chemical potential of carbon in that graphite phase, which is sitting there, which is, by definition, the chemical potential of carbon in its reference state. Good.

And let me remind you why that is. The type of thing we've been doing all semester is thinking about the conditions for equilibrium, the criteria for equilibrium, if you like. Here's graphite. Here's silicon carbide. Well, there's a gas phase, too, right? The carbon atoms are exchanging. I'm going to draw some carbon atoms in the gas.

The carbon atoms are exchanging freely, right? That's an unconstrained internal process. They're exchanging freely between silicon carbide and carbon-- well, graphite-- via vapor phase, via the vapor phase.

When we had conservation of mass with mass exchange between two phases, that led to the condition for chemical equilibrium. Chemical equilibrium. Right? That was about the middle of the term that we arrived at that. So chemical equilibrium, right? That's what I wrote down here.

OK, So that's great. That means that-- what is this term equal to? What is the term in the expression in the parentheses equal to?

AUDIENCE: 0?

RAFAEL JARAMILLO: 0. Right. Exactly. There's no difference in chemical potential for carbon between the compound and the pure state, right? Thank you, Ian. OK, great. So half the term, half the right-hand side of the equation is put to bed. Let's put the other half of the right-hand side to bed. Let's take care of part 2, which is, expressing in words, part 2 is the difference in chemical potential for silicon between the compound and its pure state.

So I'll write that out in words. How does the chemical potential of silicon differ from its pure reference state?

OK, so that's why that-- OK. OK, so this is a little harder. I'll walk you through this. Are there any initial thoughts on how to go at this? Anyone want to take a gamble? Let me give you a hint.

OK, if solid silicone, or I should say liquid because we're above the melting point condensed-- I said solid in the lecture notes. So that's a typo. If condensed silicon were present, the partial pressure, P silicon, would be equal to-- what would the partial pressure of silicon be equal to if condensed silicon were present?

If condenses silicon were present, what would the partial pressure of silicon equal to?

AUDIENCE: The saturation volume.

RAFAEL JARAMILLO: Right. Thank you. OK. So that's a hypothetical because there's no condensed silicon there. But it's a starting point if condensed silicon-- OK. So therefore, chemical potential of silicon minus chemical potential of silicon in its reference state equals-- this is a bit of an a-ha thing.

You have to see the connection here between different parts of the semester. The chemical potential of silicon in this system relative to what it would be if condensed silicon were present. If condensed silicon were present, the chemical potential would be equal to its reference state chemical potential. Also, if condensed silicone were present, the pressure would be equal to the saturation pressure.

OK, I'll just give it. Therefore, the chemical potential difference of silicon relative to the reference state is RT log P silicon over P silicon sat. Why is this? This is recognizing that silicon in silicon carbide is in equilibrium with silicon in the gas phase.

All right, here's another. You have to imagine this. Silicon carbide and there's silicon vapor. You can't see it. But it's there. And you know that the silicon vapor is in equilibrium with the silicon carbide. Those components are in equilibrium because they can freely exchange. So they're in chemical equilibrium.

So whatever the chemical potential of this vapor phase is, it's the same as the chemical potential of silicon in this compound. And you know how to calculate the chemical potential of a vapor phase. It's RT log partial pressure over the reference partial pressure. OK, that was cool. We're not done yet.

What is partial pressure of silicon? I'll remind you. The total pressure now equals 4.0 pascals. The total pressure equals 4 pascals, right? Gas phase, what are the gas phase components? What sort of molecules am I finding in the gas phase? Told you I have silicon. And what else is there?

AUDIENCE: Silicon? Oh.

RAFAEL JARAMILLO: Yep. Thanks for that. What else?

AUDIENCE: Probably nitrogen, oxygen if it's from the general air.

RAFAEL JARAMILLO: No because we pulled vacuum before we did this. That was a key thing. So there's nothing in there except what we put in there, which was silicon and silicon carbide. It's carbon and silicon carbide. So what other components are in the gas? In general, what else could be there?

AUDIENCE: Carbon?

RAFAEL   Sorry?
JARAMILLO:

AUDIENCE: Carbon.

RAFAEL   Yeah. There's carbon. And we could allow that there's maybe some silicon carbide molecules. Turns out, doesn't
JARAMILLO: matter whether there's silicon carbide molecules, right? We know that carbon and silicon carbide are saturated,
right? We know they're saturated. That's just my observation because the pure components are there. So their
vapor pressures are saturated. They're saturated.

But their saturation vapor pressures are-- they're negligible Because they're refractory materials. We talked
about that 20 minutes ago. OK, so what does that mean? Somebody?

AUDIENCE: All right, I have a quick question if that's all right.

RAFAEL   Yeah. Go ahead. Please.
JARAMILLO:

AUDIENCE: Earlier, I think we talked about how the carbon wouldn't vaporize nearly as much as the silicon. So would it make
sense to ignore it in future calculations? Or do we still need to take it into account even though it's less likely to
vaporize?

RAFAEL   So, Sara, your question is exactly my question, which is this. So what is the silicon partial pressure? And if it's not
JARAMILLO: clear right now why your question is my question, I'll make that clear. But, somebody, please. Here's your
observations and some facts and things that you know. Would somebody make a guess for the silicon partial
pressure?

AUDIENCE: It's just equal to the total pressure.

RAFAEL   Thank you. Yes. That's exactly right. The silicon partial pressure is basically the same as the total pressure. In
JARAMILLO: other words, the vapor is essentially pure silicon. That's the second big intellectual connection which you need to
make to solve this problem. The first was the change in chemical potential for gases when they're rarefied. The
second is, well, it's a more pragmatic thing, right?

You have all these things in the gas phase. But I know that the pressure of carbon in silicon carbide is really
small, unmeasurable on my gauge, definitely not making a contribution to that 4.0 pascals, maybe at, like, sixth
decimal point or something. But who cares? It's 4.0 pascals. So my gauge only has two digits of precision
anyway. So I can infer that that pressure is totally silicon.

So now I plug. And I chug. The chemical potential of silicon in this system minus the chemical potential of silicon
for condensed pure silicon, which is RT log P silicon P silicon sat is just RT log 4.0 over 4.4.

So I'm putting it all together. Therefore, delta formation G of silicon carbide-- it's two terms, chemical potential of silicon minus chemical potential of silicon in its reference state, and the chemical potential of carbon minus the chemical potential of carbon in its reference state. And that's 0. And this is RT log 4.0 over 4.4, which happens to equal to minus 1,563 joules per mole. That's the answer.

So I intentionally left a good amount of time to talk about this problem. But I want to start with a strategy for solving these types of problems and to solving all thermal problems, actually. The key to solving such problems-- this is sort of the intellectual key-- is to ask, who is in equilibrium with whom?

This is the key to getting good at these problems. What do I mean by that? Let's see. We have vapor. We have vapor, carbon, silicon, silicon carbide. We have condensed silicon carbide. We have condensed graphite. And the components are freely exchanging.

All right, so this here, we have these components freely exchanging, right? Exchanging mass. Back to the basics, right? Back when we developed chemical equilibrium as opposed to vapor, silicon. Imagine silicon carbide, silicon carbide, silicon carbide. Those are in equilibrium.

But what about solid silicon? Not in equilibrium. Not in equilibrium. Not in equilibrium with condensed silicon.

What does that mean? It means that the vapor pressure is below saturation. And because when I saturate the vapor pressure of a thing, that thing starts condensing. It starts condensing out of the air. It starts raining silicon. If the vapor pressure reached the saturation vapor pressure of silicon, it would start raining silicon in that system. That didn't happen. So the vapor pressure is below.

OK, so that was a lot of stuff all wrapped up into one problem. Good that I have 10 minutes to talk about it. So I'm happy to take questions about this or anything else. I will mention one last thing on course scheduling. Wednesday's office hours, I'm planning to do a really informal semester in review. So hopefully, that'll be useful. But back to this problem. Questions? Confusion?

AUDIENCE: I have a question about something very early on.

RAFAEL JARAMILLO: Mm-hmm?

AUDIENCE: So how is it that we knew that the vapor pressure of carbon was a lot less than silicon? Was that reading from the graph or?

RAFAEL JARAMILLO: No, no, no. So that was not-- so there's two things. First of all, I gave you reference data. So that was data given with the problem. So one way is that it was just in the problem statement. So you see it. It's fine. But it is worth asking yourself, would you have been able to infer that if that hadn't been given in the problem? And, yeah. You might guess that. You might know the silicon carbide and graphite are refractory materials, right?

You might know that they're very tightly bound molecular solids with a huge cohesion energy. It's very hard to break them up. And the phase diagram here tells you that silicone is a lot more volatile than either silicon carbide or carbon. It's got a much lower melting point, right? So you might just guess. And I wouldn't ask you to do that. But you might be able to infer that the saturation vapor pressure of silicon carbide and carbon is very low.

And if you remember, the saturation vapor pressure, it's proportional to e to the minus delta H of formation. You remember that from your phase diagram. So a material that has a very large energy of formation has a very small saturation vapor pressure. So maybe you know that silicon carbide and carbon are very happily-bonded solids.

Again, I wouldn't ask you to necessarily come up with that in the context of a big problem like this. But it could be done. It would be it would be an educated guess. Does that help?

AUDIENCE: Yeah. That helps a lot. Thanks.

RAFAEL JARAMILLO: Yeah. I mean they're-- volatile. compounds are compounds that you can smell, right? So you can't smell silicon. You can't-- I mean, maybe a dog can. But dog noses are amazing. But you can't smell silicon. You can't smell these things. And the amount that you can smell something corresponds to its volatility, right? You know this when you're dealing with solvents and paint solvents and stuff. Very volatile compounds are very smelly compounds because they have a large vapor pressure. They're just in the air. So things like that.

Can dog's smell of silicon? That is the question that everyone is dying to know. All right, what else? What else? No other questions? Well, maybe that was clear. All right. If there are no other questions, we can get out 6 minutes early. All right, well, thank you. I will see everyone on Monday. And again, homework due Sunday at 8:00 PM.