

[SQUEAKING]

[RUSTLING]

[CLICKING]

**RAFAEL  
JARAMILLO:**

All right, let's talk about intermediate phases and line compounds. So we've [AUDIO OUT] line compounds. So I want you to recall intermediate phase in a three-phase system.

And I'm going to recall it visually, and we're going to remember what the free-energy composition diagram looked like in such a case. And it looked-- let's say an alpha phase and the beta phase. We had some intermediate phase.

So the common tangents are to look like this with a common tangency there, tangency there. Let's see. I'm just going to eyeball this. Tangency there, let's say. All right, so this was your generic three-phase situation.

And I want to remind really just about this region here. This was, let's say, the [INAUDIBLE] phase. Let's call this phase epsilon. This region of composition was an epsilon solid solution. So there's a finite range over which you have a solid solution-- that is, the epsilon phase has variable composition within a range.

OK. So now suppose that instead of being a solid solution, the epsilon phase is very intolerant of deviations from stoichiometry.

So, for instance, for instance, let's say we have  $A_{1-n}B_n$ . But in this case,  $n$  is fixed. It doesn't vary in nature. So this is a little bit more like a molecule than a solution. If  $n$  is fixed, it's a little bit more like a molecule than a solution.

How does that look on the free-energy composition diagram? Let's see. What colors did I use? I used blue, green, and maroon, I guess. So all right. So here's blue, as before. Here is maroon, as before.

But now let's say that-- here's  $n$ . That's that composition. And this solution model is going to look like this.

What I drew is something that's really narrow. So there's a minimum to this curve, the composition in which we find this material in nature. But as soon as we deviate from that composition a little to the right or a little to the left, we have to pay a huge energy cost. You imagine this curve collapsing into almost the shape of a pin.

So my common tangent construction is going to now be like this. So my-- let's just call this "solution" model-- solution in quotes because it doesn't really appear, the solution in nature anymore for epsilon phase.

So the solution model becomes very narrowly shaped, like a pin. All possible common tangents are going to converge at the same point. That point is  $x$  of B equals  $n$ . That's that one composition that we find in nature.

So you see how that's a geometrical fact? As this thing gets narrower and narrower, all common tangents are going to cross at that one point. Instead of crossing at different points, giving you a finite range of composition, they're all going to cross that one point.

And what that means is I no longer need a solution model. I no longer need a solution model. I only need one point. So I no longer need a solution model. All I need is that one point, that one point, is one free energy point and one composition.

OK. So here, I can't help myself. I got to draw the mouse-face plot. So here's the point. If you have a very, very steep free-energy composition curve, like this-- very, very steep-- all possible common tangents that you could draw are going to converge at one point because of that very steep curvature down there. So this kind of, to me, looks like a mouse. So it's a mouse-face plot.

But the point here is that these whiskers are all the common tangents kind of coming together at one point. So let's look at some examples here in nature. We can start with the magnesium nickel system. So we've looked at this system before. I don't remember why and when, but we did.

And so here's a phase diagram. It's got a number of different phases. It has a liquid phase at high temperature. Let me grab a highlighter. It's got a liquid phase at high temperature.

And then how many other phases? We have magnesium, which is HCP. We have nickel, which is FCC. And then we've got two other phases which appear as line compounds.

We've got this magnesium 2 nickel phase, which is a line compound, and this magnesium nickel 2 phase, which is also known as a Laves compound. Laves is a structure type. And this line compound down here, it actually broadens. Can you see this develop some width here?

So at high temperature, this Laves phase develops some width. It can be made as a solid solution with a very, very narrow range of solid solubility. But when you drop down to low temperature, both of these intermediate phases appear as line compounds.

So that's an example. And one of the hallmarks of a line compound and phase diagrams with line compounds is that you have very different structure types. So you can kind of see how these are not-- you don't reach this hexagonal magnesium 2 nickel phase just by individually substituting our atoms from the HCP magnesium phase. And they're really fundamentally different structure.

So I grabbed some images here of the magnesium 2 nickel and this magnesium nickel 2 Laves phase. These Laves phases are of interest for people that study magnetism because they have these triangular sheets which are interesting for spin liquids and spin ices-- and then this FCC nickel. I even found a paper based on some phenomenology here in "Switchable Mirrors Based on Nickel Magnesium Films."

But this is the point I want to make here is that these are very distinct structures, and they're only occurring at very distinct compositions. That's a hallmark of an intermediate phase. That is a line compound.

So how would you draw the free-energy composition diagram for the magnesium nickel phase? It would be drawn like this. Magnesium nickel-- actually, magnesium nickel system, right?

So, for instance, at some low temperature, at some low temperature, we have here this is going to be x nickel. So here, we have HCP magnesium on the left-hand side, FCC nickel on the right-hand side. This is going to be a delta G, and here's 0.

And I simply have here a value that represents the formation of magnesium 2 nickel, a value that represents magnesium nickel 2. And my taut rope construction, or my common tangent construction, ends up being just a series of straight lines.

This is magnesium 2 nickel. This is magnesium nickel 2. And these vertical distances are related to formation-- related to formation of free energies.

My taut rope-- right. So instead of being like a taut rope, it's just now like-- well, it's just sort of a string held up between needles, needle points. There's no more curvature apparent.

All right. So now let's talk about the size of these vertical segments. Let's talk about compound formation energy. And it's often written as delta form. So what is the compound formation energy?

It is the free energy change for formation of 1 mole of compound from the elements in their reference states.

So, for example, I might have 2 moles of magnesium in its alpha phase plus alpha-- let's say HTP-- plus a mole of nickel in its alpha FCC phase. And these can react to form magnesium 2 nickel. And there's going to be a free energy of formation for that reaction.

So you can see I'm using this term reaction, and we're writing things a little bit more like molecular reactions. Even though this is an extended solid, it's an extended solid with fixed stoichiometry. Well, here's another example.

Two aluminum in its alpha phase plus 3/2 oxygen gas delta form forming alumina. And there are an infinity of examples. So line compounds formed from the elements with a formation energy delta G.

OK. But there's a detail. This formation energy is per mole of compound. When we draw free energy composition diagrams, we assume 1 mole total of the components. So there's a normalization that you need to apply in order to use formation free energies-- as you might find in databases-- in order to use those data in free-energy composition diagrams.

So, for example, we need normalization to use delta formation free energy on a free energy composition plot. So using the example of magnesium 2 nickel-- let's see. I'm going to redraw the free-energy composition plot quickly.

And what I want to measure here, I want to figure out-- let's talk about what size that vertical distance should be. This is magnesium 2 nickel. That green arrow, this is the change of free energy when 1 mole of atoms form magnesium 2/3, nickel 1/3.

I want to stop and make sure people recall that this was pretty much our definition of solution. Modeling we have a model for how the free energy changes when you combine a total fixed amount of atoms in different composition ratios. So, for example, a point on this plot represents 1 mole of total atoms-- in this case, let's say 2 to 1 magnesium to nickel.

So 2/3 a mole of magnesium, 1/3 a mole of nickel combined to form this magnesium 2 nickel 1 phase. But this is different in the formation energy, right? This measure is 1/3 times delta form magnesium 2 nickel. So it's simply 1/3 because I have 1/3 the amount of atoms.

So that is kind of an algebraically-simple point, but it's a conceptual point that it's easy to mess up. It's easy to mess up when you're trying to do a free-energy composition diagram, when you're trying to model a system, and you go to the textbook or you go to the databases and you look at formation energies of compounds. And the formation energies of compounds are listed per mole of compound.

So if I go over here-- again, there are lots of databases out there, but they're all going to list something like this, properties of selected compounds. So here's a carbide, boron 4 carbide. I know you can't read that.

But it's listing, let's say,  $\Delta H$ 's. That's not per mole of compound, not per mole of total atoms. So you have to apply that normalization if you need to draw such plots. All right.

All right, I want to give you some examples of line compounds in nature and in technology. And then we'll come back to discuss the thermodynamics a little more. Before I move on to some examples, are there questions about this algebra, this arithmetic, the concept of formation energy, the mouse-face plot, anything, anything of that nature?

So I have some examples here. I should have animated this. I didn't. We can just walk through this one at a time. There's an infinity of examples of line compounds. So I just want to show you some of different types.

So here's an example, which speaks to the problem set, actually. I lost my highlighter. What happened there? Let me get my highlighter back. OK.

So here is a copper silicon system. So you can see that you can get a fair amount of silicon into copper. That's 10%. That's this kind of purple region. There are silicon bronzes and silicon brasses-- that is, bronze and brass alloyed with silicon. Those are ternary systems. But silicon tends to be a pretty useful additive for copper-based alloys.

I used a silicon bronze when I was in grad school and we were designing high-pressure cells that needed to be actuated at low Kelvin, like below temperature, below 1 Kelvin. And below 1 Kelvin, you can't use lubricant. You can't just use WD-40 because it'll freeze.

Means you have to look for metals that slide well against each other. And it turns out there's a whole family of silicon bronzes that various space agencies around the world have developed in the last century. Because space is another application where you have moving parts sometimes, you have machinery that needs to move against each other. And you can't just have WD-40, right? There's no real lubricant that you can use.

And so there are certain silicon-based bronzes that have been developed for that application. And I didn't know anything about all that, really, when I was in grad school. But I needed something that would work for my high-pressure experiments. So we ended up with that.

So let's see. There's a couple of other solid solution phases. There's this little guy here and this little guy here and then, of course, the big liquid phase. But how many line compounds are there? Trick question. Somebody, please, how many line compounds are there in this system?

**AUDIENCE:** Is it three?

**RAFAEL** It's not three. that's why it's a trick question. Somebody else?

**JARAMILLO:**

**AUDIENCE:** Four.

**RAFAEL**  
**JARAMILLO:** Four. Yeah. I didn't see who that was. Thank you. It's four. So there are the three here, which are intermediate phases. There's this really funny composition here, 0.08, 0.17. There's this thing and there's this thing. And I don't know anything about these phases, but I do know that they're probably very distinct crystal structures with distinct properties. You can say that as an educated material scientist not knowing any details. You can just say, oh, these must have different crystal structures. They must have different properties.

So those are line compounds. They appear as lines here. But what about over here? Silicon. Silicon's not an intermediate phase, but it is a line compound. The solid silicon phase appears to have no equilibrium solubility of copper.

Now, in reality, you always have some finite solubility of a solute in a solvent. We know this from maybe a month and a half ago. We did this on a problem set. It was something called there's always a solution. Because of the driving force of entropy, you can always get some solute into a solvent.

However, in many cases, that solubility limit is very, very low. So in the case of silicon, the solubility of metals is very, very low. The solubility limit is typically parts per billion. So in principle, there is a purple region extending along this y-axis of solubility of copper into silicon. However, it's at the parts-per-billion level. So on this plot where you go from 0 to 100 atomic percent silicon, you don't see it.

And that's true of line compounds in general. There's always some solubility, but it's often so narrow that you can model as if there's no solubility. That's not just an academic point. Doping semiconductors is why we're able to talk to each other over Zoom. Without doping, there is no semiconductor devices, there is no electronics revolution.

So the fact that you can dope some metals into silicon is as important as it gets. And the solubility limits can be in the parts per billion. They can be sometimes in the parts per trillion. But they're rarely above parts per billion.

Anyway, so on the last P set, you're going to do some problems around doping semiconductors. So I do want to point that out. There's always a solution. Good, OK.

What about this one? This is gallium arsenic system. And so gallium arsenic system has a very famous line compound right up the middle, gallium arsenide. So why is gallium arsenide important? Does anyone know why gallium arsenide is important? Let's talk about technologies that are based on gallium arsenide. Does anybody know?

All right. Well, the two areas where you're going to find gallium arsenide are places where silicon either isn't fast enough for electronics or you need to use light in addition to electronics. So where silicon isn't fast enough are the transmitters and receivers of your phones, gigahertz RF networks. Silicon is not fast enough.

So the transmitters and receivers of all modern telecommunication devices, including your phones, are based on what's called III-V semiconductors, such as gallium arsenide. So there, the transistors and diodes and so forth are just made out of a gallium arsenide wafer instead out of a silicon wafer. Another place you're going to find it is anywhere you need light.

And so gallium arsenide and alloys, thereof-- which we don't show here-- are the basis for all optoelectronics and photonic technology. So right now, we're Zooming. But likely, some part of the data between me and you is carried by fiber optic. And fiber optics are ways of transmitting a lot of information over long distances at low power by using light instead of electrons. And so at the points where the light and electrons are transduced, you have gallium arsenide and similar-material-based chips doing the work. So that's an important and famous line compound.

Here's another one. Here's another system where carbon and silicon each don't really dissolve in each other. You have these apparent line compounds along the y-axis. But there's another line compound right in the middle, silicon carbide.

Silicon carbide is a refractory-- some people will say it's a ceramic. Some people say no because it doesn't contain oxygen. That's kind of immaterial. It's basically a refractory material. It's used for grinding, so it's of enormous industrial importance.

It also is an emerging semiconductor material for high-power electronics. And high-power electronics is the idea that you could replace discrete, bulky, power-handling equipment with integrated power-handling equipment. So I think these power substations that you see when you're driving by on the highway, these big-- kind of they take up a whole property lot and they buzz at 60 Hertz-- or these cans that you see hanging from the utility poles that down convert to a voltage for houses, like 220 or 115.

The idea that you could replace those discrete elements with integrated circuitry-- saving power, saving money, saving weight and so forth-- that is the field of power electronics. And the thing is, you can't do it with silicon because silicon doesn't perform well at very, very high voltages.

So you need new semiconductors that perform well on high voltages. Silicon carbide is one of the leading candidates. So in 50 years from now, if the idea of a power substation is a thing of the past, it will be due to silicon carbide and similar high-power electronics that are being developed today.

And this last one, this is a big old mess. This is the titanium-sulfur system. This is a neat system because, first of all, it has everything in it. It eutectics. It has peritectics. It has a bunch of line compounds. It has line compounds that broaden it to intermediate phases as you raise the temperature.

It has sulfur, which is a liquid below 500 C and melts at 20, and titanium, which doesn't melt till 1,670. So it has this totally wacky kind of mismatch between two elements that are nothing alike. The system contains 2D materials. 2D materials are of a lot of interest today in semiconductor technology.

Titanium-sulfur system is the basis for the original lithium-ion batteries. About a third of the Nobel Prize work that was recognized recently in 2019 with the chemistry Nobel Prize was for work on titanium-sulfide-based cathode. Why? It's a layered material, so you can shove a lot of lithium in it. Anyway, there's a lot of good stories to tell in these titanium-sulfur system.

So these are-- for example, systems that have line compounds and other things. Before I move back to the board, do we have any questions on reading these, interpreting these, using these?

**AUDIENCE:** Yeah, I have a quick question. So on the bottom left one and the top right one, do they both contain three line compounds?

**RAFAEL**

**JARAMILLO:**

Yeah. So, for example, let's look at the silicon-carbon system. Carbon here is a line compound. Line, line-- OK-- line element, I guess, it's not a compound-- so a bit of a terminology there. It has zero apparent solubility of silicon in carbon. Silicon is a line element. It has zero apparent solubility of carbon in silicon. Again, there is some, but it would be invisible on this plot.

And silicon carbide is a line compound. So again, here's a line, here's another line, and here's another line. And it doesn't have to be that way. Here's a case of a line and an element that actually does have a pretty wide, solid solution, great range. So it's not that all elements are always pure, right? That's definitely not the case.

But the low temperature-- have a look here at the silicon-carbon system, silicon-carbon system at low temperature. At low temperature-- actually, similarly to gallium arsenide at low temperature, it's going to be a really boring free-energy composition diagram at low temperature. Let's draw it. Let's draw what that looks like.

So would anyone like to take a stab at how I would draw a free-energy composition diagram for the silicon-carbon system at low temperature? Here's silicon. Here's carbon. Here's  $\Delta G$ . Here's 0. And let's say this is 50/50.

So first off, do I need any solution models? Right, I don't. I don't need solution models because nature doesn't form solutions, so no need to model solutions. So what do I need instead of solution models?

**AUDIENCE:**

Just the taut rope, like, the lines.

**RAFAEL**

**JARAMILLO:**

Yeah. All I need is a number to represent the free-energy change on forming silicon carbide. I just need that point. And similarly, carbon from carbon doesn't take any energy to form. Silicon from silicon doesn't take any energy to form, no solution models anywhere needed because nature doesn't form solutions. And here is my free-energy composition diagram. It is just a triangle.

So it's simplified. It's simplified a lot. Any other questions on the meaning or importance of this stuff? I'll go back to this slide quickly. And then if there are no more questions, I'll finish up on the board.

So getting back to my trick question, I suppose that, because silicone is not a compound, the right answer probably was that there are three line compounds. But there are 1, 2, 3, 4 if you take pure phrases in the system. Don't worry. I'm not going to ask trick questions on an exam or anything like that.

But the thermodynamics here is that this is a pure phase. This is a pure phase. This is a pure phase. This is a pure phase, meaning it's always going to be a known composition, never going to be alloy. This is a pure phase. This is a pure phase. And this is a pure phase. They just appear as single points on the free-energy composition diagram. That's what I meant to say.

OK, then we move back to the board. I'll just make a couple of conceptual points and then we'll finish up. Comparing solutions at equilibrium to line compounds at equilibrium. So this is going to be two solutions.

Let's imagine an alpha phase and a liquid phase at equilibrium. And I'm going to draw just a representative phase diagram just to have something in mind. So here's alpha. It is liquid. Here's x. Here is temperature. And I'm going to imagine now some equilibrium, alpha liquid equilibrium. I drew one tie line there, alpha liquid equilibrium.

Just an example, this is no system in particular. We know that, along that line,  $dG = \mu_1^{\alpha} - \mu_1^{\text{liquid}} + \mu_2^{\alpha} - \mu_2^{\text{liquid}}$ . This is just recalling previous stuff.

We have internal composition variables. The compositions are variable, composition variables. So we have  $n_1$  alpha, we have  $n_1$  liquid, we have  $n_2$  alpha, we have  $n_2$  liquid. And if we have conservation of mass, then we can boil this down, let's say, to  $x_1$  alpha and  $x_1$  liquid. So we have these composition variables. We're familiar with that.

And the equilibrium condition, the equilibrium condition  $dG$  equals 0 satisfied by common tangents. What do I mean? Coefficients equal to 0. That's what the common tangent ensures, that the coefficients are 0.

Chemical potentials are the same in both phases so that the coefficients are 0. Chemical potential's the same in both phases. The coefficient is 0. That's ensured by the common tangent construction. So this is just recalling, right?

Now let's imagine two line compounds. I drew an unnecessarily-complicated example. Let me just follow through on that.  $B_3A_2$  and  $B_4A_3$ . How did I come up with that? Well, I sketched an imaginary phase diagram, and then I had to follow through on my sketch.

So I had-- what do I have? I have like this and then like this and then like this and then like this. And that means I had a congruent melter. I had this. And then I drew as this and then like this, peritectic, and something like this. I had this complicated thing which I do.

And the point is not the complicated thing. It's really, I have some two-phase region down here at low temperature where I have two line compounds coexisting.

So let's see. The Gibbs free energy of  $s$  1 mole of that thing is 3 times the Gibbs free energy of B and its reference state plus 2 times the Gibbs free energy of A and its reference state plus  $\Delta G$  formation of  $B_3A_2$ .

The Gibbs free energy of  $B_4A_3$  is 4 times that of pure G times 3 times that of pure A plus the free energy of formation of  $B_4A_3$ . There are no internal composition variables.

That's a key point. Before, we had composition variables because the composition of the phases was variable. Now, we don't have that. What that means is that the equilibrium condition  $dG$  equals 0 is satisfied trivially, trivially.

There's no need to do common tangents. There's no need to equate the chemical potentials because there are no internal composition variables. The compositions aren't changing.

I can write out the total Gibbs free energy. It's going to be determined just by the phase fractions, phase fraction of the II-III phase times, let's say,  $1/5$  of the Gibbs free energy of the II-III phase plus phase fraction of the III-IV phase for A3 times

$1/7$  of the Gibbs free energy of the IV-III phase. And these phase fractions are determined by lever law.

This is really the point. This is really the point. When you have line compounds in coexistence in equilibrium, there are no internal composition variables. Whereas when you have solution phases in equilibrium, the internal compositions are variable.



And that's what's led to everything we've been enjoying over the last month and a half, is the fact that solution phase is the compositions are variable. And now we have these cases where the compositions are not there [INAUDIBLE] anymore. OK. I want to leave you with one final thought, which is leading into Wednesday's lecture, which is the case of metal oxides, which are line compounds. So it's on topic. But I want to introduce this and get this in your minds.

Let's imagine reacting metal M with 1 mole of oxygen to form an oxide. So  $z\text{M}$  plus  $\text{O}_2$  gas reacting to form  $\text{M}_z\text{O}_2$ . All right. What's z? How do I determine z? Anybody?

Does anyone know some oxides? Name for me a common oxide that you know. What is rock? What's the main component of rock? What's the main component of window glass?

**AUDIENCE:** Silicon oxide?

**RAFAEL JARAMILLO:** Silicon oxide, OK. So for silicon, z is 1. Yeah, easy. Does anyone happen to know an example of an oxide for which z is not 1?

**AUDIENCE:** Magnesium oxide?

**RAFAEL JARAMILLO:** Yeah. Magnesium oxide is 1 to 1, right? So in that case, it would be 2. Oxygen always  $\text{O}_2$  minus in compounds. So z is determined by charge balance. Oxygen is always  $\text{O}_2$  minus.

And metals have various oxidation states-- can't write anymore. Metals have various oxidation states. That's what that's supposed to mean. Some metals have more than one oxidation state. So that's z.

Here, M is in its reference state. That could be solid, liquid, or even gas-- although, we don't really encounter that so often. But oxidation of metals at low temperature, the metals are solid unless it's gallium or mercury. Oxidation in metals at high temperature, a lot of them are molten. So this matters for high temperature electrochemistry.

Oxygen always in gas phase. We're not talking about low-temperature physics here. So oxygen is always going to be in its gas phase. And these oxides are line compounds.

That z is not a variable. That z is an integer or a rational fraction, and it's fixed--  $\text{SiO}_2$ , magnesium oxide,  $\text{Al}_2\text{O}_3$ , so forth. So when we return on Wednesday, we're going to talk about the thermodynamics of this reaction. We're going to use this property of being line compounds, and we're going to use a bunch of other things as well.