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**RAFAEL**  
**JARAMILLO:** So today's lecture is the start of binary phase diagrams, which are going to occupy most of the rest of the class, meaning most of the rest of the semester. So this topic is comprehensively treated in De Hoff. But I have some reading in McAllister, in Callister, not McAllister, it's Callister associated with today's lecture.

So we just finished something on reacting chemical systems. Please don't fall behind on the reading. Turn to Callister and do that reading as well. Callister is a little bit more wordy than De Hoff, a lot nicer pictures. De Hoff is thorough and august. And Callister is a little bit more like those textbooks from high school with lots of pictures in them. So Callister's is a little bit easier to start the topic. And I like some of the examples that Callister gives.

So that reading, like with Denby reading, that reading is posted on Canvas. So binary phase diagrams, let's just start by drawing some and talking about the primary features. What are binary phase diagrams? Somebody tell me. What is a binary phase diagram? What is a binary phase diagram?

**AUDIENCE:** A phase diagram for a system with two components.

**RAFAEL**  
**JARAMILLO:** Right, thank you, So it is a phase diagram for a system with two components. And normally, it's plotted like this with temperature on the vertical axis and a mole fraction on the x-axis.

So if we have two components, we have  $x_1$  and  $x_2$ . And we know that  $x_1$  plus  $x_2$  has to be 1 by definition. And so you have two composition variables. But only one of them is independent. And so we normally plot something like this. So the mole fraction of two will go from 0 to 1. That means on the left hand side here, we're talking about pure-- pure component 1. And on the right hand side, we have pure component 2.

So it's a diagram of equilibrium for temperature and composition. Here's a typical thing that you have. You might have a solution phase. So you might have a large region where 1 and 2 mix. And often, you'll encounter something like a solubility limit. The solubility limit-- and when you hit the solubility limit, you enter two phase regions.

Two phase regions are often indicated like that, with something that we call tielines. So those horizontal lines are tielines. And what tie lines do is they connect the two phases that can coexist at equilibrium. So let's make this specific. Let's pretend that this is sugar water, that this is a water and sugar solution.

And so pure component one is, let's say, water. So let's say water. And pure component two is, let's say, sugar. All right, so what this region here is is sugar water. That's where you can dissolve sugar and water. And you often see that the solubility limits increase as you increase temperature.

That's because the process of making a solution increases the entropy, increases the mixed-ness of the universe. We saw that in the very first lecture. And so as you go to a higher temperature, entropy becomes more important. We know that because Gibbs equals  $h$  minus  $ts$ . So as you go to higher, temperature solution phases tend to broaden.

What's the solubility limit? What does that mean? Imagine you're actually making sugar water and you start off with pure water. You start off with pure water. And you start adding sugar. You're adding sugar. You're moving to the right on this phase diagram. What does that mean you hit the solubility limit?

**AUDIENCE:** It'll start to precipitate out.

**RAFAEL**  
**JARAMILLO:** Start to precipitate. So when we hit this composition, we can no longer add any more sugar to the solution. Any sugar that we add in addition will precipitate out as solid. So when that happens, I end up with two phases in coexistence, sugar water and solid sugar. That's the precipitate, stuff on the right.

And as I add more sugar to the system, more and more sugar precipitates out while the composition of the solution doesn't change. So in this region, the composition of the solution changes continuously with the overall system composition. But in this region, the composition of the solution is fixed, even as the overall system composition can vary because I have two phases. So that's the meaning of two phase regions. And the tielines connect the phases that coexist. OK, so that's just the basics. So let's do an example here. Let's look at an example.

Crystal growth by supersaturation. And this is-- if you've ever made rock candy, in fact, I've got a-- I've got a big one in my-- I'm at home. I've got a big one in my son's room. So I might take a walk and grab it in a minute. So let's see. He's at school. Otherwise, he'd get mad at me because I'd be taking his rock candy. Don't worry, I'll put it back.

So there's the same phase diagram. Here's x2. We'll call this the solvent, keep the solvent on the right. Solute on the-- solvent on the left, solute on the right. And here's temperature. And here is a two phase region with a solubility limit. And here's what I'm going to do. Has anyone made rock candy or do you remember? Somebody tell me, how do you make rock candy? What do you do first?

Well, let's do it this way. Start--

**AUDIENCE:** Start like with hot syrup.

**RAFAEL**  
**JARAMILLO:** Hot syrup, good. So let's just get there to hot syrup. Let's start with a room temperature solution. Let's start-- let's start here. One, we're going to start there. And then what we're going to do is we're going to heat up. We normally do this on the stove.

So let's see, we're going to heat up two. Now, we heat it up. And then, we're going to add more solute. Add more solute. So what we're going to do is we're going to make it more syrupy. I think that was Ali. So like Ali said, we're going to make this more syrupy. We're adding more solute. And what's the final thing we do? Maybe somebody new who hasn't contributed yet?

**AUDIENCE:** You cool it down.

**RAFAEL**  
**JARAMILLO:** Yeah, we're going to cool down into supersaturation. So we're going to cool down into supersaturation. That's step four. And then what's the final thing we do? We wait for spontaneous crystallization. I'll be right back.

What I'm showing you is a piece of-- a large piece of rock candy. And how did we make this? We took water, and then we made syrup. And then we heat it up on the stove. And made the thing even syrupier until it was really viscous on the stove. And then we cooled it down. And we poured the-- poured the syrupy solution into-- not a beaker, because we're at home, a glass-- a glass dish. And then we waited. And over the course of maybe a day, this thing grew.

And you see lots of little crystallites here. It's hard to see over the camera. And if we were really making rock candy, we would have put some strings in the solution. They grow rock candy on strings. That's how you normally see it. All right, so that's one way to use a binary phase diagram. So let's see, we're going to move on to do some formalism. I want to stop now and take questions on what we've covered so far.

Spontaneous crystallization, it means you're going to end up with sugar water and the crystal coexisting.

**AUDIENCE:** Can we get the energy from this part? Like if we get like-- if we have the [INAUDIBLE] information?

**RAFAEL JARAMILLO:** Can you get an energy from this if you have-- can you repeat one more time, if you have something information?

**AUDIENCE:** Like if I have the  $\Delta h$  of max in at 2.

**RAFAEL JARAMILLO:** Can you get energy from this? I mean, it's an exothermic process, crystallization. So this was an instant hot pack. This was the instant hot pack. This whole class is coming back to the thing we did on day one with the hot and cold pack. So this is an instant hot pack situation. You have spontaneous exothermic process. It's driven by enthalpy, not by entropy.

So there is a heat of solidification. And that heat of solidification is not something we worry about so much when we're making rock candy. But if you're growing semiconductor boules or any other solidification process that you care about quite a lot, then you have to engineer that.

Any other questions on these basics? This is introducing binary phase diagrams through, I think, a very, very gentle example. Of course, they're going to get a lot hairier than this. But I want to make sure people have seen these basic concepts of solutions, two phase regions, tielines, and how we can think about processing them.

I'll move on. So naturally because this is thermo, a lot of what we're going to do boils down to bookkeeping. So what we're going to do now is establish some necessary conventions. Let me pause for a minute and call something out. And I hope I remember to do this again at the end of class.

In the first class, I mentioned that we were going to be using the software Thermo-Calc. And so that starts on the piece that's released today. So if you haven't yet, please do go either look at the course info document or just go directly to the Thermo-Calc website. And download and install their educational version for students. It's free.

In our experience, every year, there's maybe one or two students that have a little bit of trouble installing it. That's always been with Macs. But almost everybody, including people with Macs, are able to get this running. In fact, I actually don't know anybody who wasn't able to get it running, which is to say it's a fairly well-designed software installation process because normally, there's always problems.

So get this running on your computer before you need it on the P set, you could do it today or tomorrow. It should take five to eight minutes at most. It's not a huge program. Educational version of Thermo-Calc. All right now, back to regularly scheduled programming.

So now, we're going to consider the process of making solutions. And we're going to do this really generically. We have some component A. It has a volume. We're going to spend time on notation here because the notation, when we're making solutions, it gets hairy because we have mixtures. And we have components. And we have reference phases and everything like this. So it becomes really-- again, it's all about the bookkeeping. So here, we have some volume of A, component A.

It has a volume. It has an entropy. It has a Gibbs Free energy, so forth. The subscripts label component. So maybe it's water, for instance. Maybe that's water. The dash reminds you that it's an extensive quantity. So that's not volume per mole, or entropy per mole, or Gibbs per mole. It's volume, entropy, and Gibbs.

And the circle is going to remind you that it's a reference state, which when you're making solutions, means the pure phase, the pure state. So we have pure A. And we're going to do something similar with B. So we have a container of B. It has its own volume, it's own entropy, its own-- it's own Gibbs free energy, and so on.

And now, we're going to mix them. And you get something which is new. You don't get A. You don't get B. You get A plus B. Let's do some bookkeeping. We're going to introduce quantities of mixing, quantities of mixing. So let's see. The volume of the mixed system, we're going to set it up this way.

It's the volume of A plus the volume of B in their reference states plus something we're going to call the volume of mixing. This is free. We can do this. This is no problem. This doesn't tell you anything about the science. This is just a bookkeeping scheme.

I see now the top of my screen is Sarah, Josh, and Ali. So let's say that I want to see the amount of money Ali has in his pocket right now is the amount of money that Sarah has in her pocket plus the amount of money that Josh has in his pocket plus the difference. Which doesn't tell you anything about how much money you have in your pockets. It's just a bookkeeping scheme. That's all this is. So we're going to do something similar with all of the other extensive quantities.

**AUDIENCE:** Could the  $\Delta v$  mixture value be a negative number?

**RAFAEL**  
**JARAMILLO:** It can be, it can be, sure. What's an example of when it's a negative number. I've got to think about this.

**AUDIENCE:** Like maybe like water and acid. They usually shrink when you mix them, it getting smaller than it was.

**RAFAEL**  
**JARAMILLO:** Well I love the example. But I didn't quite hear it. What exactly was it that shrinks in water?

**AUDIENCE:** It's like water and acid.

**RAFAEL**  
**JARAMILLO:** Oh, water and acid. Sure. Or sometimes it's larger, sometimes it's smaller. You shouldn't think that, oh, it should be bigger because we mixed it. So the system got bigger. It's a volume of A plus the volume of B, however it changed. So if there's chemical interactions that cause the molecules to pull more closely together than they do when they're unmixed, then that volume term is negative.

If there are chemical interactions that cause a thing to swell, that's the case with glass formers, then that becomes positive. So let me just make this clear. We have this structure here. These are the reference state--reference states of pure components.

And these are the mixing terms. And the point of having these mixing terms is because when you make solutions, the whole is not simply the sum of the parts. That's why we have these mixing terms.

There are solutions all around us. So there are solutions all around us. We know this, right? Liquid phase, this is where we started. And when people colloquially say solutions, normally, they mean a liquid, liquid phase. So ocean water, syrup, gasoline, et cetera.

Gas phase, of course, air is a solution. But in material science, in MSC, we spend most of our professional lives working on solid phase solutions. So this is less colloquial. Normally, I think we stop somebody on the street and hold up a solid chunk of something and say, is this a solution? And they would say no, it's a solid.

But everything we're doing applies definitely to solids. And that's actually where we get most of our technological impact. So would somebody like to name for me some solid phases that matter to you, or everyday life, or cool, extreme examples, or anything at all?

**AUDIENCE:** Carbon steel.

**RAFAEL JARAMILLO:** Steel. The most basic steel is carbon steel. It's iron and carbon. Iron is very, very soft, ductile. Rusts easily, not good for structure. You add a little bit of carbon, and you get steel. Good. Other metal alloys. This is-- if you go back millennia, this is where material science started, brass, bronze.

These are kind of old-fashioned metal alloys. Even though steel, there's nothing old-fashioned about it as practiced today. We also have superalloys. So now, we're getting really into late 20th century stuff. So for example, cutting edge materials research enables things like jet turbine blades.

How can you have those big turbo fans in modern jet engines? They're withstanding enormous stresses and heat. The bigger you make them, the more efficient the engine becomes. But in order to make them big, you need a material that can withstand that. And so these superalloys are developed for that application.

What else? What about lithium ion battery electrodes? Nobel Prize in chemistry from two years ago for lithium ion battery development, largely, almost 80% of the work and intellectual input on alloy design that is designing solid phase solutions for those electrodes. Semiconductors, semiconductor is pure silicon with nothing added, is useless. It doesn't do anything for us.

We alloy it. We make solid phase solutions to change its properties and enable electronic circuits. Any other examples? This is enough, I think. But this is material science. You take something, you add a little bit of something else, and you dramatically change the properties, make it more useful.

Let's take three minutes to talk about solutions and reactions. Why? Because we just finished reactions. And because many of you have worked with reactions in introductory chemistry classes. So you're used to something like this. Take two components, they react to make a third. What's the difference? This is a discrete process, a discrete process with fixed reactants and products.

What do I mean by that? Let's say we have carbon and oxygen reacting to make CO<sub>2</sub>, we're OK with that, right? We don't also have to consider carbon plus O<sub>0.71</sub>, just choosing a random number of moles of oxygen reacting to make some molecule that's CO<sub>0.71</sub>. Because on a molecular level, there's no such thing as 0.71 of an atom.

So so we don't worry about composition being a continuous variable when we're dealing with reactions. Why? Because the individual chemical components are discrete. And they undergo substantial atomic scale changes. So really, there's some bonding going on, bonds made and broken.

And we're going to contrast this with solutions. Solutions, we talk about this, A<sub>x</sub> plus B<sub>1-x</sub> forming a solution of A of x B<sub>1-x</sub>. This is a continuous process. And this is a qualitative thing. But you can say that the individual molecular components remain recognizable on an atomic scale.

So I'm not going to say too much more about solutions versus reactions until we work on reacting solid gas systems in a couple of weeks. But I do want to stop and point this out because we just did reactions. And everything I'm about to tell you in the next couple of weeks could be analyzed using the mechanism of reactions. But it would be inconvenient to do so.

Just as everything which we did in the last two lectures could have been done using the formalism of solutions. But it would have been inconvenient to do so. So we're doing solution modeling because it's a convenient way to treat systems that are solutions. Nature doesn't care. Nature doesn't care how we write this down, what I call it. So it's just about formalism and choosing the right formalism to make our lives easier.

All right, let's move on. Let's talk about solution modeling. This is basically a postulate. This is about making a postulate. So we know that to make predictions, we're in the prediction business for intellectual growth and profit. To make predictions, we need thermodynamic data.

You can't solve any problems if you don't have data. You need the data. And when we were doing reacting systems, you had carbon, and oxygen, and CO<sub>2</sub>, and other molecules. And you could say, oh, I know what that is. I've seen that before. I know how to search for that data. Maybe I'll just find that on Wikipedia. That's a well-defined thing, oxygen. It's a well-defined thing, carbon dioxide. No problem.

But every material is different. Every material is different. So for example, if we have database-- here's my database. Imagine a big cloud database. And here's the entry for carbon monoxide. And here's the entry for carbon dioxide. And they each have their own properties. You wouldn't assume that you can use something for CO<sub>2</sub> and apply it to CO. It's a different substance. Every material is different.

Does this mean we need a separate database entry for every possible composition? So this is a motivating question. Let's say we have silicon. And let's say like Professor Fitzgerald did when he developed strained silicon, which is now in every transistor below the 40 nanometer node, he started alloying it with germanium. And he added a little more germanium. And maybe added a little more.

And I'm just putting a 1 at the fourth decimal point. I could put it at the 10th decimal point. The question is, do I need a separate database entry for each and every one of these compositions, for every possible composition no matter how minutely I change it? Do I need a separate database entry as I do for molecular systems?

All right, we hope not. We hope not. So we postulate not. We postulate that we don't. We're not guaranteed it's going to work. But we do the following. We do the following. We try to model trends in thermodynamics with composition.

We try to model trends, right? This is about modeling. Modeling is another very important aspect of the shadow curriculum in 020. The shadow curriculum meaning things which are essential to being a professional scientist and engineer, but most of you won't take a separate class in. So accessing and manipulating data, basic statistics, plotting. Communication, we do explicitly tie in.

Modeling is up there. How do we model? What is that? What does it mean to model a physical system? We're going to model trends in composition. I think what modeling is. Let's say you have data. And you have some control parameter, that's the abscissa. And you have observations. And you go to the lab and you measure that. And each one of these measurements cost money.

Let's not make this that you're students. Let's make this that you're working at a company. And each time you want to run a test, you have to spend some money. And you have a boss. And that boss, they don't want to spend any more money. And you have to make a decision about what's going to be the value for that composition. How do you do it? Do you spend more of your boss's money?

No, Sarah says no. Don't spend more of my boss's money. You know what to do. You say, well, I'm going to postulate that there's an underlying model. And that model has some truth to it. Or maybe it's purely empirical. Either way, it might have predictive power. And I'm going to curve fit.

But it's not about curve fitting. It's about postulating the existence of a model and using that model to make a prediction. So you fit the model somehow. And then you say, OK, I haven't done the measurement. But I'm willing to bet that there's a value somewhere over there. And you could be wrong. But you're probably right.

We saw an example earlier with the heat capacity, where was capacity versus temperature for cobalt. I don't if you remember that. And the heat capacity data was like this. And then it had a weird spike during the magnetic transition. And then it went back. So maybe you missed the spike, and maybe you get the data wrong.

Nature always is full of surprises. But the point is that this works a lot of the time. This type of approach works a lot of the time. And when we're modeling solutions, we call it solution models. Solution models are used in two ways. First of all, we use them to understand atomic scale phenomena.

We use it for understanding. And we use it to make predictions. And this is almost always what models are used for in the science. When you're taught models, like in a physics class, it normally starts from some underlying atomic scale phenomena. And you get  $F = mg \sin \theta$ . And then you build up a model of some thing, a weight on an inclined plane. And then you can use that to make calculations.

And it's not really obvious that you're really generating a prediction engine. But once you get towards engineering and you're doing something in the material sciences and you realize how much experiments cost, the economic value of modeling for predictions starts to become a little bit more clear.

And it's always two sides of this. You do it for understanding. And you do it because it's going to let you do something else that matters to you. So let's look at some examples very qualitatively. What about water and ethanol? Water and ethanol, right? Well, these are both polar solvents, polar solvents. And they're totally miscible. What does that mean, totally miscible? Anybody?

**AUDIENCE:** Every composition, they always don't separate regardless of composition.

**RAFAEL JARAMILLO:** Yeah, that's right. So I'll repeat what Ali said. It means that there's no phase separation. There's no solubility limit. Unlike the sugar water system, these two components will always mix in any composition. So let's say the horizontal axis here is ethanol composition.

And I'm going to make the y-axis something which we'll be spending a lot of time with, which is the Gibbs free energy of mixing. I'm gonna put zero here. So if mixing will happen spontaneously at a given temperature and a given pressure, what that means is that the Gibbs free energy of mixing is strictly negative.

Not only that, it also means that the curvature is positive. But we won't mess with that now. Just draw over that there in red, so I'll make it a little more clear. So there's my free energy mixing. Now, in the next couple of lectures, we'll start developing functional forms for this. But we're not going to do that now. We're just going to look at this.

Unmixed, we have the Gibbs free energy per mole of system equals the Gibbs free energy per mole of pure water plus the mole fraction of water plus the Gibbs free energy per mole of pure ethanol plus the mole fraction of ethanol.

That's like this. We have the pure stuff, this pure stuff, and this pure stuff before we've mixed it. And then mixed, the Gibbs free energy is that Gibbs free energy before we made the mixture plus  $\Delta G$  of mixing. This is just according to that bookkeeping that we split up-- that we set up.

$\Delta G$  of mixing is less than zero, which is equivalent to saying that  $G$  mixed is less than  $G$  unmixed. The system mixes spontaneously to achieve equilibrium at a fixed temperature and pressure. So this plot here is not a phase diagram.

This is-- that's a variable you find in a phase diagram. But that's not. That Gibbs free energy, that's not found in a phase diagram. This is not a phase diagram. This is called a free energy composition diagram. And he will be very, very tired of free energy composition diagrams by the end of the semester. But anyway, that's what it is called, the free energy composition diagram.

What about-- what about water and oil? Polar and non-polar, I'll just go ahead and draw. You know they don't mix, at least not in the binary system. You can cause them to mix if you add a surfactant. So let's do  $x$  of oil. But in the binary,  $\Delta G$  mix, at a given temperature and pressure, that's typically what you find. You have a positive  $\Delta G$  of mixing with a negative curvature.

And what that means if the system is initially mixed, it will spontaneously unmix to achieve equilibrium at fixed temperature and pressure. And in the edX version of this class, there's a little bit of a separate demo of whiteboard video and a demo about the ouzo system. Which ouzo is a Greek liquor. It's also known as pastis in French.



And it's oil and water. But they're caused to mix with the addition of a surfactant. And so that gets into ternary phase diagrams, which we don't really cover in this class, we don't spend time on. But it's a fun example. So I encourage you to check that out. All right, so let me just summarize here.

Free energy composition diagrams, free energy composition diagrams are how we draw, visualize, and then evaluate solution models. So they're like the engine room of binary phase diagrams. So we have here something like  $\Delta G$  of mixing.

Let me draw this generically. And draw a curve. That could be a solution model. This is the x-axis,  $x_2$ . The solution model comes from somewhere. We'll talk about that. And it allows you to make very specific predictions. It allows you to build binary phase diagrams. And we'll talk about that.

The solution models, they represent particular phases. Or I should say structures, like FCC, or BCC, and so forth, or liquid, or gas. And the models are-- where they're derived from, they're derived from experimental data. They're derived from empirical modeling.

Or they're derive from atomistic modeling. So that is theory. All right, and and so this is the core of the class. We're getting there. This is what really enables phase diagrams, which is what enables materials processing. The solution models, we're going to deal with only the most basic ones in this class. And you can go pretty far with that.

The basic ones are what they give you in Thermo-Calc. To get the real ones, if you wanted to get the solution model that corresponds to a superalloy that say United Technologies uses for turbine fan blades, you would have to break into a very secure server. Those are databases with enormous economic value. They're trade secrets. Those are not published in the literature.

If you go into alloy development, you're going to be doing a PhD. And a lot of that's going to be doing-- building solution models. So if you were in the Allanore group, or the Tasan group, or maybe the [INAUDIBLE] group, building these models, these mathematical objects from data and using it to make predictions to design new materials, that's the core-- that's what's done.

So that's the end of the hour. I hope that I've been able to introduce you to the formalism of solution modeling without it being too boring, because at the end of the day, we're doing bookkeeping. And bookkeeping is hard to make-- it's obviously important. I think we can all agree on that. It's hard to get too very excited about it.

But we have to do it. So I'll remind you, again, Thermo-Calc. Thermo-Calc Academic, Thermo-Calc Academic, free software. Please download it. Install it well before you start working on this next P set. The reading for today is in De Hoff and Callister. So do the Callister reading. It's pretty straightforward.

There's also an accompanying light board video on binary phase diagrams, and tielines, and the lever rule. So I encourage you to watch that. You'll find that same content in De Hoff and the same content in Callister. But it's a little more colorful in the video.