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[RUSTLING]

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RAFAEL JARAMILLO: Back to thermodynamics. Happy Friday. We are going to study simple regular resolution model and spontaneous mixing and spontaneous unmixing. So the simple regular model is just a refresher from before the lecture-- sorry-- before the exam, the simple regular model. And by the way, my handwritten lecture notes are up on Canvas. Those will be replaced soon with the digitized notes. Sorry, we're a little bit behind on that. But anyway, this is a simple regular model.

So this is generic for any regular model. We assume ideal mixing and just some nonzero-- ideal entropy of mixing and nonzero enthalpy of mixing. And for the simple regular model, we have this form for the enthalpy of mixing-- sorry-- enthalpy of mixing. And this can take us a long way, just this relatively simple form, where a naught parameter rises enthalpy of mixing. a naught greater than 0 is endothermic, so we have to put heat in. And a naught less than 0 is exothermic, so we have to pull heat out from wave mixing at a fixed temperature.

And what does that actually mean? This is bonds, bonds being made and broken. When you hear endothermic and exothermic, that's what you have to remember. This is energy going into and getting pulled out of chemical bonds. All right. So that was a refresher.

So a week ago when we introduced this, there was a question of, where does this come from? Can we justify this? And I previewed this model, which I want to go into in more detail today because it's motivating. It's called the quasi chemical model. I don't quite know why it's called that, but that's what it's called. And it motivates the simple regular solution model, makes it seem less random. Model of molecules, or if you like atoms, on a lattice. So it's a lattice model. It's the latest model.

And so we're going to have species A and species B. We're going to have a lattice. So it doesn't really matter how I draw this. I just want to draw something that looks random. Can you hear the birds right out my window? They've been going crazy all morning. It's really nice. Anyway, so here we have atoms on a lattice, and the bonds are the lines connecting them. So this an A bond. It's a bond between two A's. This here is a B bond, and here over here is a BB bond.

So that's the model. And we're going to add up the bond energy. So we have bonds and the internal energy of those bonds, so bond internal energy. And so we have AA bond. We're just going to assign an energy EAA. That's the energy per bond. BB bond, we're going to go ebb. AB is going to have energy EAB and beyond nearest neighbor, no energy. So we're saying that only nearest neighbor bonds matter. That's the model. So it's very simple.

All right. So next, what we do is-- where's the pen that I need? we're going to add up the total internal energy. So U, the total internal energy, equals the number of AA bonds times the energy of AA bonds plus the number of AB bonds times the energy of AB bonds plus the number of BB bonds times the energy of BB bonds. That's it. N, I, J equals number of IJ bonds. And we know that the total number of bonds is the total number of sites times the coordination times 1/2 so that we don't double count.

M equals total site number and Z is the coordination. This is geometry. You can convince yourself of that. All right. We have conservational mass. What does that mean? Z, M, X, A, that's the total number of A species. That equals 2 times the number of AA bonds plus the number of AB bonds.

And similarly, ZMXB equals 2 times the number of BB bonds plus the number of AB bonds. So we're just counting atoms here, counting atoms, or I should say molecules to be more general, counting molecules or atoms, and then we solve for U and delta U of mixing. We can get this already. Watch.

Delta U of mixing equals U minus the pure contribution. Let's imagine pure AMZEAA and similarly for B. So now we're imagining lattices here of pure A and pure B. And if you plug in the numbers from above, you find a pretty simple expression. It's NAB times quantity EAB minus 1/2 EAA plus EBB. Welcome back to that. All right. But the math works pretty easily. All right.

So we have the energy here of mixing, depends on the number of unlike bonds, and this thing, which is the difference between the energy of an unlike bond and the average energy of the bonds. So that's a little funny. So next what we're going to do is we're going to count up NAB.

In general, NAB depends on structure. The structure of the lattice will determine how many of each type of bond there are, but if the alloy is random-- do you remember what random alloys means? Anybody want to volunteer of guess?

STUDENT: There's no general consistency for the arrangement of A's and B's.

RAFAEL JARAMILLO: Right. So a random alloy is you have some crystal lattice. That's correct, [INAUDIBLE]. You have some crystal lattice, and you have an alloy. So it's a mixture of components, and you distribute the components on the lattice at random. No order. That's opposed to ordered alloys, which there are many of. So random alloys, ordered alloys.

So if the alloy's random, as it should be if we're using the ideal entropy of mixing, which has that assumption of randomness in there, going all the way back to the baby book and lecture 1, then we have the probability of an AB bond equals-- what's the likelihood here? What's the likelihood that a given bond is AB? Well, you can have the first atom being A and the second atom being B, that's a conditional probability.

They're uncorrelated probabilities, but this is a joint probability because we want A and B. That's an AB bond. And we can also have B and A. That's also an AB bond. So we also have the probability that the first one is B and the second one is A. So this is combinatorics, the stuff that drove me crazy in high school because they didn't teach it well. So you have two XaXb. So that's the probability in a random alloy that a given bond is an AB bond.

So based on that, you can get Nab equals 1/2 Mz, total number of bonds, times this probability of AB, which equals MzXaXb. So now we're going to gather terms. Gathering terms, we have delta U of mixing equals alpha 0 XaXb-- sorry-- A0, where A0 depends on some things, the total number of sites, the coordination number per site, and this difference between the energy of unlike bond and the average energy of like bonds.

And here's a bit where we make an approximation, which you don't have to worry about too much right now, but we could talk about if you're curious. This by definition equals P minus delta H minus P delta V mixing, just by definition of enthalpy and energy. And for solid solutions, this can be well approximated by delta H of mixing.

And this is related to-- this approximation is related to what you did on a couple P sets ago, which is you estimated the energy changes for changing temperature and changing pressure of solids. And you found that temperature is a much more important knob in terrestrial conditions.

So anyway, you don't have to worry about this approximation so much right now. What I want to focus on is the form of this. We got this form. We got A0XaXb. So this pretty simple model of molecules on a lattice gave us an energy of mixing, or if you like, an enthalpy of mixing, that has this simple regular form. And there's some physical interpretation here. If the AB bond is a really low-energy thing relative to the AA and BB bonds, then this will be negative, and you'll have an exothermic process.

If the AB bond is a really high-energy thing relative to the cases of the pure materials, then this overall will be positive, and you'll have an endothermic mixing process. So let's plot this. Plotting-- so that was the end of the quasi chemical business. And I think it's useful. Plotting the simple regular model. Now we're going to step away from this quasi chemical business and just, again, analyze the simple regular model. Plotting the simple regular model.

So for the case A0 less than 0 exothermic mixing, we have delta H mix. Delta H mix is a parabola that's only negative. And we have T delta S mix, and we know what this. This is the ideal solution model with those x log x things, and it's all negative. So this thing looks like the following. The series is your increasing temperature. We have delta H mix minus T delta S mix equals delta G mix. So we can see here the enthalpy favors mixing. The entropy favors mixing, and so the Gibbs free energy is going to? Somebody?

STUDENT: Favor mixing as well.

RAFAEL
JARAMILLO: Favor mixing. All right. Thank you. So the Gibbs free is very favorable for mixing. And I have here a series of temperature. So this is qualitative. I'm just drawing lines on paper, but hopefully, you now see where this is coming from. That's exothermic. What about the endothermic case?

So in this case, we have something a little bit different. Delta H of mixing is now positive. We have to put heat in. The system absorbs heat from the environment when it mixes at fixed temperature. So now we have a 0 here, and this thing is an upwards moving parabola. But the ideal entropy of mixing is still the same, so this thing is strictly negative with the x log X's. So we still have this series, and the combination is delta G mix. And now our function is a little more interesting. So what does this look like at low temperature? Somebody, please. What does this look like at very low temperature?

STUDENT: Downward-sloping parabola.

RAFAEL JARAMILLO:	A very low temperature. Imagine temperature is zero, what does it look like?
	[INTERPOSING VOICES]
STUDENT:	--positive?
RAFAEL JARAMILLO:	Yeah, you got the parabola part, that was right, but if you look here at the sign-- if T is negative-- I'm sorry, that-- if T is 0, then you don't worry about this at. It's not here. So then you just have the upward facing. So it's an upward-facing parabola. At low temperature, you have the upward-facing parabola. It's ugly. What about a very high temperature? What about a really, really high temperature? What does this look like?
STUDENT:	You would have the negative parabola?
RAFAEL JARAMILLO:	Not the parabola, but you've got this thing that comes from the x log x. The parabola is parabolic, so that's x squared. But here you've got this downward-facing thing. That's right. So again, at high temperature, the entropy term dominates. At low temperature, the enthalpy term dominates. All right. Remember that. At high temperature, the entropy dominates. At low temperature, the enthalpy dominates.

What happens in between? In between is more interesting. So in between, you get a series of curves that interpolate between that low temperature case and the high temperature case. Sometimes I call this the duck phase plot. It kind of looks like Daffy Duck. But anyway, this is-- so now this is a little more interesting. Let me share-- I think this is useful to see plotted by-- it looks slightly more accurately than I'm able to do by hand.

So right here is the first case. This is exothermic mixing. I chose a physically reasonable number, minus 20,000 joules per mole. And you see the isentropic term here is strictly negative, downward-facing parabola. The entropy term is strictly negative, this x log x business, with increasingly negative with temperature. And when you add them up, you get this strictly negative thing, which favors mixing.

On the other hand, here, in the endothermic mixing case, we have-- and you said it's unfavorable enthalpy of mixing, takes energy to make it happen-- favorable attribute mixing. And when you combine them, you get this family of curves. And here, I've chosen physically reasonable numbers, plus 30,000 joules per mole. And you see what happens as I go from 300 Kelvin to 2,100 Kelvin. I traverse this series. So you're got to get a sense for units in temperature scales if you're going to be professional material scientists and engineers.

And so you see this is a reasonable number. I'll just tell you that now. This is a reasonable number for molecular or atomic systems that don't favor mixing, and now you see the temperature scale at which we often run materials processes. So this is typical furnace temperature. This is like 1,800 degrees. It's an aluminum furnace or maybe a graphite furnace, maybe a blast furnace.

All right. So now I want to talk about these curves a little more. Before I move on, questions, please. Questions on how that looks and why it looks the way it looks. We're going to talk about what the implications are in a minute, but-- |
| **STUDENT:** | So which sign of A favors mixing, again? |

RAFAEL JARAMILLO: So if A is positive is an endothermic, takes heat. So in general, this means the enthalpy will disfavor mixing. It means the mixing is a higher energy process. Mixing is a higher energy state than unmixed, as opposed to exothermic, where mixing is a lower energy state. So it's favorable.

And if you remember way back to lecture 1, there are processes that are spontaneous that are driven by lowering the system energy, sometimes at the expense of entropy. There are other processes that are spontaneous, that raise the energy, but they're spontaneous because the entropy also is significantly enhanced. That was the hot and cold pack example. And then as you vary composition and as you vary temperature, you have transitions between those cases. You have spontaneous processes that are driven by entropy and spontaneous processes that are driven by enthalpy.

This is a case of a spontaneous process that's driven by both. For ideal mixing for either no enthalpy or exothermic entropy, mixing is going to be spontaneous because it lowers the energy while also increasing the entropy. So this is a win-win. But in many interesting cases, you have instead a balance. You have instead of a balance. Then you have a situation where you have to put energy in, but you get an entropy benefit. And so what happens is in the balance. This goes right back to hot and cold pack.

All right. Allow me move on. I want to talk about the curvature. We haven't talked about curvature much, the curvature of this thing and solution stability, curvature and stability. So again, use a simple regular model. For a simple regular model, the curvature of delta G mix changes with temp for the case of endothermic mixing. So I'm just going to repeat what we just drew at low temp, medium temp, and high temperature.

So at low temp, we have delta G-- I'll use some colors here-- delta G of mixing is like that. So the curvature D squared DG mix DX2 squared, that curvature is everywhere negative. This is everywhere negative. This is negative curvature everywhere. Another way of putting that is that there are no inflection points.

At intermediate temp, medium temperature, we might have something like this. That individual has two inflection points. Here we got a little bit darker. That individual has two inflection points. The curvature changes sign. And it does it twice. There are two inflection points. Changes sign twice.

And at high temperature, where you go back to a situation with no inflection points, except here the sign is flipped. The curvature is now positive everywhere, and again, no inflection points. All right.

Why am I telling you this? So I want to draw a little picture here. I want you to consider spontaneous, microscopic fluctuations. For example, let's consider a system of squares and triangles at 50/50 composition. And let's go with the green and orange again. They have nice contrast.

So let's imagine at some time, maybe barely ever say time in this class, but I just said it, all right, so sometimes, I'm just going to draw-- this is very conceptual. I'm not actually drawing what a real system looks like, you know that. Let's see. How did I want this to be? I have a particular way that I want this to look, although the lesson could be taught through lots of different ways of drawing this.

1, 2, 3, 4, 5, 6 7, 1, 2 3, 4, 5, 6-- I was going to put another one somewhere. Do I have 7? 1, 2 3, 4 5, 6 7, 1, 2, 3, 4, 5, 6. Let's put another one here. It doesn't quite matter. So just imagine, we have some mixed system. This could be on a lattice. This could be on a fluctuating lattice. This could in a gas. This could be in a liquid. And now what I want to do is I'm going to imagine a thermal fluctuation that swap positions through thermal fluctuation.

And now we're looking at the system a moment later, and what does it look like? It looks like-- see if I can do this. And I wanted to have this down here and this here and this here, and then I had a triangle up here. And I have a triangle and a triangle and a triangle, and I have another triangle. And I have a triangle, and I have a triangle. All right. What on earth?

So you just had this randomly fluctuating system, but the fluctuation is such that it created a cluster of triangles. And you have to imagine that this kind of thing happens all the time, 10 to the 15 times per second in any thermal system, any sort of liquid at room temperature. Not that many times, 3 second in solids, but still many billions of times per second in solids, you have these fluctuations that are happening.

And here's the question, will this delta-rich cluster spontaneously dissolve or grow? That's a question we're going to ask. And to analyze this, we follow the money-- what do we follow? It's like follow the money but for thermodynamics.

STUDENT: Follow the Gibbs free energy.

RAFAEL JARAMILLO: The Gibbs free energy. Gibbs free energy is like thermo cache. That's it. So we follow the Gibbs free energy. So that's what we're going to do. We're going to analyze the Gibbs free energy of this little fluctuation, and that will tell us whether that fluctuation will spontaneously grow or spontaneously dissipate.

How do we do that? Well, we calculate the free energy of spontaneous composition fluctuations, and then we draw the plot. So this is the way I want you to think about it. We have delta G of mixing and we have-- this x-axis here is X_2, and we have some segment of a curve. We're zooming way in right now. We're not looking at the whole solution model. We're just zooming way, way in and looking at a segment of this curve.

And so let's imagine that we start here at overall composition X_2. So the system initially uniformly mixed at composition X_2. And then what we're going to do is we're going to spontaneously fluctuate into regions. We're going to spontaneously have a little bit of region that's X_2 rich and a little region that's X_2 poor. And I'm going to call this X_2-- r for right, you can call it whatever you want-- X_2 left. Just for today's lecture and drawing, its left and right makes some sense.

So we're going to spontaneous fluctuation inter regions with composition X_2 left and X_2 right. How much of each material is there? How much of this composition is there and how much of this composition is there? That's determined by the phase fractions. I'll come back to this in a minute. Let me just get this down on paper.

The phase fractions, that is what fraction of the system is at the left composition and what fraction of the composition, they're determined by the lever rule. So we're previewing a little bit here what you're going to be reading and working on in the future. But if these compositions are equally spaced around the central composition, that is X_{2r} minus X_2 is the same as X_2 minus X_2 left equals, let's just say, some dx, some little differential change. So this is dx, and this is the x, so the same spacing.

Then you have simply f left equals f right equals 1/2. So half the system is a little rich in component two, and half the system is a little poor in component two. And what you want to do is calculate the differential change, the change in the overall free energy of mixing.

And so what you get is something like following, phase fraction of the left stuff times the free energy of mixing evaluated at the composition of the left stuff plus phase direction of the right stuff times the free energy of mixing evaluated at the composition of the right stuff minus-- not the right stuff, that's funny-- minus what you had before the spontaneous fluctuation. So this is after fluctuation, and this is before fluctuation.

Now, a word before I go on. I'm actually helping you on the p set. So finishing this calculation is one of the problems on the p set. Reading about-- and then proving the lever rule is also on the p set. So this is all stuff for next week. So if some of these concepts are new to you, that's OK. It's coming up. And these concepts are not particularly complicated. You just want to become exposed to them. And the reading for the next week also includes a section of Callister, which I've discussed. There's more pictures. It's a little more entertaining than DeHoff. And so you can get this content from Callister or DeHoff.

And I'll make one final note, which is that I have a mini lecture of one of these-- what are these called? These lectures where I was standing in front of a piece of glass. Light board, a light board video on the lever rule. So all of that's available for you. Anyway, so this is what you do. You calculate this change, and you can show, or you will show, that negative curvature leads to spontaneous unmixing.

So that's going to be the condition for those little unmixed clusters, those little fluctuations, to grow in size and for the system to spontaneously over macroscopic length scales unmix. And we have a special name for this process, is called spinodal decomposition. In my experience, and as far as I know, spinodal decomposition is synonymous with spontaneous mixing. They exactly mean the same thing. And you can similarly show that mixtures are stable for positive curvature.

So this is neat because we get to analyze our solution model a little more. We also get to start learning about binary phase diagrams, which is coming up. So we learn some concepts, like lever rule and phase fractions. And we learn something about stability. Before pausing and stopping for questions, I want to share some pictures about spinodal decomposition.

So this is a really important general phenomenon. Here's a general spinodal phase diagram. This is from the book. This is from chapter 10 to the book. So we're not there yet, but here's a delta G of mixing for a system that undergoes spinodal decomposition. Let me grab a laser pointer here. So this delta G of mixing has this feature that its curvature changes sign, and it's got inflection points, rather like what we were showing half an hour ago. And the resulting phase diagram has this two phase region.

And we're not quite there yet analyzing phase diagrams like this, but we're going to get there within a couple of lectures. So a free energy composition diagram like this leads to a phase diagram like this. And here's an example. This is dodecane and ethanol, any system that at high temperature mixes and at low temperature separates. I think Aviva was asking earlier, which one was which, high temperature, low temperature.

This is the system, which is an endothermic mixing system. It takes energy to mix. So low temperature, where enthalpy terms tend to dominate, it prefers to unmix. At high temperature, where entropy terms dominate, it prefers to mix. And unmixed is within this region of composition called the miscibility gap. And you get this phase diagram. This is very general phenomena.

I pulled four examples here of spinodal systems, and this spinodal decomposition analysis shows up. You can't get away from it. Now that you've heard of it, you are not going to be able to get away from it. It is very general, and it's good to be introduced now. Of course, it happens in liquid phases, nucleation and growth. We just showed an example of dodecane and ethanol. Those are two liquids. And this is randomly picked pictures from the literature.

So I don't really cite these properly, but it's pictures here of nuclei forming and growing, secondary phase nuclei within a liquid. Before we move on, how can you tell this to the liquid? Anybody? How can you tell this is a liquid system and not a microscopy of a solid system? This goes beyond O2O by the way, just if someone has intuition about it.

STUDENT: Maybe because there's less order than there would be in a solid [INAUDIBLE].

RAFAEL   So that's not it. And so that's a really good point. This length scale here is not the length scale of atoms and
JARAMILLO: molecules. You can't see the atoms and molecules on this length scale, although that's a good point. This is a macroscopic length scale that you might see under a microscope. So you don't see atoms and molecules. What I'm looking for here is the fact that they're round.

Liquids tend to have isotropic surface energy. Liquid particles tend to be rounded. And droplets of one liquid in another, like your droplets of oil in your salad dressing, tend to be round. So that's a surface effect. We don't have time for surface effects in this class, but it's a good clue. All right.

Here's another example, spontaneous unmixing in high entropy alloys. So this is a micrograph now. Still not on the atomic scale, although I guess the total x and y direction here is no more than a couple tens of microns, if I had to guess, but we're still macroscopic. We're not on the atomic lever here. But here you see that there's been spontaneous unmixing of this iron, copper, nickel, manganese, copper alloy into iron, copper-rich regions and copper-rich regions. And here, the boundaries between the regions, they follow some geometrical order.

Now the boundaries seem to line up along some grid, and they don't just curve randomly. And so that's reflecting the fact that these are crystalline materials with an isotropic surface energy. So this is a counterpoint to the liquid case. And as you can imagine, this pattern formation, that's what it's called often, this pattern formation is very important to controlling the material properties.

Here's another case, slightly surprising maybe, where we see spinodal decomposition, and it's in neural activity in the cortex, where you have decomposition into regions of high activity and low activity based on the input. That the math that we developed, or started to develop, just a couple of minutes ago has been generalized and generalized again and found to apply to many, many systems, not just material. So here is neuroscience, and it applies to the structure formation of the universe. Who knows what this picture is?

STUDENT: Is that cosmic background radiation?

RAFAEL   Cosmic microwave background across the entire visible universe. And the physicists are very concerned about
JARAMILLO: the fact that the Big Bang started off with spherical symmetry and we ended up with the universe with you and me and MIT being regions of high density and most of space being regions of-- Harvard being a region of low density, for instance. And so we have this-- how did this happen?

And the mathematics of that, the physics of that is analyzed in terms of spinodal decomposition. It's called quantum spinal decomposition. Fully beyond my understanding. But I do know that if you look at current papers in the cosmology literature, you will see free energy composition diagrams very much like this one. So this is a general phenomena.

It's 10:55. I want to-- let's see-- remind folks that we're shifting towards phase diagrams here. Remember Callister, so slightly different textbook just for a short time. It's an easy read. There's also a paper that is focused on teaching spinodal decomposition that I'm going to post on the website, and that will help a little bit with understanding and also with the p set. And there's a white board-- sorry-- a light board video on the lever rule. And we're almost done with the exam grading, and there's a new p set out within minutes.