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RAFAEL JARAMILLO: So we're going to talk about equilibrium in a unary heterogeneous system. So let me give you the reason why. We are not talking about phase diagrams in exam one. But that comes next. That's what we cover next after the exam.

So today's lecture is like a bridging lecture-- we're going to talk about applying equilibrium, which we've learned about, and unary heterogeneous systems. And of course, this will lead into unary phase diagrams.

So let's set up the problem. This problem is as follows-- we're going to isolate our system. So we have a box, and it's going to have thermal insulation. Imagine that thermal insulation all around there.

And we're going to have two phases in this box. We're going to have an alpha phase. And then over here, in a different region, we're going to have a beta phase. And we're going have a phase boundary between them. And this is unary, so one component.

So system with one component and two phases. We're isolating the system. So if it's isolated from the surroundings, what is going to be its condition for equilibrium?

Equilibrium for-- what's the condition for equilibrium for an isolated system?

STUDENT: Is it that entropy is set at maximum?

RAFAEL JARAMILLO: S max, right, maximum entropy condition. That was-- right, isolated system. Thank you.

OK. The internal-- and this is part of the problem statement, this isn't always true-- so there's a boundary between the phases internally. Think the boundary between the ice and the water in your glass of ice water. That's an example.

That internal boundary is non-rigid, it's open, and it's diathermal. So it's the opposite of the external boundary. So that's the problem set-up.

And our goal is to evaluate the equilibrium condition-- so that's it. Evaluate the equilibrium condition. So let's see what we mean by that.

So let's write an expression. And if we want to evaluate the condition, ds, we have to write an expression for ds. So let's start with phase alpha.

For phase alpha, d u of alpha-- we're going to do combined statement-- equals t alpha d s alpha minus p alpha dv alpha plus mu alpha d m alpha. You'll recall a couple of lectures ago, we introduced briefly superscript phase labels. And now we're going to start using them-- now we're going to start using them a lot.

Lost my black pen. OK. All right, so this is combined statement.

You've seen this before. We're just adding superscript phase labels. So we're going to rearrange. This is a pretty easy algebra operation. We're going to rearrange and write ds equals 1 over t alpha d u alpha plus p alpha t alpha dv alpha minus mu alpha t alpha dn alpha.

Likewise-- likewise, for the beta phase, we're going to have d s of beta equals 1 over t beta d u beta plus p beta t beta dv beta minus mu beta t beta d n beta.

I'm going to try using this pen for a while. It's thinner. You guys can tell me which one you like better. So we have made an assumption here, which is that the alpha phase is everywhere at the same temperature. Also, it's everywhere at the same pressure. And it's everywhere at the same chemical potential.

Similarly, we've assumed that the beta phase is everywhere at the same temperature, everywhere at the same pressure, and everywhere at the same chemical potential. So you have to state your assumptions, it's good to know what they are.

All right, so now, entropy-- is it extensive or intensive?

STUDENT: Extensive.

RAFAEL JARAMILLO: Extensive, right. Entropy is extensive. Not intensive. So the total ds-- the thing we're trying to write-- equals ds alpha plus ds beta. I want to make sure that people understand that-- if there are questions about that concept, let's tackle them now.

No questions about that. So that means, the total change of entropy in the system equals the sum of the things which I just wrote down. So I'm going to take the pains to write it out.

All right, so this is a big differential equation. Let's count variables-- how many variables are there? Independent variables, how many independent variables are there?

STUDENT: Three?

RAFAEL JARAMILLO: So there are six here. Mu alpha, v alpha, n alpha, mu beta, v beta, and beta. Six variables and six coefficients.

So we're learning to identify variables and coefficients from differential equations. That was what we were working on for the last two lectures. So differential form, dependent variable, independent variables, coefficients.

I want you to really get to the point where you don't have to think to pick those off. All right, so now we're going to talk about optimization. For the case of unconstrained-- unconstrained optimization, ds equals 0, requires that all six coefficients equals 0.

So those of you who have done a lot of mathematical optimization, are probably familiar with this. Those of you who have not, which is probably most of you, might take a minute to think about what that means.

So I'm going to draw that in one dimension. We have a six-dimensional problem, but I'm not very good at drawing in six dimensions. But I can draw on one. So let's draw a curve in one dimension.

I have x and I have y. Where is the optimum of this curve? Optimization means finding the optimum.

STUDENT: The maximum point?

RAFAEL JARAMILLO: Right, just the maximum point. Right, right. So what would the condition for that be? Say it in calculus language.

STUDENT: The slope to be 0.

RAFAEL JARAMILLO: Yeah, d x-- sorry, d y, d x equals 0. Sorry, I messed up my y there, but at that point, the slope is 0. So what that means is let's say x is unconstrained. As x wiggles around, the value of y doesn't change. Only as long as I'm at that point with 0 slope.

If I'm at a point with non-0 slope, as x wiggles around, y will change. So if there is a potential, which tries to maximize y, it's going to force the system to the right, if I'm here. Or if I'm over here, if there's a potential that tries to maximize y, it's going to force the system to the left.

So the only condition for which the system is stationary, we might say at equilibrium, is a condition for which that slope is 0.

Now, imagine this in six dimensions. This is 1 plus 1 dimension. Now, imagine it in 6 plus 1 dimensions. I can't draw in seven dimensions any better than I can draw in six. But the same thinking applies-- that for unconstrained optimization, I would need all six coefficients-- those are partial differentials-- to be 0.

So the way to solve this problem and to figure out the equilibrium conditions, is to identify what are relevant constraints that reduce the dimensionality of the problem? So that's what we're going to do next-- we're going to think about what constraints apply in this case.

And the constraints change from case to case. So let me show you what I mean. Let's talk about constraints.

A constrained optimization is-- and you could-- if you went into business consulting, you're doing constraint optimisation. Operations research, a lot of engineering problems boil down to constraint optimization. We're just scratching the surface here.

But constraints come from physical things. Let's start for conservation of energy. I seem to have switched back to the fat pen. I'm going to switch midstream here. I want a vote at some point, you guys tell me which one you like better.

Conservation of energy. So conservation of energy, this is an isolated system. So what can we say about d u of alpha? If alpha gains energy, where does it have to come from?

STUDENT: From beta.

RAFAEL JARAMILLO: Has to come from beta. So d u alpha has equal minus d u of beta.

Again, coming back to our picture, we have an alpha phase, we have a beta phase. They're separated by a very porous, almost non-material boundary. And that boundary allows energy to pass back and forth. They can do work on each other, and they can heat each other.

OK, that's good. This reduces our number of dimensions by 1. We have an additional equation.

There's another constraint-- conservation of volume. I said, the system was rigid, it was in a box. And the box's size wasn't changing. So if we have volume conserved, what do we know about d v of alpha?

STUDENT: Minus d v beta?

RAFAEL JARAMILLO: Minus dv of beta, right. If one side is getting bigger, it has to be because the other side is getting smaller. There's nothing else in the box.

And the third conservation law we're going to apply is conservation of mass. If phase alpha gains particles, it has to come at the expense of phase beta. Because the box is closed. The mass of the overall system is fixed.

So these three conditions, which are constraints, they simplify the equilibrium condition d s equals 0, to three independent variables with three coefficients that we set to 0.

So now, instead of worrying about six slopes in [INAUDIBLE] space, now we only have to worry about it in 3 plus 1 dimensional space. I still can't draw it, but we'll see that the math is relatively simple. So let's talk about those.

Constraint optimization-- constraint optimisation down-- we're down to three. We're down to three terms-- d s equals 1 over temperature of alpha minus 1 over temperature of beta d u of alpha. See, I eliminated d u of beta. I eliminated the energy of the beta phase.

OK, likewise, p of alpha over t of alpha minus p of beta t of beta dv of alpha. I eliminated dv of beta. And similarly, you have alpha t of alpha, minus mu of beta t of beta d m of alpha.

So now, this is my problem. And this whole thing has to be equal to 0. So now, we've applied our constraints. How can I guarantee that this whole term equals 0? Under what conditions can I be guaranteed that that term will be 0?

STUDENT: If all the coefficients are 0 again.

RAFAEL JARAMILLO: Thank you, that's exactly right. The only way I can guarantee that 0 is if the coefficients are zeroed out. Why is that? Because I can't set the independent parameters to be 0.

Why is that? These two phases can exchange energy freely. They can exchange volume freely. And they can exchange a particle number freely. It's an open boundary. I can't stop those processes.

So d u of alpha and dv of alpha and d n of alpha in general can be non-zero. So the only way that I can guarantee that I'm at equilibrium is to set the coefficients equal to 0. Set coefficients equal to 0.

So let's do that. 1 over t of alpha minus 1 over t of beta equals 0. What does that give me? That gives me temperature of alpha equals temperature of beta. This is known as thermal equilibrium.

So remember how we got thermal equilibrium? Two subsystems that could exchange energy reached thermal equilibrium. What's the next one?

P of alpha over t of alpha minus p of beta over t of beta equals 0. Well, given thermal equilibrium from this, I get p of alpha equals p of beta. This is known as mechanical equilibrium.

And the third one is u of alpha over t of alpha minus mu of beta over t of beta equals 0. And again, given thermal equilibrium, this gives me mu of alpha equals mu of beta. And this is known as-- does anybody know what this is known as?

STUDENT: Chemical equilibrium.

RAFAEL JARAMILLO: Chemical equilibrium. So there are three different subsets of equilibrium-- three subsets of equilibrium. Each can be achieved on its own. Each can be engineered to be achieved on its own. But if you add them up, this equals thermodynamic equilibrium. So that's the meaning.

This is the equilibrium-- I'll write in fat red-- conditions for two-phase coexistence. So if two phases are going to coexist in equilibrium in a unary system, you must have all three of these-- thermal, mechanical, and chemical.

And the structure, the mathematical structure of this will come up again in more complicated scenarios. But if you can see past the math, I want you to see the physical origin of this. When systems can exchange energy, they come to thermal equilibrium. When systems can exchange volume, they come to mechanical equilibrium.

And when systems can exchange particles, they come to chemical equilibrium. And you, as engineers, can engineer processes to achieve selective equilibrium. You can allow systems to exchange volume, but have impermeable membrane so that they can't exchange particles.

You can allow systems to exchange energy by heating, but have rigid and impermeable membranes. Or you can have membranes that allow some particles to equilibrate, and others not to. So let's say, you're making a desalination system-- you want water to equilibrate, but dissolve solids not to.

Lots of examples here. So this seems really theoretical, it actually presents a lot of opportunity for engineering-- selective equilibrium. Let's highlight some assumptions to this point. Assumptions to this-- so assumptions to this point are at the intensive parameters, there is t and p and mu are uniform within each phase.

That's been an assumption. We also assume that the boundary has no substance or effect on properties of either phase. So this is relatively straightforward.

This-- this gets complicated. So we've assumed the boundary is a dashed line with no substance. In the real world, whether that's a good assumption depends a lot on the size scale you're talking about. So some of you may have been involved in nanoscience-- when things shrink, interface has become more and more important. It's a geometrical fact.

The thermodynamics of systems with boundary effects is a really interesting topic that goes beyond 020, but it becomes important for those of you who might work on colloidal systems, or semiconductor quantum dots, or coatings-- lots of useful materials that you don't get the right answer if you don't consider the boundary.

But in this class, we don't consider the boundary. A corollary of this assumption is that the spatial distribution doesn't matter. Spatial distribution doesn't matter. So I could have two versions of the system. What colors did I use for my phases? Orange and purple, I think? Hardly matters.

One with, let's say, orange and purple, and a single phase boundary separating them. Or I could have purple-- particles or filaments are dispersed in an orange matrix-- in this situation. As long as my total quantities are the same in both cases, there's no difference.

There's no difference. If the boundary has no substance. You can create or destroy boundaries-- they're free. So when we start caring about the differences between these, we have to start accounting for boundaries. Enough about boundaries, because we don't cover them in this class, but I want to make clear that you know where we are and where we're not.

We'll just finish here. This is the same thing-- if and only if boundaries are free. No cost.

Got it, OK, moving on. Let me make something kind of abundantly-- I might be beating a horse here, but boundary conditions affect equilibrium. The boundary conditions affect equilibrium.

So for example, here's a simplified case. Here's an isolated system. I think I used brown here for a thermal insulation, giving you an idea it really is isolated. And I'm going to have an alpha phase. Then I'm going to have a rigid but thermally conductive box containing the beta phase.

So in this case, alpha and beta separated by boundary that is rigid-- no volume exchange. Closed, no mass exchange. But diathermal-- heating is OK.

So this you grabbing a Coke out of the freezer, out of the cooler-- it might be pressurized, but it's going to come to thermal equilibrium with your hand, if you wait long enough. So this is a case of selective equilibrium. You're going to get thermal equilibrium, but not chemical and not mechanical.

In such a case, ds simplifies. All you have-- no dv, no d n terms. And t alpha equals t beta at equilibrium.

OK, so now, physically, you know that. You know you take a pressurized bottle out of the cooler, it will come to your room temperature, the temperature of your hand. But until you release the cap, it will stay pressurized and you won't have any mixing.

So I'm trying to use these examples, which you're very physically familiar with, and illustrate them in this way, this mathematical optimization framework, that you're maybe less familiar with. So you can become more familiar with it.

And why does all of this happen? Why does all of this happen? All of this happens because of entropy generation during a spontaneous processes. And this is where we need to keep our eyes on-- generation of entropy during spontaneous processes.

So let's write out ds again-- t alpha 1 over minus t beta over mu alpha plus p alpha t alpha minus p beta t beta dv alpha. Sorry that's messy. Minus mu alpha t alpha minus mu beta t beta d n alpha.

So this is our at equilibrium. So let's consider t alpha greater than t beta. Let's consider you drop a hot particle of alpha phase into a bath of beta phase. In this case, 1 over t alpha minus 1 over t beta is less than 0.

If the temperature of alpha is greater than the temperature of beta, what can you say about what will happen spontaneously? The hotter phase, alpha, it will heat or it will cool the cooler phase? It will spontaneously what?

STUDENT: Heat it up?

RAFAEL JARAMILLO: Yes, heat the colder phase. That's actually another statement of the second level-- that's Clausius statement of the second law of thermodynamics, is hot materials spontaneously heat colder materials. It's equivalent to the other ones, the other statements we've seen.

So that means d u alpha is less than 0, or d u beta is greater than 0. Those are the same thing. So if d u of alpha is less than 0, and this coefficient is less than 0, then d s is greater than 0. Good.

Entropy is generated-- entropy is generated during heat transfer from hot to cold. This is, again, a restatement of the second law, super important. So when a hot object spontaneously heats a cold object, entropy is generated. That's what we want to see, based on everything that we've postulated.

And that's what the math gives us. So it's all consistent. That's good.

Let's consider another case. Consider t of alpha equals t of beta. So they're already thermally equilibrated. But they're mechanically out of equilibrium. Or in other words, p for alpha or t of alpha minus p of beta over t of beta is greater than 0.

So what's going to happen? The higher pressure phase will spontaneously-- it'll either expand or contract. So the higher pressure phase will spontaneously expand or contract.

STUDENT: Expand.

RAFAEL JARAMILLO: Expand, right. This is not going to contract. Will spontaneously expand, and I could say, at the expense of the lower pressure. So it's elbowing the lower pressure phase out of the way.

That means d v of alpha is greater than 0, or d v of beta less than 0. And again, from the previous page, and from these, I get d s greater than 0.

So it's not just heat transfer, that increased entropy, it's also mechanical work that can increase entropy. Why is that, by the way? Let's go back to the baby book picture. Why is it that mechanical work can increase entropy? What's going on?

Let me draw a picture. Let's start at t equals 0 with a high-pressure phase, and let's imagine these are gases. And let's draw a low pressure phase.

So this is high pressure, and this is low pressure, at t equals 0. And then, I remove the partition. So the high pressure phase expands into the lower pressure phase. Why does that increase the entropy?

STUDENT: Maybe because particles are more randomly distributed and go out further from each other?

RAFAEL JARAMILLO: Yeah, it's like that. These can be more mixed up in the whole volume. There's a more random distribution of more particles. That's right.

Good, last example here. Let's consider temperature alpha equals temperature beta, but mu of alpha is greater than mu of beta. So in this situation, you have alpha over temperature of alpha minus mu of beta over temperature beta is, of course, greater than 0.

So we have phase boundary, we have the alpha phase, imagine particles in the alpha phase. I shouldn't have used a color, I should have used the same black, because it's unary, and I have one type of--

And then, we have the beta phase. And again, more of the same component. All right, so matter in phase at higher chemical potential will spontaneously convert to phase at lower chemical potential.

In other words, d n of alpha is going to be less than 0, or d n of beta is going to be greater than 0. How does this actually happen? Each individual little particle-- I'm going to anthropomorphize here-- each individual little particle samples its local environment. And it asks itself, where can I get the cheapest Gibbs free energy? It's Gibbs free energy price shopping-- it goes price shopping.

And it sees that it's in a more expensive region. It actually would like to transform into a cheaper region. So it transforms, and when it does so, the phase boundary moves a little bit. Now that particle has transformed from alpha to beta. The beta phase has grown a little bit at the expense of the alpha phase.

And then, the next particle gets to ask itself-- what would I rather be? And then the phase boundary moves a little bit more. And so on until chemical equilibrium is reached.

And again, from the combined statement, we find that this spontaneous process increases the entropy, as we expect. So this process here, by which particles transform between their phase-- sometimes in this class, I call it Gibbs free energy price shopping-- that's most of what we deal with in material science.

It's less intuitive than high-pressure, things pushing into low pressure things, but we're not mechanical engineers. And it's less intuitive than hot things heating cold things. So of these three examples, it's the least intuitive, maybe, it's the least everyday. But it provides the most rich behavior.

So this is what we're going to be worrying about. And of course, the particles don't sit down and think, right? But through spontaneous random thermal fluctuations, they sample different environments. And they will stay in the environment that's more stable.

So that's where it gets towards kinetics. Again, another topic which we don't quite have time for this semester. What we worry about this semester is chemical potential and reaching equilibrium.

And I always say you should never anthropomorphize atoms. They hate it when you do that.

On that note, I think I'll stop recording and we can leave here for the weekend. I'll stick around till 11:00 or beyond. I'm happy to answer questions.