[SQUEAKING]

[RUSTLING]

[CLICKING]

PROFESSOR: All right, let's get going.

I mentioned that a lot of what we're going to do when we model solutions is bookkeeping. So this is a really important quantity that we're going to track, and I'm going to introduce it-- partial molar properties. And we're going to use the notation as in the text.

So the partial molar property for some generic state function-- we're using B here because it can stand in for any state function-- is the partial of the total B-- this is an extensive state function-- with moles of component k at fixed temperature, fixed pressure, and fixed moles of everything that's not k. j not equal to k.

So B is an extensive property. Extensive property. n of k is moles of k. And B bar of k equals a partial molar property. Sometimes, I'll just call this PMPs.

So this is kind of formal looking, but it's not a hard concept. You could think of this in many different ways. You could think of the extensive property as the total amount of money in all of our pockets right now. But we each have different amounts of money in our pockets. So our own contribution to the total amount of money in all of our pockets right now would be our partial personal property, I guess.

You can think of this as the total area in my whole neighborhood, land area. But each of our houses has a different lot size. So we each have a different contribution to the total land area in my neighborhood over here in West Cambridge and so forth and so on. So this bookkeeping is kind of formal, but the concept is familiar.

We're going to make sure we know what the total differential of property B is. We have these coefficients. dB dT affects P and mole number dT plus dB dP. That affects T and mole number.

And here's where we get to use the partial molar properties. Plus B i dni. So as defined here, it's a coefficient. Partial molar property is this coefficient.

And one clarification. For pure phase, for a pure phase, you only have one component. Its molar fraction is 1. And the partial molar property is simply the molar property. There's no partial involved.

One thing about PMPs is PMPs are-- they're intensive. They're independent of the system size. And I'm going to use some illustrations to tell you what I mean there.

But let's see. How do we know they're intensive? A PMP is an extensive quantity divided by an extensive quantity. So if I imagine this is a partial molar property, and the system is a given size, and I double the system size, then both the numerator and the denominator here will double. And the intensive partial molar property will remain unchanged.

But there are useful consequences of this. So let's imagine a system made out of triangles and circles. So for example, let's imagine a system with X circle equals X triangle. And it's 50/50, just to be specific.

So let's imagine three different systems here. Here we have one, two, three, four, five circles. And we have five triangles. And if we have B circle equals 7 and B triangle-- I'm just making a numbers here. It doesn't matter what numbers I use. And for T and P constant, in this case, the total amount of B equals B circle n circle plus B triangle n triangle. And this is 7 times 5 plus 4 times 5.

Let's consider a slightly different case. Let's make the system a little smaller. Let's have three moles of each. In this case, the total amount of B again is sum B of i n of i equals 7 times 3 plus 4 times 3.

And then, of course, you can keep on going here. Let's imagine one circle and one triangle. The total amount of B equals 7 plus 4.

So why am I telling you this? Why did we just go through this exercise with circles and triangles? It's because we're going to add up partial molar properties a lot. We're going to be doing this quite a lot. And it comes back to this. The whole is the sum of the contributions of the parts, according to this bookkeeping scheme. It's according to this bookkeeping scheme.

Let's keep going. We need some mathematical relations between the whole that is a total amount of B and the PMPs.

We're going to consider scaling the system size by a scaling factor. And this is the unit of this thing. I'll just use lambda.

So imagine B is a function of temperature, pressure, and the scaled system size. Well, if we imagine, let's say, doubling the amount of moles of everybody, we simply double all extensive quantities. And that holds for any-- it doesn't have to be double. It could be triple. It could be half. It could be any factor. So we have this.

So if I multiply it by some constant scale factor, the size of the system, it's the same thing as multiplying the overall extensive quantity by that same scale factor. I'm going to use this. So this is not just for fun. This becomes useful.

But I will call out, for those of you who are mathematically inclined, that that means that B prime is a homogeneous function of the Mk's of order one. So for those of you who do real analysis and stuff, that comes into it. Never mind.

So what we're going to do with that is we're going to take the derivative, the total derivative, d d lambda of both sides. So let's see. The left-hand side is going to give us dB d lambda equals dB d lambda n of k. Just using the chain rule here.

This is chain rule. And this is our definition of partial molar property. And this derivative is really easy. Right-hand side, d d lambda times lambda B T P n of k. And that is also an easy derivative. That's B T P n of k.

So I took the total derivative of the left-hand side on the right-hand side. And I'm going to then compare them.

Again, this is exactly what we were doing with circles and triangles. The total extensive quantity for a system is the sum of the partial molar properties times the mole numbers. So again, circles and triangles, scaling with system size.

And this is called an Euler equation. I think it's the only one we're going to use in this class. So you don't have to worry so much about that there's this category of equations called Euler equations in thermo. But you might encounter them, if not now, then in a later class. And that's what this is. It is the consequence of that first-order homogeneous property.

Where is it stated a little more colloquially? Extensive properties of a solution phase are made up of the mole weighted PMPs of the components. That's what it means.

So for example-- this is the one we'll be using almost to the exclusion of any other in this class-- the Gibbs free entry of a system is going to be the sum of these PMPs times the mole numbers.

And because Gibbs free energy is so special, we have a special expression for the molar Gibbs free energy and its chemical potential. So the Gibbs free energy, PMP, is the chemical potential. So you've seen this expression before.

So if you ever see someone add up the Gibbs free energy of a system, and they just jump right to this, you know where it comes from. So sum of the chemical potentials weighted by the mole numbers. Unfortunately, we have to continue with more equations.

So what we're doing here is we're building up to these useful expressions, which you can use-- you will use on the homework, for instance-- without necessarily knowing where they come from. So we have an Euler equation, which is like the one we just derived, which is the total amount of B equals the sum of the partial molar B times the mole numbers.

And then we're going to use the chain rule. And we're going to calculate the total derivative dB. And that's going to be equal to chain rule stuff. Bk dn of k plus n of k d d of k. And that's relatively straightforward.

And we're going to use a coefficient relation. The coefficient relation is that dB at constant temperature and pressure equals-- that was from the beginning, when we defined the partial model property. And so what we're going to do is we're going to simply compare these expressions, this and this. And we find that one of these two sums is 0.

This is called a Gibbs-Duhem equation. And by the way, I really would not be spending the time on this if it didn't end up in a really useful place. So if you're wondering why on Earth you sign up for a class on analysis, all I can say is this is a class on thermo. And this is part of it. And I'm including it because it's going to take us somewhere really useful. Enough excuse making. This is thermo.

So n dbk, what on Earth does this mean? It means that you can't change all the partial molar properties independently of each other. If you have two components, let's say, the sum runs over 2, there's a linkage between how the partial molar properties of one change when the partial molar properties of the other change. There's this equation. They're related to those. Let me say that.

The Gibbs-Duhem equations are constraints on the variation of intensive properties. Or in other words, they express how the partial molar properties covary. That's a term from optimization. They covary with system composition.

In other words, it's a differential equation. An equation that describes how things covary with each other is a differential equation. That's what it is.

So now we're going to move towards partial molar properties of mixing and so forth. And we will finally get to graphical interpretation, which is why we're doing all of this. So for example, Gibbs-Duhem for Gibbs free energy.

If anyone's wondering, what's with Gibbs? How come he gets his name on everything? He's one of the most important and prolific American scientists ever. And he was a thermodynamics researcher, obviously, in the late 19th century. And he spent his career at Yale. And yeah. His name is all over classical thermo.

Euler, Euler gives us the following. The total of Gibbs free energy is the sum of mu of k n of k, the chain rule. It gives us dG equals mu of k dn of k plus n of k d mu of k.

And then we combine the combined statement. The combined statement is a coefficient relation. dG equals minus s dT plus VdP plus mu of k dn of k. And I'm going to use these, and I get the following. n of k du of k equals minus S dT plus V dP.

Or if I want to divide through by the total number of moles, I get an equivalent statement. Mole fraction d mu of k equals molar entropy. These are also gives qm.

So again, you see what these are is they're constraints on how the intensive properties are varying. Because intensive properties have pressure, temperature, and chemical potential, we can't all vary independently of each other. We have these constraints. Let's move on.

And this is really like actuarial science. We just keep on coming up with these bookkeeping schemes. And we have to stick with it.

So we're going to have something called the mixing quantities. So the change due to mixing is going to be the total quantity in the solution minus what you started with before you made the solution, the pure components.

We talked about this last time, that, in general, the whole is not simply the sum of the parts when you make a solution. And there were some examples given of materials which, for example, get bigger than you would expect or smaller than you would expect and so forth. So we're just going to capture that change here.

And we're going to write the total B using partial molar properties, as we just learned how to do, Bk n of k. And then we're going to introduce even more notation and say, for the pure components, you had pure molar properties. And we've got group terms.

And we're going to define that as delta B partial molar property due to mixing. Oof. Change in PMP due to mixing. My goodness.

What is this? Let me give an analogy. I don't know whether this helps.

Let's imagine this is personal space. We're calculating here the area occupied by a crowd of people. And you could define a personal space as the exclusive area around everybody such that the total area is everyone's personal space added up. Does that makes sense? Imagine a crowd of people.

What this is is an expression, acknowledgment, that your personal space in a given crowd varies with the crowd. So if you are-- let's see. If your crowd is a dispersal of people in Killian Court on a sunny day, you're going to have a lot of personal space per person.

It would be very, very strange to go up to somebody who is sitting there, having a picnic, and to sit so that your shoulders are rubbing, and you don't know the person. Total stranger. Killian Court's wide open and sunny. And you go sit with your shoulders rubbing. And that's the space you picked. That would be very unusual.

But same people in a crowded subway car or on a dance floor, you might have a very different personal space. So your personal space is not fixed by who you are as a person. It's determined by the solution you find yourself in. And different solutions will result in different personal space, space per-- area per person.

And we have this term, delta B of k, personal property of mixing, to capture how that changes. So how does your personal space change from your ideal situation, where you're in a field by yourself? If you're in a crowded subway car, you're surrounded by a crowd of people who you like. Maybe your personal space shrinks. Or you're surrounded by a crowd of people who you don't really like. Maybe your personal space expands.

And there's going to be analogies for all of these in thermo. When a molecule is surrounded by other molecules that it likes or that it wants to bond with, its purse's volume is going to shrink a little bit. Its volume per molecule will shrink a little bit. And if a molecule is surrounded by molecules that it doesn't want to bond with, its partial molar volume will expand a little bit. So these concepts depend on the surroundings.

So let's make this specific again, Gibbs free energy. The total Gibbs free energy of a system is equal to the sum of partial molar Gibbs free energy times mole number is-- because Gibbs is special, it has its own term, chemical potential, times mole number.

And according to our new bookkeeping scheme, this is the chemical potential of the pure stuff plus however it changed when it entered the solution phase. And then we'll divide through by the total mole count. And we get Gibbs free energy equals--

And again, this is the sum of the pure components. And this is change, the change upon mixing.

We have two more slides. And we're going to get to the very, very useful graphical interpretation of all this. How do we calculate these things?

So you're to do a little bit of this on the p set. So we're going to do the case of chemical potential in a binary system, binary system. So binary system-- delta G due to mixing equals delta mu of 1 X1 plus delta mu of 2 X2. And you have two components. That's good.

And so this gets-- you really have to know your d's of thermodynamics here. The change of the Gibbs free energy of mixing for fixed pressure and temperature as a system composition varies. So again, the change of the Gibbs free energy of mixing at fixed pressure and temperature as a new system composition varies.

What about the chain rule? Well, that thing equals 0 if I give 2n. So I'm left with these two terms here. And then I'm going to use X1 plus X2 equals 1, which means what? d X1 equals minus d X2. It's a binary system. So there's only one composition variable.

And get the following. D dT G dT delta G mix d X2. I chose X2 here as my independent variable. At fixed pressure and temperature equals delta mu of 2 minus delta mu of 1.

And then I'm going to eliminate delta mu of 1 using the above. What's the above? That's the above. And I get the following. Delta mu of 2 equals delta G mix plus 1 minus X2 d delta G mix d X2.

And believe it or not, this is really useful. And likewise for delta mu of 1.

And let me just show you why for each one, and we can come back for questions. It's really useful because we have a graphical interpretation of this. Graphical interpretation of PMPs using solution models.

So we're going to do this for a case of delta G mix and delta and delta mu k. So let's draw a plot. I'll show you what I mean here.

Here's a solution model. I'm just going to draw anything. I'm going to draw-- imagine someone gave you this data, or you figured this out yourself, something like that. Here's a solution model. Something. It's some trend of thermodynamics with what? With system composition. So this is X2.

So we have some solution model. And we're going to imagine sitting here at-- let's see. Let's imagine sitting here at this composition. Let me just go ahead and draw these tangents, and then we'll come back to why they matter.

So there's a point on the curve and my overall system composition. This intercept here I'm going to label. This label, this over here, and also label this over here. I'm going to label. I'm going to give these number labels P, S, R, and Q.

So here's my system composition. Here's my system composition. There's a tangent line, the tangent line. And we have a solution model.

So delta G mix is just at the height of this curve, is this QR. That's that length, the curve evaluated at P.

Quantity 1 minus X2 equals PR. It's just that length. And the slope, d delta G mix d X2. Rise over run. So the rise is RS. And the run is PR.

And so I'm going to plug these geometries into the expression, which we derived on the previous slide. And you have QR plus PR times RS over PR. And this length segments cancel each other. And you get QR plus RS, so this distance plus this distance, which, of course, equals QS.

What does that mean? It means that this point here, this intercept, is delta mu 2. And likewise for delta mu 1. You have just over here is delta mu 1.

So right. That means if we have a solution model, some data, some curve, if we draw the tangent to that, we can pick out the partial molar properties of component 1, component 2, by the intercept of the tangent on the left-hand axis and the right-hand axis.

And so that's where I'm going to leave it for today. Either this is kind of mysterious and wasn't worth the effort, in which case I would ask you just to hold on. Or it now it starts to make sense if you've seen the common tangent construction before, in which case, I'll say, all right, well, we'll get there. Right. So this was a bunch of math around solution modeling.