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PROFESSOR: Alright, so last time we started talking about more complicated mixtures. To get into colligative properties. And the example we gave was a binary system that has two components. And two phases. So we have a liquid phase on the bottom. A gas phase on top, and two components, A and B, where compositions  $x_A$  and  $x_B$  are in the liquid phase. Those are the mole fractions. And  $y_A$  and  $y_B$  in the gas phase, the mole fractions in the gas phase. And what we did last time was to begin to say how many degrees of freedom do we have, how many variables do we need to completely describe this mixture. And it turned out that for this mixture, we only needed two variables. Two degrees of freedom.

We started out with four variables; the temperature, the pressure, and the components in the composition in the liquid phase and the composition in the gas phase. We need one of these, either  $x_A$  or  $x_B$ , and one of these, either  $y_A$  or  $y_B$  because they add up to 1. So you start with four, but because you are in a mixture, an equilibrium, you have constraints. You have the chemical potentials that have to be equal to each other. The chemical potential of A in the gas phase has to be equal to the chemical potential of A in the liquid phase. And the chemical potential of B in the gas phase has to be equal to the chemical potential of B in the liquid phase. So you start with four variables. Temperature, pressure,  $x_A$ ,  $y_A$ , then you have the constraints that  $\mu_A$  in the liquid phase has to be equal to  $\mu_A$  in the gas phase. Because you're at equilibrium. And  $\mu_B$  in the liquid phase has to be equal to  $\mu_B$  in the gas phase. So four minus two constraints means you have two degrees of freedom. And so if you want to know everything about this mixture, all you need is the temperature and the total pressure. And that's enough. It's kind of amazing. Give me the temperature and pressure and these two components, like water and alcohol, for instance, and I can tell you everything about the compositions. It's very powerful.

And then we said that this turned out to be a special case, or sub-case of the more general Gibbs phase rule. where the Gibbs phase rule tells you that if you have  $C$  components, in this case here we have two, and the general case of  $C$  components with  $p$  phases, the number of degrees of freedom is  $C$  minus  $p$  plus two. This is components. And phases.

And where we're going to start today is by proving this. And then we'll do more with this problem here. So the first thing is for us to prove Gibbs' phase rule. So Gibbs phase rule. We start out with all the variables that we have. And then we add the constraints. And for the Gibbs phase rule, then we start with the two knobs that we can turn externally. Which are the temperature and the pressure. So we start with temperature and pressure, as two

variables that we have. And then we have a bunch of phases. We have  $C$  phases. And in each phase we have to describe the composition in that phase. So, for each phase  $\alpha$ , we have to describe its mole fraction. So here we needed to describe  $x_A$  for phase  $\alpha$ . And  $y_A$  for phase  $\alpha$ . For component  $A$  in the gas phase. So now we have  $\alpha$  components.

And for each component we have to describe its mole fraction in that particular phase. So we have to describe  $x_{\alpha i}$ . But we have a constraint on that. The constraint is that the sum of all the mole fractions has to be equal to one. That's what it is, to be a mole fraction. So the constraint is that  $x_{\alpha i}$ ,  $i$  from one to  $\alpha$ , is equal to one. So the constraint on the number of the components, instead of having, actually,  $i$  goes from one to  $C$ , because that's the number components. So instead of having  $C$  different compositions that we need to take care of, we only need  $C$  minus one. Just like here we only needed one, just  $x_A$ . We didn't need both  $x_A$  and  $x_B$ , because we knew the sum was equal to one.

So that means that we really need  $C$  minus one variables to describe the composition in one of the phases. But we have  $p$  phases, so let me fix this. We had  $C$  components. We have  $p$  phases. And so for each phase, we have to describe the composition. So that means that we need  $p$  times  $C$  minus one variables to describe all the components and all the phases, plus these extra two. So the total number variables then that we start out with before putting the fact that we're in equilibrium, is going to be two plus  $p$  times  $C$  minus one. So that's a basic description of the system. Then we put in the same constraints that we had up here. In terms of the chemical potentials. If I take any of the components, let's take the  $\alpha$  component, or the  $i$ 'th component. Because it's in equilibrium, the chemical potential of that particular component has to be the same in all the phases.

So let's take the  $i$ 'th component. So  $y_i$  in phase one has to be equal to  $y_i$  in phase two, has to be equal to  $y_i$  in phase three, has to be equal to  $y_i$  in phase  $p$ . All the chemical potentials have to be the same across all the phases for that component. And if you count the number of equations, the number of equals signs here, that's  $p$  minus one.  $p$  minus one equals signs, constraints due to the fact that I have an equilibrium here. So this gives me  $p$  minus one constraints. And this is true for every single component. Every single component has to have its chemical potential, its chemical potential equal throughout the phases. So  $p$  minus one's constraint for one component times  $C$  components. So for a total of  $C$  times  $p$  minus one total constraints. My variables, my constraints. So the number of degrees of freedom then becomes  $p$  times  $C$  minus one minus  $C$  times  $p$  minus one and then plus two.

And if you multiply this out,  $p$  times  $C$  gets rid of the  $p$  times  $C$  here. And you get the plus  $C$  minus  $p$  plus two. Which is the Gibbs phase rule, right? Which I'm going to bring back up here.  $C$  minus  $p$  plus two. So just purely in accounting, just accounting for the variables and the constraints. OK, any questions on how we did this? Great. OK.

So let's move on, then, to these ideal solutions. Which is this case right here. And the first thing we're going to do is look at the case where we have A is a solvent, and it's volatile. And B is a solute, which is non-volatile. So let's take the first case. We have A volatile, that's a solvent. Could be water. And B is going to be the solute. It's non-volatile. And let's interchange solute or non-volatile to be consistent here. So this could be sugar. A sweet water.

So, Mr. Raoult looked at such solutions, and found that they could be well described by the following diagram here. So if I plot on the x-axis here, from zero to one, I'm going to plot the partial molar fraction of the solute. Partial molar fractions of the solute, that's going to be  $x_B$ . So when  $x_B$  equals to zero, I have a pure water solution. When  $x_B$  is equal to one, I have pure sugar. Then on the y axis, I'm going to plot the total pressure. So when I have a pure water solution, the total pressure is going to be the same as the vapor pressure of water at a particular temperature. Let's take temperature fixed at some value. Temperature is fixed at some value. I'm going to have the total pressure is going to be the partial pressure of the water. And clearly, when I don't have any water left, all I have is the sugar, there's no pressure. We're going to assume that it's totally non-volatile. Obviously there's going to be a little bit of vapor pressure, even at room temperature. Ten to the minus, I don't know, 13 torr or something. But anyway, it's basically zero here. And what Raoult said is that while these two points are just connected by a straight line.

Simplest way to connect two points. Basically, he said that the pressure of, the vapor pressure of the water in this case, is equal to  $x_A$  times  $p_A^*$ . I could also plot this with  $x_A$ , going from one to zero, since  $x_A$  plus  $x_B$  is equal to one. Or I could write this as one minus  $x_B$  times  $p_A^*$ . Where a star, the star, means pure water. So pure A. And  $p_A$  is the vapor pressure of the mixture. Which in this case here is the total pressure, because I don't have anything else that's volatile. And this is Raoult's law.

And the first thing that you can use this for is to look at your first colligative property which is vapor pressure lowering. And let me point out another thing first. So if a solution obeys that property here, it's called an ideal solution. So if the water-sugar solution really did behave like a straight line like this, as you increase the amount of sugar, then it would be an ideal solution. Many things are very close to it. It's not such a bad approximation. Especially in that region up here. Around zero, when the amount of sugar is pretty small. You expect to obey an ideal solution behavior.

Alright, so let's look now at a glass of water that has sugar in it. We've got my glass of water,  $H_2O$ . With some sugar dissolved in it. And it's got a certain vapor pressure on top.  $p_A$ , or  $p_{H_2O}$ . And I'm going to ask the question, what's the difference between the vapor pressure what it would be without the sugar in it. What is  $p_A^*$  minus  $p_A$ ? Obeys Raoult's law.  $p_A^*$ ,  $p_A$  is  $x_A p_A^*$ , plug that in here. That's one minus  $x_A p_A^*$ , one minus  $x_A$  is  $x_B$ .  $x_B p_A^*$ . Well, the first thing I know is that this is a positive number.  $x_B$  is a positive number.  $p_A^*$  is a

positive number. This is greater than zero. That means that the act of putting some solute in my water decreases the vapor pressure of the water in the gas phase. Pretty simple. It's called vapor pressure law.

And we can actually take this one step further. We can draw a phase diagram. So our usual phase diagram here with temperature on this axis here and pressure on this axis here, and we've got our triple point sitting here. And our gas-liquid line, with a critical point here. So this is gas here, there's a liquid here. And we've got our, this is going to be water. So it's got a negative slope. I think I've got it right this time. And there's the solid phase here. OK, this is for the pure stuff. So now I can draw a similar diagram for sugared water. And I just looked at this, assuming it obeys Raoult's law. What we looked at here was the gas-liquid coexistence. And we found that the gas-liquid coexistence point, the vapor pressure of the water, was less than if it were pure. So that means that if I looked at the gas-liquid coexistence, which is this line right here. In the presence of sugar, that whole line is going to get lowered. The pressure, the vapor pressure, of the water is going to be lower when the sugar is there. So the whole thing is going to get lower.

Now, if I have a solid, if the water is a solid, it's going to crystallize the water, the sugar is going to be separated from the water. The sugar and the water are not going to really know about each other. They're just going to have big chunks of pure water, with every now and then a molecule of sugar that's in there. So you don't really expect to see any difference between the pure solid water, in terms of the gas-solid interface, and the pure liquid water. There's no sugar in the gas phase. And as far as the gas phase is concerned, that solid phase is pure water. It's just seeing pure ice crystals on the surface. Every now and then there's a molecule of sugar. So you expect this to be pretty close here. So you expect the triple point to go down. And if I now, I go up to the solid-liquid coexistence, and go up like this, I can make a prediction about solid-liquid coexistence. I can predict that if I'm looking at, let's put one bar here somewhere. One bar. Room temperature, sitting here somewhere. One bar, room temperature, water is all liquid. This is what it would usually, solid, liquid, that would be 273 degrees Kelvin. That's the melting point of water. So now if I put sugar in the water, and I follow my diagram here, what I find is that the new melting point of water is some new temperature  $T_1$ , where  $T_1$  is less than 273 degrees Kelvin. You all know this. When you put something, like an impurity, a salt or sugar in the water, the melting point gets depressed. It goes down. Straight from here. You can build it up straight from here.

When we get to the colligative properties, we'll attack it from the point of chemical potentials. We'll equate chemical potentials and we'll look at the change in the chemical potential in the water, and the presence of the sugar and we'll do it rigorously. But this is sort of the first indication that these colligative properties are all connected to each other. They're connected to this diagram here. OK.

So when I was a kid, and I knew that this was the case. Everybody knows this is the case, right? You put salt in the water and you expect all sorts of things to happen. You expect the vapor pressure to go down. And certainly

you know that you add salt to the roads and the water melts, et cetera. And my mother always told me that the reason why you added salt to the water was so that the temperature of the water would get higher when you try to boil pasta. And for, I don't know, fifteen years I believed her. Until I taught thermodynamics. And I actually calculated the change in the temperature by adding a few pinches of salt to the water. And you know how small that temperature change is? You should calculate it. It's really tiny. It won't make any difference for the water. Probably the difference in the temperature of the water will be the same as if I cooked here versus halfway up Mount Washington in New Hampshire or something. Probably even less. There's no difference. The reason why you add salt is so that it tastes better. That's the only reason. It has nothing to do with thermodynamics. Alright, any questions on this?

So we going to make it a little bit more complicated now, if there's no questions. We're going to now have, instead of having one non-volatile solute, use we're going to have two, we're going to have this mixture. Where both components are volatile. Can we erase this? Actually, I may not erase this. Because I want to keep Raoult's law here. OK, we're going to have a mixture of two volatile components. For instance, water and alcohol. Your your typical martini type situation. Or margarita. Whatever's your favorite drink.

So now we have  $x_A$ , we have  $x_B$ , we have  $y_A$ , we have  $y_B$ . And we're going to assume that both obey Raoult's law with respect to each other. So now if I draw a diagram, and I just focus on, so there's the total pressure sitting here. And I just focus on one component and ignore the other. Suppose I focus on A. And I know that A in the presence of B, the partial pressure of A is going to obey Raoult's law. And let's take A to be the more volatile component in this case here. So  $p_A^*$  is bigger than  $p_B^*$ . The partial pressure, pure A, had a particular temperature,  $T$  fixed is bigger than  $p_B^*$ , it's the more volatile of the two. So if I were to plot  $p_A$  as a function of  $x_B$ , going from zero to one, so it'll be Raoult's law, I'm going to start at  $p_A^*$ . And I'm going to go down linearly to  $x_B$  equals one. Now I can do the same thing for the partial pressure of B. And assume that in the presence of A, just looking at this component B, now, and I'm looking at the partial pressure of B, and it's got its impurity in it, A. B obeys Raoult's law with A in there. But now if I want to keep the same x axis here, I can look at  $x_A$  here, going from zero to one. So I just basically flip the thing over. So at  $x_A$  equals zero that's pure B.  $p_B^*$  is less than  $p_A^*$ . I'm starting here, on that side here.  $p_B^*$ , and I'm going down in a straight line to zero.  $p_B$  is equal to  $x_B p_B^*$ , straight line all the way to zero when  $x_B$  is equal to zero. So that's  $p_B$ . And that's  $p_A$ .

Now, the total pressure is the sum of the two.  $p_A$  plus  $p_B$ . So the total pressure in this system here, that I measure here, is just the sum of these two straight lines. Let me do it in blue. The total pressure, if you add up these two straight lines together, you got another straight line. Two straight lines make a straight line.  $p$  is  $p_A$  plus  $p_B$  is equal to  $x_A p_A^*$  plus  $x_B p_B^*$ . Now,  $x_A$  and  $x_B$  are related.  $x_B$  is one minus  $x_A$ . And so really, this is only a function of one variable here. Linearly, with respect to one variable. OK, what does this diagram tell me? So now,

let's ignore how we built it. And let's take a look at it. So I have, going to take  $x_B$  on the bottom here. From zero to one. We could choose either one, and I've got the straight line for the total pressure going from  $p_A^*$  to  $p_B^*$ .  $T$  is fixed. I need to tell you that  $T$  is fixed because I have two degrees of freedom, right? I have two degrees of freedom. My degrees of freedom are the temperature, which I'm fixing. And the composition in the liquid phase, which I'm fixing. So my two variables are  $x_B$  and  $T$ . Those are my two degrees of freedom. And I'm telling you what the total pressure is. I'm giving you total pressure as a function of  $x_B$  and  $T$ . By fixing  $T$ , I'm really telling you what the pressure is of the function of  $x_B$ . So the Gibbs phase rule then tells me that the pressure should be only a function of  $x_B$  if  $T$  is fixed. Should be a line. Not necessarily straight, but it should be a line in this diagram. To have coexistence. So what this line is, then, this line is the line of points that tells me when I have coexistence between the gas phase and the liquid phase. The coexistence line. This is the gas-liquids coexistence line for the mixture. It's not so different than this coexistence line up here.

So you can think of this as a phase diagram, kind of like you thought, you know this as a phase diagram. It's got a coexistence line. And then if I'm above this line, if I'm at a certain pressure here, I'm at this point here, this pressure well, let's go to a slightly higher different pressure here. And this composition here. I'm not on the line. That means that I don't have coexistence between liquid and gas. I'm above the line. I'm at a pressure higher than where I would get coexistence. The pressure is higher, means I probably don't have a gas any more. Probably means that the total pressure pushing down on my mixture is too high to have a gas phase around. It means that the top part here is a liquid phase. So I'm in the liquid phase if I'm above this line and I have a coexistence between the gas and the liquid if I'm on the line. Now, if I'm below this line here, well, I get in trouble. I get in trouble because my first instinct would be, well this is just gas. I go from liquid, and then I have coexistence. Then I go into the gas phase. But my x-axis here is the composition in the liquid phase. There's no liquid around. So I really can't say anything here. This diagram is a little bit meaningless down here. Because my x-axis is describing a phase which doesn't exist on the diagram. On this diagram, here. So when you see it, this diagram here with Raoult's law on it, you've got to remember that the part that's really interesting is above the line and at the line itself.

So you could do an experiment, then, on this line here.  $T$  fixed. This is the liquid phase. So suppose I start with some high pressure up here somewhere. At this point, let's call this point one. We've got my container, my piston here.  $p$  is equal to  $p_1$ . Again, I put the point in an awkward place. Let's put it right there.  $p_1$ , and composition  $x_B$ .  $p_1$  and  $x_B$  here. And I'm going to slowly decrease the pressure. I start in this composition. The composition doesn't change. I'm just decreasing the pressure. Decrease the pressure, decrease the pressure, decrease the pressure. And at some point, I get to that line. Get to that line, what happens when I get to that line? I start to see bubbles coming out of the liquid. Vapor starts to form, because it wants to be in the coexistence line. So I get to that line. And I get a little bit of bubbles forming. And a little bit of vapor. That's the liquid here. Little bit of gas. And

that's why this line here is called the bubble line. So I've gone down, decreased the pressure. So  $p$  has gone down now. Decreased the pressure. And if I keep on decreasing pressure, well, I'm not going to jump into this area of the diagram. Because this area of the diagram means there's no liquid, it's a meaningless area. If I keep decreasing the pressure, I'm still going to be in coexistence. I'm just going to make more gas. More vapor. I'm going to transfer more of the liquid into the vapor phase. I'm going to ride down that line. I'm going to ride down the line. I'm decreasing the pressure. I'm not going to skip into here. I'm going to ride down the line here. We're going to keep decreasing the pressure even more.  $p$  goes down even more. Now, I make even more vapor. There's my piston right there. There's the gas phase. There's the liquid phase. Now I've transferred material from the liquid phase to the gas phase. But I also changed the composition of my liquid phase. And if I read my new composition, this is what I started out with.  $x_B$ . My new composition in the liquid phase is going to be, let's call it  $x_B'$ . There's going to be more solute in there. Or more B in there, than what I started out with.

Now which one was the more volatile one? A or B? A was more volatile, right? So as I decreased the pressure and I started bubbling off the material, which one's going to bubble off preferentially? A is going to. So it makes sense that I would concentrate B in there. Decrease the pressure. Bubbles that are rich in A come out. Both A and B come out. But more A comes out than B. And what's left over is rich and then more than the less volatile material which is B. So we're beginning to see how distillation comes about. This is the first step in it. In a distillation process.

So let's make this a little bit more complicated now. Any questions, first? Alright, now, suppose I wanted to know. So I found out where the composition in the liquid phase is here. And I know that should tell me immediately whether the composition in the gas phase is here. So I have all, I have everything I need to know to calculate what the composition in the gas phase is. So I have everything I need, then, to calculate and draw a diagram that looks just like this. Except where my x-axis is the y's instead of the x's. Going to make the same diagram, except now I'm going to use the gas phase as my reference point. The composition in the gas phase.

So I need to get, so here I got  $p$  as a function of  $x_B$ . I want  $p$ , total pressure, as a function of  $y_B$ . So I can draw a diagram that looks just like this except now with the x-axis being the gas phase composition. Let's turn the crank. What do I know? I know Dalton's law.  $p_A$  is  $y_A$  times total pressure. I'm trying mix up the partial pressures and the total pressure in all ways that I know how to write it. And then hope that something's going to come out that's going to be helpful. So that's Dalton's law. I know Raoult's law.  $p_A$  is  $x_A$  star times  $p_A$  star. And that's Raoult. And I can write Raoult's law in a different way. I can write as  $p_B$  is equal to  $x_B$   $p_B$  star, that's just Raoult's law for B. One minus  $x_A$   $p_B$  star. And I'm looking for this. I'm looking for the composition in the gas phase. Or the total pressure as a function of the composition in the gas phase. Let's start by finding the composition in the gas phase as a function of the composition in the liquid phase. And the total pressure. Rewrite  $y_A$  is equal to  $p_A$  over  $P$ . Total

pressure is  $p_A$  plus  $p_B$ . Sum of the two partial pressures.  $p_A$  over  $p_A$  plus  $p_B$ . And I'm trying to get  $y_A$  in terms of the  $x_A$ 's. Or  $x_B$ 's, in terms of composition in the liquid phase. And I know how to relate that to a constant. Which is the vapor pressure of the pure material times the, and the composition of the liquid phase, Raoult's law. This is  $x_A p_A^*$  divided by  $x_A p_A^*$  plus  $x_B p_B^*$ . And I know that  $x_B$  is one minus  $x_A$ . So this is  $x_A p_A^*$  times  $p_B^*$  plus  $p_A^*$  minus  $p_B^*$  times  $x_A$ . Where all I did was replace  $x_B$  with one minus  $x_A$ . And rearrange my equation on the bottom.

So I've gotten the composition in the gas phase in terms of the composition in the liquid phase. They're not independent. I knew they weren't independent. And this just shows me that math works. OK. So I've got that. And I can invert this to get the composition in the liquid phase in terms of the composition in the gas phase. It's not so straightforward, but you can get  $x_A$  as a function of  $y_A$ , as well. You've got  $x_A$ , if you reverse this you get  $x_A$  is equal to  $y_A p_B^*$ . It looks kind of the same.  $p_B^*$  plus  $p_A^*$  plus  $p_B^*$  minus  $p_A^*$  times  $y_A$ .  $x_A$  as a function of  $y_A$ .

Alright. So now you can actually put everything together, starting from Dalton's law. Because really what we want is the total pressure as a function of the composition in the gas phase. So there's our total pressure here. There's the composition in the gas phase. There's  $p_A$ . We've found composition in the gas phase in terms of composition in the liquid phase.  $P$  is equal to  $y_A$  over  $p_A$ . Which is equal to  $y_A$  over  $x_A p_A^*$ . So if we could get rid of this here, in terms of  $y_A$ , we'd be all set. We'd get the total pressure as a function of the composition in the gas phase. And there's what we need. So we plug that in here. And now we have the total pressure in terms of constants like these pure vapor pressures and the composition of A in the gas phase. So let me find a way to write that somewhere. Let me write it right here in this little box here. Plug it in, you get something that's not a straight line. Unfortunately. Doesn't look like Raoult's law.  $p_A^*$   $p_B^*$ .  $p_A^*$  plus  $p_B^*$  minus  $p_A^*$  times  $y_A$ . It's not a straight line. It's a more complicated function. What does it look like?

Looks like this. I'm going to use the same sort of plot. I going to plot the total pressure on this axis here, on the y axis. I'm going to keep the T fixed. Temperature is fixed. So I'm going to find the total pressure as a function of the composition in the gas phase. I'm going to put  $y_B$  here.  $y_B$  going from zero to one. So it's kind of looking like what I had before. Total pressure is going to look the same. If you want to do it in terms of B, you just have everywhere you see B replace it with A. And everywhere you see A replace it with B. You just need to change the two. You know that if  $y_B$  is equal to zero, that you have pure A. So you know that this is going to be  $p_A^*$  here. You know if you have  $y_B$  equals to one in the gas phase, you have pure B in the gas phase. You know that what you have is the vapor pressure of the pure B, in this case the pure water.  $p_B^*$ , OK? Where A is more volatile than B. A would be the ethanol and B would be the water. And it's not a straight line. If it were Raoult, he would say just connect these two with a straight line. But it's not. It's not, we just figured out with an equation here. And it turns

out to be a line that looks like this. It's a curved line that looks a bit like this.

OK, what does this line mean? This line is also a coexistence line. That's what we started out with. We started out with Raoult. That was part of our derivation. Raoult's law tells you the composition at coexistence. Tells you the pressure of, the total pressure, or partial pressure at coexistence and the composition. So this is a coexistence line between the liquid and the gas. Coexistence between liquid and gas. But now, it's not as a function of the composition at the liquid phase. It's a function of the composition in the gas phase. Which was missing before. So now if I do my experiment, and I'm, so what does this mean? So if I have a point, if I have a pressure which is lower than the line here, then I have pure gas. Pressure, low pressure, I have pure gas. Don't have any liquids. And that's fine, because I can, I know what that point is. If I'm sitting below the line here somewhere, so I'm sitting here. Some composition in the gas phase, a certain pressure. That's fine. It's a meaningful point. So my container here has a piston on it. And I'm starting out with this pressure,  $p_1$  here.  $p_1$  pressing down. And I got  $y_B$  in this here. And I increase the pressure, pressure goes up. Composition doesn't change. I'm just increasing the pressure. Increasing the pressure, increasing the pressure.

Now, at some point the pressure becomes big enough that I start to see liquid forming. Little drops of liquid forming in my container. So now I have little drops of liquid that are forming in my container, that are going to start to rain down and form a little bit of liquid pooling at the bottom of the container. And that's called the dew line. The other one was called the bubble line, this is called the dew line. So when I reach the dew line, I start forming liquid. And again, just like in the previous case, if I keep increasing the pressure, I don't go into this area here. First of all, this area's meaningless for this diagram here. Because this area's pure liquid. But the x-axis here doesn't tell me about the composition of pure liquid. It's all  $y_B$ . It's all about the composition in the gas -- yes.

STUDENT: [INAUDIBLE]

PROFESSOR: Between the dew line and the bubble line?

STUDENT: Yeah.

PROFESSOR: This never, never world. Where you're not allowed to inhabit. We're going to go into that next time. On how to use those two curves together. OK, but the same thing happens here. If I increase the pressure, I'm going to ride the coexistence line up. I ride it up, and keep riding it up. And I get liquid forming in here. And I can find out the composition in the gas phase now. The composition in the gas phase, as I increase the pressure, I get  $y_B'$ , there's  $y_B$  that I started out with with. With  $y_B'$  is less than  $y_B$ . And remember, B was the less volatile of the two. As I increase the pressure, I am forming liquid. The composition in the gas phase changes. You decrease the mole fraction of the less volatile material in the gas phase. The more volatile A becomes more prevalent in the gas phase. And what's coming down is mostly, then, it's enriched in B. You've done an enrichment

of the less volatile material down in here.

And now you can put the two together, as the question was asked. Now we can have, we mix the two together. We mix our Raoult diagram with our dew line diagram. We mix the bubble line and the dew line together. In one diagram, which is going to be a powerful diagram to use.

Total pressure. Temperature fixed. You've got two materials,  $p_A^*$  is bigger than  $p_B^*$ . So I'm going to have  $p_A^*$  here,  $p_B^*$  down here. And if I choose, as my x-axis, to have  $x_B$  going from zero to one, I can draw a coexistence line on this axis. On this diagram. That's the coexistence line in terms of  $x_B$ . And any point up here is well-described by this  $x_B$  value, and the  $p$  value. And as long as I have  $x_B$  here, I'm not allowed to touch the bottom part of this diagram. But now if I add another x-axis, I'm going to add  $y_B$ . From zero to one. I draw a coexistence line in terms of  $y_B$ . Like this. So this line is  $p$  as a function of  $y_B$  coexistence line. This line is total pressure of function of  $x_B$ . And as long as I'm on this line or below this line, then this axis makes sense. That's how we build this diagram here. It's got a bubble line on top, and the dew line on the bottom. So I'm up here going down, I'm going to hit the bubble line. If I'm down here and go up in pressure, I'm going to hit the dew line. And next time -- well, next time we have an exam. But on Friday, we'll figure out how to use this diagram.