PROFESSOR: So. In the meantime, you've started looking at two phase equilibrium. So now we're starting to look at mixtures. And so now we have more than one constituent. And we have more than one phase present. Right? So you've started to look at things that look like this, where you've got, let's say, two components. Both in the gas phase. And now to try to figure out what the phase equilibria look like. Of course it's now a little bit more complicated than what you went through before, where you can get pressure temperature phase diagrams with just a single component. Now we want to worry about what's the composition. Of each of the components. In each of the phases. And what's the temperature and the pressure. Total and partial pressures and all of that. So you can really figure out everything about both phases. And there are all sorts of important reasons to do that, obviously lots of chemistry happens in liquid mixtures. Some in gas mixtures. Some where they're in equilibrium. All sorts of chemical processes. Distillation, for example, takes advantage of the properties of liquid and gas mixtures. Where one of them might be richer, will be richer, and the more volatile of the components. That can be used as a basis for purification. You mix ethanol and water together so you've got a liquid with a certain composition of each. The gas is going to be richer and the more volatile of the two, the ethanol. So in a distillation, where you put things up in the gas, more of the ethanol comes up. You could then collect that gas, right? And re-condense it, and make a new liquid. Which is much richer in ethanol than the original liquid was. Then you could make, then you could put some of them up into the gas phase. Where it will be still richer in ethanol. And then you could collect that and repeat the process. So the point is that properties of liquid gas, two-component or multi-component mixtures like this can be exploited. Basically, the different volatilities of the different components can be exploited for things like purification.

Also if you want to calculate chemical equilibria in the liquid and gas phase, of course, now you've seen chemical equilibrium, so the amount of reaction depends on the composition. So of course if you want reactions to go, then this also can be exploited by looking at which phase might be richer in one reactant or another. And thereby pushing the equilibrium toward one direction or the other. OK. So. we've got some total temperature and pressure. And we have compositions. So in the gas phase, we've got mole fractions y_A and y_B. In the liquid phase we've got mole fractions x_A and x_B. So that's our system. One of the things that you established last time is that, so there are the total number of variables including the temperature and the pressure. And let's say the mole fraction of A in each of the liquid and gas phases, right? But then there are constraints. Because the chemical potentials have to be equal, right? Chemical potential of A has to be equal in the liquid and gas. Same with B. Those two constraints reduce the number of independent variables. So there'll be two in this case rather than four

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independent variables. If you control those, then everything else will follow. What that means is if you've got a, if you control, if you fix the temperature and the total pressure, everything else should be determinable. No more free variables.

And then, what you saw is that in simple or ideal liquid mixtures, a result called Raoult's law would hold. Which just says that the partial pressure of A is equal to the mole fraction of A in the liquid times the pressure of pure A over the liquid. And so what this gives you is a diagram that looks like this. If we plot this versus x_B, this is mole fraction of B in the liquid going from zero to one. Then we could construct a diagram of this sort. So this is the total pressure of A and B. The partial pressures are given by these lines. So this is our pA star and pB star. The pressures over the pure liquid A and B at the limits of mole fraction of B being zero and one. So in this situation, for example, A is the more volatile of the components. So it's partial pressure over its pure liquid. At this temperature. Is higher than the partial pressure of B over its pure liquid. A would be the ethanol, for example and B the water in that mixture. OK. Then you started looking at both the gas and the liquid phase in the same diagram. So this is the mole fraction of the liquid. If you look and see, well, OK now we should be able to determine the mole fraction in the gas as well. Again, if we note total temperature and pressure, everything else must follow.

And so, you saw this worked out. Relation between p and y_A, for example. The result was p is pA star times pB star over pA star plus pB star minus pA star times y_A. And the point here is that unlike this case, where you have a linear relationship, the relationship between the pressure and the liquid mole fraction isn't linear. We can still plot it, of course. So if we do that, then we end up with a diagram that looks like the following. Now I'm going to keep both mole fractions, x_B and y_B, I've got some total pressure. I still have my linear relationship. And then I have a non-linear relationship between the pressure and the mole fraction in the gas phase. So let's just fill this in. Here is pA star still. Here's pB star. Of course, at the limits they're still, both mole fractions they're zero and one.

OK. I believe this is this is where you ended up at the end of the last lecture. But it's probably not so clear exactly how you read something like this. And use it. It's extremely useful. You just have to kind of learn how to follow what happens in a diagram like this. And that's what I want to spend some of today doing. Is just, walking through what's happening physically, with a container with a mixture of the two. And how does that correspond to what gets read off the diagram under different conditions. So. Let's just start somewhere on a phase diagram like this.

Let's start up here at some point one, so we're in the pure - well, not pure, you're in the all liquid phase. It's still a mixture. It's not a pure substance. pA star, pB star. There's the gas phase. So, if we start at one, and now there's some total pressure. And now we're going to reduce it. What happens? We start with a pure - with an all-liquid mixture. No gas. And now we're going to bring down the pressure. Allowing some of the liquid to go up into the

gas phase. So, we can do that. And once we reach point two, then we find a coexistence curve. Now the liquid and gas are going to coexist. So this is the liquid phase. And that means that this must be xB. And it's xB at one, but it's also xB at two, and I want to emphasize that. So let's put our pressure for two. And if we go over here, this is telling us about the mole fraction in the gas phase. That's what these curves are, remember. So this is the one that's showing us the mole fraction in the liquid phase. This nonlinear one in the gas phase. So that means just reading off it, this is xB, that's the liquid mole fraction. Here's yB. The gas mole fraction. They're not the same, right, because of course the components have different volatility. A's more volatile.

So that means that the mole fraction of B in the liquid phase is higher than the mole fraction of B in the gas phase. Because A is the more volatile component. So more, relatively more, of A, the mole fraction of A is going to be higher up in the gas phase. Which means the mole fraction of B is lower in the gas phase. So, yB less than xB if A is more volatile. OK, so now what's happening physically? Well, we started at a point where we only had the liquid present. So at our initial pressure, we just have all liquid. There's some xB at one. That's all there is, there isn't any gas yet. Now, what happened here? Well, now we lowered the pressure. So you could imagine, well, we made the box bigger. Now, if the liquid was under pressure, being squeezed by the box, right then you could make the box a little bit bigger. And there's still no gas. That's moving down like this. But then you get to a point where there's just barely any pressure on top of the liquid. And then you keep expanding the box. Now some gas is going to form.

So now we're going to go to our case two. We've got a bigger box. And now, right around where this was, this is going to be liquid. And there's gas up here. So up here is yB at pressure two. Here's xB at pressure two. Liquid and gas. So that's where we are at point two here.

Now, what happens if we keep going? Let's lower the pressure some more. Well, we can lower it and do this. But really if we want to see what's happening in each of the phases, we have to stay on the coexistence curves. Those are what tell us what the pressures are. What the partial pressure are going to be in each of the phases. In each of the two, in the liquid and the gas phases. So let's say we lower the pressure a little more. What's going to happen is, then we'll end up somewhere over here. In the liquid, and that'll correspond to something over here in the gas. So here's three.

So now we're going to have, that's going to be xB at pressure three. And over here is going to be yB at pressure three. And all we've done, of course, is we've just expanded this further. So now we've got a still taller box. And the liquid is going to be a little lower because some of it has evaporated, formed the gas phase. So here's xB at three. Here's yB at three, here's our gas phase. Now we could decrease even further. And this is the sort of thing that you maybe can't do in real life. But I can do on a blackboard. I'm going to give myself more room on this curve, to finish this illustration. There. Beautiful. So now we can lower a little bit further, and what I want to

illustrate is, if we keep going down, eventually we get to a pressure where now if we look over in the gas phase, we're at the same pressure, mole fraction that we had originally in the liquid phase. So let's make four even lower pressure. What does that mean? What it means is, we're running out of liquid. So what's supposed to happen is A is the more volatile component. So as we start opening up some room for gas to form, you get more of A in the gas phase. But of course, and the liquid is richer in B. But of course, eventually you run out of liquid. You make the box pretty big, and you run out, or you have the very last drop of liquid. So what's the mole fraction of B in the gas phase? It has to be the same as what it started in in the liquid phase. Because after all the total number of moles of A and B hasn't changed any. So if you take them all from the liquid and put them all up into the gas phase, it must be the same. So yB of four. Once you just have the last drop. So then yB of four is basically equal to xB of one. Because everything's now up in the gas phase. So in principle, there's still a tiny, tiny bit of xB at pressure four.

Well, we could keep lowering the pressure. We could make the box a little bigger. Then the very last of the liquid is going to be gone. And what'll happen then is, we're all here. There's no more liquid. We're not going down on the coexistence curve any more. We don't have a liquid gas coexistence any more. We just have a gas phase. Of course, we can continue to lower the pressure. And then what we're doing is just going down here. So there's five. And five is the same as this only bigger. And so forth.

OK, any questions about how this works? It's really important to just gain facility in reading these things and seeing, OK, what is it that this is telling you. And you can see it's not complicated to do it, but it takes a little bit of practice. OK.

Now, of course, we could do exactly the same thing starting from the gas phase. And raising the pressure. And although you may anticipate that it's kind of pedantic, I really do want to illustrate something by it. So let me just imagine that we're going to do that. Let's start all in the gas phase. Up here's the liquid. pA star, pB star. And now let's start somewhere here. So we're down somewhere in the gas phase with some composition. So it's the same story, except now we're starting here. It's all gas. And we're going to start squeezing. We're increasing the pressure. And eventually here's one, will reach two, so of course here's our yB. We started with all gas, no liquid. So this is yB of one. It's the same as yB of two, I'm just raising the pressure enough to just reach the coexistence curve. And of course, out here tells us xB of two, right? So what is it saying? We've squeezed and started to form some liquid. And the liquid is richer in component B. Maybe it's ethanol water again. And we squeeze, and now we've got more water in the liquid phase than in the gas phase. Because water's the less volatile component. It's what's going to condense first.

So the liquid is rich in the less volatile of the components. Now, obviously, we can continue in doing exactly the reverse of what I showed you. But all I want to really illustrate is, this is a strategy for purification of the less volatile

component. Once you've done this, well now you've got some liquid. Now you could collect that liquid in a separate vessel.

So let's collect the liquid mixture with xB of two. So it's got some mole fraction of B. So we've purified that. But now we're going to start, we've got pure liquid. Now let's make the vessel big. So it all goes into the gas phase. Then lower p. All gas. So we start with yB of three, which equals xB of two. In other words, it's the same mole fraction. So let's reconstruct that. So here's p of two. And now we're going to go to some new pressure. And the point is, now we're going to start, since the mole fraction in the gas phase that we're starting from is the same number as this was. So it's around here somewhere. That's yB of three equals xB of two. And we're down here. In other words, all we've done is make the container big enough so the pressure's low and it's all in the gas phase. That's all we have, is the gas. But the composition is whatever the composition is that we extracted here from the liquid. So this xB, which is the liquid mole fraction, is now yB, the gas mole fraction. Of course, the pressure is different. Lower than it was before.

Great. Now let's increase. So here's three. And now let's increase the pressure to four. And of course what happens, now we've got coexistence. So here's liquid. Here's gas. So, now we're over here again. There's xB at pressure four. Pure still in component B. We can repeat the same procedure. Collect it. All liquid, put it in a new vessel. Expand it, lower the pressure, all goes back into the gas phase. Do it all again. And the point is, what you're doing is walking along here. Here to here. Then you start down here, and go from here to here. From here to here. And you can purify. Now, of course, the optimal procedure, you have to think a little bit. Because if you really do precisely what I said, you're going to have a mighty little bit of material each time you do that. So yes it'll be the little bit you've gotten at the end is going to be really pure, but there's not a whole lot of it. Because, remember, what we said is let's raise the pressure until we just start being on the coexistence curve. So we've still got mostly gas. Little bit of liquid. Now, I could raise the pressure a bit higher. So that in the interest of having more of the liquid, when I do that, though, the liquid that I have at this higher pressure won't be as enriched as it was down here. Now, I could still do this procedure. I could just do more of them. So it takes a little bit of judiciousness to figure out how to optimize that. In the end, though, you can continue to walk your way down through these coexistence curves and purify repeatedly the component B, the less volatile of them, and end up with some amount of it. And there'll be some balance between the amount that you feel like you need to end up with and how pure you need it to be. Any questions about how this works?

So purification of less volatile components. Now, how much of each of these quantities in each of these phases? So, pertinent to this discussion, of course we need to know that. If you want to try to optimize a procedure like that, of course it's going to be crucial to be able to understand and calculate for any pressure that you decide to raise to, just how many moles do you have in each of the phases? So at the end of the day, you can figure out,

OK, now when I reach a certain degree of purification, here's how much of the stuff I end up with. Well, that turns out to be reasonably straightforward to do. And so what I'll go through is a simple mathematical derivation. And it turns out that it allows you to just read right off the diagram how much of each material you're going to end up with.

So, here's what happens. This is something called the lever rule. How much of each component is there in each phase? So let's consider a case like this. Let me draw yet once again, just to get the numbering consistent. With how we'll treat this. So we're going to start here. And I want to draw it right in the middle, so I've got plenty of room. And we're going to go up to some pressure. And somewhere out there, now I can go to my coexistence curves. Liquid. And gas. And I can read off my values. So this is the liquid x_B. So I'm going to go up to some point two, here's x_B of two. Here's y_B of two. Great. Now let's get these written in.

So let's just define terms a little bit. n_A, n_B. Or just our total number of moles. n_g and n liquid, of course, total number of moles. In the gas and liquid phases. So let's just do the calculation for each of these two cases. We'll start with one. That's the easier case. Because then we have only the gas. So at one, all gas. It says pure gas in the notes, but of course that isn't the pure gas. It's the mixture of the two components. So. How many moles of A? Well it's the mole fraction of A in the gas. Times the total number of moles in the gas. Let me put one in here. Just to be clear. And since we have all gas, the number of moles in the gas is just the total number of moles. So this is just y_A at one times n total. Let's just write that in. And of course n total is equal to n_A plus n_B.

So now let's look at condition two. Now we have to look a little more carefully. Because we have a liquid gas mixture. So n_A is equal to y_A at pressure two. Times the number of moles of gas at pressure two. Plus x_A, at pressure two, times the number of moles of liquid at pressure two.

Now, of course, these things have to be equal. The total number of moles of A didn't change, right? So those are equal. Then y_A of two times n_g of two. Plus x_A of two times n liquid of two, that's equal to y_A of one times n total. Which is of course equal to y_A of one times n gas at two plus n liquid at two. I suppose I could be, add that equality. Of course, it's an obvious one. But let me do it anyway. The total number of moles is equal to n_A plus n_B. But it's also equal to n liquid plus n gas. And that's all I'm taking advantage of here.

And now I'm just going to rearrange the terms. So I'm going to write y_A at one minus y_A at two, times n_g at two, is equal to, and I'm going to take the other terms, the x_A term. x_A of two minus y_A of one times n liquid at two. So I've just rearranged the terms. And I've done that because now, I think I omitted something here. y_A of one times n_g. No, I forgot a bracket, is what I did. y_A of one there. And I did this because now I want to do is look at the ratio of liquid to gas at pressure two. So, ratio of I'll put it gas to liquid, that's n_g of two over n liquid at two. And that's just equal to x_A of two minus y_A at one minus y_A at one minus y_A at two.

So what does it mean? It's the ratio of these lever arms. That's what it's telling me. I can look, so I raise the pressure up to two. And so here's x_B at two, here's y_B at two. And I'm here somewhere. And this little amount and this little amount, that's that difference. And it's just telling me that ratio of those arms is the ratio of the total number of moles of gas to liquid. And that's great. Because now when I go back to the problem that we were just looking at, where I say, well I'm going to purify the less volatile component by raising the pressure until I'm at coexistence starting in the gas phase. Raise the pressure, I've got some liquid. But I also want some finite amount of liquid. But I don't want to just, when I get the very, very first drop of liquid now collected, of course it's enriched in the less volatile component. But there may be a minuscule amount, right? So I'll raise the pressure a bit more. I'll go up in pressure. And now, of course, when I do that the amount of enrichment of the liquid isn't as big as it was if I just raised it up enough to barely have any liquid. Then I'd be out here. But I've got more material in the liquid phase to collect. And that's what this allows me to calculate. Is how much do I get in the end. So it's very handy. You can also see, if I go all the way to the limit where the mole fraction in the liquid at the end is equal to what it was in the gas when I started, what that says is that there's no more gas left any more. In other words, these two things are equal. If I go all the way to the point where I've got all the, this is the amount I started with, in the pure gas phase, now I keep raising it all the way. Until I've got the same mole fraction in the liquid. Of course, we know what that really means. That means that I've gone all the way from pure gas to pure liquid. And the mole fraction in that case has to be the same. And what this is just telling us mathematically is, when that happens this is zero. That means I don't have any gas left. Yeah.

STUDENT: [INAUDIBLE]

PROFESSOR: No. Because, so it's the mole fraction in the gas phase. But you've started with some amount that it's only going to go down from there.

STUDENT: [INAUDIBLE]

PROFESSOR: Yeah. Yeah. Any other questions? OK. Well, now what I want to do is just put up a slightly different kind of diagram, but different in an important way. Namely, instead of showing the mole fractions as a function of the pressure. And I haven't written it in, but all of these are at constant temperature, right? I've assumed the temperature is constant in all these things. Now let's consider the other possibility, the other simple possibility, which is, let's hold the pressure constant and vary the temperature. Of course, you know in the lab, that's usually what's easiest to do. Now, unfortunately, the arithmetic gets more complicated. It's not monumentally complicated, but here in this case, where you have one linear relationship, which is very convenient. From Raoult's law. And then you have one non-linear relationship there for the mole fraction of the gas. In the case of temperature, they're both, neither one is linear. Nevertheless, we can just sketch what the diagram looks like. And of course it's very useful to do that, and see how to read off it. And I should say the derivation of the curves isn't particularly

complicated. It's not particularly more complicated than what I think you saw last time to derive this. There's no complicated math involved. But the point is, the derivation doesn't yield a linear relationship for either the gas or the liquid part of the coexistence curve.

OK, so we're going to look at temperature and mole fraction phase diagrams. Again, a little more complicated mathematically but more practical in real use. And this is T. And here is the, sort of, form that these things take. So again, neither one is linear. Up here, now, of course if you raise the temperatures, that's where you end up with gas. If you lower the temperature, you condense and get the liquid. So, this is TA star. TB star. So now I want to stick with A as the more volatile component. At constant temperature, that meant that pA star is bigger than pB star. In other words, the vapor pressure over pure liquid A is higher than the vapor pressure over pure liquid B. Similarly, now I've got constant pressure and really what I'm looking at, let's say I'm at the limit where I've got the pure liquid. Or the pure A. And now I'm going to, let's say, raise the temperature until I'm at the liquid-gas equilibrium. That's just the boiling point. So if A is the more volatile component, it has the lower boiling point. And that's what this reflects. So higher pB star A corresponds to lower TA star A. Which is just the boiling point of pure A.

So, this is called the bubble line. That's called the dew line. All that means is, let's say I'm at high temperature. I've got all gas. Right no coexistence, no liquid yet. And I start to cool things off. Just to where I just barely start to get liquid. What you see that as is, dew starts forming. A little bit of condensation. If you're outside, it means on the grass a little bit of dew is forming. Similarly, if I start at low temperature, all liquid now I start raising the temperature until I just start to boil. I just start to see the first bubbles forming. And so that's why these things have those names.

So now let's just follow along what happens when I do the same sort of thing that I illustrated there. I want to start at one point in this phase diagram. And then start changing the conditions. So let's start here. So I'm going to start all in the liquid phase. That is, the temperature is low. Here's xB. And my original temperature. Now I'm going to raise it. So if I raise it a little bit, I reach a point at which I first start to boil. Start to find some gas above the liquid. And if I look right here, that'll be my composition. Let me raise it a little farther, now that we've already seen the lever rule and so forth. I'll raise it up to here. And that means that out here, I suppose I should do here.

So, here is the liquid mole fraction at temperature two. xB at temperature two. This is yB at temperature two. The gas mole fraction. So as you should expect, what's going to happen here is that the gas, this is going to be lower in B. A, that means that the mole fraction of A must be higher in the gas phase. That's one minus yB. So xA is one minus -- yA, which is one minus yB higher in gas phase. Than xA, which is one minus xB. In other words, the less volatile component is enriched up in the gas phase.

Now, what does that mean? That means I could follow the same sort of procedure that I indicated before when we looked at the pressure mole fraction phase diagram. Namely, I could do this and now I could take the gas phase. Which has less of B. It has more of A. And I can collect it. And then I can reduce the temperature. So it liquefies. So I can condense it, in other words. So now I'm going to start with, let's say I lower the temperature enough so I've got basically pure liquid. But its composition is the same as the gas here. Because of course that's what that liquid is formed from. I collected the gas and separated it. So now I could start all over again. Except instead of being here, I'll be down here. And then I can raise the temperature again. To some place where I choose. I could choose here, and go all the way to hear. A great amount of enrichment. But I know from the lever rule that if I do that, I'm going to have precious little material over here. So I might prefer to raise the temperature a little more. Still get a substantial amount of enrichment. And now I've got, in the gas phase, I'll further enriched in component A. And again I can collect the gas. Condense it. Now I'm out here somewhere, I've got all liquid and I'll raise the temperature again. And I can again keep walking my way over.

And that's what happens during an ordinary distillation. Each step of the distillation walks along in the phase diagram at some selected point. And of course what you're doing is, you're always condensing the gas. And starting with fresh liquid that now is enriched in more volatile of the components. So of course if you're really purifying, say, ethanol from an ethanol water mixture, that's how you do it. Ethanol is the more volatile component. So a still is set up. It will boil the stuff and collect the gas and and condense it. And boil it again, and so forth. And the whole thing can be set up in a very efficient way. So you have essentially continuous distillation. Where you have a whole sequence of collection and condensation and reheating and so forth events. So then, in a practical way, it's possible to walk quite far along the distillation, the coexistence curve, and distill to really a high degree of purification. Any questions about how that works? OK.

I'll leave till next time the discussion of the chemical potentials. But what we'll do, just to foreshadow a little bit, what I'll do at the beginning of the next lecture is what's at the end of your notes here. Which is just to say OK, now if we look at Raoult's law, it's straightforward to say what is the chemical potential for each of the substances in the liquid and the gas phase. Of course, it has to be equal. Given that, that's for an ideal solution. We can gain some insight from that. And then look at real solutions, non-ideal solutions, and understand a lot of their behavior as well. Just from starting from our understanding of what the chemical potential does even in a simple ideal mixture. So we'll look at the chemical potentials. And then we'll look at non-ideal solution mixtures next time. See you then.