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PROFESSOR: Let's do a one minute review, and then move onto the Clausius-Clapeyron equation and see how far we can go on that. So, reminding you then, what you learned last time about phase transitions is, you drew a phase diagram in temperature pressure space here. And then you had a triple point somewhere, which was a unique point. The triple point temperature, triple point pressure. Then there was a gas, solid, call it coexistence line. Which kept on going ad infinitum. And the a gas liquid coexistent line. With a critical point. So that allowed you to go around. You wanted to go from liquid to gas, you could actually go around this critical point, and never actually see a phase transition. Then there was a solid liquid coexistence line. Which usually has a negative slope, except for the two most important substances on Earth, which are water and silicon. So for water and silicon, we have positive slope. H<sub>2</sub>O and silicon. This is why there's life on Earth.

Did you hear the story of why there's life on Earth? This is the secret of life. Without this, this is why we're here. Because of this property. So, the reason why these slopes come from the, so I'll tell you the secret of life. But first let me remind you what the coexistence curve is.  $dp/dT$ . Coexistence is  $\Delta S$  over  $\Delta V$ , or  $\Delta H$  over  $T \Delta V$ . And that's the Clapeyron equation. Now, the slope of the curves points us by, look at this solid liquid line,  $\Delta S$ , for solid liquid. I looked at it up here. It's going to be  $S_{\text{liquid}} - S_{\text{solid}}$ . And you know that's greater than zero because the entropy in the liquid state is much bigger than it is in the solid state. You have a crystal, entropy's very small. Liquid state, much more disorder. Got a positive sign here. Yes. Questions?

STUDENT: [INAUDIBLE]

PROFESSOR: So, this is almost everything. It has this slope here. Which is a negative slope. And water has a positive slope. Right? Is that wrong? It's wrong. Let's go through the argument. All right. All right. Let's go through the argument. So, then you have  $\Delta V$ , and  $\Delta V$  is  $V_{\text{solid}} - V_{\text{liquid}}$ , this is per mole. Now, almost every substance has  $V_{\text{solid}}$  less than  $V_{\text{liquid}}$ . So this is negative. So almost every substance, you have  $\Delta S$  divided by  $\Delta V$  is negative. A negative slope. You're right. So I have it backwards. I do have it backwards. OK. See, I was really trying to make it so that my drawing was right. Which is why I inverted the solid and liquid here. So I really wanted to be right, but I ended up being wrong. Liquid is less than solid. Well this is water. Why do I have it backwards in my notes. I've got to correct that. So this is most substances, is positive. OK so, and most substances, OK? Except for water and silicon. Because for water and silicon this is reversed. Because the molar volume of solid for water is bigger than that for liquid. So this is bigger than here. Thank you. OK. Thanks for

catching it.

OK, so what happens if the molar volume for the liquid is bigger than the molar volume of the solid. The density of water which is the inverse of the mole volume, so the density, the molar density, is equal to one over the molar volume. So you've got the molar density for liquid is then smaller than the molar density for the solid. It's one over, right? So that's why ice floats. Because it's less dense than liquid water. So what do you think would happen in the winter if ice didn't float, in the Charles River. It would go to the bottom. It would freeze, solid and you would have no fish. You would have no life. It would freeze solid and that would be the end of life. And you know, five hundred million years ago there would be no fish. There would be no dinosaurs. There would be no anything, there would be no humans. That's the secret of life. And the fact that this is also the case is very useful for making silicon. For processing silicon. Another the secret of life. Where would we be without silicon? Our civilization would be, we'd still be using stones and things, right? OK, so it's super super important.

Alright, so this is a Clapeyron story. Which we ended up getting right. Even though I insisted on getting it wrong. So what happens now is Mr. Clausius came around and he realized that you can make some approximations that are very useful. So the first approximation is, you can realize that the molar volume of the gas is always much bigger than the volume of the solid or the liquid. And so as a result whenever you have these delta V's, for sublimation, or delta V for vaporization, which is the volume the gas minus the volume of the solid. Or the volume of the gas minus the volume of the liquid, you might as well ignore the volume of the liquid or of the solid. And this can just be equal to roughly the volume of the gas. So this is the first approximation he made. So now, if you go back to the Clapeyron equation up here, with this approximation then  $dp/dT$ , the coexistence line, is  $\Delta H$  divided by  $T V_{\text{gas}}$ . For sublimation. Or vaporization. You don't have the delta V down there any more.

Then the next thing that, next assumption that he realized you can make was, well, all these gases could, they're like ideal gases. So we can, instead of having the volume of the gas here, we can use the ideal gas law. This is all, let's do all this per mole. So  $V$  is equal to  $RT$  over  $p$ . You can plug this back in here. And then you end up with the Clausius-Clapeyron equation. So this is approximation now. We put in  $RT$  over  $p$  for here. We have  $p \Delta H$ , where this is either sublimation or vaporization divided by  $RT$  squared.  $dp/dT$ , sublimation or vaporization, and this is the Clausius-Clapeyron equation. Two important approximations that go in here. And it's not valid for solids or liquid. You have to have a gas in there because of the ideal gas for the approximation that goes in here.

And once you have that, you can integrate both sides. You've got to put the temperatures on one side. Put the pressures on the other side. I'll go ahead and cover this up here. So you have  $1/p dp/dT$  is equal to  $\Delta H$  over  $RT$  squared.  $1/p dp/dT$  that's just like  $d \log p$ . And that's another form that you're going to see often for the Clausius-Clapeyron approximation is  $d \log p / dT$  is equal to  $\Delta H$  over  $RT$  squared. And I'm freely dropping the sublimation and the vaporization because we know that's what I mean here. It's only valid for those

two lines. So that's another form that you'll see. And that's not  $dT$  here, that's  $d \log p$ ,  $d \log p dp$ . Yeah, that's right,  $d \log p / dT$ . And so now you can take the  $dT$  to the other side and integrate. From point one to point two  $d \log p$ , is from point one to point two,  $\Delta H$  over  $RT$  squared  $dT$ . And you make the usual approximation, which we've made before. That  $\Delta H$  is roughly independent of temperature, or very slowly changing with temperature. And that's fine as long as you're in a narrow temperature range. Which is usually the case when you have these Clausius-Clapeyron equation problems. So you can take the  $\Delta H$  out of the integral, the  $R$  out of the integral. And you can integrate both sides. To give you  $\log p_2$  minus  $\log p_1$ , is  $\Delta H$  times  $R$ , divided by  $R$ ,  $\Delta H$  divided by  $R$ .  $\Delta H$  over  $R$  times  $T_2$  minus  $T_1$  over  $T_1 T_2$ .

It looks a lot like and the temperature dependence equilibrium constant. And in fact, but it's not, right? And some people use that equation here instead of equilibrium constant. Temperature dependence. That's, can give rise to problems. Because obviously they're not the same equation. But roughly has the same form. So, another way that you'll also find this written is very often  $p_1$  and  $T_1$  will be some reference. Pressures and temperature, maybe one bar, let's say.  $T_1$ , 298 degrees Kelvin. That's your reference point and you want to find out the pressure temperature dependence in an equation. So if you rearrange your equations so  $p_1$ ,  $T_1$  are now some reference point. They become numbers. So you have  $\log$  of a reference point,  $T_1$  here is a number. So you often see this equation rewritten then as  $\log p$  is equal to  $\Delta H$  over  $RT$ . And I feel like I've got a minus sign missing somewhere. Here. Oh yeah, when you integrate this, the one over  $T$  squared, there's a minus sign. Oh, I took care of that by doing  $T_2$  minus  $T_1$  here. I think there's still a minus sign problem somewhere. I think there's a minus sign problem. Let me check up the notes here. Minus one over  $T_1$  minus  $T_2$  over  $T_1 T_2$ . Where's my minus sign?  $T_2$  minus  $T_1$ . OK, so I got minus  $T_1$ , minus  $T_2$  over  $T_1 T_2$ .  $T_2$  minus  $T_1$ . This is fine, right. There's no minus sign problem. Plus a constant. OK, so you'll often see it written like that.

And that gives you a relationship between the pressure and the temperature then, for a substance where all the reference point information is contained in this constant,  $C$ . Which is where the  $T_1$ 's and the  $p$ 's come from. OK, any questions? We'll do a little example here of how this could be used.

So let's switch to an example now. Let's go to the example, let's first do the example which is at the very end of the notes. So this is an example of RDX. RDX is a famous explosive, as I'm sure you know. And it's plastic explosive. It's got a melting point of 204 degrees Celsius. 481 degrees Kelvin. And it's a problem for, so it's a very powerful explosive and you can't see it in X-rays. So it's a problem at airports. You've got to be able to find if somebody's carrying a little piece of RDX in their luggage. And so, the question becomes what do you need to know to detect it? You want to find the vapor pressure. You've gotta have, and the machine which basically is sensitive enough to detect molecules of RDX that are in vapor at room temperature. So the way that you do that is, you do an experiment. Where you measure the pressure, the vapor pressure, as a function of temperature.

And room temperature, it turns out if it's not volatile at all, if the vapor pressure is very, really tiny. And so in order to get accurate numbers, you actually do your measurements at significantly higher temperatures than room temperature. They do it close to the melting point, so you're actually looking at the sublimation of RDX. You do it, let's say, at 400 degrees Kelvin, where the melting point is at 481 degrees Kelvin. So slightly below the melting point you're looking at sublimation.

And you plot. Log  $p$  versus one over  $T$ . And according to Clausius-Clapeyron, that should give you a straight line. And in fact, that's exactly what you see when you take RDX and do that experiment. You end up with a bunch of data points. That's fall nicely on this straight line. And then you can extrapolate to room temperature. Somewhere here, let's say, 300 degrees Kelvin. And find out what log  $p$  is, at 300 degrees Kelvin. And what you find is that, and that's the graph that's on the last page of the lecture notes, that the vapor pressure of RDX at room temperature is  $10^{-11}$  bar, That's ten parts per trillion. So it tells you that if you want to detect RDX with a sniffer machine at the airport, that machine better be able to tell you, find one molecule of RDX out of a tenth of a trillion other molecules, basically. Which is a really hard thing to do. So this gives you a design rule for these pieces of equipment. And why they're so expensive.

OK, before we do the next example, let's see if any questions on Clausius-Clapeyron. Yeah.

STUDENT: [INAUDIBLE]

PROFESSOR: So,  $p$  as some exponential here? You know, I don't recall seeing it as an exponential form. But that doesn't mean it's not used the exponential form. This is an easy way to do it, because then you've got a linear relationship. And generally we like to see straight lines. So this gives you a nice straight line.

OK, so now let's do a slightly more complicated example. Which is, so most of the time you don't have pure material. You have a mixture of some sort. For instance, if I have a glass of water on the table at room temperature. Above the glass of water, I have air, there's my  $H_2O$  here. And then I've got some air. Above the glass of water. And the air's inert to the water. It's not reacting with the water. So it's like an inert gas sitting on top of the water. Then I want to ask the question, what is the vapor pressure of the water? In the presence of this inert gas, the air. It's not really the same as the problem that we've been looking at up here. Right? Because this gas liquid coexistence line, this diagram, and this Clapeyron equation, is all done for a pure substance. And at room temperature, at room temperature, we're sitting squarely in the liquid phase. We're not on the coexistence line. At room temperature and one bar pressure. So instead of having this system here, I looked at the system where I had the water,  $H_2O$ , with nothing on top. With no air on top. Except the cylinder. Now, I'd better make the surface of my water a straight line, otherwise I'm going to get in trouble. There's the water sitting right here. And I put a cylinder with one bar pressure on top. My cylinder's going to sit squarely on the stump of the surface of the water.

This is not going to be any water vapor at one bar pressure on that cylinder. At one bar, we're way up in the liquid phase. I would have to decrease the pressure on that cylinder down to, I don't know, whatever the water vapor pressure is at room temperature here on this coexistence curve. 0.1 bar or something. 0.05 bar. Something pretty small.

So that's what we've been working on. This pure system. And now we're going to be working on this system here, where we have air. With a cylinder on top, one bar. And we want to know what is the vapor pressure of H<sub>2</sub>O in this system here. Is it zero? Anybody want to guess, if it's zero? We know there's vapor pressure there, right? And a good guess is that that vapor pressure here, it's pretty close to the pressure that you would guess by using this diagram with the pure water. But the key word is, it's pretty close. It's not exactly the same. So, let me ask you this. Without looking at the notes, now is  $p_{\text{H}_2\text{O}}$  in this problem here greater than, less than, or the same as  $p_{\text{H}_2\text{O}}$  in the pure Clapeyron case? How many people think that it's the same? How about smaller than? Smaller than? Few people think that it's smaller than. How about greater than? A bunch of people don't know what to answer. OK.

I think that if you think about it, what the difference is between here and there, you could probably reason which way it should go. Which way the partial pressure of the water should go under one bar pressure, room temperature. Compared to what you might expect it to be at room temperature with a diagram. So, I'm going to give you a little bit of time just to think about it. Without looking at the notes, what you think the right sign is here. Then we'll do the problem and then we'll figure out if you were right or wrong.

OK. How many people say it's greater than? One, two. Two brave people here. Two. How many people say it's smaller than? OK. Smaller than. So I'm going to say a large number, OK? Many. How many people think it's equal? One person thinks it's equal. Alright, let's do it out now and see how it comes out. And then we can reason why it came out the way it came out. Logically, without actually doing math. Because there's a way to reason it out that you should be able to do.

OK, so this is what we have here. Then the system is, we have this container. Let me redo it instead of writing air. So we have the liquid state here. Some substance, and it doesn't have to be water. That's a liquid, at some pressure  $p$ . And I'm going to say  $P$  capital, that's going to be the total pressure. And the total pressure is given by the piston here.  $p_{\text{total}}$ ,  $p_T$ . And on top here I'm going to have two substances. I'm going to have A, in the gas phase, that's the water vapor. Some partial pressure,  $p_{\text{sub A}}$ , temperature  $T$ . And I'm going to have the inert gas, with some partial pressure  $p_{\text{inert}}$ . Such that the sum of the partial pressure of the inert gas, plus the partial pressure of A, is the total pressure. One bar, in our case. With the water with the air on top.

And the question, oh, let me make a few more definitions. We're going to define  $p_0$  as the vapor pressure of pure

vapor pressure of pure A. So that's what you would read off the diagram here. And what we want, the question we ask is, what is the partial pressure of A as a function of the total pressure? That's what we're asking. As I'm increasing the total pressure, meaning I'm putting more and more inert gas in there, which way is this going? Is it going up, down, or staying the same? And we've got a bunch of votes up here. Most people think that it's going to go down. Because I put more gas in there. OK, I know that if  $P$ , capital P, is equal to  $p_A$ , then  $p_A$  is equal to  $p_0$ . Right? There's no inert gas. So that's the one extreme case here. There's no inert gas, then the partial pressure's going to be what you read off that graph here.

So another way of saying what is  $p$  as a function of capital P, is to ask the question what is the slope? I've got one point here. If I can integrate the slope then I have this equation. So the other way to ask the question is, what is  $dp_A/dp$ , at a constant temperature? Where I'm keeping the temperature constant. And that turns out to be easier to calculate. These slopes are always easier to calculate than the absolute things.

So we're doing an equilibrium here. We have an equilibrium between the liquid state and the gas phase. And we want to know something about this equilibrium as we change a parameter. Equilibrium, what do we always start with when we have an equilibrium. What's the first thing we think about? We think about chemical potential. Chemical potentials of A, in the gas phase has to be the same as the chemical potential of A in the liquid phase. Well, I can't think of anything else to start with. So let me start with that. So let's start by writing the chemical potentials being equal to each other. Because we know that's true. So  $\mu_A$ , in the gas phase, temperature and with a partial pressure  $p_{sub} A$ . Is equal to  $\mu_A$  in the liquid phase, where the pressure on the liquid is capital P.

What else do we know? Well, we, what else are we going to need? Before we do that, since what we're after is the derivative, let's take the derivative of both sides. We're looking at a derivative with respect to pressure here. Let's take the derivative outside with pressure and see what happens. So let's take the derivative of this with respect to total pressure. Well, this isn't total pressure. This is the partial pressure of A. But it's a function of the total pressure. It's a function of the total pressure. Partial pressure of A is total pressure minus  $p_{inert}$ . So, we have to use the chain rule. So on this side here, we have  $d\mu_A / dp_A$ . So I'm taking  $d/dp$  of both sides. Then by chain rule,  $dp_A/dP$ . Constant temperature. And then on the right-hand side, I have  $d\mu_A / dP$ , constant temperature.

Well,  $d\mu / dP$ , that may or may not seem familiar to you. I never remember these things, but I always remember that there's, that these relationships are interesting. Especially when you're talking about something like a chemical potential, which is really nothing but the Gibbs free energy. With respect to pressure, when we know that the variables that we use for Gibbs free energy are pressure and temperature. Right? So this is the variable that goes with Gibbs free energy. So this means that they were taking the derivatives of the Gibbs free energy with respect to one of its variables is something that we should know. So we go back to writing what the Gibbs free energy is. So  $dG$  is equal to  $V dp$  minus  $S dT$ . Which is the fundamental equation for Gibbs free energy. And this

is the Gibbs free energy per mole. That's just the chemical potential. The same thing. And this is the derivative with respect to pressure. And this is the derivative with respect to temperature. So this thing here is  $d\mu / dp$ . At constant temperature. It's just the volume.

So now we have this equation, where we started out with the chemical potentials. And we've got these  $d\mu_A / dp_A$ , we've got  $d\mu_A / dP$  here. That's just the molar volume of the gas. Right, because this is  $\mu$  of the gas phase here. So this is the molar volume of the gas. And I have  $dp_A/dP$ . And, this is very nice. Because this is actually what I'm trying to get. Trying to see how the partial pressure of A changes with the total pressure. That's what I'm trying to calculate here. I know what this is. This is just an experimental number. And then on this side here I have  $d\mu_A / dP$ . This is the liquid phase. Derivative with respect to total pressure, that's the molar volume of the liquid. The liquid. Great, I'm done.  $dp_A/dP$  total, constant pressure, is the ratio of the molar volume of the liquid of A divided by the molar volume of the gas. What's the sign? Volumes are positive, right? This has to be positive. There's no choice. It can't even be zero. It has to be positive, right? So that means the slope is a positive slope. As I increase the total pressure,  $p$  is going to go up. If I integrate now, this, starting at, so the total pressure is equal to  $p_A$ , I'm going to get a curve that looks like this. OK, if I write on this axis  $p_{\text{inert}}$ , so when  $p_{\text{inert}}$  is equal to zero, total pressure is  $p_A$ . I'm going to start at  $p_0$ . And I'm going to go up from there, positive slope.

So. Who was right? A couple people are right. So let's think about it in a different way. Let's think about it in a different way. So we did the math, and we found that actually it's, and that turns out to be a very small amount. You do a very good job by just taking this curve here. And using the pure substance. In fact, in the notes we have an example of how much it changes for mercury. So for mercury, at 100 degrees C, for pure mercury, the vapor pressure is 0.27 bar. If you add enough inert gas to make it 1 bar for the total pressure, you go from 0.27 to 0.2701. Not much of a change. They do a really good job of just picking this. And if you go to 100 bar, then you increase it to 0.28. So it takes a lot of pressure on top, a lot of extra inert gas to really make much of a difference. But, let's think about why it would make a difference, just logically.

So in the absence of this inert gas here, I just have the pure substance. I add some inert gas, what happens to the entropy on top? It's increasing, right? Do systems like to have more entropy? Yeah. So, I have a lot of inert gas here. A small amount of A. What if I had a little bit more A, in the presence of the inert gas? Which way would the entropy go? It would go up a little bit more, you'd have more disorder. If I have nothing, if I have no A here, up here and just the inert gas, then there's no entropy of mixing. I add a little bit of inert gas, there's a little bit more entropy of mixing. Eventually, I add more and more, entropy of mixing goes up and up and up, and eventually it comes back down to where I have pure A on top. So the entropy of mixing up here is driving the increase in the pressure of, in the partial pressure of A. Entropy is this amazingly important term. That's what we saw. Entropy of mixing was responsible for equilibrium. Without entropy of mixing, then everything would go directly to the

products. You'd never have an equilibrium. Another secret of life. So entropy of mixing here is driving this positive slope. That's another way of thinking about it. And that's why you can guess ahead of time what the signs of these things ought to be. Without doing the math. Alright, any questions?

OK. So there's another sample problem with the notes, which is sort of like a standard problem. Where you're given a Clausius-Clapeyron equation for a substance in this form. So if you look at it,  $\log p$  is minus some energy divided by  $RT$  plus some number. In this case, it's negative, the  $\Delta H$  is negative for the substance that you have there. And you're given it for the liquid phase, for the vapor pressure above the liquid and the vapor pressure above the solid. You can, because the only way it doesn't work is if you're looking at solid liquid. So, and then you're asked to manipulate this equation to find different properties. For instance the triple point. It's a very common thing to get, the triple point from this. The  $\Delta H$ , it's a way to get  $\Delta H$ . Just like we saw for the RDX, right? The data points formed a straight line. And the slope gave you  $\Delta H$ , for RDX.  $\Delta H$  of sublimation for RDX. So this is the way that this equation is used for problems. I'm not going to do this problem. Instead I'm going to go ahead and forge ahead to the next topic. And start it. This is the topic we're going to do it after spring break.

And and it really is a topic that follows this pretty straightforwardly. Well, it's more complicated, but it's similar to this problem here. So we saw that in real life yes, question?

STUDENT: [INAUDIBLE]

PROFESSOR: The exam. Oh there's an exam is, which is, oh I forgot about the exam. So let's see. There's a problem set that's due today. The exam will be up to the problem set that's due today. Which means that what I talked about today is not going to be on the exam. Because it's not covered in the problem set. So let's say it goes up to Wednesday's lecture. Which means you might still have a phase transition problem, right? In fact, you're very likely to get a phase transition problem. It's very likely to be the case. Because it's an easy problem to put together. But you don't have to worry about Clausius-Clapeyron. You do have to worry about Clapeyron, but not Clausius-Clapeyron, OK?

So, for the exam, we're going to put on the Web last year's exam, and you guys are going to do reviews. The usual thing. Yeah?

STUDENT: [INAUDIBLE]

PROFESSOR: So that you don't see the answers. Yeah, absolutely this can easily be done. We'll do that. Any other questions, about the exam? Now, I don't remember. Is there a problem set that, so I'm not assigning a problem set today, right, then? Right. OK. Good. Because I hadn't loaded it up yet. And so now I won't load it up. OK. Anything else? OK, so let me tell you where we're going to go then, after the break. So after the break, we're

going to be starting to talk about things that are called colligative properties. Colligative properties are the properties like the vapor pressure, lowering when you have a mixture in a liquid, instead of having a pure substance you have a mixture of substances here. And then the vapor pressure of both substances above gets lowered. Anybody want to guess why they got lowered? What's the magic word? Entropy of mixing, right. Right. There's more entropy of mixing if you've got a mixture in the liquid than if you have a pure gas up there. So usually, so let me back up. Usually it's when you have a solute, like salt in water. Where water is volatile and the salt is not. Right, a salt in water solution will have a lower vapor pressure than a solution of pure water. Because of the entropy of mixing in a salt and water solution. The salt and water solution we have a lowering, lower melting point. And that's significantly lower. Which is why we use it on roads, right? That's a colligative properties. Osmotic pressure. Which you've already sort of heard about. Why saltwater fish are unhappy in fresh water. That's a colligative property.

So we're going to go through these colligative properties. And the mainstay of these colligative properties is that we're going to be talking about mixtures in the liquid phase. Here we talked about a mixture in the gas phase, changing some property. From now on, we're going to be talking about mixtures in the liquid phase, pretty much. And so our goal is going to be able to, is going to be predict the way that properties change as you have these mixtures. OK. so the standard mixture that we're going to have, is to have a binary liquid gas mixture. So that means we're going to have two substances. A and B. And at first, we're going to make it as general as possible. So we're going to have liquid phase of A, the liquid phase of B. So, for instance, this could be vodka, right? Water and ethanol. And water and ethanol are both volatile. So we're going to have water and ethanol in the gas phase. There, and it's a mixture, they're perfectly miscible in the liquid phase, A and B. And there's going to be some fraction, molar fraction, of these things. We're going to have a molar fraction in the liquid phase for A and B. And some molar fraction in the gas phase, for A and B. We're going to call it  $y_A$  and  $y_B$ , that's the molar fraction in the gas phase. And there's no reason why the molar fractions in the gas phase should be the same as that in the liquid phase. And we know that. We know that ethanol is more volatile than water. And so if you have a gas of vodka, then you can smell the alcohol because it's coming out. But the water is, vapor pressure is, very slow, very small. It's the usual, it's pretty close to the usual vapor pressure.

And our question is, what we're going to be asking is, how many, if I give you the total pressure and the temperature here, what else do I need to know to find out all these molar fractions? So let's first see what all the variables are that we have. Usually, we have two variables. The temperature and pressure, and that's enough to tell us everything. But here now we have a mixture. So we're going to need more than that. We're going to need four variables. We're going to need the temperature. The pressure, and we're going to need the molar fraction of A in the liquid phase. And the molar fraction of A in the gas phase. We're not going to need any more than that. Actually we're going to need less than that. But those are the four variables that we can easily identify here. And

we don't need  $y_B$  and  $x_B$ , because the sum of the molar fraction has to be equal to one.  $y_B$  is one minus  $y_A$ ,  $x_B$  is one minus  $x_A$ . So we don't need  $y$ . So these are a priori the independent variables that we have to work with.

Now, we have some constraints here. We have a constraint. Our constraint is that we are the coexistence point. There's a coexistence between the gas phase and the liquid phase. And what does it mean for A liquid to be coexistent with A in the gas phase? Chemical potential. The chemical potential of a molecule of A in the liquid phase here is the same as the chemical potential of A in the gas phase. So we have two constraints. We have  $\mu_A$  for the liquid phase is equal to  $\mu_A$  for the gas phase, and  $\mu_B$  for the liquid phase equal to  $\mu_B$  for the gas phase. So we have four variables, two constraints. That means that the total number of independent variables we have is just two. It's the number of variables four, minus the constraints. OK? Or you could say six variables if you include  $y_B$  and  $x_B$ , and four constraints. Whatever we accounted, you just have two degrees of freedom. So we have two degrees of freedom. Which means that if you know the temperature and pressure, then you still know everything. At the coexistence point. You still know what the molar fraction is of your two substances in both phases. So that's really powerful. Or if you know just the molar fraction of A, and the temperature, then you know the pressure above. And you know everything else. So in this very complicated mixture here, you still only need to know a couple of things to tell you everything about this mixture. And this example here is a specific example of something called the Gibbs phase rule. Which you've seen before. In this diagram. In this diagram that we wrote here. Where, let me write down what the Gibbs phase rule is first. The Gibbs phase rule tells you the number of independent variables given a number of constraints. So, it tells you that the number of degrees of freedom, the number of independent variables in a mixture, in a complicated system like this, is equal to  $C$ , which is the number of components. So in this case, it would be two components. You have A and B. The components is the number of independent species that you have, minus the number of phases. So here we have two phases, the gas phase and the water phase, plus two. So for this example here, then we would have two components,  $C$  equals two. Two phases liquid and gas. A and B are the components. And then plus two. So two minus two plus two,  $F$  equals to two. Two degrees of freedom, two independent variables.

If I'm looking at this diagram here, in this diagram here I have  $C$  equals one. One component, right? If I'm sitting where there's only one phase, say, the liquid phase or the gas phase, then  $p$  equals one. Then  $F$  is one minus one plus two, is equal to two. Two degrees of freedom. And so in the pure phase, I am in a plane. The pressure and the temperature are my two degrees of freedom. I can freely move around the plane. At a coexistence line, then the number of phases equals to two. Then I have one minus two is minus one, plus two is one. The degrees of freedom is one. That's a line. I have one degree of freedom. I can move in the line, in the line in a plane. Then if I change to the triple point, where the number of phases is three, then the number of degrees of freedom is one minus three is minus two, two plus two is zero. I don't have any degrees of freedom, I'm stuck at one point. So this is an example of the Gibbs phase rule, specific where  $C$  happens to be equal to one. And then, this is a more

generalized example. So next time, then, what we'll do is we'll start by deriving the Gibbs phase rule. Which is not so hard. And then start on our way to the colligative properties. And then you'll have an exam.