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PROFESSOR: So last time you learned about the ideal solution limits with Henry's law and Raoult's law. And I just want to start with one reminder of what this is all about. So let's say that you have a mixture of CS₂ and acetone. So this is a review of what you saw last time. Acetone like this, CH₃, CH₃. And if you take the CS₂ as the solvent and the acetone as a solute, then when you plot as a function of the amount of CS₂ here as a solvent, then you have the limit where the mole fraction of CS₂ goes to one, meaning that CS is the solvent. You expect Raoult to work if it's an ideal solution. So that the vapor pressure of CS₂ is related to the mole fraction of CS₂ times the vapor pressure of CS₂ if it was pure. So you're sitting here somewhere. This is the vapor pressure of CS₂ pure and CS₂ goes from zero to one. And you expect Raoult to work. So let's do Raoult. Like this.

So in this area, if I were to plot the real curve, I would expect it to start out just like Raoult. And then there's going to be some deviation. Then if I take the other limit, where the mole fraction of CS₂ goes to zero. So now the CS₂ is the solute. And the acetone is the solvent. what happens for this particular mixture is that Henry's law is no longer valid. Raoult's law is not valid here. Instead, you have to look at Henry's law. And Henry's law tells you that for the solute now, not the solvent, so the CS₂ here is the solute, very small amount of it. Very small mole fraction. That the vapor pressure of the solute is related to the mole fraction in the solution. But instead of having the vapor pressure of the pure solute, you have another number. Another constant. Which we call K. Which is a Henry's law constant. And this constant depends on what else in the solution. It depends on the fact that you have acetone in there. You would have a different constant if the acetone were replaced with chloroform, let's say.

So this constant here cares what the solvent is. And it cares what the temperature is, also. There's a lot of stuff that's built into this constant here. It's a phenemological constant. And in the case of the mixture of CS₂ and acetone, the deviation from Raoult's law is positive. Meaning that the Henry's law constant is greater than the vapor pressure of the pure CS₂. So that means that the molecules of CS₂ would rather go in the gas phase. If there's acetone around. That means they don't like to mix so much. They're not happy with each other. So the CS₂ molecules would rather escape what would normally be a Raoult's law type of solution to go in the gas phase away from being close to the acetone. And as a result you get this positive deviation. You get a higher pressure than you expect from Raoult's law. So that the slope here This slope here is K_{CS_2} . And that slope here is $p^*_{CS_2}$.

This is a positive deviation. And you saw an example where you if you mix chloroform and acetone, you get a

negative deviation. Chloroform and acetone are happy together because of the hydrogen bonding between the oxygen here and the hydrogen in chloroform. And you get a negative deviation. So let's start by doing an example with numbers. Of how this might come about. Any questions on this first? I always got confused with Henry's law and Raoult's law. And I always got confused as to when I was supposed to use Henry's law and when I was supposed to use Raoult's law. Very confusing to me, initially.

The thing to remember is that if you're talking about something which in a very small amount, just the solute, like, well I'm going to give you an example which is a bad example, like sugar and water. Where sugar is clearly the solute, but sugar is not volatile clearly this is a bad example. But something which in a very small concentration, then Henry's law is going to apply. Raoult's law is only going to apply for the solvent. When you have a lot of stuff around. On this side here is Raoult's law. On this side here is Henry's law. Henry's law, the deviation's from Raoult's law, are going to happen where the molecules in the solution mostly see molecules that are not like themselves. If they mostly see molecules like themselves, since it's an ideal solution, then they don't know that there's other stuff around. In this case here, the CS₂ molecules don't really know. Most of them don't know that there's any acetone around. They couldn't care less. So it obeys an ideal solution. Here, they don't see any other CS₂ molecules. They mostly see acetone. And so Raoult's law is going to fall apart. Because Raoult's law assumed that you have a single component. Or mostly one component. OK. Let's do an example.

So in this case here, we're going to work the example out here. So let's take two components, A and B. Where B is, and let's look at something which is a dilute solution and non-ideal. So there's going to be some deviation from Raoult's law. And what we're told is at 50 degrees Celsius, that the vapor pressure of pure A is equal to 0.67 bar. And the vapor pressure of pure B is equal to 1.2 bar. So B is clearly the more volatile.

And we're also told, then, that at 50 degrees C we have a molar fraction of A in the liquid phase is 0.9. And the molar fraction of B in the liquid phase is 0.1. And the total pressure above the solution is 0.7 bar. And eventually what we're going to try to find out is, we're going to change these concentrations. Are we going to try to figure out how the total pressure above the solution changes. That's maybe the goal of the problem. When you change this to, eventually we'll change it to 0.95 and 0.05, and we'll want to know how does that change the total pressure. So immediately we see that this is a solvent. This is a solute. This is volatile. So, we're close to where this is zero. So if we're going to apply any, sort of, Raoult or Henry's law problem to this, this is probably going to be Henry's law for B and Raoult's law for A. We're going to be close to this area here for B. We're going to be close to this area for A.

OK. So ah the first question is, what's the composition in the gas phase. What is y_B . And it looks like this particular set of notes doesn't have the calculations. I'm going to go to my other set of notes here that has them. So, because I'm going to make a mistake if I go through it without my notes, I'm going to leave it up to you to do

part a. That's a good way out of making a mess. I'm just going to tell you the answer. Because the actual, the interesting part, is part b of the problem. Part a is the easy part. So this is something that you can do on your own. So y_B is equal to 0.139. Is going to be answer to part b, given these two molar fractions and the total pressure. So now, what we're going to do is, we're going to change the molar fractions and we're going to find out how that changes the total pressure.

So, second part is we're still at 50 degrees Celsius. And we're going to change the molar fraction of A to 0.95. And the molar fraction of B to 0.05. And we're going to ask, what is p_{total} now. So we write what we know. Which is that we expect p_{total} to be the sum of the partial pressures of A and B. A is the solvent, B is the solute. It's a dilute non-ideal solution. p_A is going to be proportional to Raoult's law, because it's a solvent. It's in large quantities. So it's going to be $x_A p_A^*$. And x_B is going, and p_B is going to be proportional to the mole fraction again. But because it's a solute, it's seen most the other molecules of A around, it's not necessarily going to be obeying Raoult's law. It's going to obey Henry's law. It's going to be close to the zero point. There's going to be a deviation because of the interactions between A and B. Which dominate now. So instead of p_A^* , we have K_B here, where this is the Henry's law constant. Which depends on the fact that A is around. We get a different constant if we have a different solvent around.

So we know this. We know this because that was given to us at the beginning. But we don't know this here. We don't know what the Henry's law constant here is. But we can get it. We can get it from part a here. Because we have all the information we need there. So from part a, we already have a mixture where we're given the total pressure. So from part a, K_B is p_B over x_B . And we calculated what y_B is over there. On part a. So we know what the partial pressure of B is. It's the molar fraction of B in the gas phase times the total pressure. That's Dalton's law. Then we divide by x_B . And then we plug in the number 0.139 times the total pressure up there is 0.7. Divided by 0.1. And we get that this is 0.973 bar.

So now we can plug this in to our equation here. We know x_A , we know x_B , we know Raoult's law, the 0.67 p_A^* . We know K_B here. We plug in all the numbers, and we get that the total pressure is now 0.685 bar. This is a pretty typical example of a problem that combines Raoult's law, Henry's law and Dalton's law together. And keeping track of these laws takes a little bit of thinking. And it's very, very common on problem sets or exams to mix these up. So it's good to go through examples like this and really keep track of where each law applies. Dalton's law applies in the gas phase. It's partial pressure in the gas phase. Henry's law is the pressure. If you know what's happening in the liquid phase, for a solute. Raoult's law is the partial pressure in the gas phase, if you know what's happening in the liquid phase. So Raoult and Henry tell you something about the pressure if you know the liquid. Dalton only deals with what's happening in the gas phase. OK, any questions on the problem?

Alright. So we did this problem here, and now let's draw the phase diagram for our solute here, or for B, rather.

Zero to one. And let's take a vote here. So if Raoult's law worked for B, for the mixture of A and B, then we would have p_B^* star here. And everything would be great. But Raoult's law doesn't work. Close to molar fraction of zero. Instead, Henry's law. There's a deviation, due to the interactions between the molecules A and B here. So we have two choices for the deviation. We can have a positive deviation, or we could have a negative deviation.

Positive deviation, if the molecules of B would rather be in the gas phase, than be in the mixture in the liquid phase. Meaning they don't like molecules of A. They don't like to be mixed with molecules of A. The energy of interaction is not favorable. The enthalpy is not favorable, for mixing A and B. In this case here, the enthalpy is favorable for mixing A and B.

So in this problem here, which do you think it is? The blue one or the green one. Let's raise hands here. How many people think it's the blue one here. Anybody else? The right answer, we have four people. How many people think it's the green one? Four. Five. Six. You didn't vote twice, did you? Vote early, vote often, right? Mayor Daley, the old Mayor Daley in Chicago. And if you know somebody who's dead, vote for them. OK, so this is the, I've got about five people here. And a bunch of people didn't vote. So it's a tie. It's basically a tie here. I think you should think about this. Maybe talk to each other a little bit. See if you can figure out, given all the numbers that are in this problem here, you know what, the pure pressure on the solvent is. We change concentrations here. Got Henry's law constant out. And Henry's law constant is going to tell you whether or not that enthalpy of interaction is favorable or not favorable. It's going to be a positive deviation or a negative deviation.

OK, shall we vote again. How many people say it's the blue one? How many people say it's the green one. Thank you. Alright. Good. Alright. We have K_B is less than p^* , therefore it's a negative deviation. The pressure is less than you'd expect. The molecules like each other better than you expect. There is a favorable enthalpy of interaction between A and B. They like to interact. It could be hydrogen bonding. Could be a lot of different things.

OK, so now if I put the whole diagram together, which I shouldn't have erased here. Right, so there's my diagram here again. There's Raoult's law. There's the deviation from Raoult's law here. For one substance, let's say for B. There's Raoult's law for A. There's a deviation for A. It could be like this. And if I now add these two together, instead of having a diagram for, this is a pressure x_B , y_B diagram, pressure x_B , y_B diagram, instead of having Raoult's law sitting right here. And then the y_B part down here below, your usual sort of ideal solution phase diagram with the high pressure of the liquid on top and the gas on the bottom. Now if you add the blue curve and the red curve together, you're not going to get a straight line like you did before. When Raoult's law applied throughout. Instead you're going to get a deviation from the straight line. You're going to get a curve that's always below the straight line. Because we have the negative deviation on both sides. So you end up with something that's curved and deviates below.

And the same thing will happen for the bubble line. It will also deviate below. In some way. Maybe not as much, maybe. So this is what you usually see. You see deviation of that whole phase diagram, like you're pushing down on it. Or maybe it didn't pulled up. If you have a positive deviation, then it's the opposite. It gets, this is negative deviation. And if you have a positive deviation, instead of having a usual phase diagram, you're going to get something that's looking like this. Which is the Henry's law coming in. Yes.

STUDENT: [INAUDIBLE]

PROFESSOR: Yes.

STUDENT: [INAUDIBLE]

PROFESSOR: Doesn't matter. Good question, though.

OK, so this is what it usually looks like. And everything you've learned so far can be applied to these diagrams here. There's one exception, though, which is an important one. Which is, sometimes, these non-ideal diagrams have a funny spot. Which is that if I draw them, so there's my x_B , y_B , on the bottom. Zero to one. I have pressure here. Sometimes, there's the dew line. And the bubble line. Sometimes, instead of having a nice separation between the bubble and the dew line, there's a special point which for some reason those two curves meet. Non-ideality. There's interaction between the molecules. In the gas phase and the liquid phase.

This special point is an interesting one. Because, well, if I'm away from this special point, let's say I'm sitting to the left of the special point, right here. And I can distill this thing. I can take my gas phase here. And increase the pressure. Say I'm sitting here in the mixture, gas phase mixture with x prime B, y prime B. Sorry, x prime B. And I go up and I increase the pressure. Start making vapor. Start making vapor, I can find out what the, I start making liquid. I can find out where the composition in the liquid is by going over to the blue line here. That tells me the composition in the liquid. And reading off the composition of the liquid down here. So this is actually the composition in the gas phase is y_B prime. y_B prime is the gas phase. I'm starting here. I start to increase the pressure. I begin the distillation process. And I get a little bit of liquid out. And I can read off the composition in the liquid. x_B prime. And I know from this diagram that x_B prime is less than y_B prime. So I'm enriching my liquid in A. I'm purifying my solution in A, right? I can get pure A out eventually. The fact of doing this, I can get pure A. So I decrease the pressure, I get the pure gas phase of my new solution here. And I increase the pressure. And go over and make a little bit of liquid. And capture that liquid. And repeat the process over and over again. And eventually I have pure A.

Now, suppose I'm sitting here at this special point. And I'm starting with y_B And let me call it a here. y_B of a. I'm sitting right here. And I'm increasing the pressure. I go all the way up here. And I start making liquid. . What's the

composition of liquid, compared to the composition of the gas phase? What's y ? What's x_B compared to y_B of this point up here? It's the same. So I'm making liquid. I got the same composition. Doesn't help me. If I make a gas again, I still have the same composition. I can't distill. I can't purify it. So if I have this special mixture here, of A and B, at this point here, I form what's called an azeotrope.

And then you can't separate it out. You can't separate out the mixtures into A and B. You can't distill it at that point here. Now, you can draw the same diagram in, instead of pressure, mole fraction, you can draw the same diagram in terms of temperature. And the same thing happens. You can have deviations from, this is the extra figures that are on the bottom page of the notes from last time here. That we've replaced here. You can have a positive deviation. With a positive azeotrope. And your T p diagram, T x diagram. Or you can have, depending on the interactions between the two molecules, you can have something that has a negative deviation. And a negative azeotrope here.

So in this case here, this is a particularly awful situation. Because there's your liquid phase down here. There's the gas phase here. And now, suppose that you're doing some sort of distillation. So you start here in the liquid phase, with some composition. You make a gas. Let's say you're doing a fractional distillation of some sort. Your gas now has a new mixture. So this is the composition in the gas phase. You take that gas phase mixture, and you condense it in your condenser. In your fractional distillation condenser. So now I've condensed it. And I heat it up again. I've condensed it. So I'm here somewhere. And cool it down so that I have a liquid. And I condense it. And slowly I move over to the azeotrope point.

And once I get there, I'm stuck. And the same thing happens if I'm on the other side. I'm on this point here, I keep my solution, my mixture. I make a gas, I read off the composition of the gas phase here. I take my gas phase composition out and I re-liquefy it. So I'm here, down here somewhere, again. And I heat it up again. And and I move to the azeotrope point. That's what happens if you have a mixture of benzene and water, for instance. You can't distill it. You work your way down to this point here. You can't use fractional distillation until you've separated it out.

So this is a real life problem. And you have to do things like change the pressure. Do your distillation under high pressure or low pressure. To try to get this point to separate out. So you can get past this point. Or to try to get the deviation to become of the opposite sign. Where you can start to do some distillation. Any questions on azeotropes, before we get to colligative properties? If you're doing organic chemistry, and you're trying to purify things, this is a real pain, right? Pain in the neck. So you've got to know, which things form azeotropes.

So we're going to start colligative properties. There are four colligative properties, and you already know what they are. And you've even seen the math behind them. And in fact, you've seen the math for one of them already

pretty clearly. And these colligative properties are properties that you use all the time in your day to day life. At least, three of them.

OK what are the four colligative properties? There is vapor pressure lowering. If you have a mixture and the vapor pressure of the mixture is less than the vapor pressure of the pure material, there's the boiling point elevation. If you add a large amount of insoluble - not insoluble, non-volatile solute to a solution, you will depress, you will increase the boiling point of that solution like the example of the salt and water that I gave. So if you need a lot of salt to increase the boiling point of water. There's the freezing point depression. That's what we use to melt ice in the winter. By adding salt to it. Then there's the osmotic pressure. Which is the example of the freshwater fish in salt water, or the saltwater fish in fresh water. Or the cells bursting when you put them in.

OK, so these colligative properties all come from the fact if I have a mixture, the chemical potential of a molecule in a mixture, in the liquid phase here, is less than the chemical potential of the pure guy. Where A is the solvent, and B is some solute. So this is always true if your number of moles of A is much larger than number of moles of B. Mix a little bit of B in there, and the chemical potential of A in the liquid is going to come down. Because of the mixing process. Because of the entropy of mixing. And that's going to give rise to these properties.

And, to do these, one more thing before we start. We're going to use a special concentration for these guys. We're going to use, call something molality. Molality. Molality is the number of moles of solute divided by kilograms of solvent. So it's moles per weight of solvent. As opposed to moles per liter, which is something that we're more used to. Moles per kilograms of solvent. It's pretty close to moles for liter for water. Because a gram of water is a milliliter, roughly. The density of water's close to one.

So let's start on these things. So we've already seen this. You've already seen vapor pressure lowering. It comes from Raoult's law. If I look at the change in the vapor pressure of A, p_A minus p_A^* . p_A is equal to $x_A p_A^*$. $x_A p_A^*$, that's Raoult's law. Minus p_A^* , that's equal to one minus x_A . Minus p_A^* . Which is minus $x_B p_A^*$. Which is less than zero.

So, that means that the vapor pressure above the solution is lowered. So I should have said vapor pressure lowering. And we also drew a phase diagram to show how this vapor pressure lowering was going to imply freezing point depression and boiling point depression.

So now let's go on and look at the freezing point depression. Number two. We're going to find that the change in the boiling point is going to be some constant K_b , which is not to be confused with Henry's law's constant. It's completely different. This is a colligative property. Times the molality of B. That's going to be the answer we're going to get. Amount of temperature change depends linearly on the molality of B, with a constant that depends on what the mixture is. And what the pressure is. Whenever we derive anything connected to phase transitions,

we usually always start with the fact that the chemical potential changes. And it has to be equal at equilibrium. So that's what we're going to do. We're going to start with the chemical potential equal of the liquid phase is equal to the chemical potential of the gas phase. For the solvent at equilibrium.

And the liquid phase obeys Raoult's law. So it's going to be the chemical potential of the pure material. The pure liquid. Plus $RT \log x_A$. So this is where the mixing of the solute comes in. And on the gas phase side, μ_A , it's going to be the same thing as the chemical potential of the pure A. Because we're going to take B to be non-volatile.

So the only thing in the gas phase is A. Same chemical potential as if it were pure. Because it is pure. So now we solve for $\log x_A$ is equal to one over RT μ_A^* in the gas phase minus μ_A^* in the liquid phase. And this is just the Gibbs free energy per mole of A in the gas phase. The Gibbs free energy per mole of A in the liquid phase. So we can replace this with the change in Gibbs free energy from going from gas to liquid. Per mole, which is just the Gibbs free energy of vaporization. We're going from liquid to gas. And I probably have a negative sign somewhere. No this is right, this is the final state. This is the initial state. Divided by RT .

OK. That's not really what we want, though. What we want is ΔT . Here I've got some complicated equation that has T in it, but not ΔT . But before we do that, before we transfer and try to get a ΔT out of this equation, let's see if we can do any sort of simplifications here. I don't like to carry logs around. There are no logs around here. So let's see if we can get rid of that log. What is $\log x_A$?

$\log x_A$, well, x_A is close to one. It's connected to x_B . And everything in here is connected to B. There's a molality of B here. The concentration of A doesn't come into play here. I don't want it there. So let me replace it with B. one minus x_B . x_B is a small number. It's a solute, it's in small amount. We're close to being a pure solvent here. So one minus something very small. The log of that. Well if you've worked with Taylor's expansions. You probably know that that's close to minus x_B . The log of one minus x where x goes to zero is close to minus x . So that's minus x_B . Now, minus x_B , in terms of the moles, is the number of moles of B divided by the number of moles of B plus the number of moles of A, the total number of moles. The number of moles of B is very small, compared to the number of moles of A. So I can get rid of this. So, and there's a minus sign here. So this is approximately minus n_B divided by n_A .

Now, the only I can do is, I'm trying to get at molality here. I said we're going to use molality. Got moles. I don't have kilograms of solvent here. I have moles of solvent. I'm not so happy with that. So, in order to get something that has kilograms out, let's multiply up and down by capital M where capital M is that total mass of A. Basically the number of kilograms of solvent. Total mass of A. So now, this fraction here, that's the molality. That's what I'm looking for. So this is minus the molality. Then I have the total mass of A divided by the number of moles of A.

Well, that's the molecular weight of it. Total mass divided by the number of moles is the molecular weight. So this is the molality of B times the molecular weight of A. OK.

So now I can plug this instead of $\log x_A$. And I get minus n_B times n_A is equal to ΔG of vaporization divided by RT . Let's rearrange a little bit. And m_B is equal to ΔG vaporization divided by n_A times RT , with a negative sign. Well, I've eliminated the log at least, but I still don't have a ΔT in there. I don't have a ΔT . How am I going to get a ΔT in there? Got to get the ΔT . Everything's very small. So one way to get a small change in temperature is to take a derivative with respect to temperature. That's going to get a ΔT in there. So I'm going to take the derivative of both sides with respect to T .

And ΔT is going to come out that. I'm going to take $d n_B / dT$, constant pressure. Minus one over m_A times R $d \Delta G$ over T . This is ΔG of vaporization. dT , constant pressure. And I wish I'd made my boards a little bit better. Because I have to cover things up.

OK, now I have this derivative of the Gibbs free energy divided by the temperature. This turns out to be something that you've seen before. It's called the Gibbs-Helmholtz equation. And it relates the temperature change in the Gibbs free energy with the enthalpy change. The Gibbs-Helmholtz equation is that the $d \Delta G$ over T dT is equal to minus ΔH over T . And you can get that from just writing fundamental equations about G and H . And turning the crank. And we've done that before. And I'll leave that as an exercise for you to go back and figure out what, you can go back to your textbook and look at, you know under the index. Gibbs-Helmholtz, and figure out why this is the case.

So now, we have this equation here. This is going to be nice, because it's going to get rid of the d/dT . On the right-hand side. And so now our equation becomes $d m_B / dT$ is equal to ΔH vaporization divided by $m_A R T$ squared. Now, I can rewrite this in a slightly different way. This is Δm over ΔT , basically. Δ the change in number of moles. I mean, the molality of B divided by the change in temperature. I'm getting very close here. There's a change in temperature here. There's a change in molality here. I can rewrite this as ΔT , then, is equal to molecular weight of A times RT squared divided by ΔH vaporization times Δm_B .

Now, I'm making a very small change in B here. Starting at zero. Basically I'm taking pure A and I'm dumping in a little bit of B. That's what I'm doing when I experiment. I'm dumping in a little bit of B in my pure A, and I'm trying to figure out how the temperature is changing. So I'm doing Δm_B is my small amount of B that I'm adding to the solution. Minus what I started out with, which was zero. So Δm_B is basically m_B . Right? That's basically what it is. So let's get rid of this Δ here. What else can I say? Well, I can say that the temperature change that I'm looking at is also pretty small. Compared to the absolute temperature. This is a small change. I'm only adding a small amount of B in there. So this temperature up here is not going to change very much. Let's

take it to be the temperature of the boiling point of the pure material. T_{B^*} , of the pure material. OK And there's my ΔT here.

So this is of the form ΔT is equal to molecular weight of A. Times R. Times the boiling point of the pure material squared. Divided by ΔH of vaporization of the pure solvent. Times the molality of B. And this combination of properties of A, the molecular weight of A, the boiling point of pure A. The heat of vaporization of pure A, this is K_b up here. Which I covered up. It's of the form ΔT is equal to K_b times m_B . And this turns out to be always greater than zero.

Now. If you want to look at freezing point depression, it's really easy. In your equations, it's the same thermodynamic picture. All you need to do, in all your equations, you replace ΔG of vaporization with minus ΔG of freezing. When we did a vaporization, we're going from liquid to gas. We had ΔG of vaporization. When we're doing freezing point depression, we're going from liquid to solid. And so we have to use minus ΔG of fusion. Minus ΔH of fusion. s to l would be the positive ΔG of fusion. So we're going from liquid to solid. We have to replace ΔG of vaporization with ΔG of fusion. We replace ΔH of vaporization, where minus ΔH of fusion. Replace the boiling point with the freezing point. And replace K_b with K_f . And the math is exactly identical. It all starts from the chemical potentials being equal. And turning the crank at equilibrium, being equal between the solid phase and the liquid phase. And turning the crank. The solid phase is like the gas phase. It's a pure A, pretty much. Because the molecules of B are stuck. And A doesn't know that B's around, in the solid phase. They know that they're around in the liquid phase because the fusion fast enough. .

And then we can write, if we turn the crank, we get an equation that looks like this. The freezing point depression is equal to minus $m_B R T_f^*$ squared. Divided by ΔH of fusion, for mole. Times the molality of B. And this number is always less than zero. There's the negative signs in here. OK. Always depressed. Any questions about those freezing point depression and boiling point elevation. Yes.

STUDENT: [INAUDIBLE] PROFESSOR: Why did I drop it here? Because the small change that I'm making in n_B is going from pure A, where n_B is zero, to a very small amount of n_B . That's why I'm allowed to say this. And then just replace Δn_B with n_B . I'm comparing every, my reference point is the pure material. I'm just adding a little bit to start with. It's a good question. Any other questions? OK. I didn't get to osmotic pressure. You'll get to that on Friday. And also start statistical mechanics. And after osmotic pressure, you'll be done with thermo. It'll be statistical mechanics and then kinetics.