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PROFESSOR: And today I'll continue with both ideal and non-ideal, or real, liquid mixtures. And let me just say the reason we're in some sense lavishing so much attention on this topic is because, after all, there's just an enormous amount of chemistry that happens in liquid mixtures. Awful lot of biology. Awful lot of just processing of stuff. Distillation and everything else. So there's so much chemistry that takes place in liquid mixtures that it is really important to have a sense of what the free energy and chemical potential of each of the species is doing in there. Because of course this is what directly guides the chemistry that happens. So I just want to start by finishing up something, a couple of things, from the topics from the last lecture.

One of them is, I derived an expression for the lever rule. And I just wanted to make a little more explicit the result. It may not have been completely clear. So, I just want to go back to that. We had looked at what happens if you start at some particular point, labeled one, and work your way up. So we're raising the pressure. So we're in the all gas region to start. All gas region of the phase diagram. This is x_B and y_B . The liquid and gas mole fractions of B. And the idea is that here is our initial value. Now we're only in the gas phase. There is no liquid. So this is y_B of one. There is no x_B at this point. We raise the pressure. And at some point, depending on where we end, we then look to both coexistence curves to determine the compositions of both the liquid and the gas phases. So when we look out here, at the liquid phase. That gives us x_B . At where I labeled point two, so there's two after we raise the pressure. We started at one.

And then over here, we look at the gas phase coexistence curve. so there's our y_B value at two, right? And I derived an expression for the ratio of the number of moles in the gas and liquid phases. Because the idea here is, let's say you're working your way up on the curve. If you just barely get to the coexistence curve, of course then you could see how much material you've got in the two phases. But there's very little material still. You've still got almost everything in the gas phase when you first reach here. And as you work your way up in pressure, you'd have more and more liquid. Of course, if you were to just keep going, you'd get into the pure liquid phase. Typically, though, you might stop somewhere in the middle and have some reasonable amount of material in both phases, and you want to find out the composition in each phase. And also, want to know how much material there is in each phase. So the result that I derived was $n_{\text{gas at two}} / n_{\text{liquid at two}}$. The ratio of total moles in the gas to the liquid. What I derived was $x_A \text{ of two} - y_A \text{ of one} / y_A \text{ of one} - y_A \text{ of two}$, and I just want to, in some sense, finish up by making the obvious substitution, which is, of course these are mole fractions. So I can just write x_A is one minus x_B . And y_A is one minus y_B . And I just want to put this in the terms that are written

here in the phase diagram. When I got to this result I pointed out that therefore you can use the lever rule. And I just want to make that a little bit more explicit. So using that relation, then we can see that n_g of two over n_l of two, total number of moles in the gas to the liquid is, now I'm going to substitute in to get y_B of one minus x_B of two over y_B of two minus y_B of one. So all I've done here is substitute in these expressions.

And now I'm going to just switch both of these. And so I'm going to multiply both sides by negative one. So I can write x_B of two minus y_B of one over y_B of one minus y_B of two. So that's the result that I want. Because if I look at the two segments of this line, on either side of the pressure value I've reached, then what I see, of course, is that over here I've got x_B of two minus y_B of one. That's this. And this part is y_B of one minus y_B of two. That is, it's this part. And that's here. And so that's the point, is that the ratio of moles in the gas and liquid phases is just given by the two segments of this on either side. And so what this allows us to see very simply is alright, I'm going to raise the pressure at some point. And depending on how much material I feel like I need to collect in the new phase, I can always determine that simply by reading off the phase diagram what the ratio of these two segment lengths is.

Now what I want to do. What we've done mostly is just go through these phase diagrams, see how to read them. How to follow events on them as you change pressure in a diagram like this. Or change temperature in diagrams like I also showed last time. Now what I'd like to do is go a little bit further and just look at expressions for the chemical potential and the free energies. So that we can, a little more quantitatively, see what's going on. So let's just see what's happening. So let's look at the chemical potentials. In ideal liquid mixtures. So everything is derived from the fact that when we have any of the constituents in both phases, the chemical potential must be equal in both phases. Right? So, we can write for A, μ_A of the liquid at some temperature and pressure must equal chemical potential of A for the gas. That's the partial pressure. So if we have an ideal gas, and certainly if we're going to assume an ideal liquid mixture, we can safely assume that it's an ideal gas above it.

Then we can write μ_A in the gas. Is just μ_A° . That's a function of the temperature plus $RT \log$ of p_A over p_0 . Nothing new here, this is just our expression for the chemical potential in the gas, with reference to a standard potential. Usually one bar. At whatever the temperature is. And, of course, this is how it varies as the partial pressure of A in the gas phase varies. So then we can just write our expression for the liquid. At our temperature and pressure, it's given by μ_A° in the gas phase. Plus $RT \log p_A$ over p_0 . So it's the same thing. Because I'm just taking advantage of this equality. But of course, this is an obvious step, having written this. But is a super important step. That's what allows us to do this treatment in such a straightforward way. We know a lot about the chemical potential of something in the gas phase. Since the gas and liquid are in equilibrium, therefore we know the chemical potential in the liquid phase too.

So we can rewrite this by recognizing that if we just go to the limit where we only have pure liquid A, so pure liquid

A. Well, in that case, μ_A or sorry, μ_A in the liquid phase, μ_A^* is μ_A in the gas phase. Plus $RT \ln \frac{p_A}{p_0}$. And so for the mixture, now all I'm going to do is just add and subtract terms. So we can write μ_A in the liquid at T and p , right? So this is in the case of the limit of the pure liquid. Now we're going to the mixture. So it's just μ_A^* plus $RT \ln \frac{p_A^*}{p_0}$ minus $RT \ln \frac{p_A^*}{p_0}$. Wait a minute, lost a term. Plus $RT \ln \frac{p_A}{p_0}$. And all I want to do now is combine terms. To write μ_A^* liquid temperature and pressure. Plus $RT \ln \frac{p_A}{p_A^*}$. So this is a very convenient form for it.

And then, of course, we have an expression for p_A , right? From Raoult's law. p_A is just the mole fraction x_A times p_A^* . That's just true for the ideal mixture. So now, finally, we can write that μ_A in the liquid at T and p is just given by μ_A^* . So that's for the pure liquid at that temperature and pressure. Plus $RT \ln$ of the mole fraction of A . So that's a very simple expression for the chemical potential of A . And of course the analogous expression will hold for any of the constituents. In an ideal liquid mixture.

By the way, it's convenient because it looks just like the chemical potential in a mixture of ideal gases. Except that we have liquid instead of gases, right? Now, of course, since this is a mole fraction, it's always between zero and one. That means this is always a negative number. So what that means is that the chemical potential in the solution is always lower than the chemical potential of the pure liquid.

Very important result. So it has all sorts of implications that we'll see. One of them is osmotic pressure. It means that if I have a biological cell, or some container with a membrane through which one of the constituents might pass. So in other words, let's say, component A , maybe it's just water. It can pass freely, let's say, from the outside to the inside of the cell, or from one side to another of a membrane. And on one side I've just got pure water. And on the other I've got saline solution or whatever is in the cells, right? What's the water going to do in that situation? What's going to happen? Anybody know?

So I've got, I just take fresh cells and plunk them into pure water solution. What happens? Yeah. They burst. Water rushes in. Because the chemical potential is lower inside. It's always lower in solution than outside. So water rushes in, and the membrane expands. Now, if the membrane is strong enough, at some point it may not burst. And the pressure might start to go up. Let's say the membrane is strong enough to resist and not burst. Eventually, the water won't keep going in indefinitely. That's because it won't be at the same temperature and pressure any more. In particular, the pressure will have changed. So you can build up some high pressure, what's called osmotic pressure. Because of the fact that at the same pressure the chemical potential of the water's lower inside the cell or inside the enclosure with the membrane. So water will keep filling. And at some point the chemical potentials will equalize because of the change in pressure. And at that point there'll be an equilibrium established. We'll see that quantitatively a little bit later.

OK. The other thing to notice is, this is familiar from the expression for a gas mixture. What drives the gas mixture? Remember back when we discussed mixing of gases and the fact that they would mix at all. What makes that happen? What's driving it? Yeah, it's entropy, right? And that's what's happening here too. Of course, in the case of the ideal liquid mixture, there's no energetic interaction. The molecules are non-interacting in this case. But of course, entropy is going to want them to mix. And that's what's resulting in the decrease in chemical potential.

Let's see that a little more explicitly by just calculating out the free energy change of mixing. So, ΔG of mixing. So we're going to start with two separated liquids. And then we'll remove the barrier. And we'll have the two mixed together. So of course, the free energy in either case is just the sum of the number of moles of each times the chemical potential of each. We have expressions for that. So starting G_1 in this case. It's $n_A \mu_A^*$ in the liquid. Plus $n_B \mu_B^*$ in the liquid. Here, G of two. After we let them mix. Then it's n -- wait a minute. It's just n . I think I've got that wrong in the notes also. Right, it's just a number of moles times the chemical potential in each case. So it's the number of moles times $x_A \mu_A$ in the mixture. Plus $n x_B \mu_B$ in the mixture.

But we've just figured it out our expressions for μ_A and μ_B , our chemical potentials of each constituent in the ideal liquid mixture. So this is just $n x_A$. And here's our expression. And of course these are going to cancel. Let's write it out. So it's $\mu_A^* + RT \ln x_A$. And then, $\mu_B^* + RT \ln x_B$. So our ΔG of mixing is just the difference between these two. So it's $n RT (x_A \ln x_A + x_B \ln x_B)$. Where have you seen that before? Yeah. The same thing that you had for the ΔG of mixing for an ideal gas mixture. Why? Because we're not accounting for any interactions between the molecules in either of the phases. And if the molecules aren't interacting, it's all entropy. And the entropy term has the same form in either case. In microscopic terms, it's just measuring the fact that there's more disorder in the mixture than in the pure liquids. Just the same it was in the gas phase.

OK. We can see this even more explicitly if we just recall that G is $V dp - S dT$. So we can just explicitly calculate the entropy of mixing. ΔS of mixing is just the partial of ΔG of mixing. Negative partial. With respect to temperature. At constant pressure. So it's just $-n R (x_A \ln x_A + x_B \ln x_B)$. So that's our entropy of mixing. We can calculate our enthalpy of mixing. Just ΔG of mixing. Plus $T \Delta S$ of mixing. But it's immediately apparent that these are just going to cancel when we multiply this by T . So there's no enthalpy of mixing. Just as we expect when there are no energetic terms involved. It's all entropy that's driving the mixture.

One more detail, it's straightforward to see that there's no volume change. That is, if we take the derivative of ΔG of mixing the partial derivative with respect to pressure, at constant temperature, of course, there's no explicit pressure dependence. This is zero. So again, in the ideal liquid mixture case, their molecules aren't

interacting. So there's no reason, when I open that barrier, that the amount of volume they occupy altogether is going to change. Any questions, so far? OK. Then, let's move on to non-ideal solutions.

By the way, just to return briefly to this topic of osmotic pressure, I just want to emphasize that result didn't need any kind of energy of mixing, either, right? Just from the entropy term you would burst the cell or do whatever. You end up with a larger pressure. So in other words, if you have a situation where, here is A, pure liquid. And here is A plus B liquid, so μ_{A^*} is greater than μ_A . We know that in all cases at the same pressure, the chemical potential of the mixture is lower than the chemical potential of the pure liquid. What's going to happen? Well, A is going to, oh, sorry, A over here is going to rush in. It's going to get through this, if I've got a semi-permeable membrane, it's permeable to A but not to B. Common situation, of course. That's certainly the case for the cell membrane. Water may flow easily in through the membrane, but all of the stuff, all the salt and everything else that's inside the cell generally won't. So of course A then flows through this, what's called a semi-permeable membrane. And you'll wind up with either a burst membrane, or something that looks like this. Where now there is additional pressure here. And you'll have some different mole fraction than you started with before.

Now let's go over to non-ideal solutions. So let's just think microscopically for a moment about how this is going to work. You know, normally, always, there are interactions between the molecules and the liquid. The liquid is a condensed phase. The molecules are in immediate proximity to each other. So it's very different from the gas phase, where it can be a pretty realistic approximation to say, well, the molecules are essentially non-interacting. The ideal gas law may turn out to be a very good approximation. In the liquid, really, it's never the case that you don't have interactions. So if we just sketch that. If we start with a bunch of molecules in A, they're interacting. So there's some interaction energy. I'll call it u_{AA} , it's the interaction between two molecules of A. In most cases it'll be less than zero. That is, there'd be a weak attraction. Same thing between molecules of B.

So that's my situation in the separated liquids. I've got molecules in each container. They're interacting. There's some energy associated with that. So here's the pure separated liquids. And now, I'll open up the barrier and let the liquids mix. And now suddenly, of course, A and B are going to interact with each other as well as other molecules of their own kind. So now, suddenly, there's going to be some interaction energy. u_{AB} . And very simplistically, we can envision that for some of the molecules, essentially, there would be exchange of this sort. So, one neighbor of this molecule and one neighbor of this molecule will wind up exchanged for some pairs of molecules with the unlike species. And essentially, like interactions will be replaced by unlike interactions. So there's some now change in energy involved. There's a Δu . And as outlined in this simple picture, it's just $2u_{AB}$ minus u_{AA} plus u_{BB} . Real liquids are very complicated.

For liquids with relatively simple non-directional interactions, things like organic liquids that might interact van der Waal's interactions. This might be a reasonable starting point. And in general, if we're going to deal with relatively

small deviations from the ideal liquid mixture, the ideal solution, then we can start with a model like this. And this difference is what's going to determine how far the liquid mixture will deviate from the ideal solution case. Of course, we could always just write a term like this. It may or may not be easily expressed in this sort of way.

So let's just think about what the possibilities are. Of course, simply, there are two. The sign could be positive or negative. And what that means is, you could have situations where it's positive because basically there's an energy of mixing now in these cases. If that's not zero, unlike the ideal case, now unlike before, where we just had entropy driving the mixture, now there's an energy of mixing. Could be positive or negative. If it's positive, that means energetically speaking, the mixture is unfavorable. In other words, the intermolecular interactions between like molecules are more favorable than the interactions between the unlike molecules, in that case.

So, Δu is greater than zero. And our ΔH of mixing is going to be close to Δu of mixing. That is, we're going to figure that ΔpV is not going to be something large. And in that case, we can say ΔG of mixing is $\frac{1}{4} n$. And that's only because there are 4 species involved here. Times Δu . In other words, I'm multiplying this molecular Δu . This is the change in energy for this collection of four molecules. Or of four molecular pairs. Plus the other stuff that we've seen for the ideal case. That is, the entropy term, of course, is still there. $x_A \log x_A$ plus $x_B \log x_B$. And because we're treating the case where this is positive, that means this is bigger than in the ideal solution case. So of course there are lots of examples of each of these. In fact, this is the more common deviation.

So, and lots of examples. An easy one is acetone. And carbon disulfide. So, if we look at that, and just see what the phase diagram is going to look like, it's the following. So let's start with the ideal case. So I'm going to make B the more volatile component. That is, B is going to be CS_2 . So here's $p^*_{\text{CS}_2}$, which I'll call p^*_B . And somewhere down here will be p^*_A , that is, p^* for acetone. And this is going to be the mole fraction of CS_2 . Or x_B .

So let's start with the ideal case. Not steep enough. Pretty good. OK. And now let's look at what's going to happen in the real mixture. Well, because we've got a positive deviation, what's going to happen is the mixing is unfavorable. The molecules aren't that happy any more about being in solution. So what that means is, relative to the ideal solution, they'd rather go up into the gas phase. They don't like being in the mixture. Compared to what they would feel in the ideal solution, where there are no interactions. Because the interactions between unlike molecules are unfavorable.

So what's going to happen, then, is the pressure is higher. You have deviations from the ideal case, in the total pressure. And in each of the individual partial pressures. That's the total pressure. p_A plus p_B . In the ideal case it's this straight line. In the non-ideal case, though, it's bigger than the straight line. Because more stuff wants to

get up into the gas phase. And it's the same for each individual component. So here's p_A . And there's p_B . Any questions?

OK, so it's obvious just from looking at this that each of the partial pressures is bigger than it is in the ideal case. And so, so is the total pressure. So in other words, if I say what's the partial pressure of CS_2 , well, since it's not the simple ideal case, actually I don't know what it is in general. It's not easy to calculate a priori what it's going to do all the way across the phase diagram for any mole fraction. What I do know, though, is it's bigger than it would be for the ideal solution case. In other words, it's bigger than $x_{CS_2} p^*_{CS_2}$, the pressure over the pure liquid CS_2 . Same for acetone. It's bigger than $x_{acetone} p^*_{acetone}$. And since both partial pressures are bigger, the total pressure has to be bigger. And of course, that's something you can read right off the diagram as well. In other words, the total pressure is bigger than in the ideal solution case. Any questions? OK.

So the negative case, of course, is exactly the opposite. So I'll just go through it quickly. So, remember positive deviations came, let's put this back up there. That came from the case where the unlike intermolecular interactions are not as favorable. There's less attraction, more repulsion than in this case. Of course, there are plenty of cases of the opposite sort. Where the unlike intermolecular interactions are attractive. More than the interactions between like molecules. And in that case, you have the opposite result. So you can have negative deviations. In other words, Δu is less than zero. Lots of examples. I've got one in the notes, it's just acetone and chloroform. So if we get rid of the carbon disulfide and put $CHCl_3$ in there, that's more favorable. Because there's weak hydrogen bonding between the unlike species. And not between the like species. So what happens is, you have acetone, it's this. And you have chloroform. And there's weak hydrogen bonding between them. There's an attraction there. That doesn't exist between either case of the like molecules. So now there's stronger attraction between them than there is between molecules in either of the pure liquid cases. So, of course, you know that the opposite result is going to happen. In this case, now you mix them together, relative to the ideal solution where there are no interactions, now they want to be together. They're clinging to each other through these hydrogen bonds. What's that mean for the pressure up in the gas phase, in the solution? They don't want to go there any more. Stuff in the gas phase now wants to condense down into the liquid. Because there they have favorable interactions. So that's, of course, what'll happen. And so then you just see the opposite sort of deviation from what I just illustrated before.

So then if we look at $p^*_{CHCl_3}$, where are these lines going? Well, may have been more artistic. But I'm afraid I'm going to have to go with reality. p^* for acetone. There's chloroform. And now our deviation is going to be in the opposite direction. So all the, both of the partial pressures and the total pressure are going to go lower than indicated here. So p_{total} is now less than, for the real case, is less than p_{total} for the ideal case. In the situation where you have attractive interactions between the unlike molecules. Any questions? OK.

Now, in general, this is complicated. To describe quantitatively throughout the entire phase diagram. The interactions are complicated. Lots of times, molecules interact with more than one neighbor. So in general, we don't have a simple analytical expression for what the pressure is going to do as a function of mole fraction all the way from zero to one. Of course, we have it in very simple form for the ideal solution. Because everything's linear. So it's very simple. These are replaced by equalities and we know everything. Now we don't. But we can at least make some progress by looking at the limiting cases. Where you have just very dilute solutions. So in that case, you can anticipate what's going to happen. So let's say we mix A and B. And one of them is in very dilute concentration. For the other one, for B, most molecules of B are just going to see themselves. They hardly know that you've mixed any molecules of A in there. For them, it's pretty much an ideal solution. They think they're in an ideal solution. Which is to say there's an entropy change in mixing. But hardly any of them experience interactions with the unlike molecules. For the dilute molecules, there is a change. You can't use Raoult's law any more. But at least we can look at the slope of the curve and say, OK, at least in the dilute solution case for a little while it's going to be linear. We can understand it. We can tabulate it. So let's look at how that works.

Alright. That limit is something that has a name, that's called the ideal dilute solution. Not to be confused with the ideal solution. Where both constituents follow Raoult's law, as we've seen before. So ideal dilute solution. We're going to just look at these limits. So, if we start with the ideal case, so let's imagine we're going to look at carbon disulfide again. Here's $p^*_{CS_2}$, which is our p^*_B . And this is x_{CS_2} , or x_B . OK, well, what happens if we've got almost pure carbon disulfide. Well, what's going to happen is in this limit, like I was mentioning, up here the CS_2 pretty much sees other CS_2 . It thinks it's in an ideal solution. It's going to look like that.

Now, let's go to the other limit. So this is the limit x_{CS_2} equals x_B approaches one. Raoult's law. Two, the other limit. x_{CS_2} approaches zero. We're down here. So it's definitely not going to be the same. Because now, every molecule, every CS_2 molecule, is completely surrounded by acetone. So they all feel the energy of mixing. Because there are hardly any of them there. So every one of them is, it's very rare for one to find a neighbor of its own kind. And this is a case where there's a positive deviation from ideality. That is, the interactions are less favorable between unlike species. So, it's up here. Doesn't like that. It says, get me out here, I'd much rather be in the gas phase, compared to the ideal case, then surrounded by all these acetone molecules, right? So that's what'll happen. And now it's up to the artist. But in some way there's going to be a set of values in between. And the ideal dilute solution by itself isn't going to tell us about that. It's telling us about the two limits. Now, if we follow this, and I can see I'm going to be in trouble. But I can do a little creative bending of the line here. If I follow this slope up to here, it'll intercept somewhere. That has a name. It's called the Henry's law constant. I can write it as K_{CS_2} , or K_B .

So the point is, that at least for some range of concentrations, the variation is linear. And what that means is, if I

know this Henry's law constant, for CS₂ mixed with acetone specifically, it would be different. If it's mixed with something else, right? Other kinds of interactions with different energies will have a different slope. But if I know that number, it's still useful. Because at least for that pair of constituents, I know the dependents for some range of concentrations. So this is Henry's law. $p_{CS_2} = x_{CS_2} K_{CS_2}$. Not quite as convenient as Raoult's law. That number, I don't need to know what the other constituent is. It's just a property of CS₂. It depends on the temperature, but not the other member of the mixture. This one does, but still there's at least a substantial number of these things tabulated. Especially for important mixtures. So it becomes useful for dilute solutions. And there's an awful lot of chemistry. There's an awful lot of biology that happens in relatively dilute solutions.

OK. I'll leave it at this point. Next time we'll look at the total phase diagram, just like we did last time looking at both the liquid and gas coexistence curves, and seeing what the behavior is as a function of mole fractions. And we'll talk about distillation and so forth in non-ideal liquids.