

Physical Properties of Solutions

Colligative Properties

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We've been looking at a variety of different physical equilibria. We started with considering the equilibria involved with phase changes, going from a liquid to a vapor, going from a solid to a liquid. Then we started to look at what happens in mixtures. What happens when we have a solute dissolved in that material? How does that affect what happens with the equilibrium of solute and solution and that equilibrium? Now we're going to look at the two ideas together. What happens when we take a solute and put it in a solvent, another material? What happens to the properties of that solvent? What happens to its vapor pressure? What happens to its boiling and freezing points? These are examples of colligative properties and we'll define that in just a moment. But again, our focus now is going to turn to how dissolving a solute in a different material affects the properties of that host material, of that solvent.

Let me start by telling you something that may not be very intuitive to you. It turns out that if you take a solvent that has a vapor pressure that we can measure, and remember that's an equilibrium between the liquid and the vapor, and you put a solute in. You dissolve a solute into that liquid phase. You actually change the vapor pressure of that material. So, again, looking at a cartoon here, what I'm saying is, if we focus on the equilibrium between a liquid and its vapor, and remember what vapor pressure was. We could measure that equilibrium, vapor pressure. It turns out that if dissolve, and I illustrate by these little red dots here, if we dissolve a solute into the liquid, we actually lower the vapor pressure of the solvent. Now, that's a tricky idea, how that works. Let's make sure we understand the experiment first and then we'll try to get into what on earth is going on here.

If we look at a plot of vapor pressure, so again, we're measuring the vapor pressure, as a function of how much solute we put in. And for the sake of simplicity, I'm going to assume our solute is ideal. What I mean by that is, I'm going to insist that the solute be absolutely non-volatile, for the moment, so we don't have to worry about that pressure, and also that it has no significant attractions to the solvent. I'm going to assume that those no strong bonding taking place at all between the solute and the solvent, just that we're dissolving it in there. And remember that's going to primarily be an entropy concept then, that this is just dissolved in there simply because there's more room for the solute to move around in, more disorder. Yet we see again a decrease in the vapor pressure.

So, let's go on to this. This again is referred to as Raoult's Law, the notion that that vapor pressure decreases in a linear fashion as we increase the amount of solute. And as I mentioned, this is an example of what we call a colligative property. Now here's the interesting thing about a colligative property. Colligative property depends only upon the concentration of the solute, but not on the properties of the solute itself. In other words, in principle, it makes no difference what the solute is, what the chemical properties of the solute are, that they will all obey the exact same laws. And it depends again only on concentration. So that says with respect to Raoult's Law, that it makes no difference what you dissolve in the solution, nonetheless, you will see the same exact behavior, that the vapor pressure of the solvent will drop as you dissolve more and more of the solute, whatever it is. So, Raoult's Law mathematically is the following: that the vapor pressure of the solvent is equal to the vapor pressure of the pure solvent (that's what this little symbol is here) times 1 minus the mole fraction of the solute. That's going to give us the same thing. Now, just rewriting this a little differently, using our definition of what a mole fraction is. Remember that's the amount of, in this case, mole fraction of solute is the amount of solute divided by total moles. So, another way to describe that then is the vapor pressure of the solvent is pure vapor pressure times the mole fraction of the solvent. Everything else, in other words. So, again, notice that these two things are exactly the same. Mole fraction of solvent is indeed 1 minus the mole fraction of the solute. Putting it simply, that's saying that $\frac{2}{3}$ is $1 - \frac{1}{3}$. That's just the same way of doing this. I'm just talking about fractions here. Now, using either of these expressions because they are saying the exact same thing, again, that's describing a linear dependence on vapor pressure. The more stuff we put in, the more this drops down. And the big question again is, why?

So, let's return to this picture very quickly. Again, in this ideal solution, the main thing going on here is solute is getting dispersed into solvent. It's free to wander throughout solution. That increases the entropy of the system by having that solute free to move around. Think what happens as we start to remove some of that liquid and put it into the gas phase. By doing that, we're reducing the volume available for the solvent to get lost in. That's actually going to decrease our entropy relative to if the solute wasn't there at all. Because of that entropy change, that actually makes the solution phase a little bit more stable than it would have been if it was pure solvent. And that's what is responsible for this vapor pressure lowering. In other words, we're shifting this equilibrium between liquid and gas, the more solute we put in the liquid, the more we stabilize the liquid, through entropy now, the more it wants to stay in the liquid phase. And so our vapor pressure decreases a little bit as a result.

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Let's actually work a problem where we illustrate that. Let's suppose, then, that we have in this problem listed the vapor pressure of pure benzene is equal to 1.25 atmospheres, and suppose now that we dissolve naphthalene, just another hydrocarbon, in the benzene, and the molecular weight is listed here and the mass is specified. We dissolve it in 78 grams of benzene, calculate the vapor pressure of the benzene in the above solution. Our expectation, again, is that the vapor pressure for benzene will decrease. Now, here's an aside. Naphthalene actually has its own vapor pressure. That won't affect the vapor pressure of benzene whatsoever, so we're not going to worry about that. All we're worried about is how much naphthalene is dissolved. And that's going to be what dictates what the vapor pressure of the benzene is.

So, what do we need to do first? We need to figure out the moles of naphthalene we're talking about. So, 6.40 grams divided by its molar mass gives us 0.0499 moles of naphthalene that we've dissolved in the solution. The mole fraction of benzene then is the moles of benzene divided by the total number of moles. So that's going to be, as it turns out, the numbers happen to work out so that that's exactly 1 mole of benzene, at least to three significant figures, divided by the moles of benzene plus moles of naphthalene. And that's our mole fraction again. That gives us, then, a mole fraction of benzene of 0.95, about 95%, 0.952 is our mole fraction of benzene. And then, finally, plugging it into Raoult's Law, the vapor pressure of the benzene then is going to be 0.95 times the vapor pressure of the pure benzene. So, notice in a way all Raoult's Law is doing is giving you a percentage of the total. It's saying, if there's 95% benzene in the solution, then the vapor pressure is only going to be 95% of its total value if it were pure. That's essentially all Raoult's Law is saying. That is what's causing this vapor pressure lowering. So, multiplying 0.95 times the vapor pressure again of pure benzene gives a value of 0.119. Notice again, it's less than the vapor pressure of the pure liquid. And that's exactly what has to happen if we're dissolving a solute, according to Raoult's Law.

Now, I've said all along that we're counting on the fact here that benzene and naphthalene have no significant interactions with each other. In other words, I'm assuming that ΔH is zero for the process of dissolving the naphthalene and the benzene. Well, what if that is not true. What if there is in fact a significant attraction between solute and solvent? Or, what if the solute disrupts significant attractions between solvent and solvent? Then we have something called a non-ideal solution, much in the same way that we talked about a non-ideal gas, in that we are now forced to not ignore anymore attractions between molecules. That's going to cause deviations from Raoult's Law. Raoult's Law will no longer be completely independent of what you're dissolving. In fact, there is no simple law that is going to describe it, but we can qualitatively predict how it's going to deviate from the ideal situation. Again, much like we did with ideal gasses.

So, let's see if we can predict what's going to happen here. Let's first of all consider a situation where when we dissolve the solute, we have very significant interactions between solute and solvent. So we have a lot of attraction. ΔH is going to be negative in that there is an overall release of energy when we dissolve it. That's going to stabilize the solution phase even more than just due to entropy. By stabilizing the solution phase, we drop from the ideal situation, the green line here, down to a little bit lower energy. That means that we have to pay an even higher price to go from the liquid phase to the vapor phase. If we have to pay more cost, our vapor pressure arguably is going to be a little bit lower than what we expect for the ideal solution. And, so, indeed, Raoult's Law starts to deviate from ideal behavior, that's the green line, in that the more solute we put in, the vapor pressure drops but it drops a little bit faster than Raoult's Law predicts. Conversely, if we have an endothermic situation, where a way to think of that is, as we put in the solute, we're causing more damage breaking bonds between solvent and solvent than we are by making up by solute/solvent. Then we have a situation where, overall, it costs us some energy to make the solute. That causes the energy to be higher. That means the difference in energy between let's say, instability between that solution and the vapor phase is less than the ideal case. That means the vapor pressure is probably a little higher than we would expect for the ideal situation. As a result, the deviation in Raoult's Law is positive, meaning there is a vapor pressure lowering, but it's not quite as significant as it would be for the ideal solution. So, again, we get this deviation in the positive direction rather than the negative interaction. By looking at that, it actually tells us about what's going on in solution. In other words, if we look at Raoult's Law and see how it deviates, or rather we do an experiment, see how the experiment deviates from Raoult's Law, that gives us some insight as to whether the overall process of dissolving is endothermic or exothermic. And so, again, we make that tie between the molecular level and talking about bonds and whether they are being broken or made and the entropy involved in mixing and so forth, and the macroscopic level where we're talking about changes in something like vapor pressure, in this case.

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Raoult's Law tells us that if we add a solute to a solvent that the vapor pressure of that solvent will decrease and it depends on how much solute you add. The more solute you add, the lower the vapor pressure goes. And what we've got to ask ourselves at this point is, who the heck cares? There's got to be some reason for us to talk about this because I mean we're not going to in general care about very small changes in vapor pressure. But what we're going to see is that small changes in vapor pressure have very profound consequences with things as common as boiling points and freezing points. So we're going to make that connection now.

First of all, let's review what Raoult's Law is telling us. Mathematically, it says again that as we increase concentration of solute, no matter what the solute is, remember this is a colligative property, that just depending upon how much we have dissolved in the liquid, that that will lower the vapor pressure of the solvent, not of the solute now, of the solvent. So, we increase amount of solute, we see a decrease, a steady decrease in the vapor pressure. Now what does that have to do with something like boiling for instance?

Well, let's take a look. Now this is a diagram we've seen before, but it can be a little intimidating so let's walk through this. First of all, I want you to ignore the pink line for a moment. Just look at these other three lines. This is a phase diagram and let's suppose that it was the phase diagram for water although, in fact, it isn't. In water, we would have this leaning this way. But this in general a generic phase diagram. And so this is the liquid gas interface here in green, for the pure liquid. This is the solid and liquid interface and this is the solid gas interface in red here. Remember, this is the triple point, the point where all three phases coexist. Now, remember that the normal boiling point, the point at which we get boiling at one atmosphere is the point at which the vapor pressure curve intersections with one atmosphere. At that point, we get boiling, as long as we're at one atmosphere, and this is the temperature at which that occurs. Now, look what happens when we lower the vapor pressure by adding a solute to the liquid. The pink line again shows the lower vapor pressure at a given temperature, and look what happens. This now intersects the one atmosphere line at a higher temperature. That insists that the boiling point, the normal boiling point is now higher than it was for the pure solvent. This is what we refer to as boiling point elevation. Another colligative property, a property that does not depend on the chemical nature of the solute, but it does depend on the chemical nature of the solvent. It depends what we're talking about boiling. But not about what we put in it, only about how much we put in it. The more we dissolve, the lower this drops, the further we push the boiling point out, the higher the boiling point becomes. So an example of that that you're all familiar with is antifreeze. Well, this also could be called anti-inflammatory-boil. It has the exact same effect in the engine. We dissolve some solute, the antifreeze in this case, into boiling water and we're going to change the boiling point of that solution. We're going to lower it. So let's do that right now. In fact, let me read the temperature. On this thermometer, it's about 98 degrees right now. And so we know that that would be 100 if we were at exactly one atmosphere. And so, we'll go ahead and pour in a little bit of this and you'll notice the boiling stopped and I can look at the temperature. Now, initially, my temperature drops a little bit because I'm adding something that is going to absorb some of the heat, but when this thing comes back to boiling again, we will look at the temperature and we'll see that in fact the boiling point has, in fact, increased. So, we'll let this thing increase while we keep talking here and we'll come back to it. But, again, the notion of antifreeze for an engine is simply, again, an example of using or exploiting a colligative property. What we're doing is taking a solute, putting it in water in the radiator and that increases the boiling point of the water. We can do the same thing with any number of different substances. Anything, as long as it dissolves in that water, it's going to change the vapor pressure of water. And, in fact, a number of different types of substances have been used in the past in engines in this way, by raising the boiling point. Now, I mentioned that this also has to do with freezing. After all, this is called "antifreeze." We're getting back to our boiling point again and now our temperature is just about 105 degrees, so we've raised our temperature a fair bit in this process by adding again a little bit of a solute.

Now, again, about freezing. Same idea here. If we dissolve something in solution, what we're going to do, just like with boiling, is we're going to stabilize the solution. Remember back to Raoult's Law, due to entropy, we stabilize the liquid phase; that makes it a little more stable than the vapor phase that caused us to have to work a little harder to get it to boil. The same thing is going to be true about freezing. It's going to be a little bit more difficult for us to freeze it. We're going to have to go to a little lower temperature. Let me show you how that works.

Once again, same diagram as before, our phase diagram here. The pink line, once again, indicates the ideal solution whereas the green line indicates our pure solvent. When the vapor pressure drops, we said that the boiling point increases, and also notice what happens to the triple point, down here. Notice that the triple point actually decreases in temperature. Again, simply because we're lowering this curve. As the triple point drops down, that ends up causing this solid liquid interface also to shift over and as a result the point at which we get freezing, at one

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atmosphere, has shifted to a lower temperature now. Bottom line is this, as we make the solution more stable by adding our solute, we make it more difficult to boil and more difficult to freeze. In other words, we have to remove more of the thermal energy before we can finally get it to freeze. Once again, because we are making the solution more stable by increasing its entropy or the entropy of the system at least. So we describe that in terms of a mathematical relationship for both boiling and freezing. They look almost identical. Delta T refers to the change in boiling temperature in this case, T_B , the change in the boiling point, that means the difference between the boiling point of the solution and the boiling point of the pure liquid that that is equal to a constant. This is called the boiling point elevation constant times concentration. Now, just to cause you grief, we're using concentration units of molal in this equation, not molar. So, unfortunately, this is not moles per liter, this is moles per kilogram of solvent. But, again, the important thing to see in this is that the change of boiling point is directly proportional to the amount. Again, that tells you it's a colligative property. Likewise, the freezing point depression is a constant times, again, molal. The higher the concentration, the lower the freezing point drops. Notice the minus signs. So our freezing point is decreasing whereas our boiling point is increasing.

Now, let's go to a table that describes various different boiling points and freezing point constants as a function of solvent. Now, remember a colligative property is independent of solute. But, it's going to depend on the chemical nature of the solvent. Different solvents boil at different points and as you might expect, their constants describing how much their boiling points change are also going to be different depending upon what the solvent is. So, for instance, water down here at the bottom, we have a boiling point elevation constant of 0.51. Notice that that's only about half of the size of ethanol, for instance, which has a much more pronounced effect. In other words, we're going to see a more sensitive change of boiling point for ethanol than we did of water. Our boiling point constant, again, that describes that relationship between concentration and change in temperature. Likewise, we can talk about the freezing point changers that we're going to see for such a system for a range of different solvents in this case. And listed in red here are just the different boiling points associated with these different solvents. So, again, it's these numbers that we're going to look up that we're going to use to make this connection between how much stuff we have in solution and what happens to the boiling point. So, in a moment we will go ahead and do an example of a problem where we make the connection between boiling point or freezing point change and concentration. And, in fact, what we're going to do is use that information to determine a molecular weight of a substance.

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When a solute is put in a solvent, the boiling point is raised and the freezing point is lowered. Now, remember this is an example of a colligative property. And again, we might want to ask ourselves, so what's the big deal. Well, there's a lot of practical applications of that simple idea. Remember that it's independent of the chemical nature of the thing you're dissolving. So, if you're worried about boiling point rising, for instance, one application we talked about is boiling in an engine. Let's suppose that you're in Denver and the atmospheric pressure is lower and so that means the water is going to boil at a lower temperature, as we have seen before. And you want to be able to somehow speed up the time it takes to cook spaghetti or bring yourself back up to a higher temperature. Well, now you know one way to do it, you can add salt, dissolve it in the water, that raises the boiling point of the water again. So, there's lots of practical things that you can do as far as manipulating the temperature at which something boils at. Another application that you're all familiar with, or certainly if you were in the East Coast. You're familiar with when the roads freeze, trucks go out and they sprinkle salt on the roads. They sprinkle the salt on the roads simply to dissolve into the liquid phase and that lowers the freezing point and that causes the roads to melt, as long as you don't get too low in temperature. Understand that if the temperature is too low, so that it is below the freezing point of the solution, well then you're not going to get any melting in that stage. So, again, there are lots of common applications for where you would want to lower a melting point or raise a boiling point of a substance.

Let me show you another one here. Let's suppose that one day, when I was upstairs, I found in my nine year-old's room, a mysterious white substance behind his socks in the drawer. And I was a little bit suspicious about the friends he had been playing with and just what this material might be. So, I very carefully removed it from the drawer and immediately took it to my lab. Well, I'm going to use the notion of boiling point elevation to determine what this substance is. Now I'm not going to just use boiling point elevation. I'm going to take some other information as well. I can use a different technique called combustion analysis and that will tell me simply the ratio of one atom type to another in this material. So, suppose I find that there is a certain percentage of carbon in this material and a certain percentage of hydrogen. And for the sake of argument, let's say that's all that there is in here, carbons and hydrogens. But I don't know what the substance is and in particular, I don't know what the molecular weight of this material is. How am I going to find that? Well, what I'm going to do is I'm going to take a solvent, in this case chloroform, that I know the boiling point for. And I can just read what the boiling point is, in fact. I'll weigh out a certain amount of material – an arbitrary amount – let's say 5 grams. And I'll put this stuff into the solvent. Now, that's going to cause a boiling point elevation when I do this. Let's suppose that I weighed that out exactly. Pretend I weighed out exactly five grams and I get a boiling point change as a result of that five grams being dissolved. Now, remember, this being a colligative property, it is independent of the chemical nature of this stuff. But it does depend on the amount of moles per kilogram solvent that I put in. So, remember this is the relationship that we're talking about. The change of temperature between the boiling point of the pure substance and then the solution. That is directly proportional to the concentration in terms of moles per kilogram solvent that I have. And what ties those ideas together, those two numbers, is this guy, the boiling point elevation constant. Which, for chloroform, I know and we will get to in just a moment. By knowing that number and by knowing the change in temperature, which I can read right off the thermometer, I can determine my concentration. Now, if I know how much mass I put in and I know how much moles per kilogram solvent I must have had to cause that temperature change, the only piece I'm missing is what my molecular weight. So I can determine my molecular weight by knowing those other things. Once I know the molecular weight, that gives me a good handle on what the substance actually is. So, again, what we're going to do is we've determined a boiling point change by putting 5 grams in. I am going to, first of all, figure out the ratio of carbon to hydrogen for you. Once we know that ratio, that will be an empirical formula but it won't tell us the molecular formula. To figure out the molecular formula, I need to know the number of moles that I put in there. The way I'm going to figure out the number of moles that I put in there in that 5 grams is by figuring out my concentration of moles per unit of volume of the solvent and that I'm going to be able to figure out from this colligative property, by knowing my change in temperature.

So, let's go ahead and do that. So here's our problem. We have an unknown sample, elemental analysis tells us that it's 93.7% carbon and 6.3% hydrogen. Now, remember, this is just percent by mass. That says the total mass of carbon divided by the total is 93.7%, and likewise for hydrogen. When I take 5 grams of this material, and again, pretend that I weighed out exactly a certain amount, I dissolve it, let's say, 100 grams of chloroform so I know my mass of solvent that I had so it's going to be easy for me to figure out the molal concentration. The boiling point is raised from 61.2 degrees to 62.6 degrees. So that's going to give me my information about what my temperature change is for the boiling point. My goal is to find the molecular formula for this stuff. And of course what I need is that tie between concentration and boiling point change and that is the boiling point elevation constant given for chloroform down here.

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So, first of all, let's go ahead and figure out what our moles of carbon to hydrogen would be. That's going to be the first important clue here. I know I've got 93.7% carbon. So let's take a convenient mass that is going to make this work out easy, because I could take any arbitrary amount. Let's suppose that I had 100 grams of this stuff. Well, 93.7 grams of that 100 grams would be due to carbon. So, I'm going to take that 93.7 grams, divide it by the atomic mass of carbon and I'm going to end up with 7.81 moles of carbon, if I had a 100 grams of this stuff. Now, I'm going to take 6.3 grams, which is the hydrogen, remember 6.3% hydrogen. So 6.3 grams of that stuff would be hydrogen. Divide that by its atomic mass and that gives me 6.3 moles of hydrogen. Now, in that 100 grams then, that hypothetical 100 grams, I've got a ratio of carbon to hydrogen of 7.81 to 6.3. That turns out to be a ratio of 5:4. If I just simply take that ratio again. So, what I know so far is that I have 5 carbon atoms for every 4 hydrogen atoms. But what I don't know is, does the molecule actually have as its formula C_5H_4 , or does it have a formula $C_{10}H_8$, or maybe its $C_{15}H_{12}$. See I don't know the molecular weight of the thing, only the ratio of one atom type to another. So, I'm going to use the colligative property to give a good estimate for what the actual molecular mass of this material is.

So, once again, we're going to start with the idea that I can measure directly the change in temperature caused by me putting that 5 grams in here. It turns out to be 1.4 degrees and that's 1.4 degrees Celsius, which is the same as 1.4 degrees Kelvin, and that remember is equal to or constant for chloroform times the concentration. That's what I want to know, my concentration. Adding 5 grams gave me a certain concentration causing that temperature change and I need to find out what that is. So, just rearranging then, $1.4 \div 3.63$ gives me my moles per kilogram solvent, remember concentration in molal is equal to 0.386 molal. So that's my concentration of the substance, 0.386 molal and I want to know specifically how many moles I put in that 5 grams. So I got my concentration but I want to know how much stuff I actually put in this beaker. So, to do that, I'm going to take my molal concentration and multiply it by the actual mass of the solvent. So, if I have 0.386 moles per kilogram of chloroform, then I would have 0.386 times point one kilograms. That's 100 grams and that's going to give me 0.0386 moles. So, again, all I did was I know I have 0.386 moles per kilogram. I'm going to have a tenth of that if I only have a tenth as much of my mass of solvent. So, now I know my moles of this white stuff that I put in, in that 5 grams that I put in to cause that boiling point change.

So, I'm almost there. 0.0386 moles is in that 5 grams. So, 5 grams divided by the number of moles that it is equivalent to. And that is going to give me my molar mass. Remember, after all, molar mass is just grams per mole. So, I'm taking five grams of stuff and how many moles I have in that 5 grams. That gives me my molar mass. So my molar mass is 128 grams per mole and if I indeed had C_5H_4 ; that would only be a molar mass of 64 grams per mole. So that's telling me that I have something twice as big as that simple empirical formula. In other words, in order to have that molar mass, I need to have a molecular formula of $C_{10}H_8$. Well, that turns out to be the molecular weight or molar mass of naphthalene. Naphthalene is mothballs. And so my son had some mothballs stashed away in his drawer, probably not put there by son but by his mother and so I guess he's out of the doghouse.

Anyway, the connection that we made here is using a colligative property, the change in this case in temperature of boiling and how that directly connects to concentration of the solute that we put in to cause that change. By knowing concentration, we can go from there to moles because we knew how much stuff we put in, the mass of it, we could figure out the number of moles by knowing the moles and how much stuff we had. That gives us then the molecular weight of the material, or the molar mass of the material.

In fact we can use this strategy for a number of different colligative properties. We could have used it for vapor pressure lowering, we could use it for freezing point depression, but in fact the one colligative property we have not spoken about yet that is coming next is the most sensitive to small changes in concentration of solute and that's the one you use most actually in laboratories to determine molar masses of materials. That last colligative property is osmosis.

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We've seen how, by taking a solute and dissolving it in a solvent, we change fundamental physical properties of that solvent. We change the boiling point, the freezing point, the vapor pressure... And our explanation for all of this had to do with the fact that when we dissolved the solute in the liquid, we increased the entropy of the system. By doing that, we're in a sense, favoring the liquid state over its gas or solid states, and as a result again, we got these changes in the physical properties.

There is one other colligative property that I want to discuss. And that is osmosis. And, like the other colligative properties, it is referred to as a colligative property because it is independent of the chemical nature of the solute. The way osmosis works – so in order to explain osmosis to you – let me start out with a thought experiment.

Imagine we took a tank and imagine that the tank, we partitioned with a membrane and the membrane was such that it had small holes in it that would allow solvent to pass freely through those holes, but would not allow the transfer of solute particles. Now the solute particles are just simply too big. We could imagine our cartoon; that would show that idea. If this is the membrane, if we're on the molecular level here, suppose the little brown dots are solvent, that they truly can pass through these holes, but the solute particles, the red dots, they are not able to get through that membrane. So remember, solute cannot pass through the membrane, solvent can move easily in and out.

Well, returning back to our thought experiment then. If we then set up the experiment such that on the right side, the right half, we introduced a solute. Then we might expect the solvent particles to transfer across the membrane such that we increase the volume of the solution, decreasing the volume of the pure solvent. That would cause a change in pressure, if we could measure again as a thought experiment, the pressure buildup as more and more volume transferred across that membrane to the right side, and we could measure what that pressure would be. Eventually the system would come to an equilibrium where the physical pressure of pushing the solvent molecules back across the membrane due to a pressure buildup equaled this driving force of the solvent molecules wanting to be over on the solution side of the barrier.

Now, we could talk about that pressure that we measured as an osmotic pressure and, in fact, that pressure would be proportional to the concentration of our solute at that equilibrium point. So, M here is just "molar" or moles per liter, our final solution concentration; R is the gas constant as it turns out in liter atmospheres per moldecree Kelvin and temperature is in Kelvins. And so that would describe then, this pressure. Now the important point about this is simply that the pressure depends on concentration. If we know what the pressure is, we can determine concentration of – let's suppose it's an unknown molecular weight solute, for instance. Now, this is not a convenient way to actually do this experiment. A much more convenient way in practice to do this is the following.

I'm going to show you an experiment that we set up yesterday, and in this particular case, what we did was we started out with just solute inside this tube – there was no solvent initially, or a very minimal amount of solvent at least – and we've got at the bottom of this tube here a semi permeable membrane which, remember, again, allows the transfer of solvent in to the tube, but does not allow for the solute to transfer out. We set that up yesterday, went home, came back, and now, look what's happened. The solvent molecules have moved inside the membrane, pushed up the volume until we reached a particular height. Now, I could come back a week from now and this wouldn't change anymore. This has leveled off at its final equilibrium value. Well, what are the forces at work here that are in balance. We have on the one hand, osmotic pressure, this notion that the solvent wants to be on the side of the membrane where the solute is. On the other hand, we have the mass of water pushing down, being pushed down by gravity, acceleration due to gravity, forcing the solvent molecules back out of the membrane. So, although again we have an equilibrium, it is dynamic in that there are solvent molecules always moving in and out of the membrane, but there is no net change in the height now, because we have this balance again between force due to gravity or pressure, if you will, due to gravity, and the osmotic pressure. Well, we can describe that in terms of the osmotic pressure being equal to the density of the liquid times acceleration due to gravity, that's g , times the height of the column. That's describing again what the pressure is pushing down on this column.

And so, it is convenient to go in the lab, set up this experiment, measure the height and by knowing acceleration due to gravity, which is just a constant, and the density of that liquid, we can relate that to osmotic pressure and from that point, relate it to concentration. That's the key link again. Relating concentration of something that is unknown to something we can easily measure.

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Now, let's go to just a little bit better picture of this so you can get a little bit better idea of what that membrane looks like. And, again, you can imagine, this is very typical of how you might set up an experiment like this. This is called a thistle tube and we could wrap a membrane around the bottom part of the thistle tube and just dip it into a beaker of pure solvent. That pure solvent can transfer across that membrane and it starts to push this liquid up. So, we might start it here, let's say, or we could start it down here; it makes no difference where we start it. It makes no difference at all. All that's important is what the final height is once we reach our equilibrium. So this is pushed up to some final height and the height that we want to measure is not from here. It's from the liquid down here, at equilibrium, compared to here. How much above the rest of the liquid have we pushed that column of water? That times density times acceleration due to gravity is going to give us the pressure pushing out across the membrane, which is going to be balanced by the pressure, the osmotic pressure, pushing in on the membrane.

Now, we'll do a calculation to show you how this works. Because the only tricky part about this is the units can be a little confusing. But before we do that, let's just compare osmosis, or osmotic pressure, with other colligative properties. Let's suppose that we had again the problem of wanting to determine the molecular weight of an unknown material and we only had a little bit of that material, what would be the most sensitive colligative property to use to connect mass to concentration, in terms of moles and that, therefore, would give us, again, a molecular mass for the material. Okay, so as an example, let's suppose that we had a protein, a very large molecule, molecular weight or molecular mass of 23,000 g/mole. And so, we'll take two grams of this stuff, which is a lot of protein to biologists or biochemists, that's a huge amount of material for them to get their hands on. So, we're being very generous by saying that we have this much material. But understand this – that the molecular weight of the protein is so big that two grams really isn't very much at all. This is not – again, the molecular weight is so large here, that two grams corresponds to a very tiny fraction of one mole for this protein. We're going to take that two grams and we'll go ahead and dissolve it in a 100 milliliters of water and ask, what are the changes to boiling point, freezing point, vapor pressure, as a result of adding the solute to the solvent. Well, the vapor pressure lowering is a whopping 4.8 times 10^{-7} atmospheres. That's a number you're going to be very hard pressed to even measure. That's such a small difference as far as the pressure is concerned. The boiling point elevation turns out to be .0004 of a degree Celsius or of a Kelvin. Very, very small change there. Again, you're going to be lucky if you can find a thermometer that you can read to that degree of accuracy. The freezing point elevation is not much better. It is about .001 of a Kelvin difference. So, again, these are all very, very small differences that are actually, for all practical purposes, not measurable differences.

Compare that to osmosis. In the case of osmosis, we end up with a 220 millimeter rise, so .2 of a meter rise a very significant difference in the height. So, even for very, very low molar concentrations of material, we can measure significant differences in osmotic pressure. So, let's go ahead and look at an example of what you might be asked to do. Let's suppose we're talking about a maple tree. This is one of the many places where osmosis shows up in nature. In a maple tree, let's suppose that we have an average concentration of sucrose of 3 percent. So, we'll say that that's about a .1 molar solution of nutrients, let's say, that are in the veins of this tree and so forth. The rising of the sap in this tree is due primarily to osmosis. So you can imagine the membrane as being the roots of the tree and water being pulled out of the ground and sucked up into this tree; again, simply by this notion that the water solvent will want to get where there's a lot of solute dissolved. Again, the nutrients of the tree, the sugar in this case, primarily. How high will the sap actually rise, given this temperature. Let's go ahead and assume that the density of the liquid is one gram per milliliter, the same as that of water.

So, using the osmotic pressure formula that we saw just a moment ago, the osmotic pressure, which again is abbreviated as p normally, is moles per liter concentration times the gas constant times temperature in Kelvins. So, our concentration times our gas constant in liter atmospheres per mole Kelvin times the temperature. That gives us an osmotic pressure of 2.4 atmospheres. Now, we want to relate that to height. After all, we're trying to figure out high the sap is going to get in this tree. So, 2.4 atmospheres. I'm going to now have to convert this to a set of units that are compatible with meters or millimeters or some measurement of height as well as meters per second squared, which is the units for gravity. So to do this, I have to convert this into Pascal. So, I'm going to multiple 2.4 atmospheres by the conversion factor 1.01×10^5 Pascals per atmosphere. That gives me 2.44×10^5 Pascals, and remember, that that is equal to density times gravity (acceleration due to gravity) times the height of the column. And that, in this case, is what we don't know. So, 2.4×10^5 is equal to – now I'm going to put in a couple of conversions here. This is the density – 1 gram per cubic centimeter. I'm going to convert grams to kilograms. I'm going to convert cubic centimeters to cubic meters. And finally, multiple this by acceleration due to gravity rather, in meters per second squared –that's just a constant again for gravity – and height is our only unknown. So taking all this into the

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denominator, we end up with a height of just about 25 meters. So, that's an enormous distance of water that we can push up into this tree, all due, again, to osmotic pressure.

So, just summarizing then – we have osmosis or osmotic pressure, vapor pressure lowering freezing point depression and boiling point elevation, all the direct result of the notion that a solute dissolved in a solvent, we end up with an increase in the stability of that system due to the entropy gain. And as a result, again, we see these changes in physical properties.

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We've been talking about how a solute dissolved in a solvent gives rise to various physical property changes, boiling point, freezing point, and so on. What about a solute, that when we added to the solution, broke apart into more than one particle? In other words, just schematically, suppose that we had a solute molecule of some kind that once we put it in solution, let's say, split into two pieces. Well, the number of particles in solution then would actually be twice as much as we would be counting on based on what we started with. And remember that colligative properties depend on the number of things in solution not the chemical nature of whatever the things are in solution. This particular situation comes up most commonly with ions and so what we're going to do now is talk about colligative properties, but of ionic materials rather than molecular materials.

When we have solutions of electrolytes, our formulas take on very, very similar meaning, but they have one additional term. If we look again, as an example, at boiling point elevation or freezing point depression, like before, they are equal to the boiling point elevation constant of the solvent times the molal concentration but there is an additional term here now, in this case, new. Now this sometimes will show up in textbooks as "i" or other letters but this extra constant here, called the van't Hoff factor, will be one if we get a one-to-one correspondence between the amount of moles of stuff we put in, and the amount of moles of stuff that is dissolved. But, for the situation I just described, where a molecule, once it is in solution, breaks into pieces, this can take on a different integer value. For example, suppose that we are thinking about sodium chloride. For every equivalent amount of sodium chloride, or I should say, for every one molecule, if you will, of sodium chloride, even though we know it is not in discreet molecules, that I put in, I get two ions, a sodium ion and a chloride ion. So one mole of sodium chloride as measured out will actually give me one mole of sodium and one mole of chloride, or two moles of ions. So, in that case, this factor here, new, would actually be two. It is simply a fudge factor that corrects for the fact that I get more particles of solution than I started with in a sense. If I look at this ionic material, ferric bromide, or FeBr_3 , I'm going to end up with a total for every one mole of iron three bromide, I'll end up with a total of four particles, or four moles rather, of ions. One iron and three bromides. Well, what about acetic acid? Why would it have a new of 1? We've written a description for acetic acid, that acetic acid goes to acetate ion plus H^+ , so why shouldn't new be 2? After all, we can write that equation down? The reason is, if you recall, acetic acid is a very weak acid, meaning that it dissociates only to a very small percentage in water and I'll remind you we looked at an example of that and we probed that using an electrical conductivity apparatus. Acetic acid, which is vinegar, starts out at neutral and when I pour it into the water, we see just a tiny bit of glow indicating that there is a very small amount of ionization but for the most part, there is virtually almost entirely acetic acid in there still, not acetate and H^+ . So new is very close to 1 because acetic acid acts very much like a neutral molecule. Again, 99.99% of it, in fact, the neutral form of acetic acid. That's in great contrast to sodium chloride, which we said had a new of 2, because in this case we get complete conversion into the ions that make it up. And so of course the light burns very brightly now because we have high amounts of ions.

So, what is this good for? Well one thing certainly it's good for is for correcting all of our colligative properties. I mean this would work for osmotic pressures well, it would work for Raoult's Law as well, for correcting those equations to also include things that will ionize in solution. In fact, you might even ask what about things that when you dissolve them, they dimerize instead of split in half? So, suppose it's the exact opposite situation. Suppose you throw in, for instance, acetic acid in solution in very dilute concentration in a different solvent than water. Acetic acid tends to dimerize, to form discreet units of two as they connect to each other and so we actually in that case have half as many particles as we're expecting to have. So, in that case, new would be a half instead of two. So, new gives us the information about whether particles are coming together and sticking more than we're expecting or whether they are splitting apart into pieces.

So let's use this to try to analyze what's going on in solution. Suppose, here's a problem. Here again, suppose that we are trying to figure out how potassium ferrous cyanide splits apart into solution. So that's our formula but how does it ionize? We're pretty sure that the potassiums break off because we're used to potassium plus ions. Does it in fact form $\text{K}_3\text{Fe}(\text{CN})_6$? Or is there some other combination that we're going to find? If it indeed split into those ions, we'd have 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 different ions for every 1 mole of the potassium ferrous cyanide. So again one mole of this salt gives us ten ions if indeed it broke apart the way I just described. Well, does it do that or is there some other connection or way that this thing separates? So, to probe that, what we're going to do is take a little under a half of a gram here, point four nine grams, of the salt, dissolve it in one hundred grams of water. We know the freezing point depression, that's found to be experimentally point eleven degrees Celsius. So I know I'm going to use, again, freezing point depression this time to tell me something about what's going on in solution. I know my freezing point depression. And I want to know how many ions are actually in solution for this particular thing. Here's my

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freezing point constant. I know my molecular weight for the ferrocyanide, the potassium ferrocyanide, so my problem is going to look this. Here's my thought process. I know what the freezing point change is. My temperature change in the freezing point for pure versus solution. I can relate that to moles, in particular concentration molal, moles per kilogram of solvent. And then I can compare that with what I actually put in. I have a pure substance that I know the molecular weight for. The only thing I don't know in this case is new freezing point. I know my change in temperature, I know my molal concentration, I know my constant. The only unknown is new. And that is going to tell me about what the salt is doing once it is dissolved. So, here we go then. We're just going to solve for new. I just said in English what I wrote down here. I need to solve for molal concentration. That, remember, is going to be, in this case, moles divided by kilograms solvent, so moles is going to be grams divided by grams per mole and that is going to give me moles of the stuff that I put in, divided by kilograms of solvent, in this case point one kilograms or one hundred grams. And that gives me a value for my molal. So, point zero one five moles of solute per kilogram. Now, not moles of ions, moles of solute in this case. Now, the only unknown is new and so new is just going to be coming back to this equation here; I've just rearranged this, new is the change of temperature divided by our constant divided by our molal of the ionic salt that we put in and what I find is that there is a four to one ratio between these three numbers. In other words, if new was one, I wouldn't need this anymore and this times this would equal this. But because new is not one, I know that I am getting ions once I dissolve this material. In particular, I'm getting almost four. This is essentially experimental error. I've got about four ions for every one potassium ferrocyanide that I dissolve and what that tells me at the end of the day is that this does not in fact break into potassium and iron and cyanide, but rather it converts into three potassium ions plus ferrocyanide, which is $[Fe(CN)_6]^{3-}$. So it's telling us that those cyanides are staying tightly bound to that iron. This is an example of what we refer to as a complex ion and we'll see more examples of this later where transition metals in particular very commonly will do this, where they have a lot of other groups attached to them still in solution. So, once again, what I got this time by taking advantage of the fact that this constant new shows up in colligative properties when we ionize materials, is colligative properties tell me, once again, how much stuff I've got dissolved. If I know how much stuff I've got dissolved, and I know how much mass I put in, I can make that connection between how many moles of ions do I have for the amount of stuff that I put in? And in this case, again, what we found was some information about the molecular level. How this compound breaks apart into pieces, in this case, specifically that the ferrocyanide unit sticks together in solution.