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PROFESSOR: Today I want to start us off on a somewhat new topic. Which is phase equilibria. So, recently you've been looking at chemical equilibria. What happens when substances change their chemical structure and interchange, and you've figured out how to calculate where equilibrium lies in the case of chemical reactions. Calculate equilibrium constants, and so forth. Now we'll introduce phase equilibria. So this is a little bit different. You still have a lot of molecules in one state changing to another state, but they're not changing their own molecular structure. They're changing what phase of matter they're in. From liquid to solid to gas. And so the treatment is a little bit different. And there's some new results that are somewhat different from what you've seen in the case of chemical reactions.

So we'll start with phase equilibria in just one component system. So in other words, we're going to start with a single substance and see how it goes from solid to liquid to gas. And we'll from there see what happens in multiple component systems. Where, for example, then we'll be able to talk about solubility and mixtures of liquids and so forth. And into which phase different constituents in a mixture will go. But let's start here.

So, let's say we just have two phases at equilibrium. And this could just look like ice and water. You could have a little bit of ice floating in water. So in this case you have solid and liquid. That could be in equilibrium. And this is going to be at some pressure and temperature. Or, you could have liquid and gas in equilibrium. So let's put a lid on our container. Still have some specified pressure and temperature. And now there's a liquid at the bottom. And a gas at the top. So, you could have equilibrium between liquid and gas phases. And in some cases you have equilibrium between solid and gas phases, depending on the pressure. And a little piece of solid could sit at the bottom and there's equilibrium with the gas above it.

And so, to start, what quantity are we going to need to look at to tell whether the different phases are in equilibrium, or if they're not in equilibrium, in which direction are things going to go? Are things going to change so that the ice will melt and we'll have water or, so the water will freeze and we'll have ice. What quantity is going to tell us about all that? Who thinks they can guess? Give you a hint. We're specifying pressure and temperature. Nobody really knows?

What quantity is it that you've seen from which you can determine everything. Yes. The Gibbs free energy is going to tell us everything. And we're going to frame the discussion in terms of the chemical potential. That is, the Gibbs free energy for a mole. And since there's only one constituent, one component at this point, we just have n . We

don't have different mole numbers for different constituents, we'll see that later.

OK, so what's going to happen is, the value of the chemical potential in the different phases is going to tell us everything. Because you know that at equilibrium, the chemical potential needs to be the same in all of these. If not, let's say the potential energy here is lower in the solid than in the gas, nothing's going to stop the molecules in the gas phase from going into the solid phase. That's what they'll do. If the chemical potential of the water is lower than the chemical potential of the ice, then the ice is going to melt. Because the molecules are going to want to go toward lowest possible accessible chemical potential. And there's the liquid right there. They have access to it, so they can, the ice will melt. And you'll have just water.

So the main point here is that at equilibrium, μ is identical everywhere. By everywhere, I mean in all phases that are at equilibrium. And so if multiple phases are present, μ has to be the same in all the phases. And if it isn't, then the molecules will go into the phase with the lower chemical potential. And this is what is going to guide everything in our consideration of phase equilibrium.

So, OK, what's going to happen? Let's consider our ice water equilibrium. So of course, if μ of the solid is equal to μ of the liquid, which for water it should happen at zero degrees Centigrade. And pressure of one bar, for example, not the only place it could happen. But certainly at that condition. Then the ice and water will be in equilibrium, they'll co-exist.

Now, what happens if you just want some ice water and you take some ice out of the freezer and put it in the cup, and you put some water in? And you see them both there. They're sitting there. Maybe for a while. And yet it's not at zero degrees Centigrade, at one bar. It may be at one bar, you might be out in the room, but it might be room temperature. Does that tell us that this isn't true? What's going to happen? The ice is going to melt. It may take a while. This doesn't tell us about the kinetics of it. And it could take a while, gradually, from the surface inward, for the ice to melt. So the fact that you might see something sitting there with two phases present, that alone of course, doesn't tell you the two phases are in equilibrium. And it may take time for equilibrium to occur.

And what's going to happen if at some pressure and temperature, you have the μ s greater than μ of the liquid. Then which way are things going to go? What's going to happen? You've got to be able to figure this out. Of course. The ice is going to melt. The chemical potential of the liquid is lower. And so molecules are going to move toward that phase. And, of course, if μ solid less than μ liquid, then the water freezes.

All this behavior is something that we can summarize in a phase diagram. So the phase diagram can tell us for all pressures and temperatures, what phase, or what phases, will be present in equilibrium. And so typically, phase diagram might look like this. Where here's our solid. Here's our liquid. Here's our gas phase. So let's just look at what's happening here. If we go to really low temperature, in general, what happens? What phase does stuff enter

when you're at the lowest accessible temperatures? Solid, right? Everything eventually freezes. In fact, really I should make this, leave some room on my axis for that effect. So of course, low temperature you get solid. How about high pressure, what usually happens? You squeeze something real hard. Tends to go into the solid phase.

Now let's warm stuff up. And depending on the pressure, you might go to the liquid phase. Certainly you'll go to the gas phase at high enough temperature. And that's what'll happen. And now, if you start changing the pressure, let's say you're at high temperature and you've got just the gas present, in some big container. Now you start squeezing it. You just apply more and more pressure to the gas at constant temperature. What's going to happen? Forget the phase diagram. You know what's going to happen. You keep squeezing, what will happen eventually? This isn't going to be part of your grade. You can speak up loud, and even if you're completely wrong, nothing bad is going to happen to you. Yeah. It's going to liquefy, of course. You're going to start getting liquid to form. It's essentially Le Chatelier's principle, of course. The liquid occupies less volume. The density of the liquid is much higher. So as you increase the pressure, the stuff wants to go from the gas phase to the liquid phase. Yeah.

STUDENT: [INAUDIBLE]

PROFESSOR: Well, with water you know that at ordinary pressure, you know where the gas-liquid coexistence would occur. So let's say you're there. Let's say you're at the boiling point. And now, you already in some sense know that that's a point that's somewhere on the gas-liquid curve. So now what's going to happen? Well, if you from there keep that temperature constant. You're at the boiling point. And you could easily do this. You've got a pot that's covered, right? And it's boiling. So there's liquid down here and there's gas here. So what'll happen? As you start squeezing, literally what'll happen is you'll squeeze out all the room for the gas. And eventually you'll have all liquid. And in fact, you know what'll happen at that point, if you keep squeezing and you keep the heat on. The liquid will get hotter than the boiling point. Normally that doesn't happen, if you're just out at atmospheric pressure. Because it'll boil. And instead of getting hotter, molecules will simply leave the liquid and go into the gas phase.

So that's what'll happen. If you increase the pressure, you'll liquefy all the gas. And obviously the opposite will also occur. If you just allow the volume to expand and keep expanding, maybe you don't have too much liquid there, you wouldn't have to expand it too much. You'll run out, all the liquid will vaporize. And you'll just have gas at 100 degrees C. You could heat it more if you wanted, but even there. So in other words, changing the pressure if you think about actually executing that in the lab, or in this case even in your kitchen, you'll get the result that you should see on the phase diagram.

So let's just look at this. So we've already talked about boiling. That's what's happening along this line. The line, and I'll explain the end of this in a while, all these lines are coexistence curves. That is, these are where you have

equilibrium between two phases. They coexist in equilibrium. and it could happen for water, for that case, for 100 degrees C and one bar. But that's not the only place. It could happen at a whole bunch of temperatures and pressure. Because as you vary the pressure, you're almost surely familiar with this, the boiling point changes. So the boiling point up in Denver at high elevation is not the same as the boiling point here in Massachusetts right at sea level. Because the pressure's lower up in Denver.

Let's just look at the others. So, of course, this is going from solid to liquid. So we're looking at melting. And then there is solid-gas equilibria in many cases. And this is sublimation. And this endpoint is called the critical point. And there's one point where all three phases are in equilibrium, called the triple point.

So let's look at the various cases. For example, let's look at the melting line. It could be water, it could be water and ice. Solid going to a liquid. Let's just look at them one at a time. What you have there is μ of the solid at some temperature and pressure. Is equal to μ of the liquid at the same temperature and pressure. Now, just if we back off and look at this essentially mathematically, there's an equation here. And there are two free variables. Temperature and pressure. The equation puts a constraint on them. So there are going to be a bunch of solutions along some line or some curve. So in other words, it's one equation in two unknowns. Temperature and pressure. So the solution is a line or a curve. In other words, we could solve for pressure as a function of temperature, or temperatures as a function of pressure, along the coexistence curve. And we'll do that shortly.

Now, if we're in one of these regions, then there aren't any equalities. There aren't any constraints. Because we don't have multiple chemical potentials that are equal to each other. Right here we have three phases in chemical equilibrium. Solid, liquid and gas. So let's just look at that triple point. μ solid equals μ liquid equals μ of the gas. We have two unknowns, or two variables, temperature and pressure. And we have two equations. What that means is there's only one solution, and that's what the phase diagram shows. There's a unique solution, the triple point temperature and the triple point pressure. So this has only one solution.

If we summarize, how many degrees of freedom, or how many free variables, we have, anywhere here, we can do that in the following way. We can write F is 3 minus p . This is the number of degrees of freedom. Or independent variables. And this is the number of phases in equilibrium. So, what's it telling us? If we have just one phase in equilibrium, or way over in the solid or just gas or just liquid part of the phase diagram. This is one. We have two independent variables. Which is exactly what we know to be the case. In other words, in those regions, temperature and pressure can vary freely without constraints.

If we go to any of the coexistence curves, now we have two phases in equilibrium. And then only one variable can be changed freely. If we want to stay on the coexistence curve, let's say we've got gas and liquid in equilibrium. It's boiling. We could change the pressure some, but if we want to keep them in equilibrium, if we've changed the

pressure, we'd better change the temperature accordingly to stay on the coexistence curve. Otherwise everything will go up into the liquid or into the gas phase. Because you'll go off of the coexistence curve if you were to change one of these variables and not the other. In other words, there's a constraint. So only one can vary freely. And if all three phases are in equilibrium at the triple point, then you have no degrees of freedom. Nothing can vary and there's only one place where that happens.

Now let's see if we can understand also, why does the whole thing have the overall structure that it does. Why are some of the slopes generally steeper than others. Turns out, we can get a qualitative understanding of phase equilibria in a pretty simple way. So in other words, can we understand how p and T change with respect to each other along any one of these coexistence curves? Can we understand the qualitative features of the phase diagrams?

And what we'll see is, we can get an equation for dp/dT at coexistence. That's, in a sense, our objective here in order to get the sort of qualitative picture. So let's say we are somewhere here. It could be the gas-solid part. And we have some T . And now we go to T plus dT , and out here is pressure. How much does the pressure change when we stay on the coexistence curve?

Well, let's go through this. Let's just consider any two phases, alpha and beta. They could be solid, liquid, gas. And the main condition, if we're going to be on the coexistence curve, is that the chemical potentials have to be equal. Well, that's fine. Now let's change the conditions a little bit. Staying on the coexistence curve. So, let's start again. μ_α at T and p is equal to μ_β at T and p . Now let's let temperature go to T plus dT , and pressure go to p plus dp . But since we're staying on the coexistence curve still, at the new temperature and pressure, μ_α and μ_β have to be equal to each other. So μ_α is going to go to μ_α plus $d\mu_\alpha$. There'll be some change in it. μ_β is going to go to μ_β plus $d\mu_\beta$.

But we already have that μ_α and μ_β at the beginning were equal to each other. And these have to be equal to each other. Because we've specified that we're staying on the coexistence curve. So what that says is $d\mu_\alpha$ equals $d\mu_\beta$. And now, remember in general $d\mu$ is dG per mole, so our fundamental equation for G , it's minus S per mole dT plus molar volume dp .

So this equality is telling us that $-\Delta S_\alpha dT + V_\alpha dp$ is equal to $-\Delta S_\beta dT + V_\beta dp$. So we're just applying the fundamental relation to the changes in each of the phases. But since the changes in μ are equal, so are these changes. And now I'm just going to rearrange these. In other words, $-\Delta S_\beta dT + V_\beta dp - (-\Delta S_\alpha dT + V_\alpha dp)$ is equal to $V_\beta dp - V_\alpha dp$. And that immediately is going to give us our derivative dp/dT .

So, dp/dT , staying the coexistence curve, is just $\Delta S_\beta - \Delta S_\alpha$ over $V_\beta - V_\alpha$. Which is to say it's just, we can say ΔS over ΔV . Going from alpha to beta. So we have a result that can guide our thinking

into what the slopes of those coexistence lines are going to be. And it's pretty useful to look at that. By the way, we can actually express this in another way if we want. And in some cases it can be advantageous. And that is, we know that of course G is H minus TS . So our μ alpha equals μ beta condition, or a $d\mu$ alpha is $d\mu$ beta condition, can be applied that way. That is, H alpha minus TS alpha equals H beta minus TS beta.

So we can do the same rearrangements. H beta minus H alpha equals T S beta minus S alpha. And what that's saying, in other words, is that we can substitute for ΔS , ΔH over T . So we can write our relation for dp/dT in two ways. We can also write dp/dT at coexistence is equal to ΔH over $T \Delta V$. Going from alpha to beta.

These are both forms of what's called the Clapeyron equation. And these are always valid. We haven't made any approximations. Yet. Later, in going to the gas phase, we'll make some approximations about having an ideal gas. We'll be able to treat this ΔV in a simple way using the ideal gas law. But for now, these are exact.

OK, so now let's look at what it tells us. Let's look at the different pieces of the phase diagram and see what we can conclude. Essentially we should be able to construct qualitatively, the features of the phase diagram using this relation. So let's try to do that. Here's p and T . We're going to start with an empty slate. And now let's look at the liquid-gas case. So, let's look at our ΔS ΔV , going from liquid to gas. Well, one thing you know, when you go from liquid to gas, what happens to the molar volume? It increases. By a little, by a lot? By a lot, right? The molar volume in the gas is enormous compared to the molar volume in the liquid. So ΔV is positive and very big. Now let's think about ΔS . What's it going to do, going from liquid to gas? It's going to increase? The disorder increases.

Now, it increases significantly. But the liquid already is a disordered phase. And the molecules and the liquid already have considerable freedom. Certainly not near as much as they have in the gas phase. But still considerable. So, to be sure, ΔS positive. And it's not small. So there's your condition. It's not nearly as big as ΔV is going to turn out to be. So what's going to happen here is, if we look at the slope going from liquid to gas, it's positive. But it's not enormous. It's not very steep. So dp/dT , for liquid-gas coexistence right, greater than zero, but small. Not steep slope.

So somewhere, we're going to put our liquid-gas curve. And I, where exactly we can worry about it. We haven't put any numbers on this scale. But the point is, wherever it is, it's not going to be a very steep slope. How about solid to gas? Well, so what's ΔV going from the solid to the gas? What happens to the molar volume? What happens to the molar volume, going from solid? Of course, by a lot, by a little? By a lot. It's an enormous increase. Even bigger than before. How about ΔS , the entropy change? Yeah, it increases. And also by a lot, because now you're going from an ordered crystalline solid, usually, so you have a very, very, low entropy there. Into a disordered phase. Not just the liquid, but the gas phase. So this is also very big. Well, ok, so now we've got ΔS

over ΔV . There's going to be a steeper slope. Because this is bigger than for liquid to gas. So typically, the solid-liquid part will have a steeper slope than the liquid to gas part.

Now, wait. Sorry, sorry, this isn't right. And that's because I've really badly misplaced things here. That was solid to gas that we just discussed. It has the steepest slope relative to liquid-gas.

OK, now let's think about solid to liquid. ΔV for going from solid to a liquid. What is it? What sign is it? How big is it? Let's forget about the sign for a minute. How much does the volume, molar volume, change going from solid to liquid? Yeah, not a very lot, right? You melt the solid. There's still a little piece of stuff down there. Didn't increase in volume enormously. Usually, it increases. So generally ΔV is greater than, or sort of equal to, zero. It's not a big amount. How about entropy? Going from solid to liquid? It increases, by a good amount. You're going from an ordered to a disordered phase. So ΔS is greater than zero. And so the result here is, now, if you look at dS/dV , or ΔS over ΔV , ΔS is positive and you have a pretty good amount. ΔV is small. The molar volume hardly changed. And so what that's going to tell us is the slope is going to be steep. And generally positive. So now, we're going to really be on the increase. Typical kind of phase diagram and individual coexistence curve.

And all these things, again, you could understand in terms of Le Chatelier's principle. In terms of going from, say, solid to liquid if you know think about two pressures. Go from p_1 to p_2 , some higher pressure. Where are you? Well, if you want to stay on the coexistence curve you need to raise the temperature quite a bit in order to do that. Because, basically, to keep on there, you know what's going to happen if you have, say, solid and liquid. It's ice and water. You know the freezing point, it does depend on the pressure, of course. But since the change in the volume isn't that big, what happens is, a modest change, if you change the temperature by a little bit, maybe easier to think about it that way, you've got to change the pressure by a lot to stay on the coexistence curve. Otherwise it'll have a great tendency to simply go into one phase or the other.

Now we've, in a sense, reconstructed the coexistence curve by our consideration of the Clapeyron equation. There's another way we can usefully understand the qualitative features of the phase diagram. And that's just by looking at μ itself. Looking at the free energy itself, at different temperature. So let's just do that. Let's just consider μ of T at some fixed pressure. Just qualitatively, what will happen? So let's go back to $d\mu = -S dT + V dp$. And just look at the derivatives. So $d\mu / dT$ at constant pressure is $-s$. Minus the molar volume. This is the one we're really going to look at. Of course, we also could look at $d\mu / dp$ at constant temperature, and just the molar volume. Let's just look at this.

We know that entropy is always a positive number, right? Entropy at the lowest, in a perfect crystal, at zero Kelvin, could be what value? Entropy of a perfect pure crystal at zero degrees Kelvin. Zero, right? And it's only going up

from there. So entropy is always positive. So what that tells us is that, then, if we just look at μ versus T , it's negative S , for whatever phase. So it's always negative. So in some sense, you say why? Well, it's because we're keeping pressure constant and we're raising the temperature and essentially the effect of the entropy is more important. Is going up. You could see it just by saying well, G is H minus TS . And as you raise temperature, the product TS is increasing. Which means the G is decreasing, because it's H minus TS . So it's always a negative slope.

Let's look at it in the different phases. So we have entropy of the gas, that's greater than the entropy of the liquid. Which is greater than the entropy of the solid. So that immediately tells us the relative slopes for the three phases. So $d\mu_{\text{gas}} / dT$ at constant pressure is minus S_{gas} . $d\mu_{\text{liquid}} / dT$ is minus S of the liquid. $d\mu_{\text{solid}} / dT$ is minus S of the solid. And the magnitude is much bigger in the gas than the liquid than the solid. And so the same goes for the slope. So now let's sketch this. There's μ . And there's temperature. So what we've seen is for the gas, first of all, the slope's always negative. And it's steepest by far, or steepest substantially, for the gas. Next steepest for the liquid. And least steep of all for the solid. Now, there can be variation. Because, of course, these do change as a function of pressure. But this, certainly the slope, the magnitudes of the slopes are always going to be like this. What could change as a function of pressure is where these happen to lie. But this is certainly typical. So what does it mean? So, it means, remember, the stuff is always going to be in the phase with the lowest value of μ . So at low temperature, down here, that's where the solid phase has the lowest chemical potential.

Now, let's keep going up. Eventually they cross. This is where, for this particular pressure, this is where the liquid and the solid are in equilibrium. In other words, we've started, we've got the solid and we're raising the pressure. Now it's going to melt. Here's our melting point at this particular pressure. And now we've got, if we keep raising the temperature, we're no longer in equilibrium, and we'll be in the one phase part of the phase diagram. It's just the liquid. Because that's the lowest chemical potential. Let's keep raising the temperature. Down here, of course, the chemical potential of the gas is way up there, right?

So it's not going to come into play now, though they're going to be in equilibrium. Here is the boiling point. So now let's keep raising the temperature. And we'll be in just the gas part of the curve. And of course that'll go on forever. So that can just help us understand, in addition to the slopes, the positions, the relative positions, of where these equilibria occur. Now if we start changing the pressure in particular, we could move this. So that you could have a sublimation point where the gas and the solid are in equilibrium because this has moved over to here.

Any questions about the overall structure of the phase diagrams and these phase equilibria? OK, let me just end with a few comments about one part of the phase diagram that we haven't talked about yet. This. What's going on there? If we were to change, of course, I've got a finite amount of space on the blackboard, so I haven't drawn T

and p out to infinity. But if I could, this line would keep going forever. There would always be some pressure and temperature at which you would have equilibrium between two different, distinct solid and liquid phases. Turns out, that's not true for the gas and the liquid. And there are a bunch of ways to see this. But one is you could think of the symmetry difference. When you go from a crystal, a crystal and solid, to a liquid or a gas, there's no question that you've changed phase. Because there's a symmetry in the solid that's no longer maintained in the isotropic liquid or gas. So clearly there's never going to be a point where these two phases become the same thing. Become somehow indistinguishable. But the gas and the liquid, I don't know, what's the difference between them? The density, right? The gas is more dense. It's condensed. Sorry, the liquid is condensed. The gas isn't.

But that starts to change when you adjust the pressure and temperature accordingly. And you can sort of see it coming. What'll happen is, you change the temperature, the molar volumes of the liquid and the gas start to get equal to each other. That's what'll end up happening. And at that point, what's the difference between them? There is no difference. There's no symmetry difference. So you can actually, instead of going through a phase transition, where there's a meniscus, you can see the top of the liquid when you heat it up. There's boiling and then there's the gas. You can actually go from the gas, let's go the other way, from the liquid to the gas phase, without ever boiling. If you change the pressure as well. So that you can actually walk all the way around the critical point.

What happens, is up here you don't have two distinguishable phases any more. And actually, material out at this region has a bunch of very unusual behaviors. Very useful behaviors, actually. Chemical behavior can be really very, very, different in what's called supercritical, the supercritical region beyond the critical point. Water behaves really unusually there. Or it turns out, in that region, it turns out to be a terrific solvent for organic stuff. Organic molecules which normally don't dissolve well in water. And it doesn't dissolve salts very well. That's pretty unusual. Carbon dioxide, CO_2 , turns out to be a pretty good solvent for organics in the supercritical region. That's what dry cleaning is. Very nice, because know CO_2 , apart from its slow effect on our atmosphere, it's not poisonous. It's not toxic. So you can do dry cleaning without organic solvents. All sorts of unusual behavior happens above the critical point. Beyond the critical point.

There's also a whole range of behavior at the critical point. Right at the critical point that's extremely unusual. That you could think of as a consequence of the fact that the molar volumes are getting to be almost equal to each other. That's unusual in a lot of ways. And what ends up happening is, you can see if you go online, actually, if you just Google critical point, you can see amazing movies of stuff that's at the critical point. Because what happens is, so you've got the liquid. And you've got a meniscus, and you've got the gas. And you can tell. You look at it. There's the liquid. There's the gas. But if you go real close to the critical point, the stuff doesn't really know what phase it's in. Because it's losing the distinction between the two phases. You start seeing globules of liquid up

there in the gas phase. And globules of the gas down in the liquid. Because their densities - I mean, the only reason the liquid's at the bottom normally is because the density is higher. If that stops being the case, it has no more right to occupy the bottom part than the gas. And so they sort of start interchanging. And if you get even closer, of course, what eventually happens is, there's just one phase. You don't see distinct meniscus's any more. But right near there, you see enormous fluctuations in the local density and in the location. The physical locations of different phases. And we'll see that come in another context later. Because when we talk about two phase equilibria solutions. You get this with you oil and water, you get critical mixtures also, where right at the special point, the meniscus goes away and the oil and water start interchanging. And in those situations, a tiny amount of force can give you a really big response. Because the two things are just teetering in the balance. So a little bit of force pushes things one way or the other. That's actually useful in a whole bunch of different cases. Because that critical behavior happens in all kinds of phase transitions. Magnetic phase transitions. Ferroelectric phase transitions. And in those situations, a tiny little magnetic field, for example, gives you a really big change in the magnetization. If the alignment of spins. And that's very useful. You can get a very big material response and change. You can switch something, for example, with a really small external field. And in these cases, you can change the density really a lot by only a small change in pressure.

OK, next time we'll extend the Clapeyron equation and also go to two component systems. So you actually, Professor Blendi will take over again on Friday. And we'll see you then.