PROFESSOR: I want to remind and clarify as needed the equilibrium constant Kp for gas phase reaction was the ratios of the partial pressures referenced to some reference pressure, which we usually take as one, one bar. To the stoichiometry , pD divided by p naught, to the mu D where species C and D are products. And the reactants are on the bottom. And usually we don't write p naught, but it's important to remember that it's there. And then we can also write this in terms of the Gibbs free energy for the reaction. The standard Gibbs free energy, minus delta G naught of the reaction, divided by RT. And what this tells us is that this is a number. This is a number, there's no pre-factor here that has units. That's a unitless number. And it doesn't depend on the total pressure.

And the other thing to remember is that delta G naught for the reaction is the process of taking the reactants separated in separate boxes, separate containers, and the final product, the final step, is the products separated in individual containers. That's what we write when we write delta G naught for the reaction. We also looked at K in terms of mole fractions. So if you replace all the partial pressures with the mole fraction times the total pressure, you get an expression for K sub x, which we define as the mole fraction of the products to the stoichiometric powers. Which is also unitless. This is true, it's unitless. But, if you write it in terms of K sub p, the total pressure comes in here. p total, divided by the reference pressure to the minus delta nu, where this is the change in the number of moles, in going from reactants to products. And there's K sub p sitting here. So unlike K sub p, which doesn't depend on the total pressure, K sub x does depend on the total pressure through this term right here.

So when we look at problems where we change the pressure, the total pressure of the system, this is going to stay the same. Because it only cares about delta G naught for the reaction. But this K sub x will depend on the total pressure. And that's often a source of confusion in doing problems. OK, any questions? We're going to do an example where we change the pressure first.

So there are examples in the notes, and I'm going to skip the first one. I'm going to go to the second one, which is the effect of the total pressure on the reaction. And Le Chatelier's principle, for pressure. And the example we're going to take is a fairly standard example, also. Which is the reaction of N2O4, which is a gas, to 2 NO2, which is a gas, the kind of reaction that happens when you have smog and, fairly common in big cities.

The question we're going to ask is, what happens when we change the total pressure in this reaction here. Which way does the equilibrium go? Does it go to the right, does it go to the left? Does it go to the products or the reactants. And so, in order to answer that question, we're going to ask a slightly different question. We're going to

ask what is the molar ratio, what is the fraction, what is fraction of the reactant, the N_2O_4 that's reacted. That has reacted. And we're going to call that alpha. It's the number of moles that have reacted divided by number of moles initially. So we're going to need to find at equilibrium what is the number of moles of N_2O_4 that has reacted.

So we have to set up the problem. And so the way that, the standard way of setting up the problem is to write the equilibrium, 2 NO_2 gas. And then on this line here, we write the initial conditions before we set up the equilibrium. And let's say that we have n moles of N_2O_4 initially in the box. And zero moles of the NO_2. So we have n moles here. And zero moles here. At equilibrium, let's write the number of moles. A certain number of moles of N_2O_4 will have reacted, let's call that x. So n minus x moles left. For every x moles of N_2O_4 that's reacted, we create two moles of NO_2. So we have 2x here. And then we're going to need the total number of moles, because we're going to be doing mole ratios, mole fractions. So the total number of moles at any time is the sum of these two, n minus x plus 2x. It's n plus x. So if we're going to be writing our equilibrium constant in terms of mole fractions, we're going to need mole fractions. So the mole fraction at any time is n minus x divided by the total number of moles, which we just calculated as n plus x. And this is 2x divided by the total number of moles, n plus x.

And what we want is this ratio here. We want the ratio of the number of moles reacted, which is x, that's the number of moles that's gone. That have reacted. Divided by the number of moles initially, which is n. That's what we want. We want to see how that is going to change with pressure. So we're going to deal first with Kp, because Kp doesn't depend on total pressure. We're going to write that down. Then we're going to go to Kx, somehow. And that's going to depend on pressure. So let's see what Kp is here. So K sub p, you've got the products on top. So it's the partial pressure of NO_2 to the second power, divided by the partial pressure of N_2O_4 to the one power. And everything is referenced to one bar, everything's in bar. And in terms of the molar fractions, it's the total pressure squared, times the mole fraction of NO_2 squared, divided by the total pressure to the first power. So the square root on top gets divided by one factor of pressure. So we have total pressure in front. Divided by x to the N_2O_4, and that's p times Kx.

So let's plug in what these mole fractions are from our table here. The mole fraction of NO_2 is 2x divided by n plus x. 2x divided by n plus x to the square power. Mole fraction of N_2O_4, n minus x over n plus x. n minus x over n plus x. Multiply, square the top, 4x squared. Divided by n plus x squared. Things sort of cancel out here. Rearrange. 4x squared divided by n squared minus x squared. What we're really interested in is, we're not interested in x. We're interested in x divided by n. So let's divide both the top and the bottom by n squared. And we're going to get alpha come up. So this is then p times 4 alpha squared divided by one minus alpha squared. This is not, there's no total pressure here. The only way, the only place, where the total pressure comes in, is right here. This is just a number that doesn't care what the total pressure is. Which is why we're using it. And not K sub x, which cares what the total pressure is.

So now we can solve for alpha. We can solve for alpha by rearranging this equation. This is just a number. And this is where the total pressure comes in. So you rearrange that, and you get alpha is equal to 1 plus 4p divided by Kp, to the minus 1/2 power. And if I rewrite that slightly to make it a little bit easier to see what's going to happen, when I change the pressure, 1 plus 4p divided by Kp, to the 1/2 power. And that's what I'm after. This tells me what happens at equilibrium to the amount of NO2 as I change the total pressure. This is the only place where it comes in.

So now I can see that if I raise the pressure in my container, raise the pressure, this is in the denominator, so this fraction gets smaller. Alpha gets smaller. I raise the pressure, the fraction of material that reacts gets smaller. Therefore, the reaction goes towards the reactants. If I decrease the pressure, this is a smaller number here. The fraction gets bigger. Alpha goes up. If I decrease the pressure and I compare what happens to the number of moles of reactants that react, more of it reacts. Equilibrium shifts towards the product. And this is Le Chatelier that you already know. Le Chatelier's principle, for pressure.

The way it works is that Le Chatelier's principle states that, this chemical system wants to stay as close to what it was before. It doesn't like change. It doesn't want to have any change happen. So if you increase the pressure, the chemical system says, hey, you know I'm not so happy that you're increasing the pressure on me. I'd like to go back to a smaller pressure. It doesn't like change. Very conservative. And the way to decrease the pressure is to decrease the number of moles in the container. How does it decrease the number of moles? Goes back to where there are fewer moles. And that's on the reactant side. How many of you know Lenz's law? In magnetism. The diamagnetic materials. Right. At least one person knows it. It's the same idea. You take a diamagnetic material in the absence of a magnetic field, and you slowly move it into a place where there's high magnetic field, what does the diamagnetic material do? It orients its magnetic moment to reverse the field. So that there's no field inside. It starts out with no field. Doesn't like change. So Lenz's law says it's going to do whatever it can so that it retains no field inside. Le Chatelier's principle is basically the same thing. Equilibrium systems are very unhappy if you try to change them. And that's what happens for Le Chatelier here with pressure. Any questions?

So before we go to Le Chatelier's with temperature, and the van 't Hoff equation. Let's do a little detour here and talk about equilibrium in solution, which is really as important, or if not important for a lot of you, then gas phase equilibrium. Although gas phase equilibrium was where everything started. And still a huge deal.

OK, so in equilibrium now, when we talk about equilibrium in solution, we still have to, still going to be the chemical potential. It's still going to be looking at how chemical potential likes to go downhill. And we're going to have to write chemical potential for a species, A, let's say, which is in solution. At some concentration c sub A in solution. And the concentration could be given in moles per liter. Or it could be in grams per liter. Or it could be in grams per 1000 grams. Whatever your favorite unit of concentration is. Use it. Stick to it. And in order to do equilibrium,

we're going to have to reference it to, so this would be the species at some arbitrary concentration. We're going to have to reference it to some reference concentration. Just like we referenced everything to one bar before, as our standard pressure. And we're going to take, usually you take one mole per liter, or one gram per liter, or one whatever. One as your reference concentration. And the reference concentration is going to disappear from the equation. It's just like the reference pressure. Disappear from the equation.

So we're going to reference this to some standard state chemical potential. Where the naught refers now to the standard concentration. And instead of having RT log p, now we're going to have RT log cA. It's kind of like considering the molecules in the solution to act like an ideal gas. Knowing fully well that behind, that underneath the cA, is this reference concentration of one. One whatever is your favorite units. Now, it's a little bit more complicated than for the ideal gas. Because your solution may contain other things than your reactants and your products. Especially if you're doing biology. It could be a buffer. It could be a buffer, it could have salt. It could have a pH that's not equal to seven, whatever.

And so this reference, chemical potential, now needs to be referenced to a particular pH or salt concentration. Or whatever the properties of your solvent are. Or your solution are. And that's the big difference. In an ideal gas, it's reference to vacuum, basically. There's nothing there. In here, in solution you have all these molecules of solvent, molecules of salt, molecules of acid, or whatever, that are going to be around to buffer the pH. And that's going to change what the chemical potential of a species is. And if I change the pH and I've got a molecule that I'm interested in, it may not have an acidic moiety on it, but it could still care what the pH is, slightly. And that would change what the reference potential is, chemical potential is. So this is really important to remember. And there are textbooks that are written on how to do this the right way. We're not going to do that here. We're just going to remember this is, we're going to assume that this is done correctly.

Once you take that as a given, that you have a way to have a reference chemical potential at a properly referenced pH and salt concentration, then you can go through the same analysis that we went to for partial pressures. This looks just like the ideal gas, where the concentration replaces the partial pressure. Or the pressure of chemical A. And you can go through, then the same argument, where you take your reaction. And you initially have some delta G for the reactants. And you have some delta G for the products. And the difference is the delta G for the reaction, delta G naught for the reaction, and then on this side here, you have a solution of A, so the reaction would be nu A times A, which is in a solution. Temperature and pressure. Plus nu B of reactant B, in a solution, temperature and pressure. Going to a nu C, C solution, temperature and pressure plus nu D, D in a solution, constant temperature and pressure. So this is taking a solution of A, in one container, a solution of B in another the container. That's the initial point. Mix them together. Let them react. Then you take the product, you put them in separate containers. And that gets you the stuff that you have the reaction.

So when you mix A and B, you're going to have the same entropy of mixing. You're going to lower the delta G. Of the solution. And you're going to have the same curve that goes down like this. To the mixture of products. And just like for the gases, where we wanted to know what is the bottom of this curve which gives us the equilibrium, we can do the same thing. Exactly the same thing, for solutions. And so we start out with a mixture of the A and B in solution and C and D, reactants and products together. And we let the reaction proceed a little bit. And we look at the change in delta G, going from, say this point here through that point here. This will be delta G of epsilon. We ask, is this positive, negative, or zero. And if it's zero, that means that we're in equilibrium, that we're actually sitting down here. And that gives us the equilibrium constant. So, just for the sake of completeness, let me just write down what we would do. We would react it for a small amount. And then we'd end up with nu C.

So you would have the chemical potentials of the products minus the chemical potentials of the reactants, nu C mu C, plus nu D mu D, minus nu A mu A, minus nu B mu B. And instead of these chemical potentials, you would write them in terms of the pure chemical potentials times their concentrations. And then you'd end up with epsilon times delta G naught of the reaction, plus RT log, and then the concentrations. And then you write them in a different way. So if it's moles per liter, you usually write that with these brackets here. That means concentration of A in moles per liter, I'd say. So C to the nu C power, D to the nu D power, A to the nu A power, and B to the nu B power, in these concentrations.

Where this ratio of logs comes from expanding out the chemical potential here. And there's the log term here. Just like an ideal gas. Then at equilibrium, this is equal to zero, you're at the bottom of that curve. And you set these two things equal to each other. And you get the chemical, you get your equation that you know well. For the equilibrium constant. And this time it's not K sub p, it's just K. And that's what you know from doing solution equilibrium. And it's just like V.

So the thing to remember, which is the slightly more advanced part, which you'll have to worry about at some point if you stay in some sort of biochemistry oriented field, is that you've got to reference your initial solution properly. To get to the right equilibrium constant. OK, any questions?

Alright, then now we can do the temperature dependence of the equilibrium constant in a general way. Whether it be a gas or a solution. It doesn't matter. It's going to be the same thing. So the question that we ask now is, suppose that I change the temperature of my equilibrium, which way is the equilibrium going to shift? And you all know the answer already, probably. But let's derive it out. So we're going to want to know basically, we want to know what is dKp/dT. How does equilibrium constant, or dK/dT, if you're doing solution, how does the equilibrium change with temperature? What's the slope? Is it positive, negative? If we have this, we can integrate it out. We can do an integral over temperature. And get an actual change. So that's our goal. To find how the equilibrium constant changes with temperature.

What do we know? Well, we know how Kp depends on temperature, through the Gibbs free energy of the reaction. The Gibbs free energy, delta G naught, has a temperature dependence. And then there's an RT sitting on the bottom. There's another temperature dependence here. Well, dKp/dT is sort of like, we could also ask what's d log Kp dT. That might be an easier question. It's basically the same question. Especially since we have something which is log K, is equal to something. So let's ask this question instead. Let's ask, what is d log Kp dT? Alright, so let's differentiate both sides. d/dT, d/dT here. Got to use the chain rule now. Because we've got temperature as part of delta G Write it out. So let's take the derivative with respect to the temperature on the bottom first. We have delta G naught, which is a function of temperature, divided by RT squared. The minus sign here disappears when you take the derivative on the bottom. Minus one over RT, d/dT of delta G naught.

So this is a derivative of delta G, where zero means here one bar. Fixed at one bar. So really, d/dT, with delta G naught fixed on one bar, is the same thing as the partial derivative of delta G with respect to temperature, keeping p is equal to constant at one bar. It's the same thing, just different notation. And we know what this is. In terms of other things that we can find in books, like delta H, or delta S. Because we can go to the fundamental equations. To find out how delta G depends on temperature. And our goal is to get rid of delta G, which clearly has a nice temperature dependence through the entropy term. And to replace delta G with delta H, if we can. Because delta h is going to be much less sensitive to temperature and it's, delta H is going to be over small temperature ranges, is going to be independent of temperature. And we know the temperature dependence of delta H, because it's through the heat capacities.

So our goal is to get rid of this delta G here. And to try to replace it with delta H, if at all possible. So we go to the fundamental equation for G, dG is equal to minus S dT plus V dp. And sitting right here is dG/dT at constant p. Which is what we have here. So we get rid of this derivative of G. And replace it with S. So now, now we have d log Kp dT, and I mentioned already that I want to get rid of G. Because it has a strong temperature dependence. And I want to somehow get H in there, which is not going to have a strong temperature dependence. And delta G naught, I can write in terms of H and S, and T. Delta H naught minus T delta S naught divided by RT squared. And then my derivative here, I have minus one over RT. Partial of G with respect to T. p is equal to one bar. Well, that's just delta S. p is equal to one bar, well, that's just delta S naught. Times delta S naught.

And that's great, because now there's minus T divided by RT squared. That's one over RT. And somewhere I've lost a sign. And there's my sign that I lost, right there. This minus sign here. d/dT of delta G naught is minus S. It actually includes this minus sign right here. Which is great, because now things work out, because this becomes a plus sign. And this and this cancel out. And this becomes delta H naught over RT squared.

Great, so we have what we want. We have how the equilibrium constant depends on temperature in a way which

is very clear. Where the top part is only very weakly dependent on temperature, usually. And this is called the van 't Hoff equation. And this will tell us what happens to equilibrium when we change the temperature. So if you want to do a finite temperature change, now what you need to do is, you need to integrate. You integrate both sides here. From some T1 to T2. From T1 to T2, and that tells you, then, that the log of the equilibrium constant at the new temperature is equal to the log of the equilibrium constant of the old temperature, T1, plus the integral from T1 to T2 of delta H over RT delta H naught, over RT squared. And this could be slightly temperature dependent. dT. And this is the integrated van 't Hoff equation. And if you're going to be designing a chemical plant where you have high temperatures and high pressures around, you better use that. Because there is some temperature dependence in delta H, through the heat capacities of the reactants and the products. And that could make the difference between your plant running nice and smoothly or your plant exploding. And you don't want to have exploding plants around.

So for heavy-duty uses of this equation, you've got to do the integral properly. But for most normal applications, like if you're doing biology, where the temperature changes by a few degrees, like today I have a little bit of a cold. I don't have a fever, but I could have a fever. So my biochemistry would change if I had a fever. The equilibrium constant of all my reactions would change a little bit. It's a small change in temperature. I'm not going to explode.

And so you can then take the approximation. In that case, the delta H naught, is independent of T. And this is fine over small temperature ranges. And that's the one that you're most used to. Is this approximation here, this approximate van 't Hoff equation. Which is really fine for most cases that you're going to be dealing with. So then, if that's the case then you can take your delta H. Ignore the temperature dependence and take it outside of the integral. And now you can do the integral fine. And then you have an analytic expression for the change in the equilibrium constant with temperature. Log Kp at a new temperature, T2, is log Kp temperature T1. And I'm carrying this little p around everywhere. But really, it doesn't have to be there. This could be solution. I shouldn't really have written this for the specific case of partial pressures. But it's equally valid for solutions. Then we have delta H naught over R. And then we have the integral from T1 to T2, over one of RT squared. And if you do that the right way, you get T2 minus T1 over T1 T2.

And that gives you the approximate van 't Hoff equation. Which is fine. And you'll know that it's fine in problem sets or exam, because we'll say assume that delta H is temperature - yes.

STUDENT: You said that the [INAUDIBLE]

PROFESSOR: For K, if K is solution K.

STUDENT: Right.

PROFESSOR: Yeah.

STUDENT: So then, can you also use Kx?

PROFESSOR: Can you use Kx? Well, as long as you keep the pressure, the total pressure, constant, then you should be able to use Kx. Let me think about this. Yeah, here you would have p, you have a log c so, you can use Kx, fine. Because then you would have log p to the minus delta nu times Kx, log p to the delta nu minus Kx. And the log of the multiplication is the sum of the logs. And the logs will just fall out. So it could be any K that you want. Doesn't matter. As long as you keep the pressure constant. If you change the pressure, then you're in trouble.

So now we can see what happens when you do change the temperature. If I have some equilibrium, and it's all going to depend on the sign of delta H. Whether the reaction is exothermic or endothermic. And it's the same thing as Le Chatelier's for pressure, or Lenz's law. The system doesn't want to have change happening. So if you have something that's, delta H is less than zero, it's exothermic. Exothermic, that means that it's putting out heat. it wants to heat up its environment. And if I take temperature and I raise the temperature, the system's not going to like that very much. It doesn't want to get hotter, and going from reactants to products makes things hotter. And if you go from products to reactants, that's the opposite. Go from reactants to products, that becomes endothermic. It sucks in heat. You raise the temperature. The system said no, no, no, I'm happy where I am at my original temperature. I'm going to start sucking in heat, to try to get the temperature down. And it's going to try to make more product. More reactants. So, equilibrium K is going to go down. and the reaction goes towards the reactants. And the opposite if you have something that's endothermic to begin with. OK, delta H is positive here. Delta H naught is positive. You raise the temperature, delta H naught is positive, T2's bigger. This is a positive number. K becomes larger at higher temperature. K goes up. The reaction goes to products. So if you think of it in terms of the system, the system is at some temperature. You raise the temperature. System doesn't like it. Says, I want to go back to my original temperature, what can I do. I can try to suck in heat that you're trying to put in the environment. That's great because if I make more products, that's endothermic. And I'm just going to make more products until I try to lower my temperature. So I move the equilibrium to the products.

OK, Le Chatelier for temperature. Any questions? On equilibrium.

OK, let's do a quick example. Because this was the example that we started out with, talking about, the Haber process. This important industrial reaction that started the chemical industry, essentially. That uses up 1%, or close to 1%, of the world's energy. If you think about it, that's an amazing number. 1% of all energy produced in the world goes to one reaction. One industrial reaction. Just shows how important it is.

OK, why does it take so much energy? We're going to find out. We're going to find out why it takes so much energy to run this here reaction. Alright, let's look at this Haber process. Take some nitrogen gas. Plus some

hydrogen gas. And this is usually done over catalysts, like an iron oxide catalyst or something. To try to speed it up. It doesn't change the thermodynamics. As you know, and you'll hear again in this class, catalysts just affect the kinetics. They don't change the thermodynamics. So this is usually done over some catalyst to try to speed things up. To make ammonia. And ammonia becomes the feedstock for fertilizers, for almost anything that contains an amine in it, or a nitrogen in it. If you're going to make proteins or whatever. You've got to have ammonia somewhere in the process.

OK, delta H naught of the reaction, we're given all these numbers. At 298 degrees Kelvin. And they're in your notes, so I'm not going to go through them in detail. Delta G naught for the reaction, we're given that number. At 298 degrees Kelvin, that's minus 16, roughly minus 16 kilojoules per mole. And we want to know, what is the equilibrium constant. Room temperature. So you know how to calculate that. Minus RT log Kp, log K is equal to minus RT. Minus delta G naught over RT. So you put that in there. You get Kp is equal to 860. A number, no units. It's a big number. It's a big number, you've got the products divided by the reactants. It means that the products are favored. This is great. What a wonderful reaction. Shouldn't take energy to for us to do that, right? It's a room temperature reaction. Thermodynamics is great. But even over a catalyst, this is a really, really, really slow reaction. We'd still be waiting here for Mr. Haber to produce his first mole of amine, if you were doing it, or ammonia if we were doing it at room temperature. It's just so slow. Thus, not at all practical. We're not going to run the world on room temperature Haber process.

But it turns out, if you raise the temperature, kinetics is wonderful in terms of the temperature dependence. It's exponential. Arrhenius rate law. Great thing, you raise the temperature by a little bit. Rates speed up, things go faster. So if you were to raise the temperature from 298 degrees Kelvin to 800 degrees Kelvin, the rate speeds up. You're going to need some energy. As input here, to feed that. Hence the 1% energy use. Rate speeds up, that's great. Things happen faster. It becomes practical. But, what happens if you raise the temperature?

Let's see. This is an endothermic, or exothermic, negative sign. And negative sign's exothermic. I raise the temperature, K goes down. I know how to calculate it here. And if I want to be super careful, because it's a fairly large temperature range, I can even use the exact form of the van 't Hoff equation. And what I find, if I do that, and putting the heat capacities for all these gases, I find that Kp does go down. In fact, it goes down quite a bit. It becomes 0.0007. Two zero's. Still really small. That's not practical. Not practical at all. No good. We can't run an industrial plant with this kind of yield. There's just no way it's going to work. So, you're a chemical engineer. Or a chemist, like Haber and Bosch were. And you're trying, you know by Le Chatelier, you know that it went in the wrong direction for you here. And then you look at your reaction and you say, how many moles of reactants do I have? 3/2 plus 1/2, that's two moles of reactants. And I've got one mole of product. Two moles reactants, one mole of product. Two moles reactant... What happens if I change the pressure?

If I change the pressure, if I increase the pressure, the system is going to say, no, I don't want the pressure increased. It's going to go to where there's less moles. And the less moles in the product area. It's going to go to my product. That's great. I've got to increase the pressure. Wonderful. Let's start increasing the pressure. Again, we need some energy to do that. We're going to go from one bar to some higher pressure. It's going to make our lives more complicated. The plant might explode now. If the pressure's too high. All sorts of problems going to come into play. But, let's do it. Let's increase the pressure.

So, you increase the pressure from one bar to 100 bar. And you calculate Kx. Which is really what you want. So Kx, in this case here, is equal to p times Kp. Kp doesn't change. Kp doesn't care what the total pressure is. It's Kx that cares. At one bar, Kx is equal Kp. Kx is p to the minus delta nu. Number of moles of products minus the number of reactants. If I go from one bar to 100 bars, Kx goes from 0.007 to 100 times 0.007, which is equal to 0.7. That's a lot better. Kx is the mole fraction or the, of products divided by reactants. And if I go to p is equal to 300 bars, then Kx goes to 2.1. three times 0.7.

This is great. Now I'm really starting to make good products. But I've got to go to 300 bar. I've got to go to 300 bar, and 800 degrees Kelvin. That is incredibly energy-intensive. But it works. That's why Haber and Bosch made this work. And why Germany stayed in the war longer than after 1916. The first world war. Ended in 1918. Nobel Prizes. Merck, Bayer, all these german companies. Because they figured how to do this at high pressure and high temperature. Without blowing everything up. OK. Any questions?

Alright. The last topic is, so far we've seen equilibria where you had things that were well mixed. equilibria of ideal gases. Or in solutions, where your solutes, your solute molecules are mixing around. And the entropy of mixing was really super important. Our curve, our going down for delta G, was all because of the entropy of mixing.

Now, suppose that I have a heterogeneous mixture. I've got some solids or some pure liquids that are refusing to share their environment. And staying as pure materials. So, for instance, if I have a beaker with some solid reactant on the bottom here. And the products are in solution. How do I deal with that equilibrium? Well, you know the answer, but let's just do it out again. So we're going to have nu A moles of A, of solid. Not mixed in the solution. Let's say we have multiple phases here. Nu B moles of B, which is a gas. Instead of a solution, let's do a gas phase reaction. Nu C moles of C, which is a pure liquid. And nu D moles of D, which is a gas. So these two gases can mix. But the pure solid and the pure liquid can't mix.

So let's think again, where does the equilibrium constant come from? It comes from looking at this delta G of the mixture and letting it react a little bit more. And taking out these chemical potentials for the species and the mixture. Expanding it out in terms of log p or log concentration. So we need to have this delta G in. Let's take epsilon equal to one, to make our life simpler here. So now we have nu C mu C of the pure. The pure solid. Plus

nu D mu C of the gas. Which is in the mixture. Minus nu A mu A of the pure liquid, minus nu B mu B of the gas. Which is in the mixture. That's what this delta G is, when we allow the reaction to proceed for a little bit more. We add a little bit of chemical potentials from the products. Subtract a little bit of chemical potential from the reactants. And then we expand it out in terms of the standard chemical potentials for everything being pure. Entropy of mixing comes in here. Comes in here. Delta G of mixing comes in here.

And we end up with something that looks like nu C mu C naught, plus nu D mu D naught, minus nu A mu A naught, minus nu B mu B naught. Plus RT log, and the only place where we have these log p's, or log concentration coming in, is for those species that were not pure. And those are only these two guys here. The ones that are in the gas phase. D and B. So we end up with partial pressure of D to the nu D power. Partial pressure of B, to the nu B power. The other two species don't come in there. Because they started out as pure. There's no mixing going on. And there's no expansion of the log for them. And so now, when we look at the Q for the reaction, the reaction quotient, it doesn't contain any of the pure species. It only contains those species that are allowed to mix. Those that are in the gas phase or in solution. And so K, then, for this reaction only takes in those products like D. Or reactants like B, which are in the gas phase. The pure solids or pure liquids don't come in. They come in for delta G naught. There's delta G naught sitting right here. Delta G naught for the reaction is sitting right there. So when you write your log K is equal to minus delta G naught over RT, the delta G naught has everything in it. The pure stuff, the solution stuff, the gas phase stuff. But the K only has the gas phase and solution stuff.

Alright, any questions? Good. Next time we'll do an example. And then we'll go on phase transitions.