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PROFESSOR: So let's start with some of the things we learned last time. So there are two things that were important. We learned that the chemical potential for a species is the Gibbs free energy for that species divided by the number of moles, this is Gibbs free energy per mole. We learned that the pressure dependence of the Gibbs free energy gives you the pressure dependence for the chemical potential. That it's equal to the chemical potential at one bar for an ideal gas plus RT $\log p$.

We also learned that a species will want to go to minimize its chemical potential, and we saw that for the cell bursting in salt, in distilled water. Or an ice cube melting at a temperature greater than 0 degrees. And what we want to prove right now is that if I take a species $A$, in a mixture, some temperature $T$, some pressure $p$, and I compare its chemical potential to the same species, $A$, when it's pure, the same temperature, the same pressure, what I want to argue is that the chemical potential in the mixture is always less than the chemical potential when it's pure. The same conditions of pressure and temperature.

And, so we can do a little thought experiment. Let's do a little thought experiment. Let's make a box, and in our box we're going to have a partition. And a flexible membrane here. And on one side of the partition we're going to have a gas, B. A gas, A, on this side here. And gas A on this side here. So let me just red chalk for A, And I don't think I have any other colors listed. Yellow chalk for B here. And everything's one bar. Everything's one bar. So one bar B here. One bar A here, one bar A here. And this membrane here only lets A through. And this membrane is deformable, but it's elastic. You can't deform it forever. It has some strength to it, right? So if you push on, it'll push back. There'll be pressure associated with that.

So the next thing I do, then, in my experiment, shouldn't have done it here. Next thing I do in my experiment is to break this partition here. I'm going to break the partition. And this will cause $A$ and $B$ to mix. So now in my box I have my partition, my membrane here. I've got A at one bar here, total pressure of one bar. And on the other side I have A plus B, with a total pressure of one bar. That's my initial point now. What's going to happen?

What's going to happen is that molecules of A here are going to want to go through the membrane to go in this area here. And there's two ways to look at it. You can look at it the thermodynamic way, which is the way that we're going to want to be looking at it. Which is that, from what we're going to prove, is that the chemical potential in the mixture is always less than for the pure substance. Here we have a mixture. One bar. Here we have the pure substance at one bar. So these molecules are going to look around and say hey, you know, I'm much
happier here. And they're all going to want to go in this area here. As a result, the volume of this area, if you want to keep the same pressure on both sides, you're going to deform the membrane. The membrane's going to get deformed. It's going to bloat on that side here. It's going to cause an increase in pressure on that side. And the increase in pressure from the membrane sort of deforming and pushing back, is going to increase until the partial pressure of $A$, here, equals the pressure of $A$ here. At which point the flow of $A$ from either side is going to be the same and you're going to be in equilibrium. And at that point the chemical potentials of both sides are going to be the same.

So I sort of gave you the other way of looking at it. Which is just purely in terms of pressures. At equilibrium, the partial pressure of $A$ here has to be the same as the pressure on this side here. So that the flow of $A$ on either side of that membrane, going from right to left or left to right is the same. And that's going to cause this mixing to happen. If you look at it from partial pressure perspective. But really, it's a chemical potential idea. Now, the chemical potential, as we saw, was the Gibbs free energy. And the Gibbs free energy, you can write it as H minus TS. So basically, in this process that I described, the enthalpy's not doing anything. These are ideal gases. They're not interacting with each other. The only thing that's changing, that's driving the chemical potential, which is basically Gibbs free energy per mole, the only thing that's driving the chemical potential to be lower on this side here, is that entropy term. It's the entropy of mixing. So entropy of mixing is really super important. When we're talking about systems where you have multiple components. That's going to drive a lot of things. And in fact that's going to drive equilibrium, as we're going to see a little bit later today.

Alright, let's quickly go through the math and prove this here. So our goal, then, is to have a mixture, chemical potential of the mixture on one side, and the chemical potential of the pure material on the other side. And so we're going to start by sort of a similar thing here. We're going to have a box, let me redo my box here, we're going to have a box with, let me get rid of these one bars here. We're going to put our membrane in the box. And we're going to have a pressure, pA , on this side here. And we're going to have a pressure pA prime for the partial pressure of $A$. And pB prime for the partial pressure of B . And the p total is going to be pA prime plus pB prime.

And I'm going to see at equilibrium, I'm going to write everything I know about equilibrium. At equilibrium, I know that the partial pressure of $A$ on that side here has to be equal to the pressure of $A$ here. The partial pressure, the pressure is basically the force of these molecules hitting that membrane per unit time, times the number of molecules hitting. So we have the same flux of molecules going this way, is equal to the flux of molecules going the other way. So at equilibrium, pA prime equals pA.

So. What else can I say? At equilibrium, in terms of the chemical potentials, I know that the chemical potential of the mixture, mu $A$ in the mixture, temperature under pressure $p$ total. Is equal to the chemical potential of the pure system, same temperature under pressure is p sub a on that side. These are the two things that I know at
equilibrium. So let's start to turn the crank. And see if we can come up with, well, we basically already have this. If we can massage the right side of our equation so that the pressure term, pA, is p total. And then we'll have an equation that will compare the chemical potential of the mixture under the same conditions as the chemical potential of $A$ in the pure state.

So, what can we use? We can use Dalton's law here, which tells us that pA prime is equal to $x A p$ total. That's from Dalton. And now, pA prime is equal to pA. So this is also just pA. And we can plug that in here, and suddenly we've got $p$ total included in here. Let's just pass these out. If you want to, thank you. Thank you.

So, this is equal to mu A pure temperature xA p total. So what else do I know? I know that l've written something here, that mu is equal to mu naught, to temp, so this is at one bar. RT $\log \mathrm{p}$. So I'm going to rewrite this as mu A pure temperature $T$ at one bar. Plus RT $\log x A p$ total. Now, the $\log$ of $x A$ times $p$ total is the $\log$ of $x A$ plus the $\log$ of $p$ total. It's equal to plus RT $\log p$ total plus RT $\log x A$. So I can lump these two things together. I have mu A pure $T$ plus RT log $p$. Well, that's just the chemical potential of $A$, in the pure state, at temperature $T$ and pressure pT . That's the equation here to relate pressure, at some variable pressure p , to what it would be at one bar. Which is that. Then we have the plus RT $\log x A$ sitting here. Plus RT $\log x A$. So we're done. We're done because on that side here I have mu $A$, the chemical potential of $A$ in the mixture, temperature $T$, pressure $p$ total. I've got mu A pure temperature T pressure $p$ total, plus a term. Plus RT $\log x A$. Can $x A$ be bigger than one? xA's the mole fraction. $x A$ 's always less than one. Log $x A$ is always less than zero. This term here is always less than or equal to zero. Therefore, this term is always less than that term. Therefore the chemical potential in the mixture is always less than the chemical potential inside the pure material. This is going to be important for the next part of the presentation. Any questions? This is what drives the death of saltwater fish in fresh water, right? Because osmotic pressure is basically given by this basic idea here. And it's all driven by entropy of mixing. Sure you don't have any questions? Speak up.

So now we have all the tools we need to look at chemical equilibrium. When we have a mixture, and we're going to start with ideal gases. But everything I'm going to say about equilibrium and ideal gases is valid for solutions. An ideal gas, and we're going to be talking about ideal solutions. And molecules in an ideal solution, an ideal solvent, are not very different than molecules in an ideal gas. They don't interact with each other. You use concentration instead of partial pressures, but pretty much all the ideas are the same. All the concepts are the same. The equations are basically the same. You just do a little bit of replacement of variables. But it pretty much is the same thing. It's easier to think about it, to learn first in terms of the ideal gas, but it applies equally well to what you're more likely to use. Which is solutions.

So let's look at the prototypical gas phase reaction that everybody writes down when they first do this sort of problems. The Haber process. Gas, temperature T, you take nitrogen. You react it with hydrogen, gas,
temperature T, p. And you make ammonia. NH3 gas T, p. And we're going to ask the question, so I take nitrogen, I take some, hydrogen, I mix them together in a container. And I make ammonia. And I'm going to ask, after I reach equilibrium, what is the partial pressure of nitrogen hydrogen and ammonia? Standard equilibrium problem. You all, I'm sure you've all seen equations about equilibrium. Equilibrium constant K , log delta G of the reaction, et cetera, et cetera. But you probably don't have a really good intuition as to why it is what it is. So the point of the class here is not to relearn $\log \mathrm{K}$ is equal to minus delta G , reaction divided by RT. The point is to learn how we get there. How we get to that equation. And what parts are important. Specifically, how entropy of mixing really becomes key to equilibrium.

But before we get there, let me give you a little bit of history as to why this is such an important reaction. This reaction, which you see in every chemistry class, was developed by Mr. Haber and Mr. Bosch. Mr. Bosch made it large-scale around 1910. And it's the reaction that you use to make fertilizer. Ammonia is the feed stock to make nitrogen-based fertilizers. So today, there are a hundred million tons of fertilizer, of nitrogen fertilizer made, using, essentially, the Haber process. It's a huge, huge, commodity. $1 \%$ of the world's energy is taken up to make this reaction. Almost $1 \%$ is about $3 / 4$ of the world's energy is used on this. In World War 1 , Germany was making explosives out of nitrogen feed stock. And it was getting its feed stock from Chile. From saltpeter mines in Chile. Chile was under British hands at the time. Well, the British didn't let Chile sell saltpeter to Germany. Germany had to find another way to make ammunitions. And the Haber process, which had just been invented by Bosch-Haber, became the way that Germany made explosives. Without this, Germany would have stopped the war in 1916. Or even before then. Way before then.

And this process was basically, and Haber and Bosch got the Nobel Prize, essentially, for this process. For showing how to take chemistry, and doing chemistry and large scale processes under high pressure and high temperature conditions. Haber got the Nobel Prize in 1918 and Bosch got it in 1931. This process, arguably, you could say, was the birth of the dominance of Germany as a chemical industry. Based on that, and the fact that they had to make liquid fuels out of coal. The syn-gas, or the syn-fuel process. Also invented during World War 1, where they had to use, they couldn't find any oil and they had to use their coal mines. And obviously this process, the syn-fuel process, is coming back in vogue with the energy crisis around now. So they developed a lot of knowledge about how to do large-scale chemical reactions. And that was the birth of, or the explosion of, companies like Merck and Bayer and Bosch, and BASF, and all these German companies that dominate, basically, the chemical industry. And when Germany lost the war, the US government confiscated the American divisions of these German companies. And I'm sure you've heard of Merck as the company. And you think of Merck as an American company that makes drugs. Well, that's true. It's a very large American company that makes drugs. But there's another Merck, which is the German Merck. Which also makes drugs. But it makes liquid crystals. And liquid crystals is where it makes all of its money right now.

And it's very confusing because they're both Merck. And they both came from the Merck family from the 1600s that were pharmacists. But after World War 1, Merck Germany was allowed to use the name Merck everywhere in the world except for the US. In the US it's called EMD. Merck USA is allowed to use the name Merck in the US and outside of the US it's called, let me remind myself, it's called MSD. It's very confusing. Bayer is the same way. So Bayer was split up. And there was Buyer in Germany and there was Bayer in the US. You've got Bayer Aspirin from the US term Bayer. And you've got all the other pharmaceuticals from Bayer Germany. All the chemicals. And a few years ago, Buyer bought Bayer, and now we have one Buyer-Bayer, depending on where you live.

And so it's very interesting to see the history of all these big chemical companies. And that's why Switzerland and Germany are still the home of, it's all due to that reaction. That's why you always see that reaction. Fertilizers, at the birth of the chemical company, and it's a great example for equilibrium.

So that's the example. Let's generalize it. We're actually not going to work on this until the very end. And we'll see it again. But let's generalize. Let's just take a mixture of gases with stoichiometries nu A, a gas, pressure, temperature plus nu $B, B$, gas, pressure, temperature, goes to nu sub $C$ moles of $C$, it's a gas, with a temperature and pressure, plus nu sub D moles of D , which is a gas, temperature, pressure. All ideal gases. For now.

So this the setup here. Now, when we write that reaction up here, what we're really writing is, in terms of the process, is take a container that contains A , plus a container that contains B , and go to a container that contains C, plus a container that contains D. And when we write delta $G$ for that reaction here, the process that we're talking about is taking the reactions separately from each other. That's the initial state. And the final state is the product. Separated in their own containers from each other. And when we say delta $G$ is less than zero, for this process, which means it's spontaneous, we mean the process to go from the separated reactions to the separated products. But in reality, that's not what you do when you do an experiment. In reality, you take these two containers and you mix them together. A plus B. And you let that react. And at the end of the day, you have a big container with A plus B plus C plus D inside, all mixed up together in equilibrium. And this is not the same as that. It's not the same as that. Because you've got entropy of mixing happening in all of this. Forget about $A$ and $B$ interacting with each other. Entropy of mixing is going to dominate equilibrium. You've got this problem to deal with.

So that means that we're going to have to worry about, if we're going to want to know at which state the process is in equilibrium, you're going to have to worry about this issue right here. It's not enough to know what delta G of the reaction is. So for instance, if I plot, as function of the reaction, I've got the reactants on that side here. And the products on this side here. And I want to plot delta $G$ as a function of the reaction. Well, my initial delta $G$ that I would write, to calculate delta $G$ of the reaction, which is the delta $G$ of the products, minus the delta $G$ of the
reactants, so initially I have delta G of the reactants. That's, in those two boxes, that aren't mixed. So I'm up here somewhere. Delta G of the reactants. And at the end of the process, in these two boxes, when I calculate this delta G naught reaction, I'm sitting somewhere here. Let's say it's a downhill process. Delta $G$ naught of the products.

Well, the first thing that happens, when I take these two boxes and mix them together, is delta G naught of the reaction's going to go up or going to go down, or stay the same. Anybody want to guess? When I go from here to here, before there's any reaction that happens. Shall we vote? How many say that it's going to go down? How many say that it's going to go up? How many say that it's going to stay the same? We have about three people that said it's going to go up. And a lot of people that say it's going to go down. And a few people that are abstaining.

OK. We're mixing things. Anybody want to change their votes? Something is happening here. And this entropy term here, when $A$ and $B$ come together and start mixing up. You're changing your vote. Alright. It's going to go down. Now we have near-unanimity. So the first thing that happens is, you're going to go down here. You're going to have delta $G$ naught of the reactants in the mixture. And if it were to go all the way, if $A$ and $B$ were to disappear, it still would be mixed. And so the end product here would actually be down here. It wouldn't be up in the products. It would be the mixture.

So that's the first thing we know. That this delta G naught reaction is not the full story. And along the way, here I have two species to begin with. I've got two species to end with. But l've got three different species here in the middle. So as soon as I form a little bit of products, in this case here, or if I start from products and go the other way in the reaction and form the reactants, the first thing that's going to happen is I'm going to decrease the delta G. Just from the entropy of mixing. And so if I plot my delta $G$ as a function of reaction conditions, I'm going to get a bowing curve like that. If the entropy wasn't there, then it would just be a straight line from one to the other. The entropy of mixing of reactants and products wasn't there. Actually, let me put it up here. If entropy of mixing wasn't there, I would start from up here. And as my stoichiometry changed, I would have a linear curve from here to there as a function of the process of reaction. But the entropy of mixing is causing my initial state and my final state to go down. And it's causing a bow in this here. Because if I have equal amounts of $A, B, C, a n d$, that's a lot of entropy of mixing there. So equilibrium is actually somewhere down here. It's where delta $G$ of the mixture is at its lowest. Delta $G$ of the mixture is at its lowest. Any questions?

Now we going to do the math. We're going to see how that comes about. Let me do it here. So the question we're going to ask is, suppose that l've got my mixture here. And I'm sitting somewhere on this curve here. So I've got pA for partial pressure of $A$, partial pressure of $B$, partial pressure of $C$, and partial pressure of $D$ in my mixture. And I want to know, I've got this mixture of reactants and products. Which way is the reaction going to go? Is it
going to go towards the products? Is it going to go towards the reactants? Or is it at equilibrium? And to answer that question, I'm going to let the reaction react a little bit more to create a little bit more products. Remove a little bit of reactants. And see what the sign of delta $G$ is for that process.

So I'm going to go from a moles of $A, b$ moles of $B, c$ moles of $C$ and d moles of $D$ in my mixture, which is that point on my graph here. Partial pressure A, partial pressure of B, partial pressure of C, and partial pressure D, and I'm going to react it a little bit more. a plus, a minus epsilon times nu A , where epsilon is a very small number. Of $A, b$ minus epsilon times nu $B$ times B. And I'm going to have, now, products being formed. $c$ moles plus epsilon times nu C, I've going to have the stoichiometry in there. For every nu A moles of A that I lose, I create mu $C$ moles of $C$. Times epsilon as the scaling factor. And d plus epsilon times nu D moles of $D$. That's going to be my new mixture.

And I'm going to ask, as I go from this initial state to that final state, I'm sitting on that curve, which sign is delta G. How do I know what the sign of delta $G$ is? What is delta $G$ for this process? Not the reaction with the isolated reactants and products, but the reaction where everything is mixed together. Where I'm going to have to worry about the chemical potentials of mixtures. And I'm going to go from one mixture to another mixture, and that's going to be the key to telling me if I'm in equilibrium or not. But we know how to do this. We know how to do this.

So I want to calculate delta $G$ for the process is delta $G$ after minus delta $G$ before. That's delta $G$ after minus delta $G$ before. And I know that delta $G$, rather, let's call it $G$ after minus $G$ before, the Gibbs free energy after minus the Gibbs free energy before. And I know the Gibbs free energy is just the sum of the chemical potentials, right? You take all the species, and you take all the chemical potentials. You add it up together times the stoichiometry. And that gives you the Gibbs free energy. That's what we learned last time. So if I want to find what the Gibbs free energy at the end here is, I look at the chemical potentials of $A, B$, and $C$ and $D$ times their number of moles. So I look at a minus epsilon times nu A times the chemical potential of A, plus b minus epsilon times nu B times the chemical potential of B plus $c$, plus epsilon times nu $C$, the chemical potential at $C$, plus d, plus epsilon times nu D, the chemical potential of D .

And then I subtract what $G$ was before. This infinitesimally small process. Was a times mu A plus b times mu B plus c times mu C, plus d times mu D. And we're assuming that my small change, the small amount of $A$ and $B$ that get destroyed to form $C$ and $D$ is small enough that the chemical potential basically stays the same during this infinitesimally small change. That's why I can use the same chemical potentials before and after.

OK, a lot of things drop out. This term drops out from that term. This term drops out from this term. This term drops out from this term. This is a minus, no, this is all plus. That's fine. There's the minus sign right here. So then this term drops out from that term. And I am left with epsilon times nu C mu C, the chemical potentials of the
products minus the sum of the chemical potentials of the reactants, nu A, mu A plus nu B mu B. That's the delta G for this small change.

Now, you remember way back, maybe from even just last semester if you've taken 5.112 last semester, or from last year, or from high school, that the partial pressure is going to the equilibrium constant. Somehow we're going to have to get partial pressures in there. But we know now how to go from chemical potentials to partial pressures. It's written right here. The chemical potentials of the, and we also know how to go from the chemical potential in the mixed species, in the, mixture to the chemical potential in a pure. We saw that mu A in the mixture, temperature, pressure was equal to mu A pure temperature, pressure plus RT $\log x A$. So those are things that we're going to be using, to go from something that has chemical potential to something where we'll be able to get back pressures, partial pressures, and delta $G$ of the reaction, because we're going to need the chemical potential of the pure stuff.

So let me go forward just a little bit. Remind you, if I look at the delta $G$ of the reaction, delta $G$ of the reaction, in terms of chemical potentials. Delta $G$ naught of the reaction. This is the delta $G$ of the products minus the delta $G$ of the reactants when they're pure, not when they're mixed. So delta $G$ naught of the reaction is nu Cmu C at one bar pure plus nu D mu D pure. Minus nu A mu A pure minus nu B mu B in the pure state. That's what delta G naught of the reaction is in terms of the chemical potentials of all these species. Everything's at one bar, and everything is pure. Somehow this is going to have to come out of this. So let's keep going. And see how it falls out.

So for each one of these chemical potentials, I'm going to write it in terms of the pressure. What I just covered up here. $\operatorname{Mu}(T, p)$ is mu naught of $T$ times RT log $p$. So now, delta $G$ is going to be equal to epsilon, and I'm going to do a little massaging quickly. And I'll let you take this, go home and see how I went from one state to the other. The secret is to put in here the pressure dependence. Nu C mu C naught, plus nu D mu D naught, minus nu A mu A naught, plus nu $B$ mu $B$ naught, plus RT log $p C$ to the nu $C$, $p D$ to the nu $D$, divided by $p A$ to the nu $A, p B$ to the nu $B$.

These log partial pressures all come from expanding out the chemical potential as mu naught plus RT log p. And then we recognize that this part right here, this part right here is delta $G$ naught reaction. So I have delta $G$ now, for this process of taking reactants to products just a little bit, let me take it as a function of epsilon here. Delta G naught of the reaction plus RT log of this ratio of partial pressures. I'm going to call that Q. I'm going to call this thing here Q , which you've seen before. The reaction quotient.

And this tells me that for this very small process, epsilon, very small, if delta $G$ naught, delta $G$, of this process, is less than zero, then the reaction will keep going forward. It means that I'll be on the side of the curve here. I'm going to go down a little bit. delta G naught is going to be great, it's going to be spontaneous. I'm not in
equilibrium. I'm going to go towards the products. If delta $G$ is equal to zero, then I'm at the bottom of this curve here. I'm here. If I go forward a little bit, the slope is zero. Delta $G$ is zero, I'm in equilibrium. And if delta $G$ is greater than zero, then I'm going to back to reactants, and I'm sitting, then, on that part of the curve here. And if I try to make more products I'm just going uphill a little bit.

So now, I've done this all for epsilon is equal to very small. What you usually find written in books is where the epsilon equals to one. Basically taking one mole of this process. So you'll see it per-mole of this reaction. But it's the same idea. It's the same thing. And in fact it doesn't really matter, because the quantity that matters is this delta $G$ naught reactions plus $R T \log Q$. It's the sign of this quantity here. This epsilon is just an arbitrary number. I can pick it, really whatever I want. So it's the sign of this thing that's important.

Let me go back. So what you'll see, then, is delta $G$ is equal to delta $G$ naught reaction plus $R T \log Q$. Basically, taking epsilon is going to zero. As determining where the equilibrium is going to be. OK, any questions? All driven by entropy of mixing. Without entropy of mixing, we would be sitting on this curve here. Delta $G$ naught of the reaction would tell us that everything should go to completion. Things don't go to completion, and that's a good thing. Otherwise there would not be life on Earth. We're basically a set of equilibria in a big membrane. Which is our skin, right? All these biochemical cycles are in equilibrium with each other. And it's a complicated process. And it's all driven by entropy. Ultimately. And other things, but entropy is very important.

Alright, so equilibrium now. Equilibrium is when we have this delta $G$ equal to zero. That's when delta $G$ naught of the reaction equals $R T \log Q$. And at that point, we replace $Q$ with to equilibrium, and we call that the equilibrium constant. And we're going to put a little p here, because it's in terms of the partial pressures. And it's equal to the partial pressures of the products raised to their stoichiometry. And divided by the partial pressures of the reactants, raised to the power of their stoichiometry. And this, you've seen before, I'm sure. At equilibrium. And there's a minus sign somewhere here. Because it's this plus that that's equal to zero, and there's the minus sign that I forgot to write down. So we define, then, equilibrium constant this way. And one of the things to note is that Kp as written here is actually unitless. It doesn't look like it. The way that l've written it. Because I did a shorthand way of writing the pressures, when I wrote RT $\log p$ here. There's the assumption, when you have the log of the pressure, that there's always one bar sitting behind there. Underneath. It's always referenced to a reference pressure. There's always a reference pressure. p naught dividing it by, because you don't want to have any units inside the log. And this reference pressure, we took as one bar. And it's pretty common to just ignore the fact that you've got one bar sitting in the denominator.

And so, actually, all these pressures here are divided by $p$ reference divided by $p$ reference, divided by $p$ reference, divided by p reference, which happens to be 1 bar. But it's there. And that means that the bars on top and the bars on the bottom cancel out. Which means that $K$ sub $p$ doesn't have any units. It is unitless. It's a
number. Straight number. Very common mistake to make, to write it and forget that there's one bar sitting on the bottom here. And you take all the bars to the new powers on top, and the bars to the new powers on the bottom. And make units there. And get Kp is equal to some number, to the, times bar to some power. That would be wrong. I know l've made that mistake before. But you are not going to make that mistake, right? Because you've been warned. That this is a common mistake. This is unitless. Now, you can invert this to get Kp as a function of delta $G$. e to the minus delta $G$ naught of the reaction divided by RT. And those are the things that you use to go back and forth between the thermodynamic quantities, like $G$ that you calculate, to equilibrium quantities like the K , to finding equilibria between something like the Haber process.

Now, there's other equilibrium constant that is used a lot. Which is the form of the equilibrium constant not in terms of the partial pressures, but in terms of the mole fraction. That's also an important one when you're looking at solution cases. Because we can rewrite the partial pressures using Dalton's law. pC is equal to the mole fraction of species C times the total pressure, I'll call it p. So if I replace every one of these partial pressures using Dalton's law, I get $K$ sub $p$ is equal to $x C p C$ times $p$ to the nu $C$, times $x D p D$ to the nu $D$, divided by $x A p A-n o$, not $p A$, total pressure. Dalton's law. To the nu $A, x B p$ to the nu $B$.

OK, so l've got p, p, p, p. They all come out. And that's p to the minus delta nu. Where delta nu is the difference in the number of moles of reactants minus the number of moles of products. So delta nu is nu C plus nu D minus nu A minus nu B. It's the moles of products minus moles of reactants. And then I have $x A$ to the nu $A, x C$ to the nu $C$, $x D$ to the nu $D, x A$ to the nu $A, x B$ to the nu $B$. And that ratio, which is in terms of mole fractions, we call $K$ sub $x$. The mole fractions. Because p, to the minus delta nu, times Kx.

Now, this was unitless. This pressure to the minus delta nu sitting here, this has bars to the minus delta nu. Kx has units. It may not look like it because it's a bunch of mole fractions, and it certainly doesn't look like it has any units. Mole fractions or ratio, but it's got units. So let's rewrite $K x$ in terms of $K p$. Rewrite $K x$ as equal to $p$ to the minus delta nu, K sub p. And the units are in terms of bars, let's say, bar to the minus delta nu. Always want to check your units at the end of the day. If your units don't work out after you've done a calculation, you're in trouble. Any questions? Because we're going to end today, at here. Yes.

## STUDENT: [INAUDIBLE]

PROFESSOR: In the notes it says Kp and Kx are both unitless. That is a mistake. I'm going to fix that, and put it on the Web. So it may be that there's a special case where the number of moles before and after are the same. But generally that is not true. Where did I say that? Oh, yeah. Both unitless. Well, that is actually true. Let me think through this.

PROFESSOR: About one bar, one bar, one bar. That is actually true. They're both, that is true. They are both unitless. Well, this is a big boob on my part here. Because you are absolutely right. Because there's one bar sitting here. one bar, one bar, one bar, one bar, and the bars cancel out. Good catch. OK, the notes are right. My notes are right. Alright. Next time we'll talk about the temperature dependence and the pressure dependence of equilibrium constants.

