[SQUEAKING]

[RUSTLING]

[CLICKING]

PROFESSOR: So let's talk about reacting gas equilibrium. We started setting this up last time. And now we're going to derive the key equation. So we're going to equilibrate. It's really hard to say the word equilibrate while writing the word equilibrium. I somehow got that right. Gas phase reaction at equilibrium at fixed T and P. So we mixed gases, and we let them react. We're going to do this in general terms. Reaction A plus B goes to 2C. And of course, everything we're going to do is general. Doesn't have to be for a reaction of this form.

OK. So we know that the condition of equilibrium at fixed temperature and pressure, exactly Gibbs energy at an extrema. And so we care about its differential. So let's use what we know.

OK. So here, we have the total differential of the Gibbs free energy for changes of temperature, changes of the pressure, and changes of mole number. And again, the independent variables for Gibbs are temperature, pressure, and mole number. You can see that right here in the differential form.

And why do we choose that free energy? Why do we choose Gibbs? Why is this convenient? Because we can ignore 2/3 of the right-hand side of the equation. For fixed temperature and pressure, right, those are fixed.

Fixed and stubborn and independent are, like, synonymous in thermo, right? If they're independent, that means they can be stubborn and not move. So those go to 0. And we care only about this term. So we're going to be spending the lecture analyzing that term.

And so equilibrium is determined by the chem potentials mu i and the mole numbers. So that's going to be it. Our entropy and our volume are not going to be explicitly part of this. Get rid of that.

All right. So at equilibrium, dG equals-- now, that's the equilibrium expression. So, all right.

How many independent variables are there in this case? I'll remind you, we have a general reaction A plus B goes to 2C. That's a reaction. Let me break that down a little bit.

Somebody tell me, what are the components? Let's list the components. And those are the i labels, components i. What are the components in the system?

AUDIENCE: A, B, and C.

PROFESSOR: Components are A, B, and C. Right. So this label runs over A, B, and C. OK. So we have three mole numbers, n of A, n of B, and n of C. How many independent variables do we have? This is carried from the previous lecture.

AUDIENCE: That's five?

PROFESSOR: Five. And how do you get five?

AUDIENCE: Number of components, and then two independent variables of thermodynamics.

PROFESSOR: So I see you're taking the numbers three and two, but you're adding them, and then you should be subtracting them.

AUDIENCE: Oh.

PROFESSOR: And the reason is the following. We have three components. We have three n_i's, right? But reaction balance means there's only one degree of freedom.

How do we know that? Because we have two constraints. What are they? The n of A over ν of A equals the n of B, remember this from last time? The ν of B equals the n of C over ν of C. There's two independent equations in here. You can count the equal signs. There are two equal signs. So we have three components, but two constraints, which means there's only one degree of freedom.

And we introduced this reaction, extent equals $d\xi$. You don't have to use ξ to answer any problem you're going to find in this class, but it is a nice, general form. So we have-- for one reaction, univariance, it can be called. We have only one degree of freedom.

All right. So now we're going to solve the reaction equilibrium condition by applying those constraints. So apply constraints. And here, I'm going to arbitrarily choose the product mole number as the independent variable.

So let's see. We have d n of A equals ν A over ν of C d n of c equals minus 1/2 d n of C. d n of B over ν C. d n of C equals minus 1/2 d n of C. You got this? This sort of makes sense? A plus B going to C. For every mole of C that's created-- sorry. Two C's. My apologies. For every 2 moles of C that are created, there's 1 mole of A and 1 mole of B that are destroyed. So it works out, right? For every 2 moles of C are created, you destroy one each mole of A and B.

So what I'm going to do is I'm going to plug these into my expression for dG. dG equals, then repeating from the previous board, μ of i, the n of i, and now I'm going to eliminate the n of e-- A and the n of B and write everything in terms of the the n of C. And you get the following. μ of A, ν of A over ν C plus μ of B, ν of B over ν of C plus μ of C.

And here is my equilibrium condition. OK. Now, this should have a certain similarity to what we did with the case of unary systems, when we derived the equilibrium condition for two phase coexistence. We had a chemical. We had an entropy, I think, in that case, on the left-hand side. And we needed it to be at an extrema or optimized, that is, its differential being 0.

So we have one independent variable here, the n of C. Write down some points here. dn_C is unconstrained. It's unconstrained. Can't-- we can't assume that this is 0. Why is that? Why can't we assume that's 0?

We call this an unconstrained internal variable. Why is it unconstrained?

AUDIENCE: Because even in equilibrium, the reaction doesn't stop.

PROFESSOR: Right. Thanks, So we can constrain pressure. We have pressure gauges and pressure regulators. Those exist. You can buy them. We can constrain temperature. We have thermostats. Those exist. You can buy them. And you can think of different experimental setups to constrain the temperature and constrain the pressure.

However, I want you to think of a box of gas. And you have molecules of A, B, and C. And they're zooming around in here. And this reaction can take place. You can't stop it. So even at equilibrium, this is going to fluctuate. The reaction is going to run a little to the right, a little to the left. And if you're away from equilibrium, the reaction will definitely either run to the right or to the left, right, depending.

That's the meaning of unconstrained. You can't fix it. You can't go in there with your atomic tweezers and stop the atoms from reacting. That's an important concept.

So if we have-- and this is rather like the case in unary, two phase system when we had a phase boundary and we couldn't stop the phase boundary from fluctuating. We couldn't stop a little bit of solid from evaporating, for instance, or a little bit of gas from condensing. That would be an equivalent example. The math worked out in a very similar way.

So if we need this expression to be zero, and this, in general, is nonzero, how do we enforce equilibrium?

AUDIENCE: So we have to assume that the coefficient is zero, then, since--

PROFESSOR: Coefficient

AUDIENCE: Yeah, zero?

PROFESSOR: Thank you. I didn't see who said that, but that's exactly right. If you have a function and you're optimizing it-- here, I draw for maximum. Same thing for a minimum. How do you enforce the condition of being optimized? You make the slope 0. That's what we're doing here.

Coefficient. The coefficient dG dnC must be 0 at equilibrium. That becomes the equilibrium condition.

Right. So there's some calculation here. There's some, in this case, one-dimensional function optimization in here. That's calculus. And then there's also some science, right? You have to recognize that this reaction is going to happen. You're not going to stop it. And so if dnC can't be enforced to be 0, then you've got to call this thing equals to 0 the equilibrium condition. So there's a lot in here, a lot to Unpack

All right. All right. Now, fortunately, we have expressions of those chemical potentials. So we're going to substitute ideal gas mixture expressions. This is from last time. For the mu i's. We have expressions for the mu i's from last time. So I'm going to substitute those in.

And I get the following. dG equals mu A0. That is component A in tis reference state, pure at 1 atmosphere, plus RT natural log partial pressure of A over standard pressure, this quantity times mu A over mu C plus mu B0 plus RT natural log partial pressure B over standard pressure, nu B over nu C plus mu C0, plus RT natural log pressure of C over standard pressure. This whole thing minus dn of C equals 0.

And as a reminder, mu i of 0 equals the reference or standard chem potential of component A-- I should say, from point i, at pressure P0 and temp T. And for P0, we almost always choose one atmosphere.

So we substitute. Now we're going to collect terms. Collect terms and multiply through by nu of C. I'm going to get the following. Nu of A, mu A0, plus nu of B, mu B0, plus nu of C, mu C not. I group these, plus RT natural log P of A over P0 to the power of mu A, P of B over P0 to tau of nu B, P of C over P0 to the power nu of C equals 0. Just manipulating the thing which we wrote down previously.

We're going to continue to simplify this. We're going to define something. Defined delta G0 equals this thing in parentheses equals the sum over i of the nu of i times the reference potentials.

Why does that make sense to define it that way? In this case, it's the following. 2 mu of C0 minus mu of A0 minus mu of B0, recalling, again, what our reaction is, it's A plus B going to 2C.

So what is this thing? It's the free energy change of the reaction when all components are in their standard state.

So for instance, if we assume that our standard pressure is 1 atmosphere, if you take one atmosphere of A and you react with one atmosphere of B and you produce C, where C is also one atmosphere, the change in Gibbs free energy is this delta G0.

And that doesn't have to ever correspond to a physically practical reaction. You might not ever realize that particular reaction in the lab. But thermo is all about state functions and reference data. And we're picking convenient reference data. And you can imagine that reaction, even if you don't carry it out. That is, 1 atmosphere of A, 1 atmosphere of B, and 1 atmosphere C at equilibrium.

So--

AUDIENCE: And--

PROFESSOR: --you will find this delta G-- one second, sorry, You will find these delta G0's in databases. That's the sort of thing you're going to find. If you're trying to engineer something and you need to design a reactor, you're going to be looking at these delta G0's and going forward from there.

OK.

AUDIENCE: Yeah, sorry. I just had a quick question. Are all those partial pressures in the natural log?

PROFESSOR: Yes, they're all in the natural. That's a natural log.

AUDIENCE: Yep, OK.

PROFESSOR: Let me make that really explicit. Does that help?

AUDIENCE: Yeah, thanks.

PROFESSOR: And that just comes from the property of the natural logs, you know. Natural log x plus natural log y equals natural log xy. So we just apply that sum product rule three-- multiple times. OK. Let me continue simplifying. We're simplifying.

I was just at Walden Pond with my kids over the weekend. I think that was Thoreau who said above all, simplify. It's like he was describing what someone should do in Mathematica.

So we're going to define this thing called the equilibrium constant, which some of you may have encountered in other classes. But here, we've derived it. K of P equals product operator over components P of i, partial pressure, normalized to standard pressure to the power of nu of i. So that is the equilibrium constant in terms of the pressure, so that's K sub P.

So that's kind of a big deal because it shows up in-- all over the place, including in some introductory chemistry classes. All right. We're going to further simplify. Simplify by assuming that total pressure, which we're simplifying here, but the total pressure is the reference pressure so that P of i over P0 equals x sub i, making that even simpler, again, using Dalton's rule. And if we make that simplification, we get a cleaner expression for the equilibrium constant, which is the one that we're going to use most often in this class.

And for this reaction, again, for the reaction of A plus B going to 2C, this equilibrium constant is the mole fraction of C squared over the mole fraction of A, mole fraction of B. Yeah.

So one more simplification, and then I'm going to stop and ask for questions. We're going to collect terms to write concise expression for reaction equilibrium constant. And this is a sort of expression that you may have been given in a chemistry class or you might find in Wikipedia for Kp equals e minus delta G0 over RT.

OK. So this is our final answer. This is what we're going to-- this is what's going to be useful for you after this class, when you're analyzing reacting gases. And so now you've seen it derived, and you know where it comes from.

I want to pause now. I went through that basically without interruption, or hardly without interruption, I want to pause and take questions. At Walden Pond I saw a great demonstration of thermo. There was one person out on the ice. This is on Saturday. I mean, it was warm. And one person was out on the ice. And everyone who wasn't on the ice was watching this person. And the ice was-- it was sunny. And they fell through.

So it was thermo in action. I saw someone fall through the ice. They were fine. I think people were laughing at them. It wasn't very deep where they were. And they struggled back onto the shore with their friends and I'm sure were laughed at for the rest of the day. So there's thermodynamics in action at Walden Pond. I don't have a picture to share with you, though.

All right. Questions on how we got this? Because we're going to be using this a lot.

AUDIENCE: Yeah, I have a question about the mole fractions. Are those-- like, I guess, where did the mole fractions come from? Are they the mole fractions that the components find themselves in at equilibrium?

PROFESSOR: Right, so first of all, let me answer your question in two parts. First of all, this is Dalton's rule, right? It's the definition of partial pressures, almost. So that's Dalton's rule. What mole fractions are we talking about here, right? That's a great point. So we're not going to do this a whole bunch in this class, but you're set up to do this.

Let's imagine nonequilibrium and equilibrium. Nonequilibrium-- there's something called-- sometimes as written as reaction quotient. Sometimes it's written as reaction constant. It has different forms. But it's written-- it's the exact same thing as the reaction constant. But in general, in general, it's not equal to is equilibrium value. In general, it's not equal to its equilibrium value.

So let's see what that means. Say that Q greater than K sub p. So the numerator is too large or the denominator is too small relative to equilibrium, right?

So if the numerator is too large or the denominator is too small relative to equilibrium, what direction will the reaction run? And we can answer the question thinking specifically about this case.

AUDIENCE: Would it go to the left, towards the reactants?

PROFESSOR: Right. Let's look at this. If this thing is too big relative to equilibrium, that means there's too much C or there's not enough A times B. Sorry, I was really messy with that x sub a. So that's telling you is that you're out of equilibrium, and you're out of equilibrium to the right. And the reaction will run spontaneously to the left.

And the math work out. You will find in this situation that running to the left decreases the Gibbs free energy. In other words, dG, dn of C. What's our situation here? Let me try to draw that.

This is a situation where Gibbs free energy versus n of C-- you want to run to the left to decrease Gibbs. So you have a curve like that. You run to the left to decrease Gibbs. The math will work out. I know I'm being qualitative here. The G d nfC is greater than 0, positive slope. And so it's telling you the reaction will run to the left.

And the difference between the reaction quotient and equilibrium content. That can be called reaction infinity or driving force. And there's all sorts of analyses of this. And it couples to rate-- and there's a lot of engineering in here, right? You want to figure out-- you want to design a reactor or how far away from equilibrium should you design it to be, stuff like that.

On the contrary, right, let's say Q is less than K of p. I mean, it's going to be the opposite. This is a case where there's not enough numerator. There's too much denominator. The quotient is small, smaller than equilibrium. So this is a case where you're going to decrease Gibbs energy by going to the right. dG d n of C less than 0. And the reaction will drive to the right.

At equilibrium, n of C, G-- they're right there, where they Gibbs free energy is minimized. So you can write down this expression out of equilibrium, right? And you might-- and compare this to this expression, which you get from the thermodynamics of the reaction and determine whether your reaction will run spontaneously to the right or to the left, or is it actually at equilibrium? did that help answer your question? I'm not sure.

AUDIENCE: Yeah. That makes sense. Thank you.

PROFESSOR: So basically, you can evaluate this instantaneously. Whether or not it's equilibrium depends, but you can always write that thing down.

And again, we're not doing really-- we don't really have the time in this class to talk about a bunch of out-of-equilibrium reactions and talk about rates and affinities and stuff. But that will come later in course 3 and other courses. And so you're well set up. Because if we understand equilibrium, we can start analyzing out-of-equilibrium situations.

And nonequilibrium thermos is-- exist. It's a fascinating topic, I think. And I teach it as part of the advanced thermo class, but we have no time for it here. Other questions?

I'd like to make sure that people-- this is a point from last lecture, but I'd like to make people-- sure that people understand how we get this numerator and denominator thing out of this expression. Remember, the reaction coefficients are positive for products and negative for reactants. So products end up with a positive power, and reactants end up in the basement here with a negative power.

So often, if you've seen this before, let's say an introductory chemistry, you were probably told just to put products on the top and reactants on the bottom. Well, this is where that comes from. So it's good to know it comes from somewhere. Maybe everyone understood that. I don't know. But worth mentioning.

So on the PSAT, you're asked to evaluate the equilibrium condition for a couple of reactions. And that often boils down to finding the delta G's. So I want to make this really explicit here before moving on. Delta G's-- delta G0 equals G0 products minus G0 reactants.

So that's G0 products at some temperature, let's say T2, equals G0 products at T1 plus some integrals. We've done those integrals already. We know how to do those integrals. For instance, you integrate entropy or temperature or something like that. G0 reactants at some temperature 2 equals G0 reactants at some temperature 1 plus integrals. So we're seeing that delta G0 at some T2 equals delta G0 at some T1 plus integrals. And these depend on the heat capacity differences.

So I'm doing this at a very high level and quickly here because I want to highlight the similarity to the case of unary transformations. We had-- in unary systems, we had transformations between phases. And we can analyze things like the change of Gibbs free energy or any other state function, change of h or change of s, across that transformation. And we could calculate the temperature dependence of that by integrating things that depended on heat capacity differences.

It's all formally the same right now. We're having a transformation from reactants and products. The delta G0 is important. That helps us determine equilibrium condition. And in general, it's temperature dependent.

And you're going to find things like delta G0's or their equivalents tabulated at standard temperatures in databases. And you might be asked to calculate reaction balance at some other temperature. And to do that you're going to need the cp's and the delta cp's. So formally, it's very similar to the unary case. I want to highlight that.

AUDIENCE: And if-- sorry. If a problem is just happening at standard temperature, can you then just use the standard Gibbs values? And--

PROFESSOR: Yep.

AUDIENCE: --I guess you wouldn't need it to integrate in that case?

PROFESSOR: Yes, indeed. Yep. h0 for elements at standard temperature and pressure is defined at 0. s0 for elements at standard temperature and pressure is a number, often in the back of the Hoff. Delta h0, delta s0, delta g0 for compounds-- those are numbers often found in the back of the Hoff for common reactions. That's right. And so if you're a standard temperature and pressure, you normally have everything you need, even in Wikipedia, for standard reactions. And I mean, we're analyzing, like, ammonia in this, so it's very common substances, easy to find the data. Thank you for that.

All right. Let me move on. At risk of repeating myself, notes reaction equilibrium. OK. A negative delta G0 drives reaction to the right. That's a straightforward point.

Adding more of a given component shifts reaction balance. It shifts the reaction balance to maintain equilibrium. That's Chatelier again.

Any change in the status quo prompts an opposing reaction in the responding system. And one more thing. For three or more components, there is no unique equilibrium condition.

So let's analyze again this case, x_C squared, x_A, x_B. And this equals-- OK. So this thing here is just a number, let's say at a given temperature. It's a number. And we have three variables. We know that x_A plus x_B plus x_C equals 1 by definition. They're mole fractions.

We still have one degree of freedom at equilibrium, so there's an infinite number of compositions that would satisfy equilibrium here. You can play with the method. If you want to parameterize-- fix-- you can fix x_C and then calculate x_A as a function of x_B here, if you like. There's lots of ways to slice this. But basically, you could shift your equilibrium balance.

So how does that work? Let's see how this works with Chatelier. Let's say you're at equilibrium. Let's say you're at equilibrium. And you add a little bit more x_B. You inject a little bit more component B into your system. So the denominator ticked up a little bit.

How's the reaction going to respond? How is the reaction going to respond? We just add a little bit more B. We kicked it out of equilibrium. How will the reaction respond?

AUDIENCE: It'll flow to the right to make more C.

PROFESSOR: Yeah, it's going to swerve to the right to try to counteract that change and bring this expression back to equilibrium. So you add more B, the reaction shifts to the right.

Likewise, if you add more C, the reaction will shift to the left. If you take away some A, reaction will shift to the left, and so forth and so on. You cannot get away from the Chatelier. It's always going to be there trying to restore equilibrium. It's in the math. It bears pointing out from time to time.

All right. Let's talk about temperature dependence. This gets to one of the problems in the homework. Temperature dependence of reaction equilibrium.

Now, I'm just going to do some math here, and we'll talk about the meaning. Let's calculate the partial with temperature at fixed pressure of reaction balance. And I'll do log of K_p because the math is easier this way. This is d/dt at fixed pressure of minus delta $G0$ over RT. And by chain rule, this equals delta $h0$ over RT squared minus 1 over RT d delta $h0$ dt at a fixed pressure plus 1 over R d delta $s0$ dt at a fixed pressure. So that's just the chain rule.

d delta $h0$ over dt at fixed pressure equals delta Cp, again, coming back to transformation quantities, and dx delta $s0$ dt at fixed pressure equals delta cp over T. We rely on this a lot.

And you might want to remind yourself of this. You might want to show this just in the minutes after class. Go back to when we introduce these potentials.

So using these expressions, we find d log of k of p, dt at fixed pressure equals delta $h0$ over RT squared. And this has a name. This is called the van 't Hoff equation.

OK. You're going to use a form of this in the homework because you are implicitly asked to calculate how the reaction balance changes with temperature. Let's see how this works out. Let's see how the math works.

So for example, let's consider an endothermic reaction. m, endothermic reaction. Q and delta h0 are greater than 0. That's an endothermic reaction. For example, that's the cold pack, right? So an instant cold pack. Delta h equals reversible heat for the reaction. Delta h greater than 0 means dx log kp dt pressure is greater than 0. What does that mean?

Reaction moves to the right or left with increasing temperature? With increasing temperature, do I move to the right or the left if this condition is true?

AUDIENCE: To the right.

PROFESSOR: Move to the right. k of p is products over reactants. So if k of p is increasing, if this slope is positive, that means I'm moving to the right. Reaction moves to the right with increasing temperature.

What does that mean? This system tries, doesn't actually know what it's doing, to oppose the temp rise by taking up heat in an endothermic reaction. If you try to raise the temperature, it's going cold pack on you. That's what van 't Hoff says. You cannot get away from the Chatelier.

And the converse, of course, is going to happen for an exothermic reaction. Let me ask you. If I just rip that-- wrote that backwards, products-- I just flip it, make product reactants and reactants products, everything I just said would be-- have a sign flipped. And it works out. Because nature doesn't know how I wrote this. Nature doesn't care how I wrote this. It doesn't know what the difference between products and reactants are.

So an exothermic reaction moves to the left with increasing temp. Right? OK.