PROFESSOR: Last time, you talked about the Gibbs free energy. And the fundamental equations. And how powerful the fundamental equations were in being able to calculate anything from pressure, volume, temperature data. And you saw that the Gibbs free energy was especially important for everyday sort of processes. Because of the constant pressure constraint. And the fact that the intrinsic variables are pressure and temperature. Well, it turns out that the Gibbs free energy is even more important than that. And this is something that it took me a while to learn. I had to take thermodynamics many times to really appreciate how important that was. Even when I was doing research, at the beginning, I was a theorist, and I was trying to calculate different quantities of liquids and polymers and in these papers the first thing they did was to calculate the Gibbs free energy and I didn't quite appreciate why they were doing that. And the reason is, is if you've got the Gibbs free energy, you got really everything you need to know. Because you can get everything from the Gibbs free energy. And it really becomes the fundamental quantity that you want to have.

So let me give you an example of how important that is, if you have an equation that describes the Gibbs free energy as a function of pressure and temperature, number of moles of different things. Different things you can calculate. So let's just start from the fundamental equation for the Gibbs free energy, dG is minus $S\, dT$ plus $V\, dp$. And let's say that you've gotten some expression, G, as a function of temperature and pressure for your system. It could be, as we're going to see today that we're going to increase the number of variables here, by making the system more complicated. So what I'm saying, now what I'm going to say now, is going to be more general than just these two variables here.

So you've gotten this. So you have this. You've got the fundamental equation. You've got all the other fundamental equations, and from there you can calculate all these quantities. For instance, you can calculate an expression for S. Because you know that S, from the fundamental equation, is just the derivative of G, with respect to T, keeping the pressure fixed. So you've got your equation for G. That translates into an equation for S. You can get volume, volume is not one of the variables. Temperature and pressure are the two knobs. But you can get volume out, because volume is the derivative of G, with respect to pressure. Keeping the temperature constant. And you've got S now, you got volume. Do you know where you, how did you define G in the first place? We define G as H minus dS. One of the many definitions of g. Reverse that, you've got now H as a function of G and temperature and entropy. Well, you've got an expression for G, we just calculated, we just showed we could get an expression for S, which is sitting right here. Temperature is a variable here, so now we have an expression for

H. And you can go on like that with every variable that you've learned in this class already.

For instance, u is H minus pV. Well, there's the H here. We have that equation for H. We have an equation for V, coming from here. So there's nothing unknown here. If we have an equation for G here in terms of temperature and pressure. Same thing for the Helmholtz free energy. You can even get the heat capacities out. Every single one of these interesting, useful quantities that one would want to calculate falls out from the Gibbs free energy here. Any questions on that important step?

And, really, I can't believe how clueless I was when I started doing research. Because I would go through the process of calculating G, and getting G, and et cetera, et cetera. I wrote papers, you know, G equals blah blah blah. And I didn't realize that that's why people wanted to know G. Anyway, I know better now.

So, there are a few things we can say about G that are fairly easy to calculate. For instance, if I look at liquids or solids. And I want to know how G changes with pressure. So, I know that the volume here dG/dp, that dG/dp is the volume here. So if I look under constant temperature, I pick my fundamental equation under constant temperature, and I want to know how G is changing, I integrate. So I have dG is equal to V dp. So if I change my, and I look at per mole, and if I change my pressure from p1 to p2, I integrate from p1 to p2, p1 to p2 here, final state minus the initial state is equal to the integral from p1 to p2, V dp per mole.

And what can I say, for a liquid or a solid, the volume per mole, over a liquid or a solid, is small and it doesn't change very much. So V is small. And usually these solids and liquids, you can assume to be incompressible. Meaning, as you change the pressure, the volume doesn't change. It's a good approximation. So when you do your integral here, you get that G at the new pressure is G at the old pressure, then if this isn't changing very much with pressure, or not at all, then you can take it out. It's just a constant. Plus V times p2 minus p1. And so, this is the incompressible part, you take it out. The fact that it's small means that you can assume that this is zero, this whole thing is zero, that it's small enough. And then you see that G, approximately doesn't change with pressure. Tells you that G, for a liquid or solid, most of the time you can assume that it's just a function of temperature. Just like we saw for an ideal gas, that the energy and the enthalpy were just functions of temperature.

And that's a useful approximation. It's useful, but it's not completely true. And if it were true, then there would not be any pressure dependents to phase transitions. And we know that's not the case. We know that if you press on water when it's close to the water liquid-solid transition, that you can lower the melting point of ice. You press on ice, and you press hard enough, and ice will melt, the temperature is closer to melting point. And we'll go through that. So, that means that there has to be some sort of pressure dependence, eventually. And we'll see that. This is just an approximation.

What else can we do? We can calculate, also, for an ideal gas. Liquid and solid, we can do an ideal gas. So for an ideal gas, again, starting from the fundamental equation, we have dG equals V dp. We can do it per mole. So integrate both sides, G(T, p2) is equal to G at the initial pressure, plus the integral from p1 to p2, the volume. So instead of putting the volume, this is an ideal gas now, we can put the ideal gas law. So V is really RT over p. RT over p dp. We can integrate this. Get a log term out. G(T, p1) plus RT log p2 over p1. And then it's very useful to reference everything to the center state. p1 is equal to one bar, let's say. So if you take p1 equals one bar as our reference point, and get rid of the little subscript two here, we can write G of T at some pressure p, then is G and the little naught on top here means standard state one bar plus RT log p divided by one bar. And I put in a little dotted line here because very often you just write it without the one bar and bar. And you know that there has to be a one bar, because inside a log you can't have something with units. It has to be unitless. So you know if you have something with bar here, you've got to divide with something with bar, and there happens to be one bar here. So pressure p is G at its standard state plus RT log p. And this becomes a very useful, very useful, quantity to know.

OK, so G is so important. And G per mole is so fundamental, that we're going to give it a special name. Not to make your life more complicated but just because it's just so important. We're going to call it the chemical potential. So G per mole, we're going to call mu. And that's going to be a chemical potential. We're going to do a lot more with the chemical potential today. And the reason why we call potential is because we already saw that if you've got something under constant pressure, temperature, that you want to use G as the variable to tell you whether something is going to be spontaneous or not. So you want G to go downhill. And so, we're going to be talking about chemical species. And instead of having a car up and down mountains, trying to go down to the valleys, we're going to have chemical species trying to find the valleys. The potential valleys. To get to equilibrium. And so we're going to be looking at the Gibbs free energy, or the Gibbs free energy per mole at that particular species, and it's going to want to be as small as possible. We're going to want to minimize the chemical potentials. And that's why it's called potential. It's like an energy.

So, that's the end of the one component, thermodynamic background, before we get to multi-components. So it's a good time to stop again and see if there's any questions. Any issues.

OK. So, so far we've done everything with one species. One ideal gas, one liquid, one solid. We haven't done anything with mixtures, except for maybe looking at the entropy of mixing. We saw the entropy of mixing was really important, because it drove processes where energy was constant. But most of what we care about in chemistry, at least in chemical reactions, species change. They get destroyed. New species get created. There are mixtures. It's pretty complicated. For instance, if I take a reaction of hydrogen gas plus chlorine gas to form two moles of HCl gas, I'm destroying hydrogen, I'm destroying chlorine, I'm making HCl in the gas phase. I get a

big mixture at the end. I get three different kinds of species at the end. So the fundamental equations that I've been talking about, that we've been talking about, they're too simple for such a system. Because they all care about one species. Even more complicated, for instance, if I take hydrogen gas and oxygen gas and I mix them together to make water, liquid, for instance, not only do I have species that are changing, that are getting destroyed or created, in this case here the total number of moles is changing. And the phase is changing. Got all sorts of changes going on here. And so if I want to understand equilibrium, if I want to understand the direction of time for these more complicated processes, I have to be able to take into account, in an easy way, these mixing processes, these phase changes, these changes in the number of moles.

And that's what we're going to talk about today. We're going to try to change our fundamental equations to make them a little bit more complicated so that we can deal with these sorts of problems. Because those are the real problems we need to keep track of. And the ultimate goal, then, of changing our fundamental questions is to derive equilibrium from first principles. To really understand chemical equilibrium, which you've all seen before. You've all used the chemical equilibrium constant K, you've done problems. But you've been given, basically, the equilibrium constant, and not really derived it, understood where it came from.

OK, another simple example here, which is actually the one that we're going to be looking at in the first case. Where there's a change going on, is just to look at a phase change. H_2O liquid going to H_2O solid. There's a phase change, you can think of it as one species, the H_2O liquid sort of changing into an H_2O a solid. It's the same chemical in this case here, there's no change in the molecules. But it's still a change that we have to account for.

Another example that's also simple like this, that you all, I'm sure, have seen before, suppose I take a cell. My cell here, full of water. And then I put my cell, let's say I take a human cell. My skin or something. And I take it and I put it in distilled water. What's going to happen to the cell? Is it going to be happy? What's going to happen to it? It's going to burst, right?

Why is it going to burst? Anybody have an idea why it's going to burst? Yes.

STUDENT: [INAUDIBLE]

PROFESSOR: That's right. So the water wants to go from, you're completely right. But let me rephrase it in a thermodynamic language here. The water is going to go from a place of high chemical potential to low chemical potential. And the cell can't take all that water in there. The membrane's going to try to swell. And eventually burst, right? Same thing if you if you take a, go fishing, go to the Atlantic Ocean and then get a nice cod or something. Bring it back and on your sailboat, you dump it in a tub of fresh water. Is that cod going to be happy? It's not going to be happy at all, right, because its biology is geared towards living in salt water. And turns out that the chemical

potential of water, in salt water, is lower than the chemical potential of pure water. And so when you put the cod in there, the chemical potential of the water and the cod, is lower than the chemical potential of the fresh water you have on the outside. And the fresh water wants to be at a lower chemical potential. It rushes into the cod, and well, the cod does what the cell does, when you put it in distilled water. It sort of bloats. It isn't very happy.

OK, so but all these things are basically the same idea here. Where you have a complicated change, where species are mixing, and things like this. And it turns out the chemical potential is going to tell us all about how to think about that. That's why the chemical potential is so important. So we're going to go back to these two examples here many times.

So let's take the simplest example here. Let's go back and derive some equations. Let's take our simplest example that's not a one species system, but has two species. Species 1 and 2. And n1 and n2 are the number of moles of species 1 and 2. And then we're going to see if I make a perturbation in my system. I change the number of moles of 1, or the number of moles of 2. How does this affect the Gibbs free energy? That's the question we're going to post. And our goal is to find a new fundamental equation for G that includes the number of moles of the different species as they change. Because in chemistry they're going to be changing. They're not going to be fixed. So what we want is just purely mathematically formally, take the differential of the Gibbs free energy, which we know is dG/dT, keeping pressure, the number of moles of 1, the number of 2 constant, dT. That is, dG/dp constant temperature, n1 and n2 dp.

And then we have our two more variables now, dG/dn1, remember this is just a formal statement keeping temperature and pressure and n2 constant. dn1 plus dG/dn2, dn2 keeping temperature and pressure and n1 constant here. I'm not writing anything new here, I'm just telling you what the definition of the differential is here, for G. We already know what some of these quantities are. We know that this is the entropy, minus the entropy. This here is the volume. And I know the answer already. But I'm going to define it anyways. And we're going to prove it. I'm going to define this as the chemical potential for species 1.

I'm going to define this, I'm going to give it a symbol, chemical potential mu, for species 2. So that I can write my new fundamental equation as dG as minus S dT. Plus V dp plus, and if I have more than two species present, the sum of all species in my mixture times the chemical potential of that species, dni. The change in the number of moles of that species.

So, this quantity mu, that I've just defined, dG/dni, keeping the temperature, the pressure and all the n's, except for the i'th one constant, that is an intensive quantity. Because G scales with size, scales, with size of system. G is intensive. n, obviously, scales with the size of the system. Also intensive, and you take the ratio of two extensive variables, you get an intensive variable which doesn't care about the size of the system. Which is a good thing.

For what we've been talking about. Intensive.

If I'm talking about putting a freshwater fish and dumping it in the, putting it in the Atlantic Ocean, the chemical potential of the water in the Atlantic ocean better not care whether the Atlantic Ocean is huge or even huger. It just cares about the local environment. Just cares that it that wants to be in that freshwater fish. So the chemical potential is intensive. Just as we've written it down here for a single species system. It's the Gibbs energy, free energy per mole. Which we haven't proven yet. We haven't proven yet here. We've just defined it this way and we're going to prove that in fact the mu's are the Gibbs free energies per mole for each of the species in our system.

OK, so this is now our first new fundamental equation. All we did was to add the sum here. Now, we started the lecture by saying that if you have the Gibbs free energy, you've got everything. And we wrote equations that are covered, were we can get S, we can get V, we can get H, we can get u, we can get A. So now that we have a fundamental question for G, we've got our new fundamental equations for everything else. Without really thinking too much. We go back to our definitions. Enthalpy is G minus TS. So dH is dG minus d of TS. dG, we've got our new fundamental equation for G. We plug it in here. Expand things out with a T dS here, we can write immediately a fundamental equation for H. dH is T dS. The beginning is going to look just like what you've seen before. Plus V dp. Plus an extra term, which is exactly the same extra term that we had in the fundamental equation for G. Exactly the same. And every one of the other fundamental questions can be derived in the similar way from G. And they're going to be what you had before minus S dT plus minus p dV plus the sum of the mu i's, dni, and du is T dS minus p dV plus i mu i dni.

So immediately we can see that this mu, this quantity mu that we've defined as the derivative of G with respect to the n's, we can write many other equations for mu. There are many other ways to derive it. Because this is the differential for H. This is the first derivative of H with respect to entropy. This is the derivative of H with respect to pressure. And this is the derivative of H with respect to n. Just formally, that's what it is. When you write a differential. So formally, this is also mu i, is dH/dni, keeping, now, we have to be very careful, keeping the entropy and the pressure constant. Because those are the variables. Keeping the entropy, and the pressure, and all the other n's, constant. We can also write it as dA/dni, keeping the temperature and the volume constant. And all the other n's, or we can write it as du/dni, keeping that this entropy and the volume, and all the other n's, constant. So we have many ways to write the chemical potential. They give you all the same result.

So this is the formal. Sort of the formal part of the chemical potential. Now, what we really want to show is that the chemical potential really is connected to the Gibbs free energy per mole. That's going to be the useful part. Let me get rid of this here.

So I said earlier, at the beginning of the lecture, that the Gibbs free energy per mole was so important, we were going to call it the chemical potential. And I said that here. And then I said, well, we're going to define this here, the chemical. But I haven't equated the two yet. I haven't proven to you that in fact this quantity here, which we've formally defined as the derivative of G with respect to n, is the Gibbs free energy per mole, for this species. In fact, what we want to show is that if I take the sum of all the chemical potentials, times the number of moles per species, that that is the total Gibbs free energy. In other words, that the chemical potential for one species in the mixture is the Gibbs free energy per mole for that species. Once we have that idea, then we'll be able to talk about the concept of chemical potential as this thing that we can use to look at equilibrium. To look at going downhill for the species. To see why the cell bursts and all these things. Because now we understand that Gibbs free energy is so important for equilibrium. We don't understand that quite yet, with the chemical potential. So we got to make that relation here. We need to go from the formal definition to a relation that we can understand better, because it includes the Gibbs free energy.

OK, so that's our goal now. So let's see. Let's formally do this now. Let's define, let's derive this.

OK. So remember, our goal in this derivation is to show that this is true. Or that this is true, here. And again, we're going to start with the simplest system possible. We're going to start with a two component system. And we can easily generalize to multi-component. And in our derivation, what we're going to be after is, we're going to start with the Gibbs free energy, because that's where we always start with. And we're going to remember that by definition, mu i is dG/dni, So if somehow in our derivation dG/dni falls out, that would be great. Because we'll be able to replace this derivative with the chemical potential. So the goal was to find something where this falls out, so we can replace it with the chemical potential.

We're going to start with the fact that G is an extensive variable. So if I take G at a temperature and pressure times some scaling factor for the size of my system, lambda, number of moles of n1, lambda times the number of moles of n2, if I double the size of the system, lambda is equal to 2. If I half it, lambda is equal to 1/2. Because it's extensive, this is the same thing as lambda times G of temperature and pressure, n1, n2. Just rewriting the fact that Gibbs free energy is an extensive property. And lambda is an arbitrary number here. Arbitrary variable. Now I'm going to take the derivative of both sides with respect to lambda. So I'm going to take d d lambda of this side here. And d d lambda of that side here.

Now, lambda here is inside the variable here. So I'm going to have to use the chain rule. To do this properly. So this is going to be dG/d lambda n1, there's lambda sitting in the variable lambda n1 here, times d lambda n1 d lambda. Plus dG/d lambda n2 times d lambda n2 d lambda. Using the chain rule. And on this side here, lambda's sitting straight out here. So this is very easy. This is G(T, p, n1, n2).

Now, this is good. Because this is what I'm looking for. I'm looking for the derivative of g with respect to the number of moles. Because that's the chemical potential. That was my goal up here, to make sure in the derivation, somehow, this came out. And so it's coming out right there. Right here and right here. Since the number of moles is lambda n1, that first derivative here is just the chemical potential of species 1 there. So mu 1, then we have d lambda n1 d lambda. Well, d lambda n1 d lambda, that's just n1. It's lambda times the number n1 that doesn't have anything to do with lambda. So this is n1. This is the chemical potential of species 2. Again, the derivative of lambda n2 with respect to lambda is just n2. And there is G here.

It's a fairly simple derivation, but it gets us exactly what we want. An association between this formal definition of mu, up here, directly from taking the differential. How much more formal can you be, mathematically, here? To associating this formal definition to the Gibbs free energy. Number of moles times mu 1, number of moles times mu 2, this is the Gibbs free energy per mole of species 1. Gibbs free energy per mole of species 2. The sum of all the species of the Gibbs free energy per mole of species i times the number of moles of species i is G. Or, mu i. Voila, we've done it. This is what we wanted. The chemical potential is the Gibbs free energy per mole. And in the mixture, it's the Gibbs free energy per mole of the individual species in that mixture. And if you want to know what the total Gibbs free energy is, because if you have an equilibrium, what you care about is the total Gibbs free energy. It's not the Gibbs free energy for one particular species. What's going to tell you whether you have a minimum or not in your system, whether you're at equilibrium, where you're at the lowest state possible, is the total Gibbs free energy. Now we'll be able to manipulate chemical potentials, of the individual species, to get at this number here. Any questions? This is really, we're going to see this over and over again now. This chemical potential. This idea. And it's not an easy concept.

OK, let me give you an example, then, of the water melting. And how the chemical potential comes in, now, instead of using the chemical potential. Instead of the Gibbs free energy. This is the phase transition. But it's not very different than the cell bursting when you put it in distilled water. So, we take a glass of water with an ice cube in it. H_2O liquid. This is H_2O solid. And I'm looking at the melting process. I'm looking at a process where I take a small number of molecules of water from the solid phase. And I bring them to the liquid phase. And I want to know, is this process spontaneous or in equilibrium, or not possible? Is this process going to go on? Is the direction of time that this is melting. And I want to do this formally thermodynamically. In terms of the chemical potentials. That's going to be what we're going to be talking about.

So, formally then, what's going on is, I'm taking nl moles of liquid water, H_2O liquid, which is in here. Plus ns moles of solid water. And I'm, this is my initial state. My final state is nl, plus a small number of moles, dn, of H_2O liquids, H_2O liquid, plus ns minus dn, there's a conservation of the number of molecules here. Whatever I add to the liquid has to come from the solid here. Of H_2O solid, of ice. And to know if this is spontaneous or not, if this is done

under constant temperature and pressure, what variable should we look at? G, right. We want to look at the Gibbs free energy. So what is G doing during this process here? What is delta G here? Well, we have a way of doing it now, in terms of the chemical potentials. Because we've just shown that this is the case here. So G is the sum of the chemical potentials times the number of moles in the species. Therefore, delta G is going to be equal to mu for the number of moles of l. Liquid, dn, number of moles of liquid, plus mu s dns. So the change in G is going to be equal to the chemical potential times the change in the species, which is in a liquid form, plus the chemical potential of the solid. Times the change in the species in the solid form.

Now, dns is equal to minus dnl. This is what we did right here. You take a certain number of moles from the solid form. You put it to the liquid form. That the dn up here. And you've got to have the negative of it, up here. So dns is minus dnl. Which is minus dn. Delta G is dn times mu l minus mu solid. So now we can rephrase this, it's all rephrasing. It's all basically the same thing. But, we can rephrase this process by asking the question, is the chemical potential of the liquid greater than, equal to, or less than the chemical potential of the solid? Of the water in the solid. So the chemical potential of the water in the liquid phase is greater than the chemical potential of the water in the solid phase, mu l is greater than mu s, then delta G becomes positive. In that case, delta G is greater than zero. And that's not going to happen. On the other hand, if the chemical potential of the water molecules in the liquid phase is smaller than the chemical potential of the water in the solid phase, mu s is bigger than mu l, this becomes a negative number. Delta G is less than zero. And this will happen spontaneously.

So that illustrates this idea, that the chemical potential of a species will want to go, so the species will want to go, where it can minimize its chemical potential. So in this case here, when we have the spontaneous process of the water, of the ice cube, melting, you can think of it as these water molecules that are in the ice phase looking around. They know what their chemical potential here is in the ice phase. They're looking around, they're looking to see the water phase. And they see that in the water phase, those water molecules have a smaller chemical potential. They're happier. And so these solid water molecules are jealous. And they want to go in the water phase. And the ice cube's going to melt. And it all has to do with this difference in chemical potentials for the water. And the same thing happens for the water molecules that are inside or outside of that cell that you put in the distilled water. The water molecules in the distilled water have a chemical potential which is higher than the water molecules inside the cell. And they don't want to be like that. They want to change, the system wants to change, until the water molecules couldn't care less whether they're in the water phase, or outside or inside the cell. The system is going to change until the water molecules have the same chemical potential everywhere. Where they don't have to choose one place or the other.

And so that gives us, immediately, what we're going to need when we talk about equilibrium. Equilibrium, chemical equilibrium, is going to be where the chemical potential of a species is the same everywhere in the system. So at

0 degrees Celsius, one bar, which is the melting point of water, the chemical potential of a molecule of water in the ice phase and in the liquid phase is the same. That's the definition of the melting point. It doesn't care. It could go either way. It's an equilibrium. You take an ice cube, water, liquid water, 0 degrees Celsius, one bar. You come back three days later. It's the same. Come back a week later, it's the same. It's an equilibrium. Chemical potential of the water species is the same everywhere. It's an equilibrium. And I'm just repeating that because this is so important.

OK, any questions? The last thing we're going to do is to illustrate also the importance of mixing to the chemical potential. So I'm going to set up sort of an arbitrary system here. This is kind of like the cell, or the fish, also, idea. I'm going to put a system where on one side I have a pure gas, A. On the other side, I have a mixture of A and B. And here is going to be a membrane that only allows A to go through. Only A can go through that membrane. They're going to be partial pressures in here, p prime B, and p prime A. For the gas pressures on that side, and pressure on that side is p sub A.

And my goal in this example here is to show that if I compare the chemical potential of a species in a mixture, where the temperature and the pressure total are T and p, and I compare that to the chemical potential of the same species when it's pure, when it's not mixed with anything else, under the same temperature and pressure conditions, that, in fact that that equals sign is not there. That's not what I'm trying to show. I'm trying to show that there's a less-than sign right here. To show that if you take, again, this is the cell idea. If you take the water and the distilled water, under constant temperature and pressure conditions, it's pure. And it's looking at the cell. And inside the cell is there, boy, is there a mixture of things. There's salts, there are proteins, there are all sorts of things, right? It's a mixed system. The water in that mixed system, under the same temperature and pressure conditions, the chemical potential of that water molecule is less. And that's just an entropy thing. Entropy wants to increase. It just wants to be in a place with high energy. It's the Gibbs free energy. Gibbs free energy has enthalpy and entropy incorporated into it. The enthalpy's not doing anything. It's all driven by entropy. So this is what we're going to try to show. And I'm not going to get to it today. We'll start with it on Wednesday. And I'll let your ruminate on this for the next few days.