[SQUEAKING]

[RUSTLING]

[CLICKING]

PROFESSOR: On Friday, we had a very almost philosophical lecture. And the second law can get like that. It gets sometimes a little bit head in the clouds. So today is going to be pretty mathematical. But, actually, it's very practical.

We're going to start moving from this very highfalutin concept of the second law towards useful equations that we can use, things that we can use to make predictions. So I'm going to tell you about thermodynamic potentials and equilibrium. And I'm going to start off just by listing them. These are going to be presented without proof or motivation [INAUDIBLE] we'll discuss.

So the first one is what we already know now. For fixed U entropy is max at equilibrium. So you already know that. But there are others. There are other conditions and other potentials. So for fixed entropy and volume, the internal energy U is minimum at equilibrium.

So this is a condition that you encounter in your introductory physics classes. They don't really state that, but that's the condition. Is there ever really a way to fix the entropy? Is there a way? How can we fix the entropy?

There's no entropy reservoir. We can't connect the system to an entropy reservoir like we can with a pressure reservoir or a temperature reservoir. So I'll tell you-- it's a little bit of an aside. But the only way to fix entropy is to be at 0 Kelvin. When you're at absolute zero, there's no entropy. So the physicists like it that way. But for the rest of us, it's not terribly useful.

For fixed S and P, new term here, the enthalpy H equals U plus PV is minimized at equilibrium. OK. So that's enthalpy. This condition, minimum enthalpy and equilibrium, is not terribly useful.

But the enthalpy is useful. It's a useful thing. And one of the problems on the current p set is making connection between enthalpy and the heat of a process. Sometimes those terms enthalpy and heat are actually used interchangeably. That's not strictly correct, but you'll see why.

More perfect temperature and volume-- so now we're getting a little more practical, fixed temperature. That's something we know how to do. We all have thermostats. That's what your thermostat does. The Helmholtz, F equals U minus TS is min at equilibrium.

So I'll tell you, we spent almost no time at all on Helmholtz in this class because fixed temperature and volume are much less practical and useful than fixed temperature and pressure for materials processing. However, in other disciplines, especially in semiconductors and semiconductor physics, it's the Helmholtz free energy that matters because your device is typically operated at a fixed temperature, and your electrons are confined in the volume of the semiconductor device.

So if we were to do things like calculate the theoretical limiting efficiency of a solar cell, we'd be worrying about Helmholtz. But as it is, you almost never hear us discuss that at all in the rest of the class. This is the one that matters, perfect temperature and pressure. Anybody know what's the relevant potential for these conditions? Who's read ahead?

AUDIENCE: Gibbs free energy.

PROFESSOR: Gibbs, right. So this is the one that matters for material science. And one way to see the rest of this class, actually the rest of the term, is we're just calculating the Gibbs for different scenarios. And we're doing price shopping for Gibbs, I call it. We calculate the Gibbs free energy for different scenarios. And we choose the lowest one as the equilibrium case. So that is thermodynamic potentials.

Now these are presented without proof. It's not worth the time here to motivate each and every one of those. On the piece that you're going to convince yourselves that given this, then this. So one of the exercises is going through a form of proof of this. And that's useful because Gibbs is the one we care about.

Now I have to make some mathematical asides because without this, my math note, a lot of what comes is kind of weird and confusing. So in 3.020, state functions and state variables are functions of at most three independent variables and both stay independent variables. And this is where that comes from. It comes from-- sorry, this pen is kind of smushy. It doesn't come from nowhere. It comes from the combined statement. So it comes from physical reasoning.

dU equals TdS minus PdV plus mu. Yeah. This implies the existence of a state function. U is a function of S, V, and N.

This is a critical link here. If you write down a differential form, we're going to learn how to identify the independent variables, the coefficients, and the dependent variable. And the existence of this differential form implies a state function.

Now, in most cases, we may never know this, but can-- we can still use this. That is, we may never know the closed form of the state function. But we can still use its differential form.

In fact, outside of the ideal gas situation, we almost never write down any state functions in this class. You can't find a complete state function for something useful like a high-entropy alloy. It doesn't exist. It's too complicated.

So a corollary of this is that thermodynamic potentials have what I'll call natural independent variables, which we will see aplenty in the case of Gibbs. So for example, entropy is a function of energy and volume.

If you remember, at equilibrium, entropy was max for fixed energy and fixed volume. That tells you that those are its natural variables. At equilibrium, internal energy was maximum for fixed entropy and volume. Those are its natural variables.

Enthalpy was equilibrium for a minimum at equilibrium for fixed entropy and pressure. Those are its natural variables. For Helmholtz, its natural variables are T and V. And for Gibbs, its natural variables are T and P.

Before you ding me here, I'm not writing the ends for compactness. So everything is also a function of the size of a system. I'm just leaving that off to keep the lines short.

One more note. Where on Earth does this stuff come from? When I learned thermo, these potentials were just told to me the way I just told them to you. And I think in the back of my mind, I said, where does that come from? And then I forgot the question. And I didn't come back to it for years. It does come from somewhere.

The potentials are related by a change of variables via Legendre transforms. So this is something we don't have time for in this class, and probably I wouldn't be able to teach very well anyway. This is the math concept.

And so for those of you who have seen Legendre transforms in your math classes, that's great. For those of you who are curious, you can start with a wiki entry. We're not going to cover it in detail.

You can think of it as just one more type of a transform, like a Fourier transform or Laplace transform. Fourier transform, for example, changes your natural variables from time to frequency. That's an example.

Legendre transform will change natural variables, for example, from U as a function of S and V to H as a function of S and P, exchanging V for P. And if you'll remember, H equals U plus PV. And this comes from somewhere. This is all beyond-- this is beyond 020. I just want you to know it comes from somewhere. It comes from somewhere. For most of the class, you can just memorize.

Try a bit a little more.

Let's start with the combined statement. dU equals T dS minus PdV plus mu. I'll let this be a multi-component system. So I'll keep the labels there. Somebody please remind me, what are the independent variables in this differential form?

AUDIENCE: S, V, and I.

PROFESSOR: Correct. Those are the independent variables.

The other things we call-- having fun with color today. The other things we call coefficients. So the coefficients describe how the dependent variable varies with the independent variables.

And we can write down by inspection coefficient relations. And here they are. dU dS. DU dS at fixed volume and fixed particle number equals what? What is partial U by S? You can pick it off of--

AUDIENCE: p?

PROFESSOR: Yep, you just look at the equation. Put the terms apart. And pick these off. dU dV at fixed entropy and particle number equals minus p. And dU d Ni at fixed entropy and volume and particle number J not equal to i equals mu i.

Where's your coefficient? Good call. You can them O. I just picked partial differentials. But they're called coefficient relations.

A lot of problem solving in thermo comes down to calculating these coefficients. The whole chapter, actually, in-- get to chapter 10 of the book. The most useful chapter is chapter 4. If you read only one chapter of this book, pick chapter 4 because it contains all that we need to actually solve problems. To actually solve problems, you just have to understand chapter 4. And I say just. It's actually one of the hairier chapters.

But there it is. And it's all about these coefficient relations and identifying independent variables and calculating coefficients. So let's see how to do that.

I wouldn't have called this a strategy. I think it's a little funny. Besides, it's a tactic, not a strategy. But that's what it's called in DeHoff. So I'll stick with it.

The general strategy for deriving thermodynamic relations. This is really best illustrated by an example. So that's what we're going to do.

Here is the general problem, the general problem statement. Given a dependent state variable Z, independent state variables x and y, calculate-- so this is a word problem-- delta V for a given process.

So this is like-- probably half of all thermo problems boil down to something like this. There's some kind of state variable, which you identify through the problem statement. There are some independent variables, which usually you're not told. You figure them out through the problem statement or the situation in hand. And you want to calculate the change for a given process.

So what example are we going to do? Example.

Calculate delta V for a process involving a change of pressure at fixed entropy, which is also is a reversible adiabatic process. This is helpful, remembering that fixed entropy and reversible adiabatic processes are related. That's really helpful.

So now I'm going to step through this example. We want to write down the differential for the change in the dependent variable. And this is going to depend on some coefficient times dP plus some coefficient times dS.

And our job is to find-- we want to find those coefficients, and then integrate-- this is the approach. Once you find these coefficients, then you can integrate this term, which for fixed entropy gives you the thing you're looking for, which is the change in volume. That's what we need to do.

Questions before I go on to actually do that? OK. Then we're going to start.

1-- we're going to write the exact differential. Rewriting what we did. dV equals x dP plus Y dS. x equals dV dP at s. Y equals dV dS at p. OK, good.

Then, we're going to do a change of variables. There's a really useful reference, DeHoff table 4.5. To express dP and dS in terms of dP and dT.

DeHoff chooses P and T because it's a materials science text. Another text might have chosen a different two. You can choose any two.

So we're going to look up in table 4.5. And it has the coefficients for every state variable as a function of dP and dT. So here, this is trivial. There's going to be no-- this is 0 because dP equals dP. That's trivial. The entropy is nontrivial.

We could derive this, but we're not going to take the time. We're just going to copy it from the table. It happens to be equal to Cp over temperature times dT minus V alpha dP.

That's not obvious to me. I have to think about it. This I could figure out if I thought about it long enough. This, it doesn't make sense to me. I just have to derive it. But you don't have to derive it or think about it. It's right there in the table. So here is pressure and entropy written now as dependent variables, dependent on temperature and pressure.

So we're going to combine now, and we get the following. dV equals x-- then we combine-- --equals dP-- that's easy-- plus Y. What's Cs? Cs equals Cp over T dT minus V alpha dP. I just plugged in, substituted, substituted for dS here. So that's the second step.

Then I'm going to collect terms. The third step-- collect terms. Collect terms. So I have the following. I have dV equals Y tP over temperature dT plus X minus YV alpha dP.

I still don't have X and Y. I still don't know what they are. But I can say by inspection, dV dT at fixed pressure equals Y Cp over T. That's this coefficient. dV by temperature at fixed pressure is that coefficient.

And dV dP at fixed temperature equals this coefficient, X minus YV alpha. We get the coefficients by inspection.

The fourth step is you compare to the known coefficients, again referring to table 4.5. So in table 4.5, you will find the differential form of volume written as a function of temperature and pressure. And this is what you'll find. V alpha dT minus V beta dP.

So here's the thing. This coefficient and this thing have to be equal. And this thing and this thing have to be equal because they're both the same mathematical objects. They are these partials. I always say if it walks like a duck, talks like a duck, it's the same thing.

Compare the known coefficients and equate. So we're going to equate. We're going to equate them. And we're to get the following. dV dT at fixed pressure-- well, that was this-- equals Y Cp over T-- but it's also this-- equals V alpha.

And dV dP at fixed temperature equals this. X minus Y V alpha. But it's also this. It goes minus V beta. So now, we have our answer. How? We have a system of two equations and two unknowns, X and Y. Two equations and two unknowns.

So now you can solve. 5-- solve for unknowns. I'll spare you the algebra there because it's pretty easy. Solving for Y V alpha T over Cp. And solving for X equals V squared alpha squared T over Cp minus V beta.

And these are complicated and nonobvious. That's why you need a tactic, set of tactics, to get to the answers. Because if you follow this approach, you will always get the right answer even if it doesn't make sense to you.

So here's the final answer. dV equals V squared alpha squared T over a Cp minus V beta times dP plus V alpha T over Cp times dS. This is the thing we were looking for. That's it.

We integrate this to find change delta V for given delta P at fixed entropy.

Again, this is mechanics. This will work for you even if you don't have a physical intuition for every step. This strategy works.

Question. For a real material, when you are-- this is very realistic. I mean, now we go from multivariable calculus to money on the line. You are calculating the effect of a pressure change on the volume of components.

Let's say you're going to send this into outer space. And you have a system made out of components. And the components are made out of materials. And you want to make sure that the pressure change that your device experience isn't going to cause the thing to fall apart. So now this matters a lot. You need to know how to do that calculation. Here's how.

Question. Where are you going to get this? This is the integrant. How are you going to evaluate the integrant? How are you're probably going to end up evaluating the integrant when you're working at SpaceX, and you need the answer in five minutes?

Let me set up a straw man. Are you going to do density functional theory calculations to calculate the thermal expansion coefficient, and specific heat, and volume, and compressibility for your material from first principles?

AUDIENCE: You're going to probably look at databases.

PROFESSOR: Databases. Thanks. That's my favorite word. You're going to look at databases. This stuff is in databases.

You're going to parameterize what you need using databases. You're going to plug that in. And you're going to do this integral numerically. The computer is going to do it for you.

You're going to make sure you have good sources of data. You're going to make sure the data is inputted correctly. You're going to make sure your units are right. And then the computer is going to do this for you as a numerical integration. That's how it works in the real world.

So this hairy-looking challenge is why we hammer on this stuff in 020. And they make you talk to the-- you get to meet the librarians and such because being able to go from those data resources to answers is really an important skill. It's really an important skill.

There is one case where you don't need to do any of that. And we'll discuss this a little more next lecture. And you can work this out on your own if you're curious. It's also worked out plenty in the textbook.

For an ideal gas, as with many things, it simplifies. So you don't need any databases to evaluate this for an ideal gas. It simplifies to the following. X equals minus V over P times Cp minus R or Cp is also equal to V over P Cv over Cp.

And this leads to an expression, which before we just gave you. P final over P initial equals V initial over V final. This is where that comes from. And if you use this expression for adiabatic process for an ideal gas, it comes from this.

So I'm not going to take time to derive that now. It's kind of an interesting calculation. You can just evaluate all this stuff.

And I'll just mention that in p set 2, in p set 2, you're doing a related problem, which is you're calculating change in Gibbs free energy with current pressure and entropy. So we just did volume with pressure and entropy. And in p set 2, you're going to do Gibbs with pressure and entropy. But the overall what they call the general strategy is the same.

So for the remaining minutes, we're going to get a little bit specific and talk about Gibbs free strategy. Let's talk about equilibrium-- fixed pressure and temperature. So now we're reprocessing materials.

Gibbs free energy equals U plus PV minus TS is minimized. Let's play with a differential form, dG. So I'm going to use the chain rule. dG [AUDIO OUT] dS minus S dT. And that was just chain rule.

And now, I can use the combined statement. dU equals TdS minus PdV plus mu of i dN of i. That is all dU. I carry the rest of the terms. Plus PdV plus VdP minus TdS minus S dT. So here I use combined statement.

And I'm going to see a bunch of things cancel. I'm going to see a bunch of things cancel. So we have TdS cancels TdS. Minus PdV cancels PdV.

And so this simplifies a little bit. And I get the following. Equals minus SdT plus VdP plus mu i dN of i.

Good. This is what we wanted because I told you the natural variables for Gibbs were temperature, pressure, and particle number. And that's what we get. That's what the calculus gives us.

So there's a little clue there into how the Legendre transform works. But again, we won't go there.

So the independent variables are T, P, and N sub i. And what are the coefficients? Somebody? Please?

AUDIENCE: S, V, and mu of i.

PROFESSOR: Right. Minus S, V, and mu of i.

I'll make a note here. A lot of times, in this class, I use implicit summation. You probably picked up on that. But this implies i, mu of i, and i. It's just a little bit more compact. There's no i index on the left-hand side. So that means it has to resolve on the right-hand side. So you implicitly sum.

And by inspection, by inspection, minus S describes the change of Gibbs with temperature at fixed pressure and particle number. Volume describes the change of Gibbs with pressure at fixed temperature and particle number. And finally, our favorite-- chemical potential describes the change of Gibbs with particle number i have fixed temperature, pressure, and particles j not equal to i.

So already, we can say something about the slope of these things. On a slope of-- let's see. Here's pressure. And here's Gibbs free energy. And we're fixing temperature and particle number.

What's the slope? What's the slope? Is it positive or negative? Gibbs versus pressure for fixed temperature and particle number.

AUDIENCE: It's positive.

PROFESSOR: Positive because volume is always positive. Can't have negative volume. So that's good. Being able to pick off the slope and the curvature of these things is really useful. It's really, really useful, as you'll see.

What about this? What about temperature? Change of Gibbs with temperature for fixed pressure and particle number.

AUDIENCE: Negative.

PROFESSOR: Yeah, it's negative because entropy is strictly positive. So negative entropy is strictly negative.

You got to think about these slopes. If Gibbs free energy increases when we squeeze, that's related to the enthalpy. That's related to the enthalpy.

When we squeeze something, we're increasing the energy content of all the bonds that make up that thing. When we squeeze something, we're increasing the entropy content of all the bonds that make up that thing. So this is Gibbs free energy getting higher as we squeeze.

When we heat something, Gibbs decreases. When we heat something, we're increasing the entropy. We're Increasing the amount of mixedupness. And Gibbs depends negatively with entropy. Well see this in many examples. So up with pressure, down with temperature.

What about conditions that we're interrupting? At fixed temperature T, at fixed temperature and pressure, dT equals 0. That's pretty easy. And dP equals 0. That means the equilibrium, the equilibrium condition, reduces to dG equals minus SdT plus VdP plus mu of i dN of i.

And we're holding that fixed. And we're holding that fixed. That means it basically reduces to this-- equals 0 because G is min at equilibrium.

So if you think back to calculus, when you would calculate extrema. The extrema positions of a function are where its slope is 0. So equilibrium condition is that the change of Gibbs with particle number i is 0.

So for most of the cases of interest to us as practicing materials scientists, that is multi-component, heterogeneous systems. This becomes dG sum over i component k dN i component k.

I'm introducing a new notation here. Superscript labels phases. And the subscript labels components.

So now we can picture something in our minds. We have a phase boundary here, two phases. And each phase has two components.

This was a purple-rich phase, and this was an orange-rich phase. And evaluating the equilibrium condition is going to come down to knowing how the components can exchange between phases and what the effect of that exchange is on the chemical potential. Let me write that out.

What determines whether or not components can exchange between the phases? It's the boundary. The property of the boundary tells us what components can exchange between phases. And that can be engineered. So there's a lot of engineering around choosing boundaries to get the desired equilibrium condition.

But much of what comes later in this class is calculating composition dependence, calculating the composition dependence of those chemical potentials. And we're going to develop models for that and graphical tools for that, finally leading to binary phase diagrams.

One last note. Going to do one last note about independent variables, sometimes called natural. If a state variable is regulated, regulated, what does that mean? Controlled. Regulations are controls.

If you go to a McMaster-Carr, you can buy a regulator for pressure. If you go to Home Depot, you can get a regulator for temperature. We call it a thermostat. And those things that you would buy have analogs in-- not the real world, but in R&D and materials science, as well.

If a state variable is regulated-- that's why I'm using that term, because it will help you in the future. If it's regulated, then it must be independent.

So choosing your independent variables is one of the major intellectual challenges of thermo. It helps even know that that's the challenge you're facing. Knowing that that's the challenge you're facing, it gives you a good start.

Identifying independent and dependent variables from the problem at hand, that's key to success. So for example, if the problem statement says something about fixed pressure, then you need to choose pressure as an independent variable.

If the problem says adiabatic, you need to choose what? What should be your independent variable if the problem statement said adiabatic? What should be one of your two independent variables?

AUDIENCE: Entropy.

PROFESSOR: Yeah, entropy. And if the problem statement says in a thermal bath, then you need to choose temperature as one of your independent variables and so on.

So this is like a key for turning problems that you encounter on problem sets or in the real world into things you can solve using thermo.