[SQUEAKING]

[RUSTLING]

[CLICKING]

RAFAEL JARAMILLO: And all right, so let's go, ideal gas processes. How to motivate this? It's not just that we like ideal gases because they have a simple equation of state. What we're going to see in a couple of lectures is that the process of mixing ideal gases is a model for the process of mixing real materials.

So in case you're wondering why are we spending all this time on gases-- and ideal gases, for that matter-- there is a material science motivation for it. OK. Let's start with reversible adiabatic expansion. You looked at this a little bit at the last lecture. I want to look at it some more because it is really important.

Reversible adiabatic expansion. So what to choose for independent variables? So this thought exercise again, you have a problem, you want to calculate something about that process. What are you going to choose for independent variables?

Well, adiabatic means no heat. And we said it's reversible. So what does that mean? Is anything fixed? And what does that imply we should use for an independent variable?

AUDIENCE: Pressure and temperature.

RAFAEL JARAMILLO: So here's a rule of thumb. If something is fixed, meaning constant, then it's independent. Let's call this stubborn. If something is fixed or constant, you can also say it's stubborn. Something that's stubborn is independent.

So what is a state variable, which is fixed, for a adiabatic reversible process?

AUDIENCE: Would it be entropy?

RAFAEL JARAMILLO: Entropy, right. This is a process for dS equals 0, which means we need to use x as an independent variable. If something stubborn, it's independent.

All right. And I said expansion. So you could say P or V change. Let's use P. So these are going to be our independent variables here, S and P.

So we want to find the equation of state that describes, let's say, temperature as a function of entropy and pressure. Just for example, let's say the problem asked, calculate the temperature change for a reversible adiabatic process moving from pressure 1 to pressure 2, something like that. So that would be a useful equation of state to find.

All right. So now this is going to be more practice on the general strategy. That's really one of the reasons I'm doing this here. So you see this. Use general strategy to find dT equals-- let's say M dS plus N dP, where M and N are the unknown coefficients.

So then we substitute in. We do a change of variables. We change from S and P to T and P, as we did the last time. Pardon me. Minus V alpha dP plus NdP. Change-- that's a change of variables. And then we gather terms.

Just gathering terms. Then we can say by inspection, M Cp over T equals 1. Why is that? dT has to equal dT. So this got to be equal 1. This has to be equal to 1.

And so it's equal-- M equals T over Cp. All right. And likewise, if we have T as an independent variable-- dependent, sorry-- and the two independent variables here are T and P-- it's kind of silly-- this thing has to be 0. dT has to be equal to dT, end of story.

So N minus MV alpha equals 0. And so N equals TV alpha over Cp. All right, so these are the coefficients that we were looking for. I did this more quickly than I did it on Monday. Again, there's lots more examples in the book, but this is the general strategy. So we found our coefficients there. That's what we were looking for.

Now we can plug in. We can use properties of the ideal gas. What are some properties of ideal gases? V equals RT over P. Let's just keep the number of moles equals 1 first because it's easier that way and also because I did this thing where I used N and M, because the textbook does it that way.

I don't like to do it that way because N is also the number of moles. So we're going to just pretend I didn't do that. All right. And alpha equals 1/T. We calculated on that first or second day. And another result, which you're probably familiar with from the book-- we haven't explicitly mentioned in class-- which is that Cp equals 5/2 R for a monatomic gas, monatomic.

All right. So now we can calculate the thing which we are looking for. dT at fixed entropy equals dT dP at fixed entropy dP. And this we have from the previous board. That's what our general strategy gave us. TV alpha over Cp dP.

And we can plug in stuff from the ideal gas-- equals TRT Cp TP. All right. We're using ideal gas properties there. And we're going to simplify R over Cp T/P dP equals-- you can also say 2/5 T/P dP. I'm writing off the edge there. Sorry about that.

I can separate variables. This is a separable differential equation. This is a separable differential equation. There's dT. There's dP. There's T. There's P. It's separable. Separate and integrate.

DT over T equals R over Cp dP over p. Integrate that, and I get T final over T initial equals P final over P initial R over Cp.

So I gave you this in the P set and in a lecture a couple of lectures ago. And then on Monday, we did something like this. We used the general strategy, and we reduced it to the case of ideal gases. And then today, we just went a little farther because we went a little faster. And we actually derived an expression for the adiabatic reversible expansion of an ideal gas.

So we've kind of seen the same thing now at three different levels. And this is just one expression which you'll find. If you look up on Wikipedia ideal gas adiabatic process, you'll find several expressions. They're all equivalent. There are alternative forms.

There are alternative forms for adiabatic of the original IG. PV to gamma equals constant. That's an alternative form. TV to the gamma minus 1 equals constant. These are simply related by [INAUDIBLE]. It does use the ideal gas equation of state. You can get from one to the other.

Here again, gamma equals the ratio of Cp over Cv, which we know is greater than 1 for physical reasons we've discussed before. Or if you want, P final over P initial equals V initial over V final. I think we've seen that already. So these are all equivalent. These are all the same thing.

And we know that we have-- on a VP plot, if we have isotherms, the adiabat is going to be something steeper. So if these are isotherms, this is the adiabat. Right. OK.

So we've seen this before. There's an interesting alternative derivation of this that does not use the general strategy. I think it's interesting. You should check it out. DeHoff section is-- I wrote this down-- 4.2.4. He uses the fact that for an ideal gas, the internal energy depends only on temperature.

And you can also start from this expression and derive these. So if you're interested, let's do that. Let's do that. dQ equals 0 alternative. Alternatively, dQ equals 0. That means that dU equals work-- because there's no Q-- equals minus PdV. All right.

Previous-- we're going to use that. And we will use both of these combined, substituting Cv dT equals minus p dV equals minus RT V dV.

Again, separate and integrate. We got-- well, this is separable, right? Cv dT over T equals-- minus R dV over V. And we can integrate that, and we get T final over T initial equals V initial over V final R over Cv-- which, again, is the same thing. So we're dancing around the same thing here.

Good. OK. So by now, you've probably had more than enough of reversible adiabatic expansion of an ideal gas. Let's do isothermal expansion.

All right. Isothermal expansion-- this is our second one. Here, same question I asked in the beginning, what to use four independent variables? What should we use for independent variables?

AUDIENCE: Temperature and then either pressure or volume again.

RAFAEL JARAMILLO: Good, thank you. Isothermal dT equals 0. That means you use T. Temperature is stubborn. It's independent. And expansion, you're going to control something. Something that's controlled sounds like it should be an independent variable expansion. So we're going to-- in this case, we use pressure. We could use volume, but we'll use pressure. All right.

And what I want to do now is find the equation of state Gibbs free energy T and P. So this is an example where-- let's say someone said-- or your problem statement boil down to, we have an isothermal expansion and we want to calculate the change of Gibbs free energy for some process going from pressure 1 to pressure 2. That's a very common scenario that you'll find. To do this calculation is very, very common.

So let's see how to do it. We want to find a change, so we want to use calculus. So let's use the proper differential form. dG equals-- well dG equals minus SdT plus P dV. That, we know.

But we also said this was isothermal. So this is really pretty simple. It's a single-variable calculus problem. I point this out over and over again, so forgive me for pointing out again. This is why if something is stubborn or something is fixed, it's independent. Not only does that make sense, it also makes your life easier.

When you have multivariable calculus and you have an opportunity to reduce it to single-variable calculus, you should take that opportunity. So here's an example. If you have two terms on the right-hand side and you can set one of them to 0, the math gets easier. That's why a correct choice of independent variables is so important.

This boils is way down here. PdV for an ideal gas is RT P dP-- wait, I'm sorry. No one called me out. Right. Gibbs free energy, independent variables are T and P. And I get to ignore half of the right-hand side. So things simplify.

And this is pretty easy integral. So dG equals G final minus G initial-- we'll call that delta G-- equals RT plug P final over P initial. The math is easy when we set the problem up right.

I'm going to put two boxes around this. The math-- oh it's like a-- it's a Christmas equation. The math you just saw is very easy, but this is something which will stick in your mind. Because you will see expressions like this in other classes over and over and over again.

So, for example, if you do electrochemistry, this equation sets the voltage of your device, be it a reactor or a battery. This is called the Nernst equation in another context. If you do chemical engineering and you calculate change in chemical potential with

fugacity-- we're not going to use that word in this class because this is course 3. But if you're in course 10, it's like fugacity this, fugacity that-- you're going to have log of fugacities, and it's going to be the same equation-- and so forth and so on. This is really foundational, so that's why I put it in two colors.

AUDIENCE: Sorry, right have a quick question. Are we assuming that we're using molar volume here?

RAFAEL JARAMILLO: I've kept N equals 1 moles. N equals 1 for simplicity here.

AUDIENCE: OK, thank you.

RAFAEL JARAMILLO: Yeah. So thanks for clarifying. Yeah, sure. It's molar volume because it's 1 moles. I just didn't want to carry an extra term. If you wanted to, you could put an N there. And then you have an N there, and that would be fine. So let me we put a go to N here.

Here's an N, and you can put an N there. And everything else is the same, same thing. Good. All right.

Now, again, I don't expect you to have the skies part and the angels singing now, because we haven't gotten to the usefulness of this expression. But I want it to lodge in your mind because we're going to come back to this over and over.

All right, let's talk about another ideal gas process, adiabatic free expansion. So this is a little bit of a kooky example when you first see it, if you haven't seen it before. So just bear with me.

So here's what we have. Here's the situation. We're going to have a piston. So we're going to have a piston. And this is a cylinder, and it's thermally insulated. So I'm drawing insulation. Insulated. Pardon me, that's not very clear-- insulated.

And let's make the gas orange. Simple picture, right? So what we're going to do is we're going to withdraw the piston instantaneously, instantaneously, so much faster than the gas molecules can move, definitely much faster than their sound velocity.

I made it bigger by accident, didn't mean to do that. Here's the original position of the piston. And I'm going to pull it back very quickly. So it's now going to sit here.

The same picture. And the point is that at T equals 0-- let's call it at-- instantaneously, none of the gas molecules have had time to move anywhere.

So the gas molecules are occupying the space here. And in the space evacuated by the piston, we have a vacuum. So that's the setup. Like I said, it's a little kooky. There are actual, useful, real-world scenarios that approximate this. But for now, it's just a thought experiment.

All right. So what's going to happen spontaneously next? Gas will spontaneously do something.

AUDIENCE: Expand?

AUDIENCE: Diffuse into the vacuum?

RAFAEL JARAMILLO: Freely expand into the free volume. It's kind of spontaneous to expand into the free volume. And this word spontaneously in thermodynamics it also means irreversibly. So when you see one, I want you to think of the other.

If you remember, we did this with the baby book, right? This was the baby book from as well. This gets beyond 0.2.0, but somebody said diffuse. The process here would be initially something that's super diffusive. Because initially, the molecules that are moving to the right encounter no collisions with any molecules coming from the left or coming from the right, moving to the left.

So you can imagine almost, like, a shock wave of expansion, followed by a diffusive mixing process-- so anyway, again, just because somebody mentioned diffusion. So this is the setup.

All right. You got that picture? So let's calculate something about that process. Let's calculate the work and heat during free expansion. Start with the work.

Work equals minus dV times P. And here's the sort of kooky thing which we tell you, but it's true. The pressure of the expansion is 0 because the gas is expanding into-- or, here, better say-- against vacuum.

So the gas is doing no work in order to expand. There's nothing pushing back. So work equals 0. What about heat?

AUDIENCE: I have a quick question about homework.

RAFAEL JARAMILLO: Yeah.

AUDIENCE: So since it's like an integral dV and the volume, isn't the volume changing?

RAFAEL JARAMILLO: Volume's changing.

AUDIENCE:	So, like, mathematically, how would it work out to 0?
RAFAEL JARAMILLO:	The pressure is 0.
AUDIENCE:	Is it the pressure? Oh, I see. Sorry.
RAFAEL JARAMILLO:	If you think about-- work comes back to energy, which is forced by distance. Go way back to the beginning. So if you're pushing something, something's pushing back, right? That's Newton's third law or something like that. If nothing's pushing back, there's no work.

So that's one reason it's free. I mean, this term free expansion is as old as the hill, so I'm not going to change the term even though sometimes I think it's confusing. But that's one way to think of the meaning of free. The expansion comes for free. You don't have to do any work to move into that space.

All right. So dV here is finite, but the pressure is 0, the pressure during the expansion. And heat Q equals 0 because I said it was adiabatic. So the change of energy during adiabatic free expansion, this implies dT equals 0 for ideal gas. Right?

For an ideal gas, remember temperature and energy are one to one. So if there's no change of energy, there's no change of temperature. OK. Let's keep talking about this.

Adiabatic free expansion is spontaneous, so delta entropy has to be positive. That goes back a couple lectures. It's spontaneous. That means that it has to change the entropy, has to change the entropy. And it has to change it with a positive sign.

How do we calculate-- how to calculate delta S? How do we calculate it? We want to find a differential form and integrate. dS equals-- delta S equals dS equals something.

All right. So here's one of the first cases where we're going to, in this class, see how we can calculate the results of processes using thermo even if we can't calculate the specific processes themselves. So we have this spontaneous process, which involves this nutty expansion into a vacuum, takes place very quickly. That doesn't sound like something we know how to calculate.

We can't use PV equals nRT because during that process, the system is not at equilibrium. So the challenge is, can we think of an equivalent reversible process that brings us to the same endpoint?

Reversible process with same initial and final states. So we're going to have start, end. And we have this free expansion process, which I'll draw as being kind of nutty.

And we want to come up with a reversible process with the same starting and ending points. Because if we can do that, we can calculate delta S. And we'll know it's the same, regardless of whether I take this path or that path.

So let's imagine a reversible process. What do we know about this process? We know that delta T equals 0. We know that delta T equals 0. So let's consider isothermal.

As before, isothermal process, no change in temperature. We're going to use T as an independent variable. We'll do expansion. Let's use volume this time. Isothermal expansion.

So this isn't saying that the adiabatic free expansion is the same as isothermal expansion. But if I want to calculate a change in state variables, I can use this path instead of this path. OK. So does anybody want to-- let's see. I have some-- let's see.

I want to pause here before we do that calculation. I'm going to pause here before that calculation. Because that was a lot of stuff. I'll take questions before moving on.

AUDIENCE: Can you go back and explain again why heat equals 0?

RAFAEL JARAMILLO: For this process?

AUDIENCE: Yes.

RAFAEL JARAMILLO: Yeah. And part of this is-- shoot, I was about to-- just the way the problem was set up. So I told you the setup is a little bit kooky. I'm imagining a thermally-insulated piston.

So a thermally-insulated piston, it's in the title, adiabatic. So thermal insulation, heat equals 0. So for that process, for that process, work equals 0, and heat equals 0.

Remember, those are process variables, right? So that means that a different process might have different process variables that still go between the same start and end state. So I'm going to calculate delta S next, but I want to gather more questions.

AUDIENCE: So for isothermal expansion, previously, you had used P as your independent variable. Is there a reason why you're changing it to V now? Or is there a way that we should--

RAFAEL JARAMILLO: It's about the same. For ideal gas, of course, PV equals RT. For ideal gas with N equals 1, PV equals RT. And for isothermal processes, this is just a constant. So you can always swap P and V. They just end up being the inverse of each other.

AUDIENCE: I see. OK, thank you.

RAFAEL JARAMILLO: That's always easy. I just did this because before, I did the other way, and just see it both ways.

AUDIENCE: I have a question-- sorry-- going back to the reversible adiabatic expansion. And you mentioned the step by inspection. And that was when we identified the variables M and N. Would you mind clarifying how you got to there?

RAFAEL JARAMILLO: Sure. So that was back here, right? That was back here?

AUDIENCE: Yes.

RAFAEL JARAMILLO: Yeah. So let's talk about coefficients, coefficients. I'll ask you, tell me, what is dT at fixed pressure? Obviously, that's 1, but forget about the fact that you know that's 1. Just pick it off of this line. What is dT dT at fixed pressure?

I'm glad you asked. Because this is a very common mental exercise in thermal, and maybe you're less familiar with it coming into this class. All right, differential form, dependent variable, independent variable, coefficients. The coefficients are the partial differentials. So dT and fixed pressure is this coefficient.

Likewise, dT dP at fixed temperature equals N minus MV alpha. Now, this is sort of silly in some sense, a silly example. I mean, it's useful. The result is useful. It's a little bit of a silly example because dT has to be 1. You don't need to go to table 4.5 in DeHoff for that. You can just go ahead and say that's 1.

And dT dP at fixed temperature, what's the dT when temperature is not changing?

AUDIENCE: Oh, that would be 0.

RAFAEL JARAMILLO: Has to be 0, yeah. So what we have here is we have a system of equations, right? We have two equations and two unknowns. And that's what I'm doing here, is I'm solving for those two unknowns given those two equations.

The example that you're doing in the P set is a little bit less-- I don't want to call this silly, but it does require that you look up the coefficients in table 4.5. It's not as immediately apparent what these should be in the problem you're working on the P set.

But that's what I meant by inspection. It means you look at the differential form, you pick off the partial differentials, and you equate them to what you know them to be. In this case, it's 1 and 0.

AUDIENCE: OK, that makes sense. Thank you so much.

RAFAEL JARAMILLO: Yeah, thanks. So to finish here, coefficients, coefficients, those are coefficients. Let me calculate the change in entropy here, because I think that it's another example of using these differential forms. And so maybe it will help right now.

So let me give you let me give you something. We have T and V, and I want to calculate delta S. So I need to integrate dS-- sorry. I need to integrate dS, which is going to be dS d-- no change in temperature-- so dV, dS dV at fixed temperature dV.

This is the thing I need to integrate to get my answer, which means I need to be able to write this down. I need to know what is this coefficient. That's what I need to know.

So the implied differential form here is dS equals dS dV at fixed temperature dV plus dS as dT at fixed volume dT. I'm going to skip a couple of steps here because we have 8 minutes remaining. So I'm going to use the general strategy-- or I think this particular case is also just worked in the book, so I could also go look it up.

And I get dS equals-- and we have to copy this-- Cp over T minus V alpha squared over beta. A lot of times, again, these coefficients are non-obvious. You just have to trust that you're doing the process correctly and use the result. OK. So this happens to be what you get.

So for dT equals 0-- again, good choice of an independent variable because I get to ignore half the right-hand side of the equation. For dT equals 0, dS equals alpha over beta dV. For an ideal gas, we have alpha equals 1/T. Beta equals 1/P.

dS equals P over T dV-- again, using ideal gas equation of state. So this is pretty simple in the end.

I can integrate dS. It's going to be the integral by dV of R/V equals simply R log V2 over V1 dS. This is my answer. This is the answer I was looking for, the change of entropy for a reversible process isothermal expansion.

And here's an important thing. It's greater than 0. So what does this mean? If I start with my gas molecules here in vacuum on the right, spontaneous process is going to bring me to gas molecules everywhere.

V2 over V1 greater than 1, delta S greater than 0. Spontaneous entropy generation.

What happens if I tried to run this movie backwards? If I ran this movie backwards, everything would be the same in terms of the calculation, except V2 and V1 would be switched. The final volume would be smaller than the initial volume. So the change of entropy would be negative.

So it's our experience that you won't spontaneously have the gas molecules uniformly distributed in the box and then going through a situation where they leave a vacuum on the right-hand side. That's not our experience. Here's uniform gas molecules going to-- that red pen is causing trouble here-- going to a situation.

But they segregated themselves spontaneously on one side. We know this would never happen spontaneously. Again, this sort of goes back to the baby book we discussed. This happens spontaneously, this doesn't happen spontaneously. Now we have some math to support that. We have something called the second law. We know that spontaneously, entropy has to always increase or stay the same. It can never decrease. And now the math of this backs us up.

In this case, over here, we have V2 over V1 would be less than 1. And delta S would be less than 0. So that doesn't happen.