

**RAFAEL**

**JARAMILLO:**

All right, so let's talk about processes and thermodynamics. So we talked about thermo being this weird thing that can tell you about starting state and the final state. But it doesn't really have a clue as to the process that takes you from one to the other. That is thermo doesn't describe real world processes.

But that doesn't mean it's useless. The concept of state functions, which are history independent, allows us to make predictions. So for example, if someone told you the pressure, temperature, and volume of the system at the beginning and then told you the pressure and temperature of the system at the end, with that information you could calculate the volume without knowing the process that took it from A to B. So that's useful.

So here's the property of state functions. Any process connecting A to B will give same results for the final state. These are the final state variables, because they are state variables. So you want to calculate something. You want to do the easiest calculation you can, conceptualize the simplest process to calculate it.

So in the same way that we choose a system, its components, and its boundaries out of convenience depending on the problem we're trying to solve, you calculate the simplest process to calculate out of convenience, not necessarily the process that nature actually takes. So the simplest processes to calculate are reversible. So reversible process, that's a new concept. That's a new concept for us. And it has a very deep and important thermodynamic meaning.

It means a process that does not change the entropy of the universe. That is a system plus its surroundings. And we'll see that in the next couple of lectures.

Reversible processes have these properties-- the system plus surroundings are in equilibrium at all times. That's an assumption. This violates our day-to-day notion of an arrow of time. It's really inconsistent with most of our experience.

In practice, a reversible process would take forever. So we're imagining a process, which doesn't actually exist. But it makes a calculation easier. So in order for a process to be in equilibrium at all times, it has to go arbitrarily slowly. In order for our process to be able to go forwards or backwards, we need to be able to play the movie forwards or backwards without being able to tell which one is forwards and which one is backwards. That violates our day-to-day notion of the arrow of time.

And the requirement to go arbitrarily slowly means that in practice, a reversible process would take forever. But it makes calculations really easy. Is that surprising to anybody? Or we're comfortable with the concept of a reversible process? None of your day-to-day processes are reversible.

If you think you can think of one, just toss it out. And we can try to figure out why it's not. Those are kind of fun thought experiments.

Let's describe processes. In the last lecture, we described systems. Now we're going to describe processes.

So things you can do to a system-- you can work on it, you can heat it, or you can add or subtract stuff. These are things you can do. These are verbs in thermo. All of these are verbs in thermo. They're actions that you do on a system.

Work, what is work? It's a mechanical way of exchanging energy, mechanical exchange of energy. So we use  $w$ , and what's that? Kilogram meter squared per second squared, that's the units of energy. Just a little bit of dimensional analysis-- you guys separate that out, it's kilogram meter per second squared per meter equals force times distance. That's force, and that's distance. That's fine.

In thermo, we normally separate that out a little bit differently. We grab kilogram per meter per second squared. What do I need? What do I need to multiply this by in order to get the same units?

What do I need?

**STUDENT:** Volume, meters.

**RAFAEL JARAMILLO:** Volume, yeah, meters cubed. So what's this? This is a pressure times a volume. So when you take Intro Mechanics, let's say in a physics class, you normally do force times distance work. But when you take Intro Thermodynamics, you normally do pressure volume work. Course C is where I got this at.

But this is  $P, PV$  work, we call it. That's work. What about heat?

Well, it's kind difficult to define, actually. Heat is a process that exchanges energy without mechanical work or mass exchanges. So heat is defined by what it's not. It's kind of a weird thing.

And for heat, we're going to use  $q$ . So work is  $w$ , heat is  $q$ . They both have units of energy, joules.

So we have described state variables, which are history-independent. But we also have process variables that are process-dependent. So infinitesimal increments, infinitesimal of process variables are denoted as-- I'm going to put this in quotes, "inexact differentials." That is  $dq/d$  work. Using  $d$ , not  $D$ .

This is annoying. Don't blame, don't shoot the messenger. This is one really key area where thermo deviates from multivariable calculus. So try not to get confused because it is confusing.

There's a mini lecture I recorded. It's up on the website called, the Three d's of Thermodynamics, because it gets kind of hairy. We use a lot of d's to denote differences. So hopefully, that's useful at some point, if not now, then maybe in a week or two in the class.

In thermodynamics this Greek  $dx$  means path dependent. That's what it means. So what is a process variable? If you have a state A and a state B, a process variable is a variable, which depends on the process it takes to get from A to B.

So you might have path 1 with work 1 and heat 1, and path 2 with work 2 and heat 2. And those are different because they're not state variables. They're process variables.

If we were on campus, the nice analogy to use is the amount of work you need to get from the second floor of building 1 to the fifth floor of building 32, or just pick a pair like that. There is myriad ways of connecting those two. Because the campus is connected. You can go upstairs and downstairs, you can take elevators, you could get between those two points in a very large number of different combinations.

And the amount of mechanical work you need to do will vary with combination. But the change in your gravitational potential energy between the starting and final point, that's a fixed change. That's an example of process variables versus state variables.

But we're not on campus. That's so sad. You're just going to have to imagine all the work you'd have to do to get from building 1 to building 32.

So this is infinitesimal increments and process variables. Infinitesimal-- I think I need new markers. And state variables are denoted as exact differentials. So for example,  $dT$ ,  $dP$ ,  $dV$ , and so on, using regular lowercase  $d$  as in a total differentiable in calculus. So all I can do is tell you that understanding that can only come through practice, for sure at the beginning of the class. So all I can do is tell you-- I'm going to try to switch the purple so things show up a little better.

So let's talk about how we classify processes. So an isothermal process is a process at fixed temperature. What about an adiabatic process? Anybody know?

**STUDENT:** It's like very fast.

**STUDENT:** Does it permeate through a boundary?

**STUDENT:** Heat is 0.

**RAFAEL JARAMILLO:** I heard a couple of things which are equivalent, actually. Somebody said very fast. Somebody else said, no heat flow across the boundary. So the strict definition is no heating across the boundary.

In reality, heat will always flow from a hot object through a cold object. But if you've insulated your system, whether it's your house or a beaker in the lab, then that heat flow could be slowed down. So one way of approximating an adiabatic process is to run it quickly. If you run a process very quickly, the entire process can run before an appreciable amount of heat flows across the boundary. So that's why a fast process can be equivalent, so I like both of those answers.

Isobaric-- isobaric process is that fixed  $P$ . And isochoric, we don't use as much, it's fixed  $V$ . And we'll see that means that there can be no work done on the system if the volume is fixed. And then there is classifying boundaries. We've seen this a little bit so far.

But as a practical matter, the way that we set up processes are by defining boundaries. So for example, an insulating boundary, and no or say, slow heat flow. Diathermal-- heat but no mass transfer. Open or closed, is mass the transfer allowed or disallowed? And rigid, fixed volume.

So when we run processes, we can somewhat determine what kind of process we're going to run by setting up the boundary conditions. And this is a practical thing. This is a practical matter. And all of us who run labs, we do this every day in various ways.

So classifying processes, classifying boundaries, and so forth-- let's talk about other things associated with processes. What about heat capacity? Most folks have encountered heat capacity before. Heat capacity, we're going to use  $C$ . And it is the change in heat, an incremental amount of heat for an incremental change of temperature, heat increment, temp increment.

Is heat capacity a state variable or a process variable?

**STUDENT:** Process.

**RAFAEL** Process is right. Why is it a process very well?

**JARAMILLO:**

**STUDENT:** Because the  $dq$  is path-dependent.

**RAFAEL** Yeah, exactly. It's a process variable because it depends on a process variable. One corollary of the postulate that there exists state functions, is that state functions can only depend on other state functions. So if something depends on a process variable, it itself, is a process variable.  $C$  is path dependent.  $Dq$  is a process variable.

**JARAMILLO:**

So it's useful to define common processes. I should say define for common processes. And the ones that we encounter in this class are  $CV$  equals  $dq/dt$  at fixed volume and  $CP$ , which is  $dq/dt$  at fixed pressure. And the reason these are what you encounter is because these are the most useful.

How do you keep a system at fixed pressure? Let's say, you want to keep a system at atmospheric pressure. What's the easiest way to do that?

**STUDENT:** Use it like a piston.

**RAFAEL** It's actually, I would think the opposite. Expose it to the atmosphere, remove the piston. Because if a system is exposed to the atmosphere, it can exchange volume with the atmosphere. It can get bigger or get smaller.

**JARAMILLO:**

If it's higher pressure in atmosphere, it'll push against the atmosphere and return back to atmospheric pressure. If it's at lower pressure, it will get compressed by the atmosphere and return back to atmospheric pressure. So the existence of a free surface regulates the pressure.

Cost in volume, that would be a case like a piston, where you have something rigid, a really rigid container. You can fix the volume and then run the process. The volume is not going to change.

Which one of these is bigger? That requires a little more thought. We're going to increase the energy of the system by heating it. We're going to increase the energy by heating it. For a given increase in temperature, do I need to hear it more of a fixed volume or a fixed pressure? We haven't really gotten there yet. But I'm wondering if somebody wants to venture a guess with an explanation.

**STUDENT:** Maybe for fixed pressure.

**RAFAEL** Fixed pressure, how do you figure?

**JARAMILLO:**

**STUDENT:** I mean, I think if the system is like half fixed volume, it wouldn't be able to use the heat as work. But with fixed pressure, it can expand.

**RAFAEL** Yeah. So your reasoning is right, but your answer is wrong. So I'm glad-- the reason there is when you have a system that's at fixed volume, it can't do any work on the surroundings. It's hemmed in. So all of these thermal energy you put in will go into a change in the internal energy of the system, increase in temperature.

**JARAMILLO:**

Whereas if you have a system that's fixed pressure, it can do work. It can expand against its surroundings. So as you pour energy in the form of heat, it can lose energy in the form of doing work. So it's like filling up a leaky cup. You have to pour more water in because there's stuff leaking out at the bottom of the cup.

In this case, the stuff leaking out is energy in the form of work on the surroundings. So CV is smaller. CP is larger. But your thinking about work was correct.

C is an empirical observable recorded in devices. That's really important. Maybe you know that, maybe you don't. But the heat capacity of a system tells you so much about that system.

But most of those things, you can't calculate from first principles. They need to be measured and then reported. So for example, what has larger-- here's some, here's-- entry level, what has a bigger capacity, a big pot of water or a small pot of water?

**STUDENT:** They have the same.

**RAFAEL JARAMILLO:** Well, yeah, it depends. Heat capacity could be extensive or intensive. So I think I know what you're saying, water is water. But when we want to regulate the temperature of something, we want to prevent a temperature change, it helps to have a large heat capacity object nearby, a large thermal reservoir.

That's one reason why the temperatures are more moderate on the coasts of continents than inland. Our temperature in Boston doesn't swing nearly as much as it does in Iowa. You could say the same about any inland versus coastal community in the world. And the reason is that the oceans are a big thermal reservoir. They have a larger heat capacity than the Great Lakes do. So our temperature swings are less.

What about bread or cheese? Same quantity, now, same mass, bread or cheese?

**STUDENT:** Bread?

**STUDENT:** Cheese, maybe.

**RAFAEL JARAMILLO:** I think it's cheese. When you eat pizza, the bread is not the one that burns the top of your mouth. It's the cheese. It has a larger capacity. Cheese has a larger capacity.

That has to do with, of course, the chemistry. A big pot of water has a larger heat capacity. What about aluminum foil or a potato?

**STUDENT:** Isn't a larger heat capacity and ability to absorb more thermal energy without changing temperature, though?

**RAFAEL JARAMILLO:** Yes, exactly.

**STUDENT:** So isn't the cheese changing more in temperature than the bread?

**RAFAEL JARAMILLO:** No. What it means is that you have to put in more energy from your mouth to cool down the cheese than you do to cool down the bread. So here's another example, which should help. Aluminum foil versus potato-- you bake a potato that's wrapped in foil.

**STUDENT:** Potato.

**RAFAEL JARAMILLO:** You take it out of the oven. Someone said potato. The answer is going to be the foil. When you take something out of the oven, it's wrapped in foil. You can often open the foil. Even if the oven was at 400 degrees, you can open the foil without burning your fingers. You have to avoid the steam.

But you could grab that foil and very quickly bring that foil down to room temperature without burning your fingers. But if you grab the potato, you're going to burn your hands. Because it takes more energy out of you, in this case, to cool the potato than it does to cool the foil.

**STUDENT:** Doesn't that mean the potato is actually the one with a high C?

**RAFAEL JARAMILLO:** Larger C, yeah, sorry, sorry. Everything I said, but reverse. Exactly, it's easier to bring down. And this is lots of examples here that are every day, why certain surfaces outside feel colder or hotter than other surfaces on a very cold or very hot day, lots of examples like this.

So what do I mean to say here? C can be calculated for simple, we call toy problems. But in most cases, especially in cases that we rely on as engineers, measurements are necessary. And I actually did record some numbers here.

So heat capacity in joules per gram Kelvin-- let's see, water. Water has a large capacity. It has to do with all of the vibrational degrees of freedom in water. Aluminum is very small, 0.897. So this right here is why you can touch the aluminum foil, but you have to avoid getting a steam burn when you open up the food you packed in foil.

Potato is actually large, close to water. Because anything that's food-related, basically is set by the water content. Cheese has a lower water content than potato. I grabbed the number 3.15. If you are a gourmet chef, you have a table of capacities of things like cheese. And 3.15 is this one number. I mean, I don't know cheddar.

But anyway, so let's move on. Let's move on. So, let's talk about something really important, the first law of thermodynamics. So here's the first law of thermodynamics, as you sometimes encounter it in a physics class. And I'm here to tell you this is totally useless. Because if this is all it were, who cares? I mean, it's interesting, but you can't use that.

And that's not how we arrived at it. Intellectually, it's sort of intellectually being dishonest. Because this is very non-obvious, very non-obvious and rather hard to prove also. How is this useful? The answer is because it applies locally. And this is where the real intellectual thread comes from.

So we talk about the energy of a system plus the surroundings. System plus surroundings, you could call universe. It's kind of highfalutin language. Sometimes I'll slip, and I'll say universe, but I don't mean to. Systems plus surroundings-- energy of system plus surroundings is constant.

But here's where it gets useful. We use the boundary for bookkeeping. And like it or not, a lot of thermo is bookkeeping. So we have a system, we have a boundary, and we have flows of energy. I mean, you can keep track of them. And we can keep track of the forms that energy can flow.

So there are three ways that energy can flow between a system and the surroundings in 3020. We have encountered two of them so far about 20 minutes ago. Somebody want to tell me what the three of them are, all three?

**STUDENT:** Convection, radiation, and conduction. Nope. Sorry, so those are forms of heat transfer. But we are not going to talk about fluid dynamics or radiative processes in any detail in 020. So what you said was scientifically true. It's not specifically what the three forms are in 020.

**RAFAEL** We've talked about two of them so far. One is heat, which is everything you just described. What's another way energy can flow?  
**JARAMILLO:**

**STUDENT:** Work.

**RAFAEL** Work, heat, work, mechanical work. And there's a third way that energy can flow. We haven't introduced it yet.

**JARAMILLO:** Would anyone like to venture a guess?

**STUDENT:** Mass transfer.

**RAFAEL** Mass transfer, right. Matter has energy. And so you can exchange matter and transfer energy that way. So this is the bookkeeping that we're going to do in this class. So this gets me to first law of bookkeeping. I wish I had a week to teach fluid dynamics and talk about convection and then talk about heat transfer, talk about conduction, and do radiative. But that goes well beyond this class.

**JARAMILLO:**

You'll learn about those things in other classes. Or come to office hours, we can talk about heat transfer. First law bookkeeping-- this is where we hopefully resolve some ambiguity about 020 with the other classes you've taken. So types of energy include kinetic, potential, and internal, which we u.

So kinetic energy depends on how fast a system is moving. You know that. So if your system is a baseball, kinetic energy is how fast it's moving. Potential energy depends on where a system is in some reference frame. So again, if your system is a baseball, the potential energy depends on where it is, relative to the center of mass of the Earth.

Internal energy is everything else. It's all of the energy which is independent of the velocity of the system and independent of the location of the system. So again, if your system is the baseball, the internal energy is all the molecular bonds that make up the baseball plus the binding energy of the electrons to the nuclei. So this is the one that we use in thermo. This is the last time we'll talk about kinetic energy in the last time we'll talk about potential energy.

We might get to a 20 minutes of electrochemistry later in the term. And then potential might sneak back in. But basically, this is where we are for 3020.

What about processes that exchange energy? That would just be, we just answered. There's heating, there's work, and there's mass transfer. So this is some first law of bookkeeping. I hope this helps a little bit as we try to recall what counts and what doesn't in equilibrium thermo.

So we can do this mathematically. Energy is a state function, but it's changed by processes. So  $du$  equals change in heat energy plus change in mechanical work plus something new, a term which accounts for a change in mass. So  $dq$  equals heat applied to the system. There's a sign convention here. We're going to follow the sign convention in the DeHoff textbook.

So if you're heating a system, let's say that's the endothermic reaction, the instant cold pack, then  $dq$  is positive.  $Dw$  is work performed on a system. So there's a consistent convention there. These have the same sign. Positive  $dq$  increases the energy of the system, positive  $dw$  increases the energy of the system.

So for example, for mechanical work that we encounter in this class,  $dw$  equals  $P dV$ , and here I ask is it positive or minus? Which one is it? This is the pressure. This is the change in volume of a system.

So a positive  $P dV$  means the system is doing work on the surroundings. It's expanding against the surroundings. So what should be the sign here to stick with our new convention?

**STUDENT:** Negative.

**RAFAEL JARAMILLO:** Negative right, it's negative. Because the system is losing energy as it expands, negative. So it equals minus  $P dV$ . A little mathematical note here-- this is a process variable. This is a state variable.

This is not an equation of state. This is a differentiable form of an equation of state. So it's not the same thing. But it has this funny property, that you have on the one hand, process variable, on the other hand, is state variable. This could be considered an integration constant.

If you don't care about that comment, ignore that comment. We don't really talk about integration concepts in this class, we don't have time. But they are kind of hidden there and the structure of thermo. All right so  $dq/dw$  and  $\mu_i dN_i$  equals the energy of change  $dN_i$  of moles of component  $i$  where  $i$  has to run over all the different components of the system. So  $N_i$  equals number moles of component  $i$ .

And  $\mu_i$  is defined as partial  $u$ , partial  $N_i$ , for a fixed-- and we'll get to this-- entropy, volume, and moles of  $j$  not equal to  $i$ .  $i$  is a component label. And this whole thing is called the chemical potential, which is a really central concept for material science and chemical engineering. So we will be spending an entire term on the chemical potential. That's where I wanted to get to today.