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RAFAEL JARAMILLO: Good, all right, so let's get started. Today is lecture 2, 3020, and we're going to talk about the scope of thermodynamics. And one last note-- I'm in another location, so getting used to the configuration here with the camera. My face is hidden behind the camera half the time. I'm sorry for that. I think that by Monday I'm going to have this all worked out. But at least you can see me, so there we go.

All right, so what does thermodynamics treat and what does it not? That's the topic of the day, the scope of thermodynamics. So first we're going to talk about states of matter. What is a state of matter? There's different ways to define it, of course, but we're going to define it as something that has well-defined responses to, let's say, squeezing, heating, adding more of the same stuff, and adding different stuff.

And we're using colloquial language here, but there is way that matter responds to stimuli like these is characterized by response functions. And we're going to write these down. So these are the types of things that we're going to do throughout the term.

Another thing that we often do to states of matter is we apply fields. We don't treat that in 020. We don't get there, but the types of fields we might apply are strange fields, gravitational fields, magnetic fields, or electric fields. We might just get to a little bit of electrochemistry in the class. We'll see if we get there. But, otherwise, we're not really going to spend time talking about applying fields.

So we have this stuff, and we're characterizing it. And we characterize it by how it responds. So that's one thing that thermodynamics treats. Thermodynamics also treats transformations between states. So this is pretty generic. We have some state A, and it transforms to some state B. It treats transformations.

So we have starting and final states described certainly. So we have certainty over what those states are, how they behave. These diagrams are really useful for that. You say here's the state that you expect. Let's change the temperature pressure. Here's the final state that you expect. So we can use phase diagrams to make these predictions with certainty.

One thing that's-- and knowing about thermo when you first learn it is that the process is abstract, meaning thermo tells you how things start out and how they end up. But a process of transformation-- it's very much a black box in thermo, and we don't really treat it. There's a class for that. It's kinetics. You take it in the fall, so we'll be specific. Kinetics is not described. There's no time in thermo-- at least in equilibrium thermo-- when you first see it, like in 020. So we will never do this to you.

Never going to do that-- we're never going to take any time derivatives. We're never going to calculate rates. We only calculate what you get at the end of a process if you wait sufficiently long. What is sufficient? I don't know. This is one way to think about it. Thermo describes the why and only hints at the how.

I find this an interesting way to remember what thermo does and what it doesn't. So, for instance, when we rupture the hot pack or we rupture the cold pack, we could understand those spontaneous reactions. We understood why. One of them was driven by entropy. The other was driven by energy. That was the why.

But the how, we didn't talk about it. In fact, somebody thankfully asked me a question how that worked. What was actually going on inside the bag? It had to do with two different bags and the surface preparation and supersaturation. Thermo doesn't really treat the how. It just gives you some ideas. So it's a starting point for understanding the how, but it does tell you the why.

All right, what about the use of thermodynamics? You're here-- you're here because thermo is useful. It's really useful, whether you become scientists or engineers. It's really useful, and that's why we make you take it. So how is it useful? How do we use it?

We use it to predict and control matter. And we use it to transfer knowledge-- again, an example being phase diagrams, which are great summaries of knowledge. So let me give you an example. Let's have it a temperature axis here.

This is temperature in degrees C. And we're going to study water at one atmospheric pressure. So it's one-dimensional system here, temperature. And here it is boiling. All right, so what is the freezing point of water? Somebody? You know this. What's the freezing point in water in C?

AUDIENCE: 0 degree Celsius.

RAFAEL JARAMILLO: Zero, right. I'm freezing right now in this basement in the woods in Vermont. So I'm freezing. What about if we're here in the summer? It wouldn't be boiling, but what is the boiling point of water in degrees C? 100, someone put the chat. Well, I don't really monitor the chat. Not because I'm anti chat-- it's just one too many screens cluttering up my thing. So next time, please use the mic. But yeah, it's 100. Thanks.

So here's a question. How did you know that? Anyone who just did a quantum chemical calculation from first principles, I want you to raise your hand. Nobody did that. In fact, if you did, you'd probably be writing a paper right now because that's still a very, very, very hard calculation. In fact, I've never seen it-- an accurate prediction of the freezing point of a liquid from first principles using theory. So how did you know that?

AUDIENCE: These are material properties of water.

RAFAEL JARAMILLO: These are the material properties of water. You know that because you know that. And you know that because the data that's out there you have access to. Materials have properties, and some of these are so commonplace that you know them without having ever taken a class.

So these are observations. These are observations. These are two of the huge number of observations on materials that mankind has taken over millennia. Thermal gives you a framework for ingesting those observations and using them to make predictions about states that you have never seen before.

So this is the way to think about it. Empirical observations-- so it's a bunch of observations, observation 1, observation 2, observation 3. All these little pieces of data, they get fed into something called the laws of thermodynamics. This is the conceptual framework. And then, from these observations and the laws of thermodynamics, you can deduce predictions, or what I like to call it, decisions.

Because when we're scientists, we talk about hypotheses and predictions. But when we're engineers, we have to make a decision. What temperature will they run this furnace? How high can this autoclave run without ruining my product? What's the maximum temperature that this product can see during shipping? And you don't have time to run a million experiments. So you need a deductive framework to make decisions. And that's what thermo gives you.

How do we store observations? We store them in databases. So as you'll see starting in the first piece, thermo concerns itself very much with the maintenance of databases. Without materials data, these laws of thermo are just text on a page. They're utterly useless. You need this-- the data fed into the deductive framework to make decisions.

So the databases have huge economic value. When you download the student version of thermo calc, they're giving you a very minimal set of databases. First of all, you'd have to pay a fair amount to get a larger set. But if you want to get the real stuff, these are trade secrets. So companies like Alcoa, they guard their thermodynamic databases the way a company like Intel guards its lithography maps. It's like the key to the entire operation.

So the economic value of data is huge in thermo and material science more generally. Now, fortunately, we don't need to sit down with our pen and paper and figure out what the law of thermodynamics predict every time. We have software for that. So databases fed into software allows you to make predictions and helps you make decisions in a reasonable time frame. That's how you'll use thermo in the real world. This is how you use thermo in the real world.

OK, our next topic, systems in thermodynamics. All right, systems are characterized by temperature, pressure, volume, and composition, also boundaries. So here's an example. Here is a balloon. There's a boundary. This is in. And this is out.

All right, so let's say we want to calculate some properties of the gas inside of this balloon. What should we take as the boundary of our system? It's kind of painfully obvious, right? You take the plastic. You take the actual balloon, the actual balloon that-- you choose that as your boundary. That makes sense. It's kind of obvious, but it's good to start from an obvious example.

Why do you choose the physical balloon as a boundary of your system to analyze the gas inside? Why not just choose an arbitrary volume? Why not say no, I'm going to choose as my system the lower half of the balloon? And this is an imaginary line or surface separating the two parts of the balloon. Why not choose this lower volume to analyze?

AUDIENCE: Because there's nothing separating it from the upper volume of gas.

RAFAEL JARAMILLO: There's nothing separating it. And so as a result, particles can move between the lower volume and the upper volume. So if I choose the whole balloon, I get to use conservation of particle number. That's convenient. If I now treat these as two subsystems-- system A and system B-- now I need to keep track of how they exchange particles. It's more work. We get the same answer if you do it, but it's more work.

So this is, again, a painfully obvious example. But starting as soon as this p set, we hope to make it-- give you some slightly less obvious examples, which is how you choose boundaries. You draw-- you choose boundaries-- boundaries chosen out of convenience. You choose a boundary when you analyze a system to make your life easier. It depends on what questions you're asking

So I believe in problem 1 on the p set, we asked you to run through some of these mental exercises for different examples-- right, boundaries chosen out of convenience. So let's do an example. Example, adding sugar to a glass of water and stirring.

So let's see. Let's draw a beaker. And there's water, good. And here's sugar. There's sugar, and the sugar gets added. And I'm going to have a stir bar. I have to stir. So I have a stir bar-- a little swizzle stick or something-- and stirring that around so it's moving. This is why. All right.

Let's talk about this system. First, I'm going to write down a list of all the things in this picture. So the things are water, sugar, the glass, the atmosphere-- I didn't really draw it, but it's there-- and the stir stick and the stir bar. I want to get an answer like how sweet will the water become? That's the answer I need. What system-- so to analyze, what should be in the system, and what should not be in the system? So would somebody say should the water be in the system?

AUDIENCE: Yes, because it's one of the main components of all the mixture.

RAFAEL JARAMILLO: Yeah, OK, so we're going to choose the water and the sugar I will say also. It's one of the main components of the mixture. So let's go. What about the glass? Should that be part of the system?

AUDIENCE: No.

RAFAEL JARAMILLO: Probably not, unless we expect some kind of maybe reaction with the glass. But the sugar water, it's not going to etch the glass. If this were a hydrogen fluoride solution, it would etch the glass. We'd have to include the glass. But we're not going to include the glass. The atmosphere-- do we have to include that?

AUDIENCE: No, because it's not changing.

RAFAEL JARAMILLO: Yeah, if this is just something you're doing in your kitchen, probably not. If you're running a factory making sugar water, like a simple syrup or something, you probably want to include the atmosphere because you want really good process control. And the humidity in the atmosphere might make a difference. That's an example.

Or if you're a monk brewing a farmhouse ale-- and we know that the stuff in the air from the surrounding farms makes it into the beer and helps change. So there are examples where you do want to include the atmosphere in the system, but here not. And the stir bar, not-- the stir bar has a function, but it's not going to be a part of the thermodynamic system.

What about the boundaries? All right, these are the types of boundaries. And before we go through these, this is as good a time as any to remind you that the associated reading is every bit as much a part of the course as the lecture. So if you keep up with the reading and do the associated reading before lecture, you'll get a lot more out of the entire experience. So thank you for keeping up with the reading.

All right, boundaries-- open or closed? Somebody please tell me. Is this open or closed system? Which would you choose and why? And what does that mean, open or closed? Somebody.

AUDIENCE: I would say it was closed because nothing is leaving the system. There's no evaporation happening or particles leaving.

RAFAEL JARAMILLO: Good, OK, that's what I would choose too. Closed means no loss of particles or no gain of particles. Particle number remains the same. So the example given there was that if you included evaporation-- loss of water-- it would be an open system. You'd have to include the atmosphere in your system.

And if you're growing-- if you're in a crystal growth experiment where you slowly let the water evaporate-- the supernatant-- then it's an open system. But we're doing this quickly, and we're not going to wait for water evaporates. So closed, thank you. All right, rigid or not rigid?

AUDIENCE: Maybe not rigid since the top is, like not like a hard solid surface.

RAFAEL JARAMILLO: OK, good. So the top, it's not rigid. That's what I would choose too Let's talk a little bit more about what that means. It means that the volume can change. The volume is free to change. That's what was said there.

The top is not a hard surface. So we assume that the walls of the glass are rigid. They're not going to change. But the top surface is what's called a free surface. It can exchange volume with the atmosphere. And the ability to exchange volume-- that's the mechanism by which two systems arrive at the same pressure.

So there's notion of pressure regulation. Temperature regulation becomes very important in thermo. Non rigid systems are pressure regulated because they can exchange volume with the atmosphere. If there is a fluctuation in atmospheric pressure, that same temperature-- the same pressure fluctuation will be felt by the water bath, for instance.

As opposed to a rigid system, a rigid system can build pressure. You can have a bomb or a high pressure vessel. That's a different pressure from the outside. Why? Because it's fixed volume, rigid. All right, good.

And finally, adiabatic or diathermal? Right, so the non rigid meant that you're going to be at atmospheric pressure throughout. In my view, the Zoom video camera webcam review is blocking this text right here. Is it blocking this text in anyone else's view?

AUDIENCE: No.

RAFAEL JARAMILLO: OK, good. Thanks. All right, so what about adiabatic or diathermal? Is this adiabatic, or is it diathermal? The boundaries-- adiabatic or diathermal? So adiabatic means a process or a boundary that does not allow heating-- so a thermally insulating battery. Diathermal is the opposite. Diathermal thermal is a process or a boundary that allows heating, allows heat to flow, allows heat exchange.

AUDIENCE: So it'd be diathermal.

RAFAEL JARAMILLO: It'd be diathermal, right. So in the same way that the free surface allows the atmosphere to regulate the pressure in the water, keeping it at atmospheric pressure throughout, the diathermal boundaries in glass might be a little slow-- slow thermal transport, but definitely have a very fast thermal transport there at the surface. This is going to keep temperature of the room-- this is the temperature there the room throughout.

So the diathermal thermal boundary regulates the temperature. The non rigid boundary regulates the pressure. I'm taking my time here, intentionally introducing a bunch of new terms. Or if they're not new terms, the meaning of all these terms is very specific in thermo, so the idea of regulation, the idea of choosing boundaries. So you'll do some examples like this in the p set.

All right, let's talk about types of systems, classifying systems. Classifications. All right, so this is just getting some essentials out of the way here-- unary, one component. All right, so an example of a component would be water.

OK, so here's an example. A unary system has one component, one molecular component. A multi component system has more than one. So, for example, the binary system of water and sugar. I've got hydrogen, oxygen, and carbon here. How come it's not three components? Anybody?

AUDIENCE: Because at no point are we discussing like, the separation of those components.

RAFAEL JARAMILLO: That's right. At no point are we breaking bonds or in reforming molecules. This is remaining water throughout. This is remaining sucrose throughout. This is not a digestive system, and you break down the sugar. This is not an electrochemical water-splitting system where you might be using some source of energy to electrochemically generate hydrogen gas from water. So that's good.

So your choice of unary, multi component-- there can be more than one answer. And the same molecular components can be analyzed as unary, or a multi component system, depending on the situation. So, again, you make these decisions out of convenience because you understand the process that you're engineering, that you're designing. All right, OK, good, so that's urinary versus multi component. And this kind of gets-- sometimes can get a little bit easy to get tripped up there.

All right, two different types of classification-- homogeneous first, heterogeneous. So homogeneous means one phase. So, for example, sodium acetate-- the sodium acetate solution. That was-- the supersaturated sodium acetate solution was a starting point for the incident and hot plate, sodium acetate solution.

What about heterogeneous? More than one phase, right-- solution plus solid, sodium acetate. So that's-- because I think a little bit less description. What about closed versus open? This we've already discussed-- no mass exchange with surroundings versus can exchange mass with surroundings. So those are some basic and important classifications.

Next category-- we're going through the necessary stuff here to get started on real thermal problems. State functions or, if you like, variables. We'll use these interchangeably, state functions and state variables. So these characterize the system. They are independent of history. This is a really subtle point. This will trip you up. It trips me up.

It seems obvious, right. The fact that you could characterize a system with variables which are independent of the history of that system is very non obvious. That was a major intellectual accomplishment. It shouldn't sit easily with you. That takes some getting used to. You shouldn't trust me on this yet. Common state functions found in 020-- so would somebody like to volunteer a state function, a common state function you might find in thermo?

AUDIENCE: Temperature

RAFAEL JARAMILLO: Yeah, temp. So that's a state function. We use t. To denote volume, we use v. Pressure is p. Any others?

AUDIENCE: Enthalpy.

RAFAEL JARAMILLO: Enthalpy, OK. That's a state function. What about one that's not so specific in thermo? Are there others that are more colloquial?

AUDIENCE: Concentration.

RAFAEL JARAMILLO: Concentration, I'll say composition. Yeah, composition-- and we'll use atomic percent often in this class. What about mole number, total system size, like that? And then there's enthalpy. And then there are others which are more specific to thermodynamics. There's entropy. There's Gibbs free energy. And there's Helmholtz free energy.

If we were course 2-- if we were mechanical engineers-- we would be spending a lot more time on Helmholtz free energy and enthalpy. If we were physicists, we'd be spending a lot more time on Helmholtz free energy and energy, which we're going to use u for internal energy.

But as material scientists, we spend most of our time on Gibbs free energy and enthalpy for reasons that we'll discuss at length in a couple of lectures. But there are more. There are more. Like magnetization, that's one we don't-- that electric polarization. There're many.

OK, so we have state functions. We have state variables. We also have equations of state. So an equation of state, in general, is some state function X equals a function of other state functions Y1, Y2, Y3. And in this formulism, that's a state function. And these are state variables. But I'm going to use this interchangeably-- state functions, state variables.

All right, so you all know one state function. What's the state function everybody knows, even on the T-shirts? When I do this lecture in person, I wear my MIT T-shirt with a state function on it.

AUDIENCE: It'd be PV=nRT.

RAFAEL JARAMILLO: Yeah, PV=nRT, right. PV equals nRT. OK, so that's a state function. That's a state function for an ideal gas. This is true always for an ideal gas at equilibrium. That's pretty cool, and you can do a lot with that. But before we do a lot with that, I want to warn you this is the exception rather than the rule.

For almost every system, every material which you'll use in your careers, we do not have a state function like this. Maybe we have some that are empirically determined. You might find some magnetic systems for which state functions have been exactly derived from fundamental principles like this one. But this is the exception rather than the rule.

Usually, you can't write down a closed form like this. Usually, you have to deal with much more complicated data resources. Something on units here-- try to sneak this in. R equals PV over nT. What are the units of that? Pressure is Pascals. Volume is meters cubed-- make this so that it looks like Pascals.

Mole is unitless, just a number. And temperature is Kelvin. In fundamental SI units, a Pascal is a Newton per meter squared. Force over area, that's pressure. We have a meter cubed, and we have a Kelvin. So then, you get Newton meter by-- and what's a force displaced over a meter, Newton meter?

AUDIENCE: The joule.

RAFAEL JARAMILLO: Joule, joule Kelvin. So R equals 8.314 joules per Kelvin. It's a handy thing to remember. We're going to be sticklers for units in this stuff. I was going to say more things-- thermodynamic properties.

All right, so at the very beginning, I told you that states of matter had certain responses when you squeeze them or you added stuff or you heated them. And these are going to be described by thermodynamic response functions. So that response function term sounds kind of fancy. Don't let it scare you. It describes how a system responds to something. So someone screams, you cover your ear. That's your response function.

So some common response functions that we use in thermo are compressibility, isothermal compressibility, a fixed temperature. And, of course, this is the same as d log V dP. So you see this a lot. The only real prerequisite for thermo is multivariable calculus. And I think the first time I learned thermo and probably a second time even, I didn't appreciate just how much I relied on multivariable calculus. So just know that now so that you're not surprised later.

All right, thermal expansion-- it's another common one. Alpha equals-- again, we're going to make this volume independent. And we're going to do that at fixed pressure. And there are others, but these are the easiest ones to write down. I'm giving you an idea of the sorts of properties that we're going to calculate in thermo.

So let's consider ideal gas compression at fixed temp-- volume initial at pressure initial going to volume final at pressure final. All right, so compressibility Bose minus 1 over V dV dP at fixed temperature. And for an ideal gas, this is very, very simple. This is minus 1 over V dVP at fixed temperature nRT over P. This equals nRT over VP. 1 over P equals 1 over P. This is really simple for an ideal gas and only for an ideal gas.

So the final volume after compression is going to be the initial volume plus the change. So it's like second fundamental theorem of calculus. So we're going to plug in-- what's the integrand? It's minus V beta. You continue to plug in. This is volume initial minus-- so hang on-- dP nRT over P. 1 over P equals V initial minus nRT P initial plus nRT P final, which, of course, just equals V final.

So this calculation is really trivial for an ideal, guys. You get exactly what you think you would get. The reason why I took the time to do it is to show you the manipulations that you'll need to do later on for non ideal gasses. Now, thinking about this, you've got to put your multivariable calculus hat on.

Of course, for an ideal gas we get this-- 1 over x, these relationships-- P initial, V initial, P final, V final. And this curve is an isotherm. So we'll come back to these when we do heat engines and the Carnot cycle at lecture 4.

We're almost done. Let's see, one last-- two last points here, intensive versus extensive properties. All right, intensive properties can be defined and measured at any point within a system. Would somebody like to volunteer an example of an intensive property?

AUDIENCE: Temperature.

RAFAEL JARAMILLO: Yeah, temp. When they take your body temperature, they assume that you have one body temperature. And they can take it-- there's different places they can stick the thermometer, but you should get the same number. Density-- now, you can locally define density, and you can measure it locally. Composition for a uniform system, composition. Pressure-- and there are more. Extensive properties depend on the extent of the system. And they scale with system size.

So some examples here would be energy, volume, mass, entropy, and so forth. The doctor can take your temperature at several different places, but the way you-- your whole body has to be on a scale. They can't weigh you just by weighing your arm. So extensive, you need to know the extent. Intensive, it can be defined and measured at any point inside or within a system. Easy way to remember that.

All right, we're going to end today with definition of the phases-- a phase of matter. So I'm going to define a phase the following way. Phase is a region within which all intensive properties are uniform. All intensive properties are uniform. That's a phase of matter. So, for example, solid sucrose, some things we've seen here-- water, simple syrup, grass, some examples on length scales.

It's an important caveat. If I zoomed down to atomic length scales, I might say this isn't uniform. I've got different metal elements, depending on where I'm looking. So this has to be on length scale of large and molecular length scales. And phase boundaries, which, of course, are a really important topic in thermo and material science, are classified similarly to system boundaries.

All right, so we have a two-phase system. For example, sugar and water-- we have some sugar, and it's in water. We have a sugar water system. And we're going to think about this boundary in the same way that we classified system boundaries.

And so that's an open boundary because sugar molecules can go across the boundary into the water. And similarly, sugar molecules can come out of solution and go back into the solid. This is a boundary that exchanges volume. It exchanges heat energy, and it exchanges mass.

Good, so that's all I had prepared for today. It is 10:54, almost perfect. Thanks for joining. As usual, hang out until at least 11:00 if folks want to talk or ask any questions. Otherwise, I'll see you Monday.