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Hi. Today we're going to discuss the many D's of thermodynamics. So what do I mean? We're going to talk about lowercase d, lowercase Greek d, and uppercase Greek D. And I wanted to clarify why we have different D's that we use, when we use them, and give some physical intuition for what they mean.

So, for example, when we write the combined statement of the first and second law, we have  $du$  equals  $TdS$  minus  $PdV$ . In this case, the d's indicate exact differentials, which is equal to infinitesimal changes in state variables. I'll write that out.

OK. The next D we want to talk about are the lowercase Greek d's. So, for example, conservation of energy gives us the following expression.  $dU$  equals  $dQ$  plus  $dW$ , which tells us that the total change of internal energy for a system equals the sum of heat and work.

Heat and work our process variables. In this case, the lowercase Greek d's indicate inexact differentials.

That is infinitesimal changes in process variables.

These terms, exact and inexact differentials, they have a specific meaning in thermodynamics, which is related to, but not identical to, meanings they have in mathematics. So this is a statement about thermodynamics.

OK, this brings us to the third D, the capital Greek D. So I'll write an example. In the context of the Clausius-Clapeyron equation.  $dP$  equals  $\frac{dS}{dV}$ . In this case, the capital D's indicate transformations, transformations.

So in materials thermodynamics, the most common transformations that we talk about are transformations that take place at constant pressure and constant temperature. That is isobaric and isothermal transformations.

So of the three D's-- lowercase d, lowercase Greek d, and uppercase Greek D-- this uppercase Greek D is the one that contains the most physical, unstated assumptions. It contains the most information about this system. But as a result, it also is often the hardest for students to understand when you first encounter it. So we're going to take some time to draw out what is meant by transformations and transformation quantities.

So to illustrate the concept of transformation quantities, it helps to draw state function surfaces. So as a reminder, for a given phase and composition, we can draw state functions of two-- we can draw these as surfaces-- that is, state function of two independent variables.

So, for example, we could have the entropy of phase alpha drawn as a function of temperature and pressure. So I'm going to draw a representative state function surface now. Let's see. We'll keep the axes. So here we go. Here is-- for some hypothetical phase. That's a state function surface. Let's draw the axes.

We'll make the vertical axis entropy. One of the axes in the plane can be pressure, and the other would be temperature. So this is a 3D visualization of how the entropy for a given phase might vary with pressure and temperature at a fixed composition.

And to keep track of the fact that it's for a given phase, I'll label it alpha. So this is the state function surface for a given, particular phase. So to illustrate transformation quantities, I want to draw the transformation entropy for an isobaric, isothermal phase transformation.

So it's a isobaric-- we're going to consider a transformation between two phases, alpha and beta. So we're going to be two different state function services, one for each phase.

We'll label this beta. And I'll draw another state function service for phase alpha. Alpha. And as before, we'll say that we're measuring the transformation entropy. So the vertical axis is entropy.

And the independent variables are temperature and pressure, pressure and temperature. All right. So at a given pressure and temperature, we can visualize the transformation entropy for a transformation between phase alpha and phase beta. So we're going to pick a given temperature and pressure-- that is, a point down here on the PT plane-- and we're going to draw a vertical line and see where it intercepts these surfaces.

We come up from the plane. And at some point, we're going to cut that state function surface and then keep coming. We'll cut that state function service and keep going.

So a given point of pressure and temperature-- we now have a visualization of the transformation entropy. It's exactly the vertical distance between these two surfaces. So this is the transformation entropy between phase alpha and beta at a given pressure and temperature.

And using this visualization-- at least, in your mind's eye-- you can see that this transformation quantity is a function of pressure and temperature. Because as I move this point around in pressure and temperature, the vertical distance between the surfaces might change. So this is illustration for an isobaric, isothermal transformation, and we're illustrating this for entropy. But in thermodynamics, we have many different transformation quantities that we keep track of.

In material science, our most common independent variables are pressure and temperature, because those are often the easiest for us to regulate in the laboratory. But for any transformation quantity, you can at least imagine, if not draw out on a piece of paper, state function surfaces corresponding to the quantity that you're trying to measure, independent variables corresponding to the variables that you're regulating, and a vertical distance, which is a function of those independent variables that measures the transformation quantity for the transformation between two different phases.