

# Name the experiment! Interpreting thermodynamic derivatives as thought experiments

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We introduce a series of activities to help students understand the partial derivatives that arise in thermodynamics. Students construct thought experiments that would allow them to measure given partial derivatives. These activities are constructed with a number of learning goals in mind, beginning with helping students to learn to think of thermodynamic quantities in terms of how one can measure or change them. A second learning goal is for students to understand the importance of the quantities held fixed in either a partial derivative or an experiment. Students additionally are given an experimental perspective—particularly when this activity is combined with real laboratory experiments—on the meaning of either fixing or changing entropy. In this paper, we introduce the activities and explain their learning goals. We also include examples of student work from classroom video and follow-up interviews.

## I. INTRODUCTION

In thermodynamics, most experiments are designed to measure how one thermodynamic quantity changes as another is controlled by the experimenter. This change is represented by a partial derivative. Understanding this role of experiment is challenging for students in several ways.<sup>1–8</sup> Students have been shown to struggle with the operational definitions of pressure, temperature, and volume, and commonly fail to recognize the covariation among these three variables.<sup>4</sup> At the upper-division level, we add in entropy—a particularly challenging quantity—as a fourth canonical variable. We go on to express “simple” quantities such as pressure or temperature as partial derivatives of the internal energy. Even the notation used to describe partial derivatives in thermodynamics,

$$\left(\frac{\partial A}{\partial B}\right)_C, \quad (1)$$

is rarely used in other subfields of physics, and is not typically taught in math classes. Much of thermodynamics involves mathematically deriving relations between different experiments that measure different partial derivatives. This is a challenge when students struggle to understand these partial derivatives.

We have developed a sequence of activities to address some of the student difficulties with partial derivatives in thermodynamics. This sequence was developed in the context of *Energy and Entropy*, the junior-level thermodynamics course at Oregon State University.<sup>9</sup> This two-credit course teaches basic thermodynamics followed by a brief introduction to statistical mechanics. *Energy and Entropy* features three laboratory experiments: a rubber band lab described in a previous paper<sup>10</sup> and two calorimetry experiments involving ice and water.

In this paper, we present three “name-the-experiment” activities, which involve the instructor providing student groups with a partial derivative, and asking the students to draw a picture of an experiment that could be used to measure that derivative. We introduce each activity by announcing “Name the experiment!” The intent of

this announcement—which sounds like a game show—is to tap into students’ intuitive understanding that this is a new epistemological game, with its own rules and victory conditions for them to learn. We assign one partial derivative to each group of three students and we end the activity by having groups present to the entire class their solution to each different partial derivative. Each activity typically requires half an hour of class time, including the wrap-up discussion. We do each activity on a separate day, with progressively more challenging derivatives addressing different learning goals spread throughout the course.

There are several overall learning goals for these activities. The primary objective is for students to be able to identify partial derivatives as descriptions of experiments in which one quantity is changed, while certain others are held fixed. There are also several smaller—but still important—learning goals that span all three activities. One of these goals is for students to understand how to measure all the thermodynamic variables. In the past, we have observed students failing to recognize that adding weights to a piston will increase the pressure! In these activities, students are repeatedly forced to remember and describe how to control or measure each of the thermodynamic variables. Another aim is for students to discover for themselves that some variables are easier than others to change, to constrain, or to measure. Finally, we desire for students to be able to use “canonical” thought experiments such as a gas in a piston or the idea of a heat bath as a big tub of water. Canonical thought experiments are ubiquitous in physics—they exist in every subfield—and allow us to easily apply physical intuition to problems. This goal is usually accomplished through the discussions that wrap up the activities.

One reason for these “big picture” learning goals is to enculturate these physics majors into the physics community and aid their development as expert physicists. As experts, we smoothly move from a symbolic representation of a partial derivative to a description of an experiment that would measure that derivative. For example, experts can identify the derivative  $(\partial p/\partial V)_S$  as

essentially the adiabatic compressibility—even though it differs in sign, and by a factor of volume, and has been inverted. The *essence* of adiabatic compressibility is present in this derivative. Why is this? In order to find this derivative, one must perform the same measurement that gives the adiabatic compressibility. As was nicely summarized by Jeppsson *et al.*, “. . . there is increasing plausibility to the claim that expert scientists’ formal conceptual understanding draws on concrete notions of material substance.”<sup>11</sup>

In addition to the overall learning goals discussed above, there are others specific to each activity. In this paper, we describe each name-the-experiment activity, explain the learning goals for that activity, and discuss some particular student difficulties that are addressed. For more detailed information about how name-the-experiment fits into our course, see the thermodynamics activities presented on the Paradigms in Physics Activities wiki.<sup>9</sup> This website also includes narratives, which are annotated transcripts of videos of class sessions. These narratives provide examples of how these activities can be enacted in the classroom and of what an instructor and students might say and do during such activities.

The final reason for all these learning goals is affective—we believe that if students understand that the derivatives they are manipulating are physically measurable quantities, they are likely to be more interested in understanding relationships between these derivatives. How can students understand the the laws of thermodynamics as real scientific laws if they cannot connect the mathematical expressions involved with experimental measurements?

## II. ACTIVITY 1A: SIMPLE DERIVATIVES

We begin the first name-the-experiment activity with derivatives that relate to experiments that the students can simply envision. At this stage, we have introduced students to operational definitions for the thermodynamic quantities, which are descriptions of how one could measure these quantities. We have talked about entropy and the concept of adiabatic processes as quasi-static processes in which there is no heat exchange and the entropy is held fixed. Finally, students have been presented the first law of thermodynamics, which is that the change in the internal energy of a system is the sum of the energy added to it by heating, and energy provided by doing work on it:<sup>12–14</sup>

$$dU = dQ + dW. \quad (2)$$

Table I lists the derivatives that we give students in this first activity. We group these derivatives into four categories: easy derivatives for a three-dimensional fluid system (involving only pressure  $p$ , temperature  $T$ , and volume  $V$ ); easy derivatives for a one-dimensional system (involving temperature, length  $L$ , and tension  $\tau$ );

TABLE I. Easy derivatives for the first activity, grouped into four categories, according to the physics concepts required.

Simple 3D:	$\left(\frac{\partial V}{\partial p}\right)_T$	$\left(\frac{\partial V}{\partial T}\right)_p$
Simple 1D:	$\left(\frac{\partial L}{\partial \tau}\right)_T$	$\left(\frac{\partial L}{\partial T}\right)_\tau$
Simple adiabatic:	$\left(\frac{\partial T}{\partial V}\right)_S$	$\left(\frac{\partial V}{\partial p}\right)_S$
First law:	$\left(\frac{\partial U}{\partial T}\right)_V$	$\left(\frac{\partial U}{\partial p}\right)_S$

adiabatic processes (with fixed entropy  $S$ ); and derivatives of the internal energy that require students to use first-law reasoning. The first-law derivatives (discussed in Section III) are the most challenging in this set, and are assigned as a second task to groups that quickly finish describing their first experiment.

This first name-the-experiment activity is designed to address several learning goals. Some of these are general, addressed by all of the partial derivatives in Table I; others are specific to only some of these partial derivatives. The challenge of exposing the entire class to these specific learning goals is addressed by having each group report on their solution to the class.

The first general learning goal for this first activity is to reinforce the operational definitions of thermodynamic quantities that students have already been shown. For instance, students need to formulate how they will measure or fix the pressure in terms of a force measurement divided by an area, reinforcing the definition of pressure.

The second, and primary, general learning goal is for students to appreciate the meaning and importance of the quantity that is held fixed. Many students expect that this quantity is redundant; they have been taught in their mathematics course, and sometimes in earlier physics courses, that when taking a partial derivative, “everything else” is held constant. The belief that the quantity held fixed is redundant is surprisingly persistent, even in problems that aren’t explicitly asking about a partial derivative. Research has shown that students also commonly—and incorrectly—hold fixed any variables that are not currently under consideration in questions involving finite changes.<sup>15</sup> In fact, the idea of measuring the effect of changing one variable while holding “everything else” constant is taught as early as elementary school, where it is called “control of variables” and used to teach the scientific process.<sup>16</sup> By having students design their experiment in a way that explicitly constrains the quantity held fixed, students are given a physical perspective as to why this matters.

One of the specific learning goals is addressed by the “adiabatic” derivatives, which require students to remember that fixing the entropy corresponds to thermally insulating the system. An example from the list of adia-

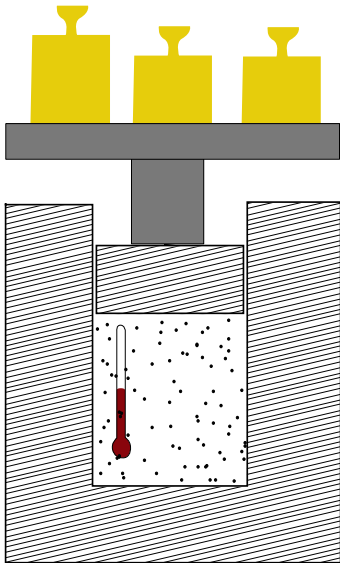


FIG. 1. Sketch of an experiment to measure the derivative  $(\partial p/\partial T)_S$ . The procedure involves slowly adding weights to the top of the piston to change its pressure, having measured the area. The piston itself is insulated to keep the process adiabatic, and we use a thermometer inside to measure the resulting change in temperature.

batic derivatives is

$$\left(\frac{\partial p}{\partial T}\right)_S, \quad (3)$$

which showcases several of the student learning opportunities at this stage. Since entropy is being held fixed, this corresponds to an adiabatic process, in which the system is thermally insulated from its environment. We are changing the temperature, while at the same time *not* heating the system! This is a source of confusion for students, an issue that will be more forcefully addressed by the isothermal derivatives in the second activity (described in Section IV).

This experiment is actually much easier to imagine if we turn the derivative upside down,

$$\left(\frac{\partial p}{\partial T}\right)_S = \frac{1}{\left(\frac{\partial T}{\partial p}\right)_S}. \quad (4)$$

By examining this inverse, we see that we can change the *pressure* on an insulated piston, for instance by putting weights on it, and measure how much the temperature changes with a thermometer, as illustrated in Fig. 1, which is far easier than trying to directly change the temperature of a thermally insulated piston. Inverting partial derivatives in this way blurs the distinction between the dependent and independent variables, and the distinction between controlled and measured variables.

Most students (and even some faculty) are unsure of the validity of Eq. (4). In both abstract math courses

and other fields of physics, it is rare to invert partial derivatives in this way. It is hard to imagine the meaning of the derivative  $(\partial t/\partial \psi)_{x,y,z}$  in quantum mechanics, for instance. In their math classes, students are likely to be taught that such a relationship is, in fact, *not* true for partial derivatives. Notationally, Eq. 4 is close to meaningless when expressed in standard math notation:

$$\frac{\partial u}{\partial x} = \frac{1}{\frac{\partial u}{\partial x}} \quad (5)$$

because  $u$  here is a function, while  $x$  is not a function but an independent variable. If we *do* understand  $x$  to represent a function, it is not clear what variables it is a function of, which would determine which variables are being held constant. In short, even the simple process of inverting a partial derivative, which on its face may seem obvious to experts, requires assistance for students to grasp.

### III. ACTIVITY 1B: THE FIRST LAW

In the same first activity in which we do simple derivatives, as described in the previous section, we also include derivatives that require the use of the first law, which states that the change in internal energy of a system is found by adding together its changes due to heating and working.<sup>12–14</sup> One of the first-law derivatives from Table I is

$$\left(\frac{\partial U}{\partial p}\right)_S, \quad (6)$$

which corresponds to another adiabatic process and is thus easiest to understand by imagining an insulated piston. We are changing the pressure, which is easy to manage by placing weights on the piston. However, we don't have a way to directly measure the change in internal energy, so we must relate this change to something else using the first law. Since the change is adiabatic, there is no heating ( $Q = 0$ ), and the change in internal energy is equal to the amount of work done, so  $\Delta U = -p\Delta V$  for small  $\Delta V$ . Thus,

$$\begin{aligned} \left(\frac{\partial U}{\partial p}\right)_S &= \left(\frac{\Delta U}{\Delta p}\right)_S \\ &= \left(\frac{-p\Delta V}{\Delta p}\right)_S \\ &= -p \left(\frac{\partial V}{\partial p}\right)_S, \end{aligned} \quad (7)$$

which is a result we could also obtain using the ordinary chain rule together with the definition

$$p = -\left(\frac{\partial U}{\partial V}\right)_S. \quad (8)$$

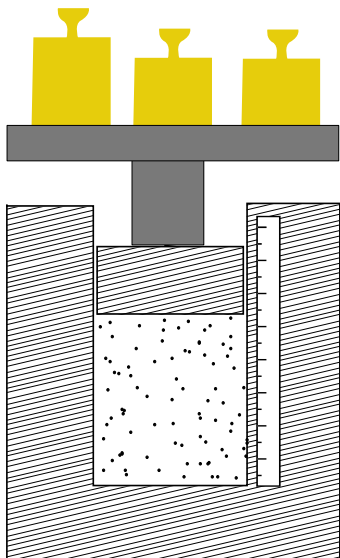


FIG. 2. Sketch of an experiment to measure the derivative  $(\partial U/\partial p)_S$  in Eq. (6). The piston is the same as that described in Fig. 1. As mentioned in the text, the procedure involves slowly adding weights to the top of the piston to change the pressure, and measuring the change in volume using a ruler. From this, the work is found, and from that the change in internal energy.

Our students seldom arrive at Eq. (7) mathematically, but students are able to express that they measure the work by seeing how the volume changes, in order to find the change in internal energy as pressure changes. Using Eq. (7), we can design an experiment to measure the change in volume as we change the pressure adiabatically, as illustrated in Fig. 2.

Devising an experiment to measure derivative (6) is a challenging task, which requires students to recognize that the first law is needed to describe a measurement of work needed to change the volume slightly, to realize that changing the pressure requires that they change the force on a piston, and to realize that the system must be insulated. When this name-the-experiment question was given on a final exam, over half of the students (16 out of 27) were correctly able to express either Eq. (7) or the idea that they would measure the work in order to find  $\Delta U$ . The same number of students—although not the same set of students—recognized that the system must be insulated in order to measure a process at fixed entropy.

As a part of a separate study,<sup>17</sup> one of the authors (MBK) conducted interviews with six students just after they had completed the *Energy and Entropy* course. Part of the interview involved asking them to draw and describe an experiment to measure  $(\partial U/\partial p)_S$ , a derivative that these students had not encountered in class. We present here an analysis of Bob’s response as an example

of a somewhat weak (C+) student’s response.

Bob began by identifying that one must isolate the system to maintain constant entropy.

“First I’m just thinking, I guess just reading this out loud in my head to conceptually understand what it’s asking, measure the change in internal energy as a function of pressure at constant entropy, which [inaudible] entropy, constant entropy is a little bit interesting, although it’s not as hard as constant pressure. **Alright, so, the experiment’s going to be isolated from its surroundings if you want the entropy to be constant.**”

As Bob proceeded to address the question of how to measure internal energy, he correctly identified measuring the change in height as a way of measuring work, with the implicit assumption that this told him something about internal energy. However, he became confused about what is being held constant, and decided to change the height of the piston by heating the gas with the pressure held fixed. At this point, Bob was describing a measurement of  $(\partial V/\partial T)_p$ .

“So, measure the change in internal energy, at constant pressure [long pause]. I imagine I’d have some sort of insulated channel [begins drawing Fig. 3] and then, a piston that can be raised freely. It’s a little bit harder with real world experiments, cause you have to think about the friction of the piston. But there’s some gas in here and we have measured, we know the weight of the piston, all of that and we can measure the height here [makes a mark and labels ‘h’] and maybe some height it gets raised to [makes second mark and labels ‘h’] when we increase the temperature of the gas. There’d be some isolated heating element inside here [draws at the bottom left] and if you measure the heights, you can find the work done to move this weight in the gravitational potential energy, from this point to this point.”

The unusual phrase “isolated heating element” is telling, as it suggests that Bob is confusing an “isolated system” with one that is surrounded by insulation, as the combined system of gas and heating element is in this case. As Bob began to summarize his approach, he returned to the idea of a thermally isolated system with no heat exchange, correctly using the first law to find the change in internal energy under those conditions, but the heating element is still present.

“And how I’d essentially model [pause]. **The work done would be the internal energy because we’re not adding or removing heat from the system and so you’d essentially be measuring the work done at**

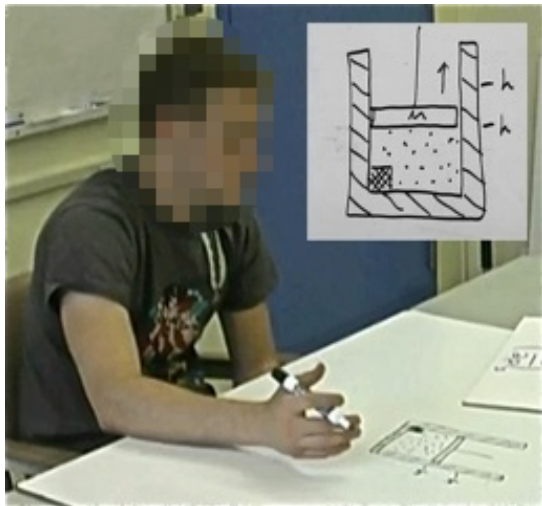


FIG. 3. Interviewed student’s sketch of an experiment to measure the derivative  $(\partial U/\partial p)_S$  in Eq. (6) (compare to Fig. 2).

**constant entropy**, as a function of increase in pressure, because from the temperature increase of our monitored heating element, we can know the pressure of the gas. We put the gas in there, we know what it is, and all about it.”

Bob is clearly struggling with the concept of thermal isolation. He recognizes that an isentropic process means the the system cannot be heated, and therefore adds thermal insulation to isolate the piston from its surroundings. However, he proceeds to add a heating element to the system, failing to recognize that the energy from the heating element comes from the surroundings. Throughout this episode, Bob is also inconsistent about whether he sees the pressure as changing or held constant.

We include a discussion of this episode because it is typical of the student reasoning that is addressed both in small groups and in the whole-class discussion. The activities presented in this paper give students the chance to wrestle with these issues through interactions with their peers, as well as the instructors and teaching assistants. Additionally, observing the conversations between students during these activities can help instructors to better tailor their instruction to the needs and confusions of that particular set of students.

#### IV. ACTIVITY 2: CHANGING ENTROPY

After we have spent some more time in the class talking about entropy, we have a second name-the-experiment activity, in which students examine derivatives in which the entropy itself is changing, as listed in Table II. This set is composed of two easier derivatives, which correspond to measurements of the heat capacities  $C_V$  and

TABLE II. Derivatives for the second activity, in which we change the entropy, grouped according to the type of experiment required.

Heat capacity measurement:	$\left(\frac{\partial S}{\partial T}\right)_V$	$\left(\frac{\partial S}{\partial T}\right)_p$
Isothermal (challenging):	$\left(\frac{\partial S}{\partial V}\right)_T$	$\left(\frac{\partial S}{\partial p}\right)_T$

$C_p$ , along with two more challenging isothermal derivatives. Since we don’t have a direct way to measure entropy itself, all of these derivatives are more challenging than those in the first activity. Instead of measuring entropy directly, we must infer the change in entropy by measuring the energy transferred by heating and using the thermodynamic definition of entropy:

$$\Delta S = \int \frac{dQ_{\text{quasistatic}}}{T}. \quad (9)$$

The energy transferred by heating can be measured by heating the system with a resistor, as our students do in an experiment measuring the heat capacity of water.

One of the primary goals of the heat capacity derivatives is to provide a review of the concept of heat capacity. At this stage of the course, students have already measured the heat capacity of water, and many groups recognize that these derivatives correspond to an experiment that they have already performed.<sup>18</sup> This name-the-experiment activity highlights the distinction between  $C_V$  and  $C_p$ , because students are required to explain how they hold the volume or pressure fixed. We find this an excellent opportunity to discuss the difficulty of keeping the volume fixed and to introduce the term “bomb calorimeter” for a device to measure  $C_V$ . Students appreciate the humor of this term.

The isothermal derivatives with changing entropy are considerably more challenging, but also provide several excellent learning opportunities. In particular, these isothermal derivatives address a common student difficulty: many students assume that when a system is held at fixed temperature, it is not being heated and since  $Q$  is zero, its entropy must also be held constant. This is complementary to the issue mentioned in Section II, in which an adiabatic process resulted in a changing temperature. During this activity, this difficulty comes up early in student discussions, and many groups are able to overcome it without the need for instructor intervention.

In one of these isothermal derivatives,

$$\left(\frac{\partial S}{\partial V}\right)_T, \quad (10)$$

we need to change the volume at fixed temperature, and measure the energy transferred between the system and environment by heating. There are two mechanisms one can imagine for this, neither of which is very easy.

One approach is to create a thermostat, described by one group this way:

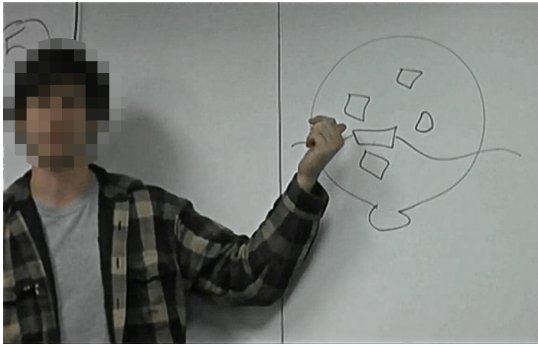


FIG. 4. Student sketch of an experiment to measure the derivative  $(\partial S/\partial V)_T$  in Eq. (10). The students assumed that the material being measured was ice water, and put the ice water in a balloon. The mixture is then heated with a resistor and the resulting change in volume is measured.

“We were just thinking that we could have like something, an object that we can change the volume and then we’d have like a resistor and thermometer and, say like we expand it so it cools off and measure how much heat we have to put into the system to keep the temperature constant.”

This approach is somewhat awkward and does require that the temperature change somewhat, so that the thermostat can respond.

The second approach, proposed by a different group, would be to use a mixture of ice and water to hold the temperature fixed. Figure 4 shows a student presenting this group’s solution. The material that is being measured is ice water that is held in a balloon. A resistor heats the ice water, and the volume of the balloon is then measured. This student solution has a few disadvantages: it is hard to imagine thermally insulating the balloon, and measuring the change in volume could be tricky.

As mentioned in Section I, we desire to aid in the development of these students as expert physicists. A significant part of the culture of physics involves peer evaluation and critique. Having students present their solutions to the rest of the class can provide opportunities for students to engage in this practice. For example, consider the discussion between the instructor (IN) and two students (S1 and S2) from different groups that followed the presentation of Fig. 4:

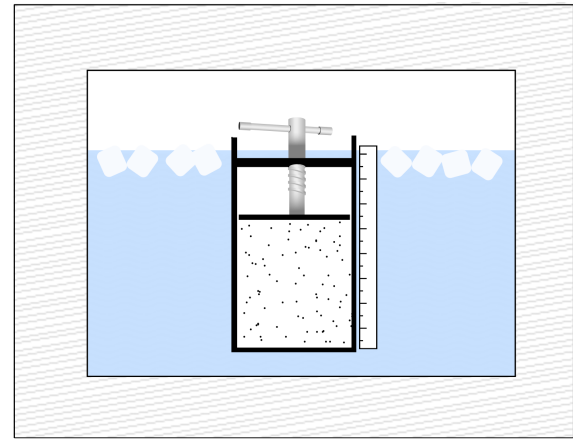


FIG. 5. Sketch of experiment to measure the derivative  $(\partial S/\partial V)_T$  in Eq. (10). The system of interest is inside a metal cylinder that is immersed in ice water with a known quantity of ice. The cylinder and ice water are inside an insulated container. The volume of the cylinder is slowly changed, and afterwards the mass of the ice is measured.

- S1: Does that work because when you change phase in water, uh, like, water is larger as a solid than a liquid, which is not, most things aren’t like that, and that’s because of the hydrogen bonds?
- IN: Uh huh.
- S1: So, it seems like that’s adding in an extra factor that doesn’t really have anything to do with the heat, necessarily.
- IN: [furrows brow]
- S1: Or like, thermodynamics in general.
- IN: Well it does certainly does have to do, I mean, thermodynamics is all about what do things actually do.
- S1: But, I mean, I guess what I’m saying is if you use something that wasn’t water, like just some other.
- IN: If you use...
- S2: The change of volume would just be different.
- IN: [nods] mmhmm, yeah. So, your change of volume would be different in that case.
- S1: But, [pause] ok.
- IN: [shifts the discussion to other issue related to phase changes]

At the end of this exchange, it is not clear that S1 is completely convinced by S2’s answer. However, both S1’s critique of the previous group’s methodology and S2’s willingness to try to address S1’s question demonstrate that they understand that they are a part of a culture that values peer feedback. In addition, both students recognize that the experiment should be able to measure this property for an arbitrary system.

A more satisfactory variant of this solution is displayed in Fig. 5, which uses a piston such that the volume is eas-

TABLE III. Derivatives for the third activity, in which we use Maxwell relations to find an easier experiment. In the upside down cases, the Maxwell relation required involves the inverse of the derivative requested.

Right side up:	$\left(\frac{\partial S}{\partial V}\right)_T$	$\left(\frac{\partial S}{\partial p}\right)_T$
Upside down:	$\left(\frac{\partial S}{\partial p}\right)_V$	$\left(\frac{\partial S}{\partial V}\right)_p$

ily controlled, and the system is taken to be separate from the ice water. In this case, the challenge is to measure how much ice remains after changing the volume of the system. One could use a sieve to pull out the ice and measure its mass. Both of these solutions (Figs. 4 and 5) have the disadvantage of requiring that we make our measurement at  $0^\circ\text{C}$ , but the advantage of reinforcing the concept that fixed temperature does not mean zero heating, and they build on the ice-water calorimetry experiments that we do earlier in the course.

During this second name-the-experiment activity, students encounter their first really “hard” derivatives, and experience the difference between quantities that are conceptually easy to measure and those that are inherently challenging. In this case the heat capacities are easy to measure, while the isothermal derivatives of entropy are challenging, since it is hard to fix the temperature while changing the entropy by a measured amount. Understanding this distinction is one of the primary learning goals of this second activity. Allowing students time to struggle with this challenging task that has no particularly elegant solution helps them to appreciate the difference between an easily measurable quantity and one that is less so, an appreciation that will pay off in the next activity.

### V. ACTIVITY 3: MAXWELL RELATIONS

Before the final name-the-experiment activity, we have shown students the Legendre transforms, and asked them find the total differentials for enthalpy, Helmholtz free energy, and Gibbs free energy. We discuss how each of these total differentials gives us a new set of expressions for the thermodynamic variables  $p$ ,  $V$ ,  $S$ , and  $T$ , and then remind students of Clairaut’s theorem regarding the equality of mixed partial derivatives. We then introduce Maxwell relations to our students and have students find a given Maxwell relation in small groups.

At this point, we use a final name-the-experiment activity. The students are given a partial derivative to “measure.” They then use a Maxwell relation to find a second (ideally easier) experiment that is equivalent to their given partial derivative. We actually ask students to find *two* experiments for their derivative, one easy experiment and one hard experiment. Table III lists the derivatives that may be assigned in this activity, each

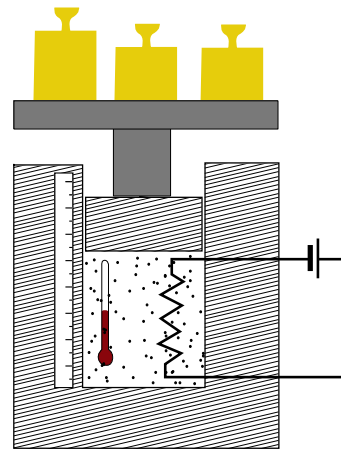


FIG. 6. Sketch of an experiment to directly measure the derivative  $(\partial p/\partial T)_V$  in Eq. (11). The procedure involves heating the contents of an insulated cylinder with a resistor, and measuring how much weight needs to be added to the piston in order to return the system to its original volume.

expressed as a derivative of entropy. In two of the four cases, this results in a derivative that is the inverse of the derivative that occurs in a Maxwell relation, which creates an additional challenge for students. This idea of turning derivatives “upside down” can be used at any stage in the name-the-experiment sequence, to add one more step for students to consider in analyzing a derivative.

Two of the derivatives in Table III are also present in Table II. One of these,  $(\partial S/\partial V)_T$ , was discussed in detail in the previous section. This derivative required a “hard” experiment to measure, performed with good thermal insulation and either a thermostat or some ice water, but we can find a Maxwell relation involving  $(\partial S/\partial V)_T$  from the Helmholtz free energy. From the total differential  $dF = -S dT - p dV$  we have

$$-\left(\frac{\partial^2 F}{\partial T \partial V}\right) = \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V. \quad (11)$$

This gives us a “simple” derivative to measure, which involves changing the temperature of a system and measuring the change in pressure required to keep the volume fixed, as illustrated in Fig. 6. This experiment is far easier than the difficult experiment shown in Fig. 5 in which the quantity of ice melted must be measured.

In the case above, we were able to reuse the hard experiment that we had discussed earlier. When assigning derivatives to students, however, we prefer to avoid assigning a derivative to the same students who have already tackled it during a previous name-the-experiment activity. This policy provides the opportunity to reinforce their learning by designing a new experiment, instead of merely attempting to recall a solution that they previously created. In many cases students will have seen an applicable experiment described by another group during an earlier wrap-up discussion, so the derivative

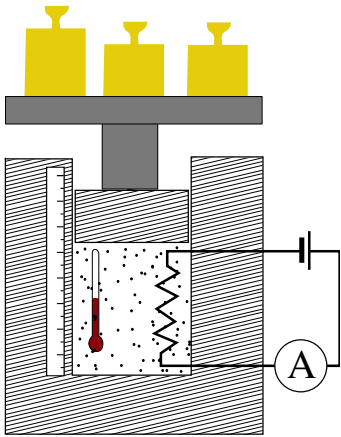


FIG. 7. Sketch of an experiment to directly measure the derivative  $(\partial S/\partial V)_p$  in Eq. (12). The procedure involves heating the contents of an insulated cylinder with a resistor, while measuring the current (and thus power) and the temperature, and measuring the change in volume.

will still feel somewhat familiar to them.

Let us consider another of the derivatives from Table III, which we have not previously discussed:

$$\left(\frac{\partial S}{\partial V}\right)_p. \quad (12)$$

Interpreted directly, this derivative requires us to change the volume at fixed pressure, and measure the change in entropy. Practically, it is easier to change the entropy and measure the change in volume, which we can do by heating a thermally insulated system with a resistive heating element, keeping track of the amount of power dissipated and the temperature. This direct experiment is illustrated in Fig. 7.

We can construct an alternative experiment that does not require a heat measurement by seeking a Maxwell relation that involves  $(\partial S/\partial V)_p$ . As discussed above, there is no Maxwell relation that explicitly uses this derivative, since Maxwell relations come from mixed partial derivatives between two thermodynamic variables that are *not* conjugate pairs as  $p$  and  $V$  are. We present students with these “upside down” derivatives in order to encourage them to think about how else to look at any given derivative. In this case, we seek a Maxwell relation involving  $(\partial V/\partial S)_p$ , which we can find using the enthalpy. From the total differential  $dH = T dS + V dp$  we have

$$\left(\frac{\partial^2 H}{\partial S \partial p}\right) = \left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S. \quad (13)$$

In this case, the “simple” derivative is the inverse of the first derivative we discussed in Section II, which could be measured with a simple insulated piston with a thermometer and a set of weights, as illustrated in Fig. 1. Through this activity, students encounter unfamiliar derivatives that can be related to much more familiar experiments.

This final activity allows students to gain experience in the lessons of the previous activities, while at the same time demonstrating how a seemingly obscure relationship between derivatives is actually a powerful experimental tool. We follow this activity with a laboratory in which we use a Maxwell relation to enable us to measure the entropy change when isothermally stretching a rubber band without resorting to calorimetry.<sup>10</sup>

## VI. CONCLUSIONS

We have introduced a sequence of three activities in which students describe an experiment corresponding to a given partial derivative. These activities provide students the opportunity to think of thermodynamic derivatives as descriptions of experiments. Students also gain practice with the operational definitions of thermodynamic quantities, and experience with constructing canonical thought experiments. These concrete ways of thinking about abstract concepts further enculturate students into ways of thinking like expert physicists. Finally, these activities explicitly address student difficulties with partial derivatives and thermodynamics that have been previously documented in the literature.

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