A thermodynamic derivative means an experiment

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All too often, courses in thermodynamics and statistical mechanics barrage their students with numerous equations that are left unexamined and uninvestigated. This note explains how to pause, examine a thermodynamic equation, and render it more meaningful. Three techniques are discussed: (1) design two experiments that would measure the quantities on either side of the equality; (2) examine special cases; (3) consider the consequences if the equality failed to hold. © *1999 American Association of Physics Teachers.*

Thermodynamics is full of equations relating various partial derivatives. Left unexamined, such formulas are jumbles of symbols with little meaning and little to excite the mind of most students. But because a thermodynamic partial derivative suggests an experiment which measures it, equations relating partial derivatives imply that two very different experiments must, remarkably, always produce the same results. This note examines one of many such thermodynamic relations to illustrate general techniques for investing thermodynamic results with meaning. (The widely applicable scheme of examining equations for meaning is called[1] ''reading an equation.'' Additional techniques for reading equations are described in Refs. 2 and 3.)

The thermodynamic relation I choose to discuss,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \tag{1}$$

holds for equilibrium fluid systems with constant particle number (no particles enter or leave the system either at the boundaries or through chemical reactions). It is the Maxwell relation associated with the Helmholtz free energy $F(T,V)$, and is frequently derived as an intermediate step in uncovering the relation between heat capacity at constant pressure and heat capacity at constant volume.

Experiments. Each of the above derivatives is not only a mathematical expression, but also an invitation to perform an experiment. The derivative on the left is measured as follows: A sample in a container of variable volume (such as a piston) is placed within a thermostatically controlled bath (so that the temperature does not change) and is heated in a slow and carefully monitored way (so that the heat absorbed quasistatically can be divided by the temperature to find the entropy change). As the substance is heated at constant temperature, the volume of the piston must change. Dividing the heat absorbed by the temperature and the volume change gives (for small volume changes) the derivative on the left. This experiment is not impossible, but clearly it is difficult and expensive.

Consider in turn the experiment on the right. The sample is in a ''strong box'' container of fixed volume and its pressure and temperature are measured as both of them change. The change need not be controlled carefully and the heat absorbed need not be monitored: You can just blast your sample with a propane torch. Dividing the measured change in pressure by the measured change in temperature gives (for small temperature changes) the derivative on the right.

It is far from obvious that the results of these two very different experiments should always be the same. The fact that they are shows how thermodynamics can save a lot of experimental labor!

Special cases. A commonly encountered special case is the ideal gas that has the pressure equation of state

$$pV = Nk_BT. \tag{2}$$

For this case

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{Nk_B}{V}, \tag{3}$$

so

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{Nk_B}{V}. \tag{4}$$

At a given temperature, the entropy always increases with volume, and the rate of increase is larger at high densities (small volumes). Integrating Eq. (4) gives

$$S(T,V) = Nk_B \ln(V/V_0(T)), \tag{5}$$

where $V_0(T)$ is an undetermined function of integration which differs from one ideal gas to another. The remarkable character of our Maxwell relation comes into sharp focus when applied to this special case: The ''mechanical-type'' experiments which uncover the equation of state enable us to determine much about the entropy function even in the absence of any ''heat-type'' experiments.

The fact that the ideal gas is so commonly discussed has the unfortunate consequence that students might spend an inordinate amount of time on the thermodynamics of the ideal gas, getting the misimpression that thermodynamics applies *only* to the ideal gas. In fact, thermodynamics applies to *all* equilibrium systems: fluids, crystals, mixtures, magnets, polymers, even light.[4] It is a pity to waste the beautiful, powerful, and wide-ranging subject of thermodynamics on the study of only one substance, especially since that substance does not even exist in nature! Another special case of interest is two-phase coexistence of, say, liquid and gas. It is not difficult to see that for ''typical'' two-phase coexistence—in which the low-temperature phase has higher density than the high-temperature phase—both of the derivatives in our Maxwell relation are equal to positive infinity.

For ''backwards sloping'' two-phase coexistence—such as water and ice—both of the derivatives are equal to negative infinity.

What if it were false? What would happen if we discovered a substance for which the Maxwell relation Eq. (1) did not hold? The relation is derived from the existence of the Helmholtz free energy $F(T,V)$, which in turn is derived from the existence of entropy, which in turn is derived from the fact that one cannot build a perpetual motion machine. Hence if the two experiments discussed above *did* happen to give different results for some newly discovered substance, then you could use that substance to build a perpetual motion machine.

Anyone whose sense of wonder[5] is not excited by this remarkable chain of reasoning needs a better-developed sense of wonder.

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[1] Robert H. Romer, ''Reading the equations and confronting the phenomena—The delights and dilemmas of physics teaching,'' Am. J. Phys. **61**, 128–142 (1993).

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[3] Jeffrey J. Prentis, ''Equation poems,'' Am. J. Phys. **64**, 532–538 (1996).

[4] Robert E. Kelly, ''Thermodynamics of blackbody radiation,'' Am. J. Phys. **49**, 714–719 (1981).

[5] Philip Morrison, *Nothing Is Too Wonderful To Be True* (American Institute of Physics Press, Woodbury, NY, 1995).

OBJECTIVE MEASURES

Publishing more papers rather than fewer will help you in several ways with the ''bean-counters'' among those who judge you. They will not only look at the number of papers you have published, but will also consult the *Science Citation Index* to see how many inches of citations your papers have attracted. If you have published twice as many articles, this ''objective measure'' of their impact will be roughly twice as great. You may find this idea crass. I do. But it is safe to assume that there will be bean-counters among those who determine your future, and it certainly does you no harm to please them.

Peter J. Feibelman, *A Ph.D. Is Not Enough—A Guide to Survival in Science* (Addison–Wesley, Reading, MA, 1993), p. 101.