4.10 Special Application: Thermodynamics

A sealed canister is filled with gas. A thermometer allows you to constantly monitor the temperature of the gas, a manometer lets you monitor its pressure, and a heating coil allows you to add controlled amounts of energy to it. In one experiment you tighten the lid of the container and slowly add energy until the temperature of the gas has gone up by 5 K. You record the amount of energy you added and the change in pressure that resulted. In a second experiment the lid is a piston that can slide up or down freely, allowing the gas to expand or contract. The piston is still sealed so no gas can enter or leave, and it's insulated so the only cooling or heating comes from the coil that you control. This time as you add energy you find that the gas expands, pushing the piston up, and the pressure of the gas remains constant. You also find that you need to add more energy to the gas to raise its temperature by 5 K than you had needed when the lid was locked in place.

These experiments fall within the domain of "thermodynamics," which deals with the flow of energy between systems. It is one of the fields that most heavily uses partial derivatives and differentials. In Problem 4.178 you'll come back to these two experiments and calculate the changes in pressure, volume and energy in both cases. In order to get there, you'll need some of the central formulas of thermodynamics:

1. The "first law of thermodynamics," which can be rewritten as the "thermodynamic identity," addresses the ways in which energy transfers into and out of a system.
2. "Heat capacity" addresses the change in temperature that results from such a transfer of energy.

The first law, and the application of heat capacity to a system, are universal. To figure out the heat capacity of a specific system, you need more information about that system. This brings us to our last topic:

3. The "ideal gas law" and "equipartition theorem" describe specific systems in enough detail to allow you to figure out their heat capacities in many cases. Although these laws are not universal, they apply in a broad variety of important real-world situations.

The First Law of Thermodynamics and the Thermodynamic Identity

A brick lying on the ground has an "internal energy" U due to the motions of its molecules and the forces between them. A brick falling from a roof has a "total energy" E which is the sum of internal, kinetic, and potential energies. In this section we will consider containers of gas at rest. They may expand or contract, but they won't move, so their only energy changes will be in their internal energy. There are two ways a system's environment can change the system's internal energy. Heat (Q) is the spontaneous transfer of energy from a hot object to a cold object. Work (W) is essentially any other transfer of energy, which can include mechanical work (pushing or pulling the system), electrical work (running a current through it), and more.[5] The relationship between energy, heat, and work is expressed in the "first law of thermodynamics":

$$dU = Q + W \quad \textit{the first law of thermodynamics} \tag{4.10.1}$$

We don't usually set a differential equal to a normal quantity, but Q and W are not normal variables. Q is the *heat entering the system*; it is not an energy, but the increase in energy due to one specific cause. (Some texts use ΔQ and dQ for normal and infinitesimal flows of heat respectively, but that seems to imply "a change in heat" which is not completely accurate; rather, heat itself is a change in energy.) W is also a change, the energy added to the system

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[5]We are assuming that each system maintains a constant number of particles, which rules out energy exchange by direct transfer of particles from one system to another.

due to all other causes. (Some texts define W as the work *done by* the system, and therefore write $dU = Q - W$.) We will use Q and W without a prior Δ or d, and you will need to know from context whether we are referring to a regular change in energy or an infinitesimal one.

In this section we will consider the relatively simple case of a gas in a closed container, and we will only consider work done by compressing or expanding the gas. You will show in Problem 4.189 that the work done on a gas when it is compressed by a small amount dV is $-P\,dV$, where P is the pressure of the gas and V is its volume. The sign is negative because positive work is done on the system when dV is negative. The heat entering a system can similarly be written as $T\,dS$ where T is the temperature and S is the "entropy."[6] That expression can be derived from a more fundamental definition of entropy having to do with the microscopic properties of the system, but for our purposes you can think of $dS = Q/T$ as the definition of entropy. (It's how entropy was first defined.) Putting all this together gives the "thermodynamic identity," which (among its other virtues) looks more like a good equation with differentials should.

$$dU = T\,dS - P\,dV \quad \textit{the thermodynamic identity} \tag{4.10.2}$$

Heat Capacity

When you add energy to a system you generally increase its temperature. The amount of heat required per unit increase in temperature is the "heat capacity" (C) of the system. This definition can be written as $C = Q/dT$. Using $dS = Q/T$ (from above) we get:

$$C = T\frac{dS}{dT} \tag{4.10.3}$$

In this form, however, the definition of heat capacity is ambiguous because the entropy depends on all three of the state variables T, P, and V. How fast entropy changes with respect to temperature depends on what is happening to the other two variables at the same time. The simplest possibility is to hold the volume constant ($dV = 0$), so Equation 4.10.2 becomes $dU = T\,dS$. Putting that together with Equation 4.10.3 and the chain rule,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \textit{heat capacity at constant volume}$$

Recall that the subscript V on this partial derivative means V is the variable you are holding constant as you differentiate with respect to T. We'll discuss this issue in more detail below.

Physically, this is the heat capacity of a system assuming there is no work being done on or by the system ($P\,dV = 0$). While C_V is relatively simple to calculate for many systems, it is not usually the heat capacity of interest. That's because when you heat something it tends to expand, which causes it to do work on its environment: it is the pressure, rather than the volume, that stays constant. Most tabulated values of heat capacity refer to "heat capacity at constant pressure." In Problem 4.198 you will show that

$$C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \quad \textit{heat capacity at constant pressure} \tag{4.10.4}$$

Since some of the energy you put in as heat is going into work on the environment, the heat you need to add to get a certain increase in temperature is greater, so C_P is always larger than C_V.

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[6]This section will contain many formulas with temperature in them. Those formulas only work if temperature is measured in Kelvin, or some other scale where $T = 0$ means the absolute zero of temperature. If you think about the familiar ideal gas law $PV = nRT$ (which we discuss below), it should be clear that if a gas is at $0°$ Fahrenheit that doesn't mean P or V is zero. The ideal gas law, like most thermodynamic formulas, simply isn't true for temperatures in Fahrenheit or Celsius.

Ideal Gases

To make calculations about a particular fluid, you need to know the relationships between properties such as pressure, volume, temperature, and energy. Different relationships lead to different behavior. Here we address only one case, an "ideal gas." But this case is not just a textbook oversimplification: more complicated systems can often be approximated by the ideal gas law in cases of low densities, such as the densities typically found at room temperature and pressure, so these equations serve as a useful model for most gases an engineer is likely to encounter. You'll consider some other systems in the problems.

We will need two equations to model an ideal gas. The first, the "equation of state," relates pressure, volume, and temperature:

$$PV = nRT \quad \textit{the ideal gas equation}$$

Here n is the number of moles (number of molecules divided by a constant called "Avogadro's number") and $R = 8.3 \, \text{J}/(\text{mol K})$ is a constant.[7]

The second equation, which applies to ideal gases and a variety of other systems, relates the internal energy to the temperature:

$$U = \frac{f}{2} nRT \quad \textit{the equipartition theorem}$$

Here f is the number of "degrees of freedom," which essentially means how many ways the molecules can move. A monatomic molecule such as helium has three degrees of freedom because it can move in three independent directions. A diatomic molecule such as hydrogen can also move in three directions, but in addition it can rotate around two independent axes, so it has five degrees of freedom. (Technically you could consider other degrees of freedom such as vibrations or rotations about the long axis of a diatomic molecule, but for quantum mechanical reasons those motions cannot be excited at room temperature for most gases.)

The equation of state and the equipartition theorem allow you to predict measurable quantities. For example, the heat capacity at constant volume of an ideal gas is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{f}{2} nR \tag{4.10.5}$$

For a container with five moles of helium gas, C_V is thus $20.8 \, J/K$.

Another look at $(\partial f / \partial x)_y$

Throughout this section, and throughout thermodynamics more generally, frequent use is made of the notation $(\partial f / \partial x)_y$, meaning the partial derivative of f with respect to x, holding y constant. To consider in more detail what such a derivative means, we turn briefly to a non-thermodynamic example from basic Geometry.

The area of a right triangle can be written[8] as $A = (bc^2 - b^3)/(2a)$, where a and b are the legs and c is the hypotenuse. If the side lengths are changing, then the chain rule gives us $dA/dt = (\partial A/\partial a)(da/dt) + (\partial A/\partial b)(db/dt) + (\partial A/\partial c)(dc/dt)$, which becomes:

$$\frac{dA}{dt} = \left(\frac{-(bc^2 - b^3)}{2a^2} \right) \left(\frac{da}{dt} \right) + \left(\frac{c^2 - 3b^2}{2a} \right) \left(\frac{db}{dt} \right) + \left(\frac{bc}{a} \right) \left(\frac{dc}{dt} \right) \tag{4.10.6}$$

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[7]Physicists often write the ideal gas equation in terms of the number of molecules rather than the number of moles: $PV = Nk_B T$. "Boltzmann's constant" k_B is just R divided by Avogadro's number.

[8]You can easily confirm this formula for yourself. Your next question might be "Who would write it that way, and why?" We would, because we're writing a math book. So there.

We're about to say some unflattering things about this equation, but first a word of reassurance: if we tell you the side lengths of a right triangle and how fast those lengths are changing, Equation 4.10.6 will correctly tell you how fast the area is growing. We are not about to take back everything we've promised about the chain rule.

But we are about to point out that $(\partial A/\partial a)$ is a fictitious quantity.

You know by now that $(\partial A/\partial a)$ means "Find how much A changes if you change a while holding b and c constant." But you also know that you *cannot possibly* change a while holding b and c constant! The three variables are related by the Pythagorean theorem: $a^2 + b^2 = c^2$. If you change one side, one or both of the others must change. (You can't have a 3.01-4-5 right triangle.) So $\partial A/\partial a$ is a *useful* quantity, as a step toward finding a total dA, but it is not *physically meaningful* by itself. In fact, as you will show in Problem 4.191, different forms of the area formula lead to completely different values for $\partial A/\partial a$.

EXAMPLE   **Same Partial Derivative, Different Answers**

Question: The function $f(x, y) = x + y$ is defined on the domain $y = x$. Find $\partial f/\partial x$.

One solution:
If we take the function as given, $f(x + y) = x + y$, then clearly $\partial f/\partial x = 1$.

Some other solutions:
Because this function is subject to a constraint, we can use the equation $y = x$ to rewrite the function. If we write it as $f(x, y) = 2y$ then $\partial f/\partial x = 0$. And if we rewrite it as $f(x, y) = 2x$ then $\partial f/\partial x = 2$.

Why did we get three answers for one question? Because the question involves a useful fiction. You cannot "change x while holding y constant" while also maintaining the constraint $y = x$.

So why did you write a whole chapter about partial derivatives if they don't mean anything? Two reasons. First, sometimes they do mean something. If x and y were truly independent, then $\partial f/\partial x$ would be a real and meaningful quantity. And as we will see below, even when there is a constraint, we can frame partial derivatives in a perfectly meaningful way by carefully specifying what stays constant and what doesn't.

But the second reason is even more important: as we stressed above, the chain rule still works! In this example, if you write $df/dt = (\partial f/\partial x)(dx/dt) + (\partial f/\partial y)(dy/dt)$ you will get the right answer, $df/dt = 2(dx/dt)$, no matter what form you use.

In short, there are two kinds of partial derivatives: the ones that are physically meaningful (and have one unique answer), and the ones that are not physically meaningful (and may have different answers). Both kinds can be used to find correct total derivatives.


Thermodynamics is rife with constrained multivariate functions. For instance, $\partial U/\partial T$ falls into the "useful but not physical" category because you can't change T while holding P and V constant. But we can get physically meaningful derivatives by specifying one variable to hold constant, and allowing the others to change as they must. Consider how we can apply this strategy to our triangle.

- $\partial A/\partial a$, as discussed above, means "see what happens to A if you change a while holding b and c constant." It can be a useful step on the road to finding a total dA, but it has no intrinsic meaning, and its value depends on the specific form of your $A(a, b, c)$ function.

- $(\partial A/\partial a)_b$ asks about the change in area if you change a while holding b constant. This is real: the change in a causes a change in c, and the area of the triangle changes in response to both of these changes. Mathematically, you would find this quantity by solving $a^2 + b^2 = c^2$ for c and then plugging in to find $A(a, b) = (1/2)ab$ before evaluating the partial derivative.
- $(\partial A/\partial a)_c$ is also real: you change a while holding c constant, which causes a change in b, and the area of the triangle changes in response to both of these changes. Mathematically, you would find this quantity by solving $a^2 + b^2 = c^2$ for b and then plugging in to find $A(a, c) = (1/2)a\sqrt{c^2 - a^2}$ before taking the derivative.
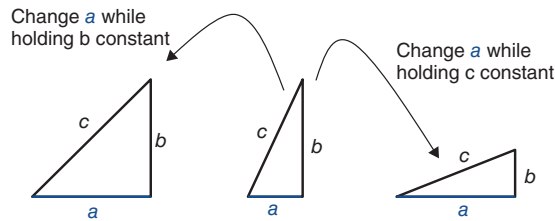
Please don't think that we are saying "partial derivatives are physically meaningful only when they have parentheses." The message is quite different: "Partial derivatives are physically meaningful when they represent a possible change." For instance, if $T(x, y, z)$ represents the temperature in the room, then $\partial T/\partial x$ (which implicitly means "holding y and z constant") is perfectly meaningful, since x, y, and z are all independent. But if our function is confined to the plane $3x + 2y + 5z = 7$ then a change in x must be accompanied by a change in either y or z. In that case, $\partial T/\partial x$ would be helpful only as part of a total dT, but $(\partial T/\partial x)_y$ would mean more than that.

Perhaps surprisingly, this distinction between "only useful" and "actually physical" partial derivatives can be important in how you use them in equations. As an example, suppose that three quantities E, F, and G are related by:

$$dE = dF + F \, dG \qquad \textit{given} \qquad (4.10.7)$$

You can take this at face value as a statement about small changes: "If F and G each changes by a small amount, then here is how much E will change." If all three variables depend on time, then you can also divide both sides by dt:

$$\frac{dE}{dt} = \frac{dF}{dt} + F\frac{dG}{dt} \qquad \textit{follows from Equation 4.10.7}$$

This is now a statement about *rates* of change: "If F and G are changing this fast right now, then here is how fast E is changing."

But what if E, F, and G are all functions of x and y? Since we have stressed that dx is a meaningful (and manipulable) variable and ∂x is not, you should be suspicious if we assert this.

$$\left(\frac{\partial E}{\partial x}\right)_y = \left(\frac{\partial F}{\partial x}\right)_y + F\left(\frac{\partial G}{\partial x}\right)_y \qquad \textit{Does this follow from Equation 4.10.7?} \qquad (4.10.8)$$

Does Equation 4.10.7 imply Equation 4.10.8? If x and y are independent, so all of these partial derivatives have unique physical values, then the answer is yes. If x and y are related by some external constraint, however, then you can change the values of these partials simply by rewriting your functions as we did for $\partial A/\partial a$ above, and Equation 4.10.8 doesn't follow from Equation 4.10.7. You'll see an example where you are not allowed to do this division in

Problem 4.196, and in Problem 4.198 you'll apply a valid use of "dividing by ∂x" to derive an important thermodynamic equation.

Thermodynamics makes frequent use of this notation and this trick, generally without explanation. So let's be clear: you cannot get from Equation 4.10.7 to Equation 4.10.8 by "dividing both sides by ∂x" (there's no such thing), or by taking derivatives with the chain rule. You can't get there by any mathematical step, because it is not always true. But if x and y are independent of each other, then changing x while holding y constant will lead to real values of dE, dF, and dG, and under those circumstances the leap to Equation 4.10.8 is safe.

4.10.1 Problems: Thermodynamics

4.178 A canister contains 5 moles of hydrogen gas at 300 K and 10^5 Pa (the SI unit of pressure). You may consider the hydrogen to be an ideal gas.

  (a) How much thermal energy does the hydrogen contain?

  (b) How much more thermal energy would the hydrogen contain if it were at 350 K?

  (c) Use Equation 4.10.5 to find C_V for the hydrogen and use that to calculate how much heat you have to add to the gas to raise it from 300 K to 350 K at constant volume. Verify that your answer matches the energy difference you found in Part (b).

  (d) How much would the pressure of the gas increase as you heated it at constant volume?

  (e) Use Equation 4.10.4 to find C_P for the hydrogen.

  (f) Use your answer to Part (e) to calculate how much heat would be required to raise the gas from 300 K to 350 K at constant pressure.

  (g) Use the first law of thermodynamics and your answers to the previous parts to calculate how much work is done on or by the gas as you heat it from 300 K to 350 K at constant pressure.

  (h) Recall that we define W to be positive when work is done *on* the system and negative when it is done *by* the system. Based on the sign you found for the work, is work being done on the hydrogen by its surroundings, or on the surroundings by the hydrogen? Based on that, is the hydrogen gas expanding or contracting as you heat it? (*Hint*: Don't forget to use common sense and experience. If your answer to this question contradicts what you would physically expect, go back and see if you made a sign error.)

  (i) Using $W = -P\,dV$, find the amount by which the volume of the gas increased or decreased as you heated it at a constant pressure of 10^{-5} Pa.

4.179 **(a)** What is $(\partial U/\partial V)_S$? (*Hint*: If you spend more than 30 s on this problem you're making it harder than it needs to be.)

  (b) Briefly describe an experiment you could perform to vary V while holding S constant. *Hint*: look at the definition of entropy.

4.180 For a system that obeys the equipartition theorem we could have written the definition of C_V as a total derivative, dU/dT. Explain why this is equivalent to the definition we gave for systems that obey equipartition, but not necessarily for other systems.

For Problems 4.181–4.185 you should assume all gases are ideal. At normal temperatures and pressures this is usually a good approximation. Pay attention to how many degrees of freedom f the gas in each problem has.

4.181 An "isothermal" process is one that takes place at a constant temperature. Assume a container with n moles of helium at volume V and pressure P is being expanded isothermally at a rate dV/dt.

  (a) At what rate is the internal energy of the helium changing? (*Hint*: This requires no calculations.)

  (b) Using the thermodynamic identity and your answer to Part (a), find the rate of change of the helium's entropy.

4.182 An "adiabatic" process is one in which no heat enters or leaves the system. Assume a container with n moles of helium at volume V and pressure P is being expanded adiabatically at a rate dV/dt.

(a) At what rate is the entropy of the helium changing? (*Hint*: This requires no calculations.)

(b) Using the thermodynamic identity and your answer to Part (a), find the rate of change of the helium's energy.

(c) Is the helium's temperature remaining constant, increasing, or decreasing?

4.183 An "isobaric" process is one that takes place at constant pressure. Assume a container with n moles of helium at volume V and pressure P is being expanded isobarically at a rate dV/dt.

(a) At what rate is the temperature of the helium changing?

(b) At what rate is the energy of the helium changing?

(c) Using the thermodynamic identity and your answer to Part (b), find the rate of change of the helium's entropy.

(d) Is heat entering the system, leaving the system, or neither?

4.184 A container with a movable piston that can allow it to expand and contract contains n moles of helium. The container walls are thin enough that the helium remains at a constant room temperature T. You slowly compress the container so that the volume goes from V_0 to V_f.

(a) Write an expression for $P(V)$, the pressure as a function of volume while the helium is being compressed.

(b) Recall that a *small* amount of compression $-dV$ requires an amount of work $-P\,dV$ to be done on the system. To find the total work done in going from V_0 to V_f take an integral to add up all the infinitesimal amounts of work done along the way.

(c) Did the sign of your answer to Part (b) come out the way you would expect? Explain.

(d) How much did the energy of the helium change during the process? (*Hint*: This should be trivial to answer.)

(e) How much heat entered or left the system during the process?

(f) Find the change in entropy of the helium during the compression.

4.185 Methane is a "polyatomic" molecule, meaning it has more than two atoms.

(a) A polyatomic molecule can rotate about any of the three axes. How many degrees of freedom f does it have?

(b) How much heat is required to raise 30 moles of methane gas from 300 K to 350 K at constant pressure?

4.186 **(a)** What is C_P for an ideal gas with f degrees of freedom?

(b) Is the expression you just found for C_P larger than or smaller than Equation 4.10.5 for C_V?

(c) Explain why your answer to Part (b) makes sense physically.

4.187 The ideal gas approximation assumes that the molecules of a gas don't interact with each other. At high densities, an approximation that takes into account some molecular interactions is the van der Waals equation of state:

$$PV + \frac{an^2}{V} - nbP - \frac{abn^3}{V^2} = nRT$$

The energy of a van der Waals gas is:

$$U = \frac{fnRT}{2} - \frac{an^2}{V}$$

(a) Calculate C_V for a van der Waals gas.

(b) From the energy equation you can conclude that $(\partial U/\partial T)_P = fnR/2 + (an^2/V^2)(\partial V/\partial T)_P$. Use implicit differentiation and the van der Waals equation of state to find $(\partial V/\partial T)_P$ and thus derive an expression for C_P for a van der Waals gas.

4.188 Electromagnetic radiation can be considered a gas of particles called "photons." The gas is ideal (not just approximately ideal, like normal gases), but instead of the usual equipartition theorem it obeys the relation $U = 3nRT$. Derive C_V and C_P for n moles of photons.

4.189 Consider a container of gas with a movable piston. Suppose the gas is allowed to expand in such a way that the piston moves by a distance L. As it expands the gas exerts a force on the piston given by the pressure P of the gas times the cross-sectional area A of the piston. Recall from introductory mechanics that the mechanical work you do on an object is the force you exert on it times the distance it moves (assuming they are in the same direction).

(a) Show that the work done by the gas on the piston is $P\,dV$.

(b) Argue using Newton's third law that the work done by the piston on the gas is $-P\,dV$.

4.190 The Explanation above discussed the different meanings of $\partial A/\partial a$, $(\partial A/\partial a)_b$, and $(\partial A/\partial a)_c$ in a right triangle. Give a similar discussion of the different meanings of $\partial S/\partial T$, $(\partial S/\partial T)_V$, and $(\partial S/\partial T)_P$ where S, the entropy, depends on temperature, pressure, and volume, which are in turn constrained by an equation of state such as the ideal gas law.

4.191 In the Explanation above, we analyzed a right triangle using the admittedly perverse (but correct!) area formula $A = (bc^2 - b^3)/(2a)$. In this problem you will replicate our analysis based on the more conventional $A = (1/2)ab$.

   (a) Find $\partial A/\partial a$, $\partial A/\partial b$, and $\partial A/\partial c$ and use them to write a general expression for dA/dt.

   (b) Based on the Pythagorean $c^2 = a^2 + b^2$, write a formula for dc/dt based on a, b, c, da/dt, and db/dt.

   (c) If $a = 3$, $b = 4$, $c = 5$, $da/dt = -2$, and $db/dt = 6$, find dc/dt.

   (d) Plug the numbers from Part (c) into your formula from Part (a). Show that your $\partial A/\partial a$ is not the same as ours, but our final dA/dt answers are the same.

4.192 Consider the function $f = x^2 + yz$ where $2x - yz^2 = 3$.

   (a) Using the function in the form given above, find $\partial f/\partial x$.

   (b) Rewrite f as a function of x and z only. When you take the derivative of the resulting equation with respect to x, you will find $(\partial f/\partial x)_z$.

   (c) Find $(\partial f/\partial x)_y$.

4.193 The entropy of a monatomic ideal gas is $S = C + nR\ln(V) + (3/2)nR\ln T$ where C is a constant.

   (a) Calculate $(\partial S/\partial T)_V$.

   (b) Calculate $(\partial S/\partial T)_P$. (*Hint*: Start by using the ideal gas law to eliminate V from the equation for S.)

   (c) Show that you can rewrite the entropy of an ideal gas as either $C + nR\ln((1/2)V + (1/2)nRT/P) + (3/2)nR\ln T$ or $C + nR\ln((1/3)V + (2/3)nRT/P) + (3/2)nR\ln T$.

   (d) Using the two expressions for entropy in Part (c), calculate $(\partial S/\partial T)$ holding P and V constant. Prove that your two answers are *not* equivalent.

   (e) We seem to have a problem. If you do an experiment where you change T while holding P and V constant, and measure the resulting change in S, you cannot possibly get two different results. So how can a series of valid mathematical steps lead to two different values of $\partial S/\partial T$?

4.194 A light bulb has a constant resistance R. A battery supplies a voltage V across it, which causes a current $I = V/R$ to flow through it. The power emitted by the light bulb (in the form of light and heat) is $P = IV$. The voltage, and thus the current, are changing with time.

   (a) Draw the dependency tree for the power in this arrangement.

   (b) Write the chain rule for dP/dt.

   (c) Using the equations $P = IV$ and $I = V/R$, calculate dP/dt as a function of V and dV/dt.

   (d) Redo Parts (a)–(c) starting from the equations $P = I^2R$ and $I = V/R$.

   (e) Note that $\partial P/\partial I$ came out differently in your two calculations, but in both cases led to the same dP/dt. Why must dP/dt come out the same no matter how you calculate it?

4.195 Consider a function f defined everywhere on a plane. We use ρ and ϕ for the polar coordinates on the plane.

   (a) The derivative $(\partial f/\partial x)_y$ looks for a change in f when you advance x by a small amount while holding y constant. Draw a picture of a point (x, y). Then draw a small line segment from that point that allows x to change but holds y constant. Label dx on your drawing.

   (b) The derivative $(\partial f/\partial x)_\rho$ looks for a change in f when you advance x by a small amount while holding ρ constant. Draw a picture of a point (x, y) and a small line segment from that point that allows x to change but holds ρ constant. Label dx on your drawing.

   (c) The derivative $(\partial f/\partial x)_\phi$ looks for a change in f when you advance x by a small amount while holding ϕ constant. Draw a picture of a point (x, y) and a small line segment from that point that allows x to change but holds ϕ constant. Label dx on your drawing.

Now we consider the specific function $f = y$ at the point $(4, 3)$.

   (d) Calculate $(\partial f/\partial x)_y$ at the given point.

   (e) Rewrite f as a function of x and ρ. Using this form, calculate $(\partial f/\partial x)_\rho$ at the given point.

(f) Rewrite f as a function of x and ϕ. Using this form, calculate $(\partial f/\partial x)_\phi$ at the given point.

4.196 In this problem you will prove by example that you cannot generally divide both sides of an equation by ∂x when x and y are not independent. Consider three quantities $f(x, y) = 3x^2y + 2$, $a(x, y) = 2x^4$, and $b(x, y) = y^2$, where $y = x^2$.

(a) Use the chain rule to calculate df/dx, da/dx, and db/dx, and verify that $df/dx = da/dx + db/dx$. Because these are total derivatives you can multiply both sides of the equation by dx and conclude that $df = da + db$.

(b) Using the forms given in the problem for f, a, and b, show that the equation $(\partial f/\partial x) = (\partial a/\partial x) + (\partial b/\partial x)$ is false.

4.197 Consider a function of x and y, which are themselves related by $y = x^2$.

(a) Let $a_1 = x + xy^2$.
   i. Calculate $\partial a_1/\partial x$ and $\partial a_1/\partial y$.
   ii. Use the chain rule to write a formula for da_1 as a function of x, y, dx, and dy.
   iii. Now plug in $y = x^2$ to find da_1 as a function of x and dx only.

(b) Let $a_2 = \sqrt{y} + x^3y$.
   i. Calculate $\partial a_2/\partial x$ and $\partial a_2/\partial y$.
   ii. Use the chain rule to write a formula for da_2 as a function of x, y, dx, and dy.
   iii. Now plug in $y = x^2$ to find da_2 as a function of x and dx only.

(c) Show that $a_1 = a_2$. (Assume $x > 0$.)

(d) What was the same in these two examples, and what was different?

4.198 **(a)** Derive Equation 4.10.4, starting from the thermodynamic identity.

(b) Equation 4.10.4 looks like the thermodynamic identity divided by ∂T, but in general dividing by a partial is not legal. Why is it OK in this case?

4.199 The "enthalpy" H of a system is defined as $H = U + PV$.

(a) Express the differential dH in terms of T, S, P, and V and their differentials. In other words write a formula for dH without U in it.

(b) Using your formula for dH, show that for any process done at constant pressure the change in enthalpy equals the amount of heat that enters your system. (Many reactions occur at constant pressure because they are open to the atmosphere. Chemists often refer to tables listing the enthalpy of gases in different states to figure out how much heat will enter or leave when they undergo certain reactions.)

4.200 **Maxwell Relations** The thermodynamic identity can be used to derive non-obvious relationships between certain derivatives.

(a) What is

$$\left(\frac{\partial U}{\partial S}\right)_V$$

Hint: If you spend more than 30 s on this problem you're making it harder than it needs to be.

(b) Take the derivative $(\partial/\partial V)_S$ of your answer to Part (a) to get an expression for $(\partial^2 U/\partial V\partial S)$. Your answer should be in the form of a *first* derivative.

(c) Derive a similar expression for $(\partial^2 U/\partial S\partial V)$. Using the equality of mixed partial derivatives, write an equation relating two first derivatives. This equation is known as a "Maxwell relation."

(d) Describe experiments that you could perform to directly measure each of the two derivatives that you just said should be equal to each other. When you think of these derivatives as descriptions of physical processes in this way it is *far* from obvious that these two quantities would be equal.

4.201 *[This problem depends on Problems 4.199 and 4.200.]* Use the formula you derived for dH in Problem 4.199 to derive another Maxwell relation similar to the one you derived in Problem 4.200.