For each one of the partial derivatives below, describe and draw a picture of *two* experiments that you could perform to measure that derivative. One of these experiments should "directly" measure the derivative you are given, while the other will "directly" measure a derivative that is related to the first one by means of a Maxwell relation.

$$\left(\frac{\partial S}{\partial V}\right)_T \quad \left(\frac{\partial S}{\partial p}\right)_V \quad \left(\frac{\partial S}{\partial p}\right)_T \quad \left(\frac{\partial S}{\partial V}\right)_p \tag{1}$$

At the end of class, you will report to the class on the experiments you developed to measure your partial derivative, and will comment on which of the two is the easier experiment.

Solution I'll give solutions for just two of these partial derivatives, which I think form a good balance of effort versus learning.

$\left(\frac{\partial S}{\partial V}\right)_T$ measured directly Measuring this one directly is a bit of a pain. The only way we know to "directly" measure a change in entropy is to control the amount of energy added by heating. So we'll stick our sample in a microwave oven, so we can use the time to measure the energy added by heating. And we'll need insulation (transparent to microwaves) to ensure that there is no accidental heating going on. We'll need to measure a change in volume, which is most easily managed with a nice frictionless piston. The trickiest bit here will be to keep the temperature from changing while we heat the system up.

FIXME ADD FIGURE HERE

I would do this experiment in two steps. I would start by microwaving the system at fixed volume for a short amount of time (giving me Q). This will raise its temperature. Then I'll take it out of the oven (remember that it is insulated!) and slowly adjust the volume until the temperature returns to its original value. Probably this will require expanding the system a bit.

Once I have done this measurement, I can find the derivative with

$$\left(\frac{\partial S}{\partial V}\right)_T \approx \frac{\frac{Q}{T}}{\Delta V} \tag{2}$$

$\left(\frac{\partial S}{\partial V}\right)_T$ using a Maxwell relation We have to start by finding a Maxwell relation involving this derivative. Clearly holding temperature fixed will be relevant, which suggests using the Helmholtz free energy or Gibbs free energy. Since we

FIXME ADD FIGURE HERE

don't see pressure, Helmholtz is probably what we want:

$$F = U - TS \tag{3}$$
$$dF = dU - TdS - SdT \tag{4}$$
$$= -SdT - pdV \tag{5}$$
$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \tag{6}$$
$$\left(\frac{\partial\left(\frac{\partial F}{\partial V}\right)_T}{\partial T}\right)_V = \left(\frac{\partial\left(\frac{\partial F}{\partial T}\right)_V}{\partial V}\right)_T \tag{7}$$
$$\left(\frac{\partial(-p)}{\partial T}\right)_V = \left(\frac{\partial(-S)}{\partial V}\right)_T \tag{8}$$
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{9}$$

So now we have a different derivative, which we might hope will be easier to measure. And indeed, this does seem considerably easier, with no entropy in sight!

We can again use a standard piston, and we can adjust the temperature a bit (by setting the thermostat in our house, perhaps), and then see how much we need to change the force (by adding or removing weights on top) to get the volume back to where it started. Once I have done this measurement, I can find the derivative with

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \tag{10}$$
$$\approx \frac{\Delta p}{\Delta T} \tag{11}$$
$$= \frac{\Delta F}{A \Delta T} \tag{12}$$

where A is the area of the piston.

$\left(\frac{\partial S}{\partial p}\right)_T$ **measured directly** Measuring this one directly is a bit of a pain in the same way as $\left(\frac{\partial S}{\partial V}\right)_T$. As in that case, we'll want to microwave an insulated piston, so we will know how much energy is transferred by heating. In fact, the experiment looks almost identical to the first case, with the only difference being that when we take the piston out of the microwave and tweak it to return the temperature to its original value, we will now need to add or remove weights from the piston to get it back to its original temperature.

FIXME ADD FIGURE HERE

Once I have done this measurement, I can find the derivative with

$$\left(\frac{\partial S}{\partial p}\right)_T \approx \frac{\frac{Q}{T}}{\frac{\Delta F}{A}} \tag{13}$$

$\left(\frac{\partial S}{\partial p}\right)_T$ **using a Maxwell relation** With temperature held fixed, we can guess that we want to use a free energy. Since we already used the Helmholtz free energy above (and it didn't give us) this derivative, we can try using the Gibbs free energy.

$$G = U - TS + pV \tag{14}$$
$$dG = dU - TdS - SdT + pdV + Vdp \tag{15}$$
$$= -SdT + Vdp \tag{16}$$
$$\frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T} \tag{17}$$
$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \tag{18}$$

I'll keep this shorter than you should, but basically we're measuring the thermal expansion of something at fixed pressure.

$\left(\frac{\partial S}{\partial V}\right)_p$ **measured directly** This derivative isn't so bad to measure directly as some of the others. We need to know how much energy was transfered by heating, so we can use a microwave oven or a resistor to heat our system. We're holding the pressure fixed, so that happens for free if the object is in the atmosphere. So I can measure doing this with a solid cube of a semiconductor for variety. Since I don't want to microwave a conductor (even a semiconductor), I'll instead run a current through it. As long as my wires have a very low resistance compared with the cube, I can just measure the current and voltage and find the energy dissipated as heat. Then I just need to carefully measure the volume before and after to find the change in volume. Maybe I use calipers to carefully measure the dimensions of the cube.

FIXME ADD FIGURE HERE

$$\left(\frac{\partial S}{\partial V}\right)_p \approx \frac{\frac{Q}{T}}{\Delta V} \tag{19}$$

where I calculate $Q = IV\Delta t$ and get ΔV from the measurements of the cube.

$\left(\frac{\partial S}{\partial V}\right)_p$ **via a Maxwell relation** Since we're holding p fixed, we can guess that we want either the enthalpy or the Gibbs free energy. Since I used the Gibbs free energy on the last one, we can guess to use the enthalpy here. In practice, you're likely to have to try both.

FIXME ADD FIGURE HERE

$$H = U + pV \tag{20}$$
$$dH = dU + pdV + Vdp \tag{21}$$
$$= TdS + Vdp \tag{22}$$
$$\frac{\partial^2 H}{\partial S \partial p} = \frac{\partial^2 H}{\partial p \partial S} \tag{23}$$
$$\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S \tag{24}$$

> So our derivative showed up upside down, but we can always invert the other derivative. Since the other derivative holds entropy fixed, we're going to need to insulate our system, and will want to adjust the pressure (by adding some weight to a piston) and measure the change in temperature.
>
> $$\left(\frac{\partial S}{\partial V}\right)_p = \frac{1}{\left(\frac{\partial T}{\partial p}\right)_S} \tag{25}$$
>
> $$\approx \frac{\Delta F/A}{\Delta T} \tag{26}$$