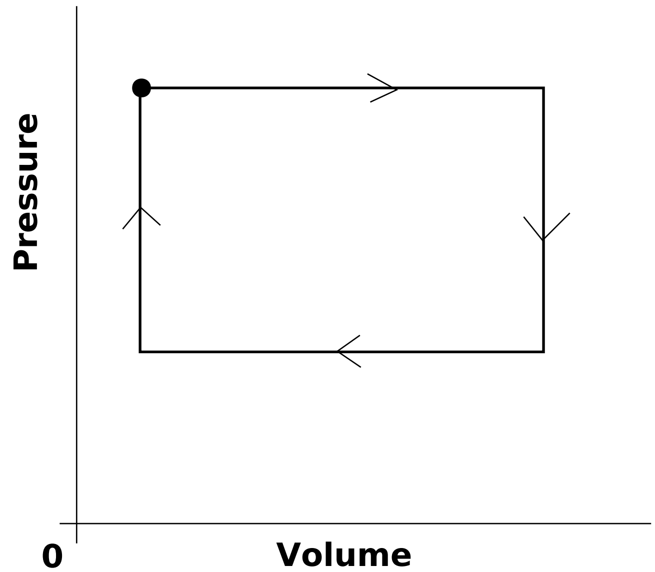
1 pV rectangle

This worksheet considers processes that happen at constant pressure, volume, temperature or entropy.

Earlier in PH423, we spent time discussing partial derivatives and how they relate to measurements. Today we will analyze a different type of measurement. The analysis will involve integrals. To visualize this analysis, it's common to use what are called pV diagrams such as the square shown in the Figure.



Note When you consider a pV diagram, you cannot assume that the substance which has pressure p and volume V is an ideal gas. It could equally well be water, or a strange gooey substance that you found on a distant planet. *You can* ***never*** *assume that we are talking about an ideal gas unless it is stated in the problem, or you have explained why the ideal gas as a suitable approximation!*

In your groups, work out the following questions:

1. What does this figure describe? Is p a function of V?

> **Solution** This figure describes a system which is expanded at constant pressure (which probably involves increasing the temperature), then has the pressure drop at constant volume (probably by lowering its temperature). Then it is compressed at fixed pressure (probably with the temperature dropping) and finally the pressure is increased at fixed volume (probably by raising the temperature).
> The pressure is *not* a function of volume, because as you can see there are volumes that have two different pressures. Instead, this plot is like a map that shows us where we went with our system in the space of possible states.

2. What is the net work done after one cycle of this process? How much work was done at each step?

> **Solution** We can integrate to find the work, starting with the first step.

$$W_A = \int đW \tag{1}$$
$$= \int_{V_0}^{V_f} (-pdV) \tag{2}$$
$$= -p_H(V_f - V_0) \tag{3}$$
$$W_B = 0 \tag{4}$$
$$W_C = p_L(V_f - V_0) \tag{5}$$
$$W_{\text{net}} = -(p_H - p_L)(V_f - V_0) \tag{6}$$

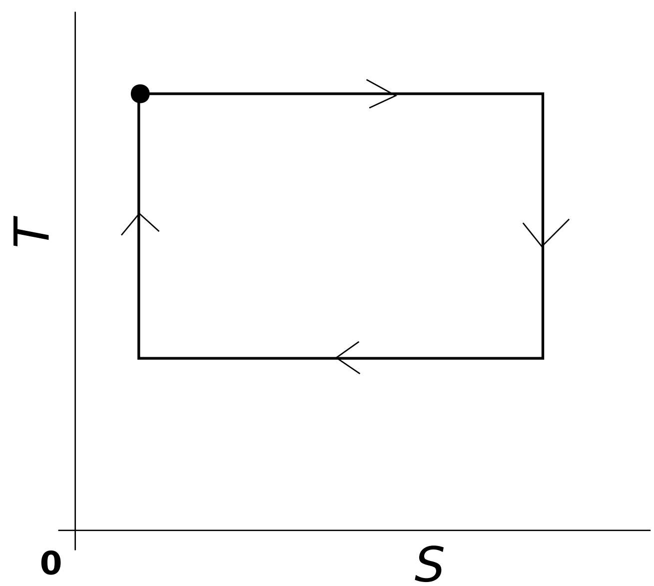
> There is non-zero net work (negative) over the cycle, which is find because work is not a state function.

3. What is the net energy transfered by heating over one cycle of this process? Try to find the energy transfered by heating at each step.

> **Solution** To find the net heat, we just need to invoke the First Law. Because U is a state function, when we return to our original state after one cycle (since the state can be defined by any pair of state variables), the internal energy must return to the same value, so
>
> $$\begin{aligned} \Delta A &= Q_{\text{net}} + W_{\text{net}} \quad (7) \\ &= 0 \quad (8) \\ Q_{\text{net}} &= -W_{\text{net}} \quad (9) \end{aligned}$$
>
> We do not have enough information however to solve for the heat on the individual steps of the cycle. We would need to know either the internal energy at the corners, or the entropy and temprature along the paths.

2 TS rectangle

Now let's look at another cycle. Let's consider the following figure, which looks similar, but is now a plot of T vs. S, and answer the following questions:



1. What is this cycle? How would you go about running a cycle like this?

> **Solution** The system is isothermally expanded (which means it was expanded slowly without insulation), and then adiabatically cooled (probably expanded). You could imagine doing this with insulation, but in practice it might be simpler to just expand fast enough that there isn't much time for the system to be warmed up by the room. There is a hierarchy of speeds, so you can often go slowly enough to be quasisatic, while still going fast enough to neglect energy transfer by heating through the walls (if they aren't too good thermal conductors). Then we do the two reverses, of isothermal compression (most likely) and adiabatic compression (most likely).
>
> In case you're wondering about all the "most likely" and "probably" that are showing up, they relate to thermal expansion. Most materials if their temperature is raised at fixed pressure will expand. But a few materials will contract. So on these sorts of diagrams we can't

predict with certainty whether we are doing expansion or contraction, but we *can* describe what is happending for an "ordinary" system.

2. What is the net heat transfer over one cycle of this process? How much was transfered on each step?

Solution This process is much like for the work on the pV rectangle, with areas under curves because of $đQ = TdS$.

3. What is the net work done after one cycle of this process? How much work was done at each step?

Solution This process is much like becore, invoking the First Law, and being unable to predict the work for each step individually, only the net.