

_____Sept. 25 2002: Lecture 9: _____

Quasistatic Processes

Last Time

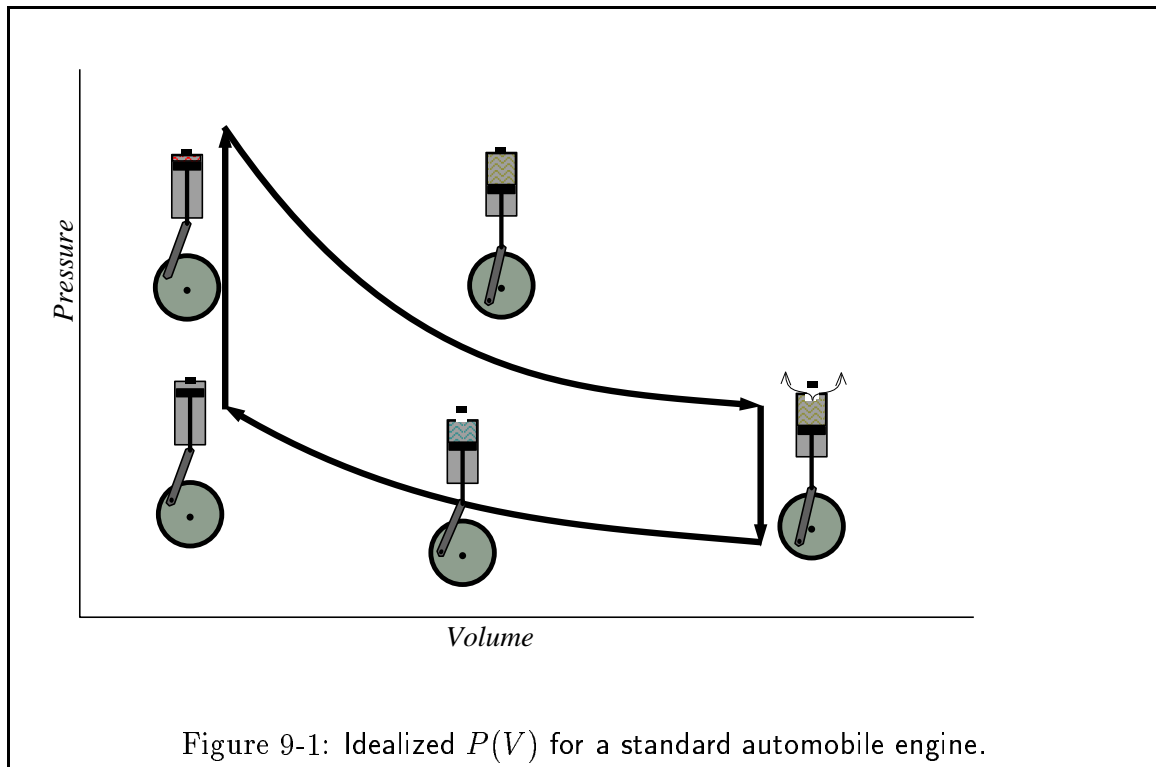
Forms of Work

Elastic Solids: Stress and Strain

Fluids: Pressure and Volume

PV work

Reversibility



Recall that we showed that the work performed cannot be a state function because:

$$\oint dw = - \oint PdV \neq 0 \quad (9-1)$$

Question: Why does the inequality in Eq. 9-1 show that the the integral of dw is path dependent?

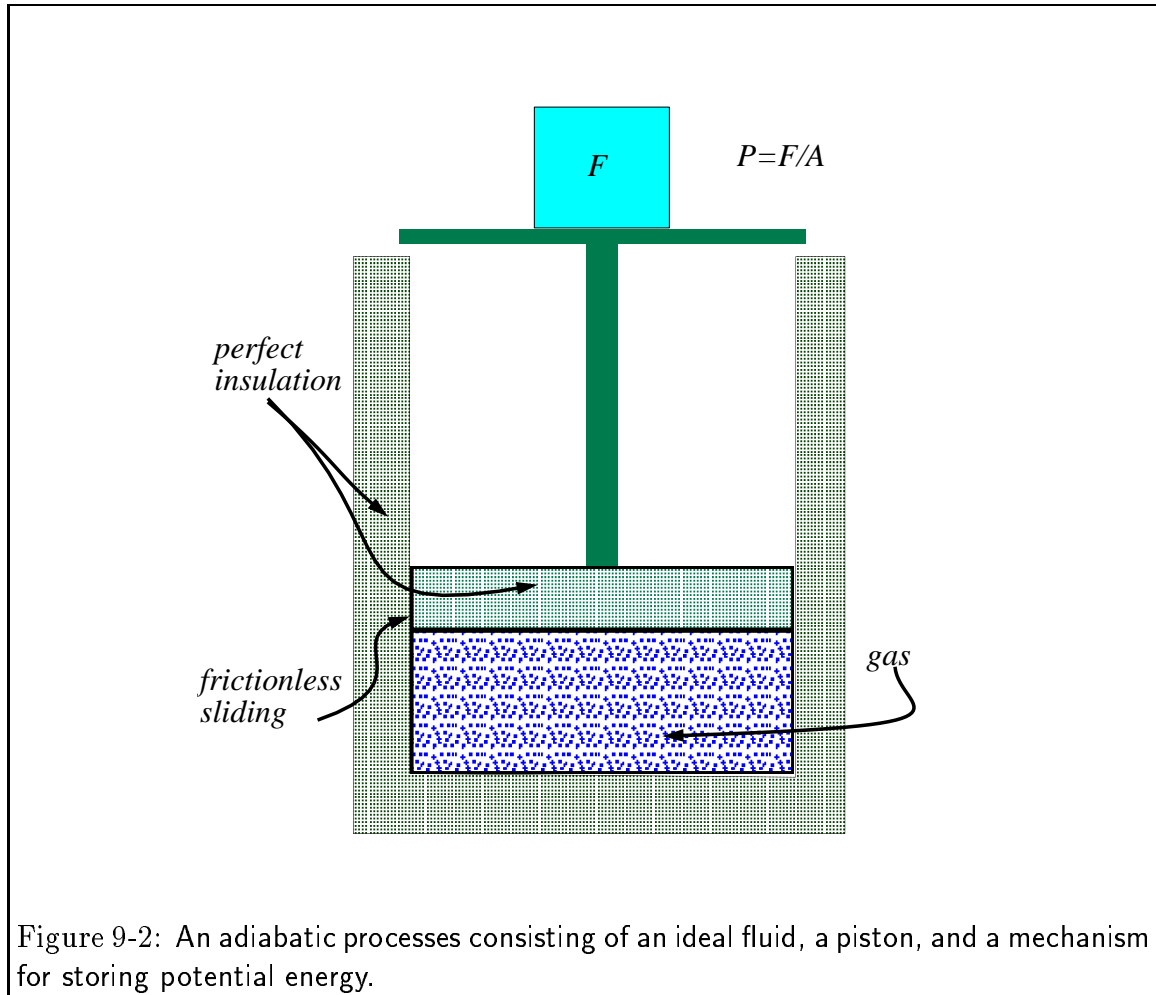
The differential work dw is sometimes called “not a perfect differential” because of this property. It simply means that you need even more information to integrate it—namely the path: $\int dw$ is “path dependent”.

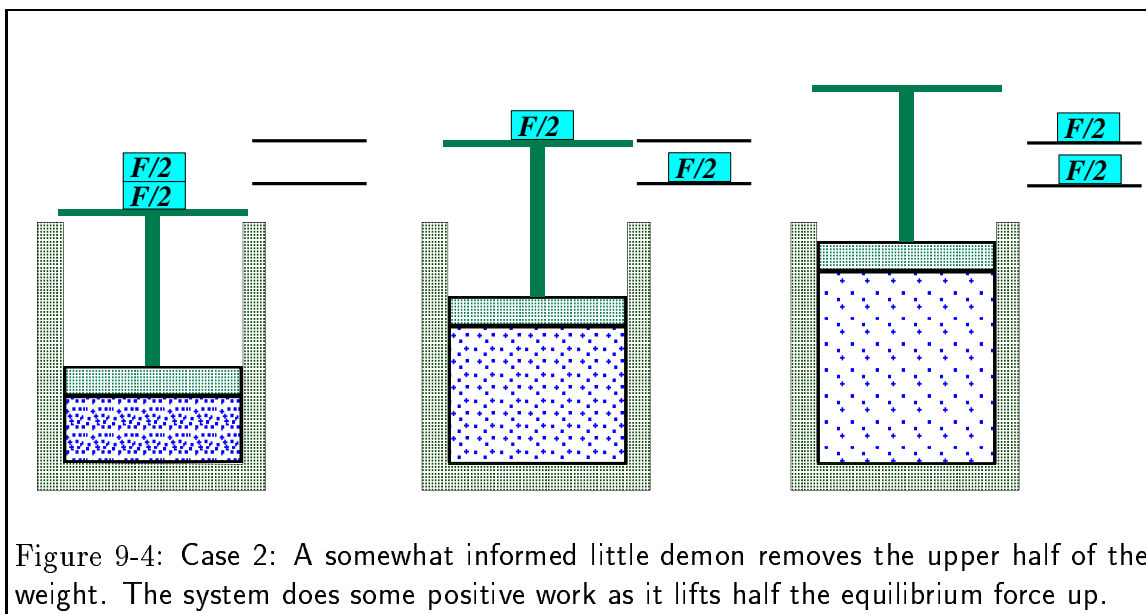
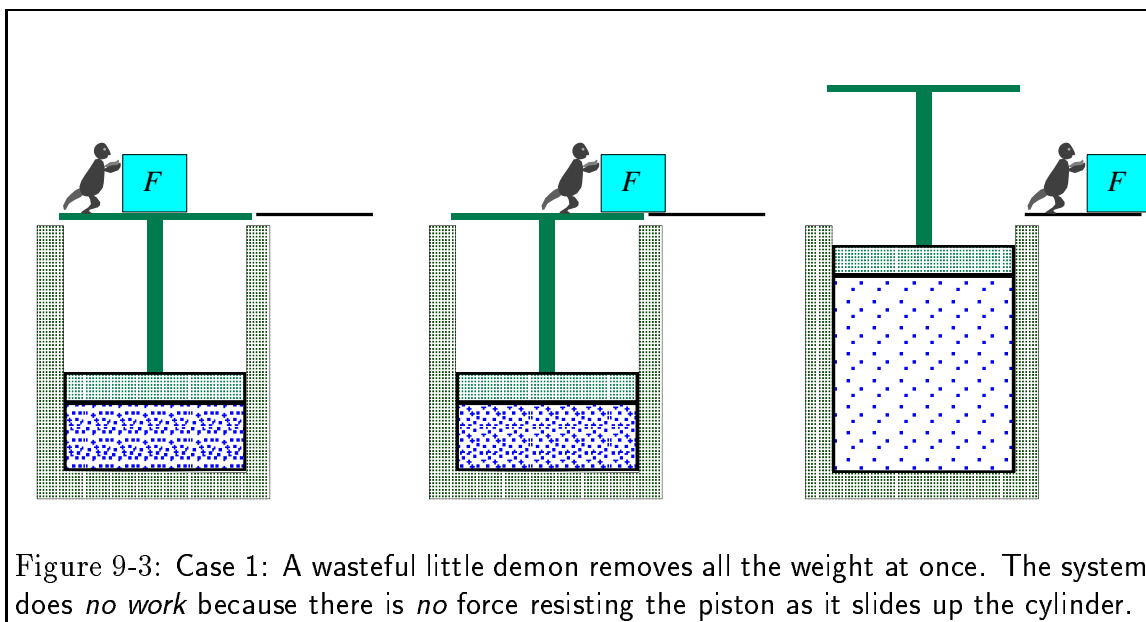
Furthermore, the idealization in Figure 8-1 is a somewhat misleading.

It is easy to specify what the volume is in such a system, but what about the pressure, P , just after the beginning of the “spark” as the system expands rapidly? The pressure is not uniform and cannot be represented for the system by a point—so the curve cannot be represented by a series of points.

The idealization in Figure 8-1 introduces the topic of *reversibility*. (Sometimes, the terms *quasi-equilibrium* or *quasi-static* are used, they are effectively synonyms for reversible processes).

To illustrate what is meant by reversibility, consider the following simple processes:





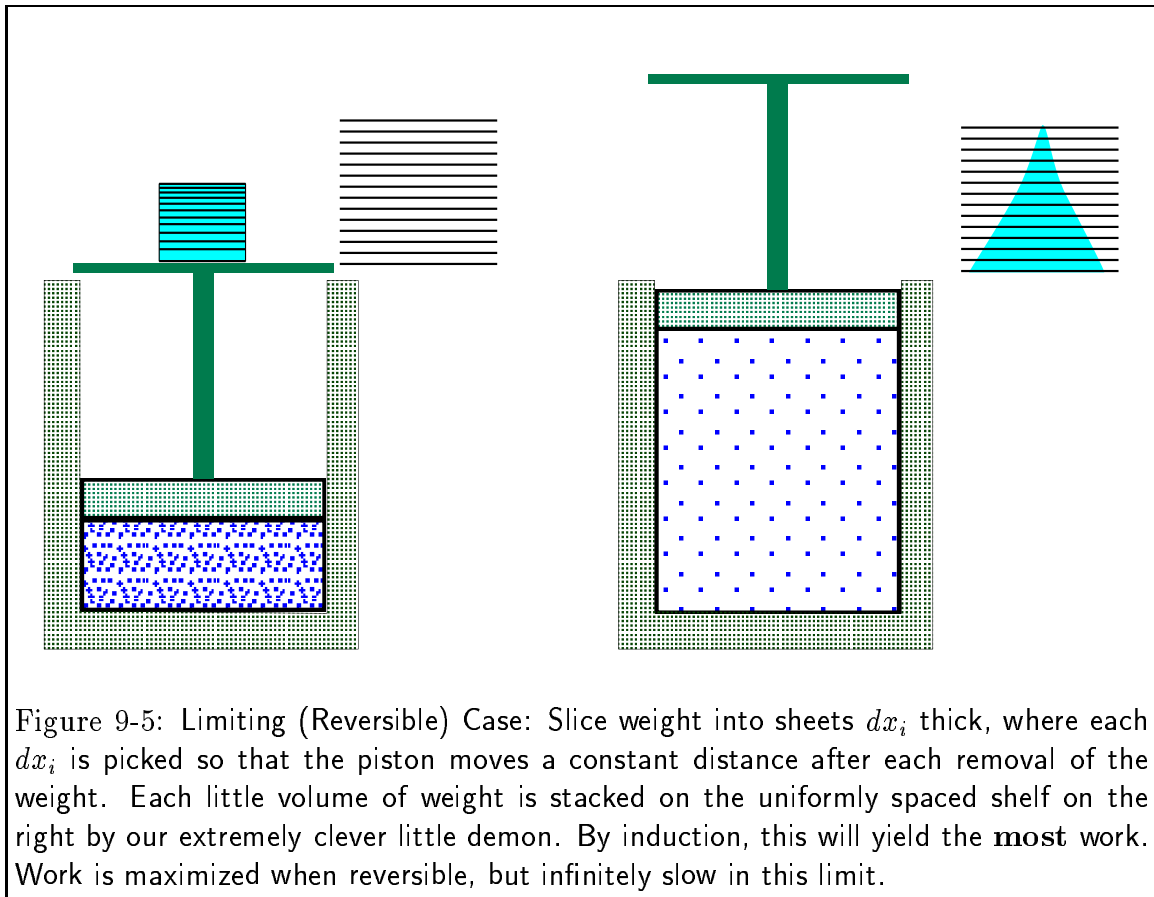


Figure 9-5: Limiting (Reversible) Case: Slice weight into sheets dx_i thick, where each dx_i is picked so that the piston moves a constant distance after each removal of the weight. Each little volume of weight is stacked on the uniformly spaced shelf on the right by our extremely clever little demon. By induction, this will yield the **most** work. Work is maximized when reversible, but infinitely slow in this limit.

Question: Why is the word “reversible” applied to the case in Figure 9-5?

Therefore, the curves in Figure 8-1 are idealizations of a sequence of equilibrium states (P, V) . This idealization is called “quasi-static” and applies only if the system is changing **very** slowly. A quasi-static process is also called “reversible.”

Because U is a state function, then it must be true in general that

$$\oint dU = 0 = \oint dq + \oint dw = \oint (dw + dq) \quad (9-2)$$

Because dw depends on the path, so must dq ; it is also not a perfect differential.

Heat Capacities

The fact that dq is not a perfect differential is reflected by the observation that the heat capacity depends on path as well.

$$dq = C_V dT \quad (\text{constant volume}) \quad (9-3)$$

$$dq = C_P dT \quad (\text{constant pressure}) \quad (9-4)$$

C_V is the heat capacity at constant V . C_P is the heat capacity at constant P .

Question: In materials that expand while heating, they differ considerably. Question: which one should be bigger? Why?

For larger thermal expansion, the difference in heat capacities will be greater.

Gases, which expand considerably with temperature, have a large difference in their heat capacities.

Liquids do not expand as much. For H_2O at 15°C and $P = 1 \text{ atm}$, $c_P = 1 \text{ cal}/(^{\circ}\text{Kgram})$. (Note use of little c for the derived intensive quantity on a per mass basis), and c_V is only slightly different.

For solids, the difference is very small and usually neglected.