

Sept. 25 2002: Lecture 9:

Quasistatic Processes

Last Time

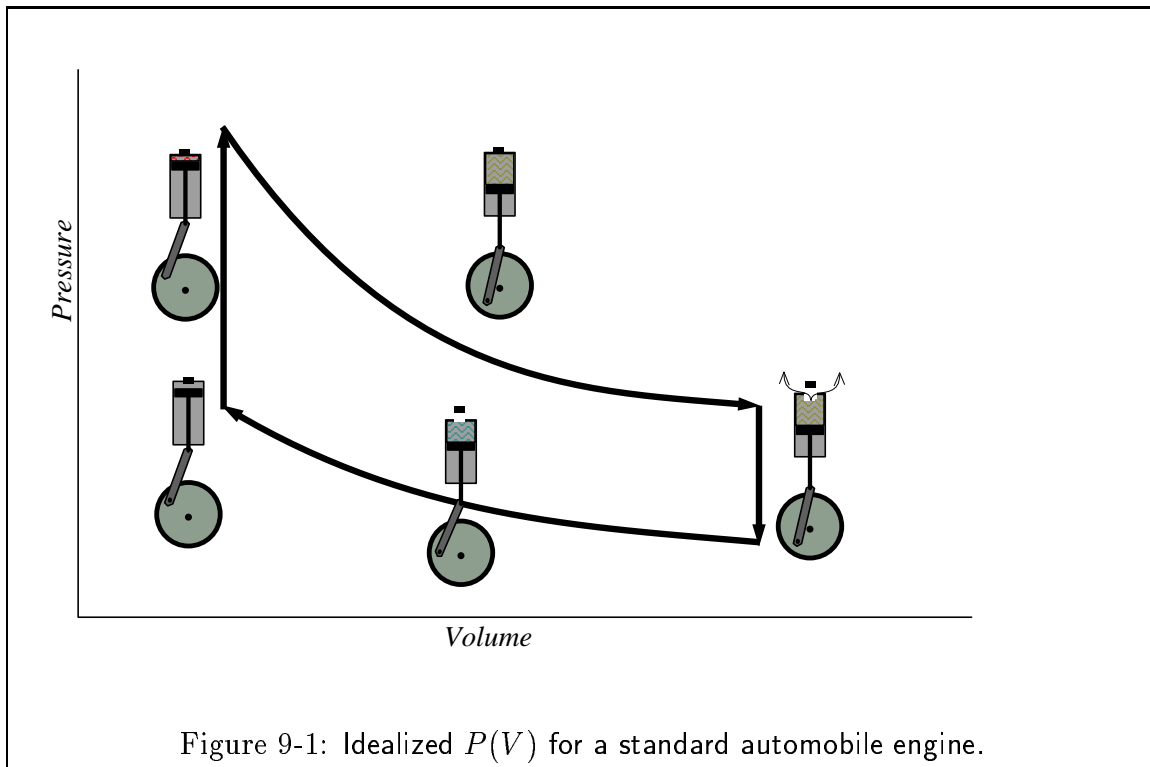
Forms of Work

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?

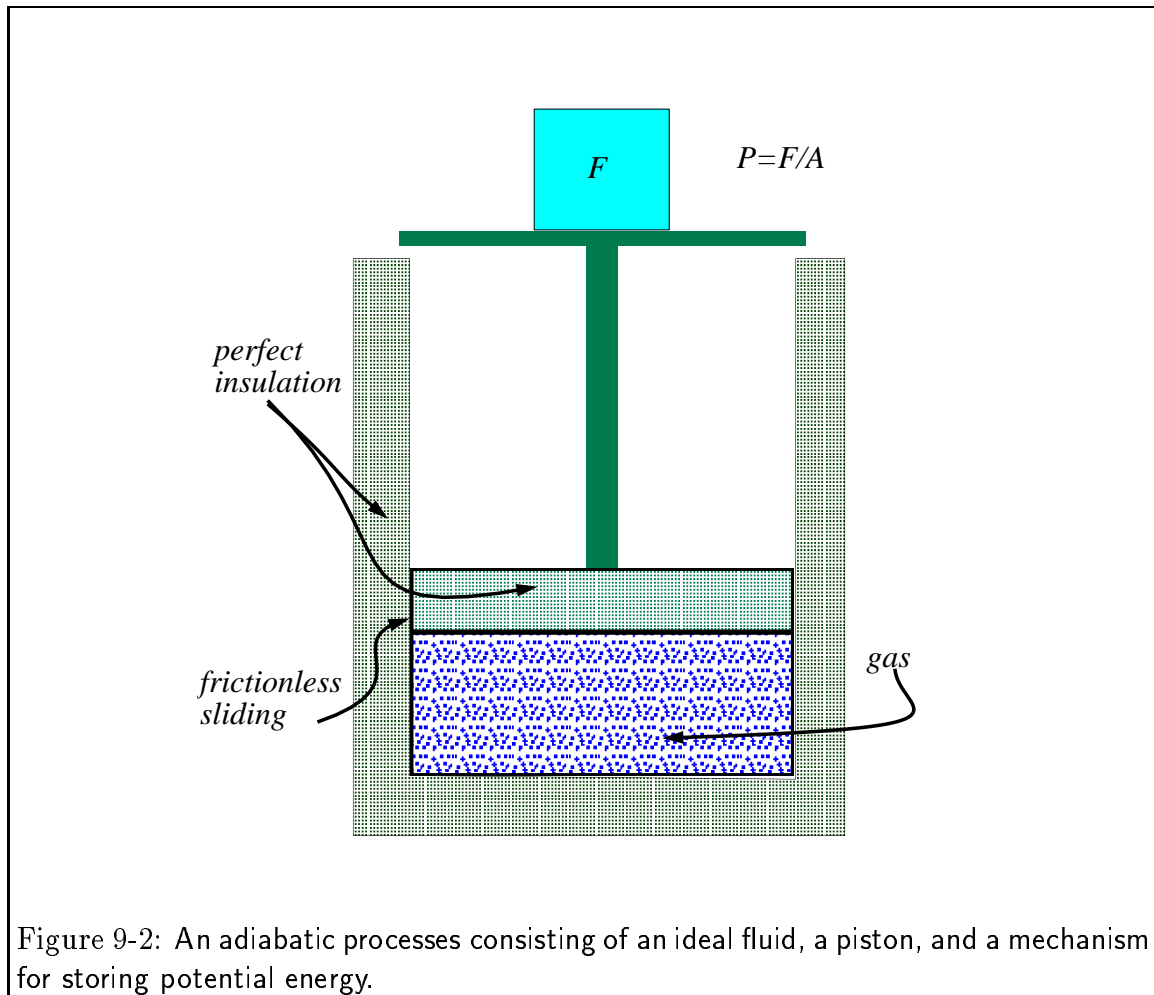
The differential work dw is sometimes called “not a perfect differential” because of this property. It simply means that you need even more information to integrate it—namely the path: $\int dw$ is “path dependent”.

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:



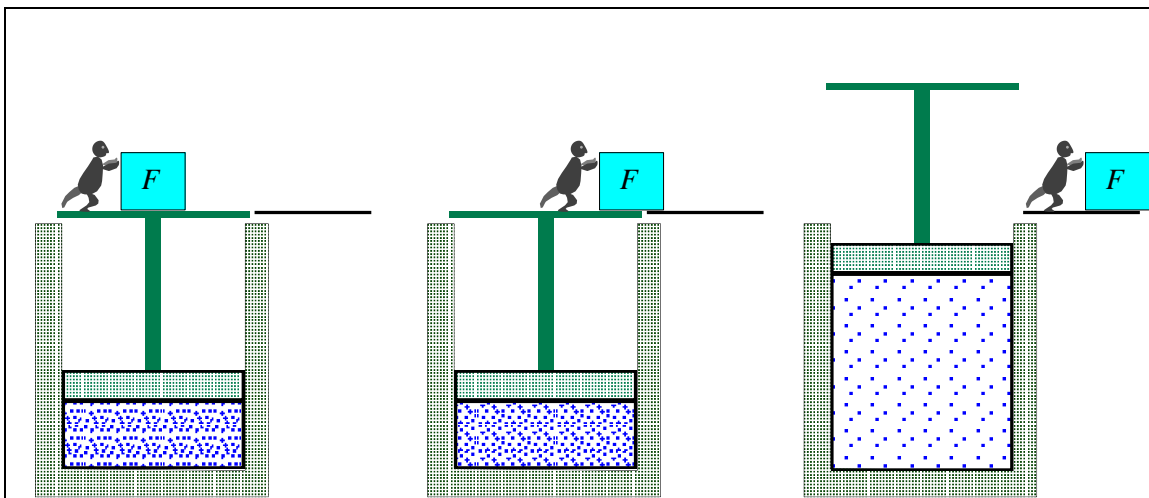


Figure 9-3: Case 1: A wasteful little demon removes all the weight at once. The system does *no work* because there is *no force* resisting the piston as it slides up the cylinder.

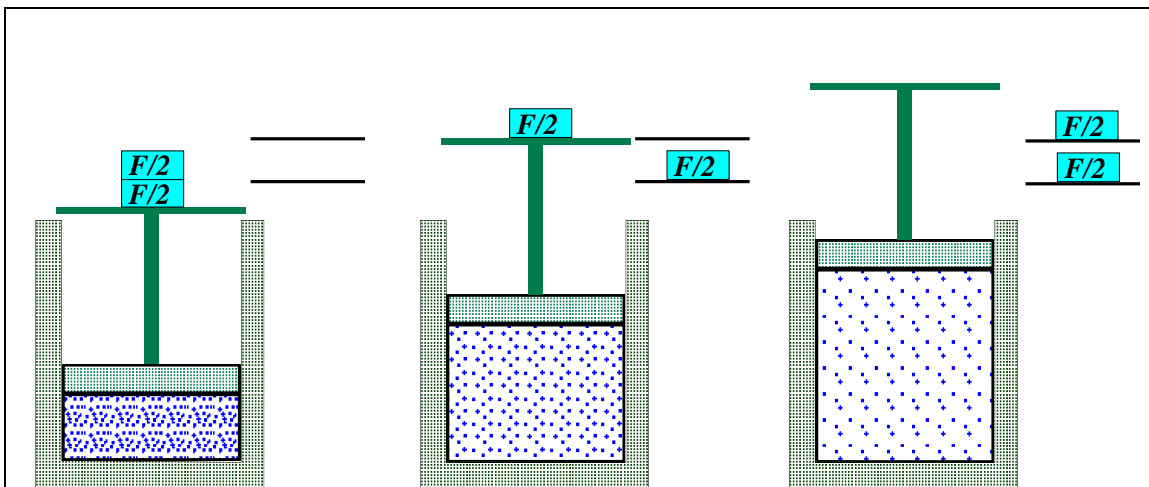
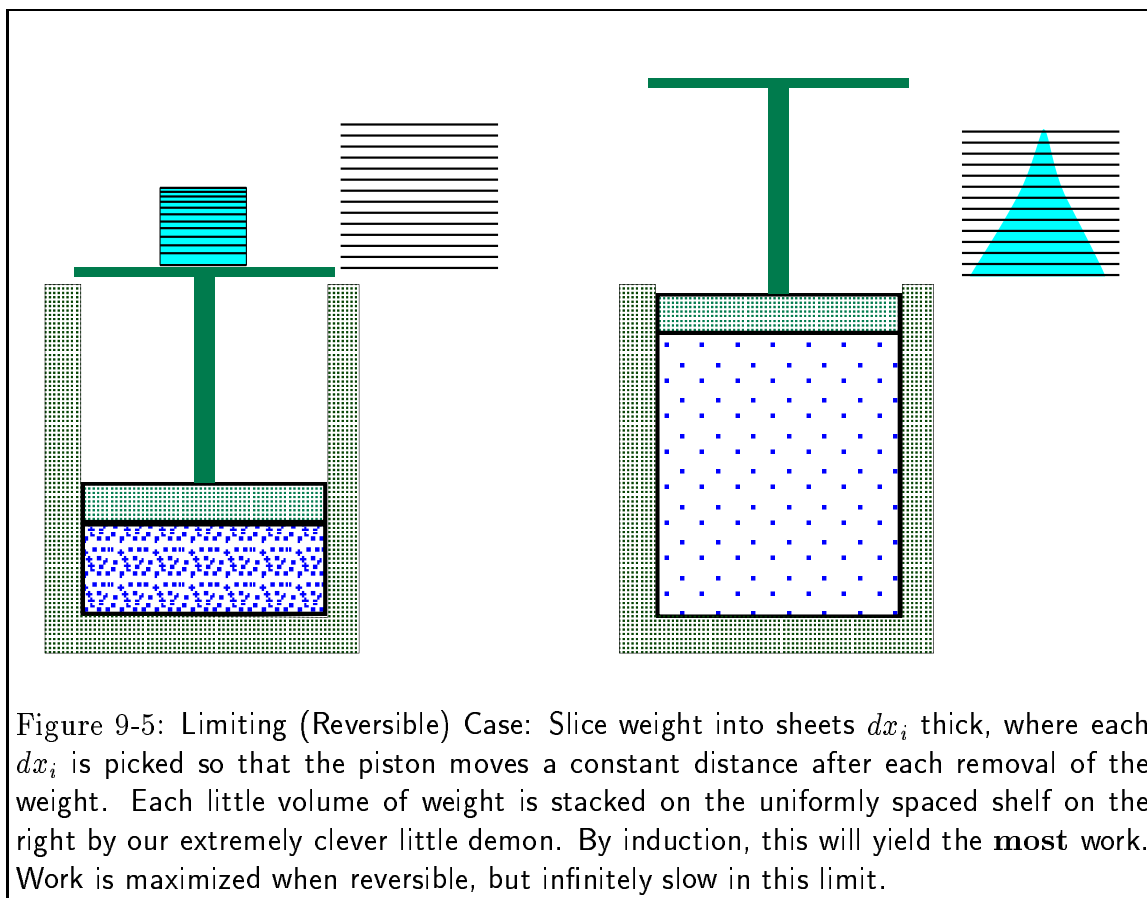


Figure 9-4: Case 2: A somewhat informed little demon removes the upper half of the weight. The system does some positive work as it lifts half the equilibrium force up.



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.