PHY 171
Lecture 15
(February 20, 2012)

§ Thermodynamics

In the last lecture, we learned that the internal energy E_{int} is defined as the *total* energy of all the molecules.

- So, if work is done *on* the system, the internal energy E_{int} should *increase*.

- Likewise, if heat is *added to* the system, E_{int} should *increase*.

- On the other hand, if work was done *by* the system , its internal energy would *decrease*.

- If heat *flowed out* of the system, its internal energy would *decrease*.

First Law of Thermodynamics

The change in internal energy of a closed system is equal to the heat ***added to*** *the system minus the work done* ***by*** *the system.*

In math notation

$$\Delta E_{\text{int}} = Q - W$$

where Q is the net heat *added to* the system, and W is the net work done *by* the system.

Note the sign conventions for Q and W:

- If work is done ***by*** the system, W will be ***positive***.
- If work is done ***on*** the system, W will be ***negative***.
- If heat ***enters*** the system, Q will be ***positive***.
- If heat ***goes out*** of the system, Q will be ***negative***.

We completed a worksheet in class to reinforce the above concepts.

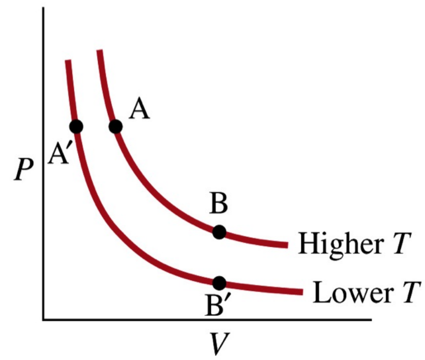
Some simple processes

Isothermal Processes ($\Delta T = 0$)

Thermodynamic processes carried out at ***constant temperature*** are known as *isothermal processes.*

An example of an isothermal process is the Boyle's law experiment.

A graphical representation of two isothermal processes is shown in the graph on the right. Since $PV = nRT$ from the ideal gas law, we get $PV =$ constant, for an isothermal process (because T does not change). Each point on the curves in the graph (e.g., A, B) represents the state (P, V, T) of the system at a given moment. The upper curve shows an isothermal process at a higher temperature T. The lower curve shows an isothermal process at a different (lower) temperature T.



Since T and mass are kept constant, the internal energy E_{int} does not change in an isothermal process, because $E_{\text{int}} = \frac{3}{2}nRT$. So we have

$$\Delta E_{\text{int}} = 0$$

and since $\Delta E_{\text{int}} = Q - W$, this means that

$$Q = W$$

That is, the *work done by the gas in an isothermal process equals the heat added to the gas.*

Adiabatic Processes ($Q = 0$)

Thermodynamic processes in which no heat is allowed to flow into or out of a system are known as *adiabatic processes.*

Such processes can occur if system is extremely well insulated, or the process happens so quickly that heat has no time to flow in or out.

Example: Rapid expansion of gas in an internal combustion engine.

Demo: We demonstrated adiabatic processes using a "fire piston" tube; an example is shown in the figure on the right. The fire-piston tube is a thick-walled glass tube with a plunger and piston. A piece of cotton kept inside the tube can be set on fire by quickly depressing the plunger. This is, therefore, an example of an adiabatic process.

Since $Q = 0$ in an adiabatic process, we now have from the 1st law of thermodynamics that

$$\Delta E_{\text{int}} = Q - W = 0 - W$$

which gives

$$\Delta E_{\text{int}} = -W$$

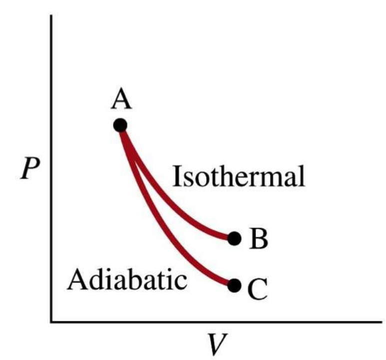
This makes sense. Since no heat is allowed into or out of the system, any change in the internal energy must come from the work done on, or by, the system.

- If the gas is compressed, as in our fire piston tube demo above, work is done on the system; by our convention, W will then be negative. Then, $\Delta E_{\text{int}} = -$ (a negative number), so ΔE_{int} is positive, meaning that the internal energy E_{int} will increase if the gas is compressed.

- If the gas is allowed to expand, work will be done by the system; by our convention, W will then be positive. Then, $\Delta E_{\text{int}} = -$ (a positive number), so ΔE_{int} is negative, meaning that the internal energy E_{int} will decrease if the gas is allowed to expand.

Comparison of $P - V$ graphs of isothermal and adiabatic processes

An interesting exercise is to contrast the graphs of isothermal expansion and adiabatic expansion of an ideal gas. This is shown on the right. Notice that an adiabatic curve is steeper than the isothermal curve.

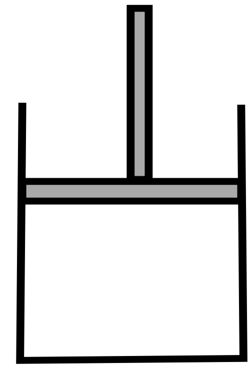


To understand the contrast between the two graphs, recall that $E_{\text{int}} = \frac{3}{2}nRT$. This relation implies that T will decrease during an adiabatic expansion, because E_{int} decreases in an adiabatic expansion (as we have described above). Since the ideal gas law holds for both isothermal and adiabatic processes, $PV = nRT$ implies that due to the decrease in T during an adiabatic expansion, the pressure will be lower for an adiabatic expansion than for an isothermal expansion, if we compare the same volumes V of the gas (which we are doing when we compare points B and C on the curve). Therefore, an adiabatic $P - V$ curve is steeper than an isothermal $P - V$ curve, as seen in the figure.

In contrast, during an adiabatic compression ($C \rightarrow A$ in the figure above), work is done *on* the gas; therefore, internal energy increases, so temperature rises. In a diesel engine, for example, the rapid adiabatic compression reduces the volume by $\sim$15 times or more; the temperature rise is so great that the air-fuel mixture ignites spontaneously.

Work done in volume changes

Consider a gas confined in a container with a movable piston, as shown in the figure on the right. Choose the system to be the gas, so the walls and piston are parts of the environment.



Let the gas expand quasistatically — this means that P and T are defined in the system at all instants. If you expanded very fast, P and T would take time to stabilize at different parts of the gas, and you would have different parts of the gas at different P or T.

If the area of the piston is A, the gas exerts a force PA on the piston, so the work done by the gas to move the piston an infinitesimal displacement $d\vec{l}$ is given by

$$dW = \vec{F} \cdot d\vec{l} = F(dl)\cos\theta$$

where θ is the angle between $\vec{F}$ and $d\vec{l}$, equal to zero in this case because the pressure on the piston is the force per unit area applied perpendicular to the piston. So, we get

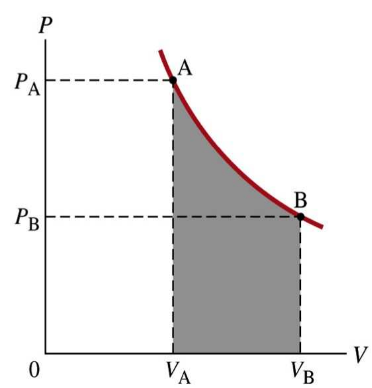
$$dW = F\,dl = \big(PA\big)dl = PdV$$

because the change in volume is $V = Adl$, assuming the cross sectional area of the tube does not change.

Integrate to find the total work:

$$W = \int_{V_A}^{V_B} PdV$$

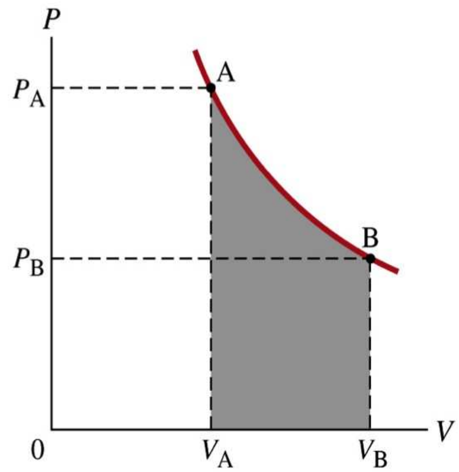
Geometric Interpretation: You know that integration measures the area under the curve. So, in the integral above, if we imagine a large number of infinitesimal rectangular strips of width dV along the horizontal (volume) axis, then their vertical value P multiplied by dV, and added for all such strips between V_A and V_B will correspond to the integral above.

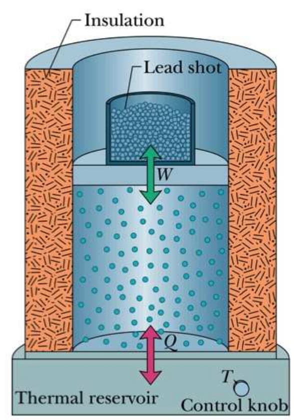


While we will not do the integration in class (you will get practice doing it on the homework for isothermal processes), note that the integration depends on the process, e.g., if P is constant, it can be taken outside the integral. So, *work done in taking a system from one state to another is dependent not only on the initial and final states, but also on the type of process or path* — we will study more about this below.

Finally, note that if initial and final volumes are known for a constant pressure process, the work can be found by simply doing $W = P\Delta V$, because the constant pressure can now be taken outside the integral.

Now, there are an infinite number of ways to go from point A to point B (or from B to A). We will see below that the work done (and thermal energy transferred, if any) will depend on the path followed.





Explanation of figures:

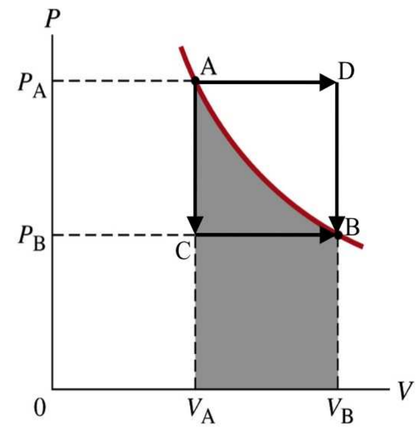
On the left above is a figure we have seen before; it is a $P - V$ graph depicting a thermodynamic process. Each point on the red curve represents a state of the system described by the variables P, V, T. The area shaded in gray represents the work done in expanding the volume from V_A to V_B.

On the right above is a physical system in which we can depict the states represented in the $P-V$ graph on the left. The walls of this system, and the piston at the top, are well insulated, and the system rests on a "thermal reservoir" at the bottom. A thermal reservoir could mean a heat source (which can supply heat to the gas, so Q is positive), or a heat sink (which can take away heat from the gas, so Q is negative).

If the piston is raised (increasing the volume), work done *by* the gas (W) will be positive. We can think of this in the following way (in order to connect to principles learned in PHY 170): the gas always exerts an outward perpendicular force on the piston, and the displacement of the piston is in the direction of this force; therefore, work done by the gas is positive. The convention is to write W as positive, signifying that work was done by the gas.

If, instead, you push down on the piston (decreasing the volume), work will be done *on* the gas, so the work done by the gas (W) will be negative. We can think of this in the following way: the gas always exerts an outward perpendicular force on the piston, while the displacement of the piston is opposite to the direction of this force; therefore, work done by the gas is negative. The convention is to write W as negative, signifying that work was done on the gas.

Now, consider again the $P-V$ diagram shown above, which is reproduced on the right. If we go from state A to state B along the red curve, what will this process look like in the physical picture of the cylinder and piston resting on the thermal reservoir shown above? In going from A to B on the $P-V$ curve (keeping T constant), the system has undergone an increase in volume. In the cylinder shown on the previous page, the pressure of the gas must be equal to the pressure due to the lead shot resting on the piston. So, we can increase the volume at constant temperature if we take away some of the lead shot resting on the piston. If we decrease the amount of lead shot in this way, the gas will increase in volume until the gas pressure balances that due to the lead shot again. Since there is an expansion, the work is done *by* the gas, so $W > 0$.



Another way to go from state A to state B, however, is to go from A to C, then from C to B, as shown by the arrows AC and CB respectively, in the figure above. How will we carry out this sequence of processes in the cylinder with the piston shown on the previous page?

> For the first part AC, we need to decrease the gas pressure, while keeping the volume constant. This can be done be drawing thermal energy out of the system to lower its temperature. At the same time, we should put a wedge on the piston so it cannot move, in order to maintain constant volume. No work is done during this part because the volume remains constant.
>
> For the second part CB, we need to keep the pressure constant and increase the volume. We can keep the pressure constant by leaving the same amount of lead shot on the piston. Meanwhile, we can increase the volume by supplying thermal energy to the gas, thereby raising its temperature. Since the volume increases, $W > 0$ for this part (i.e., the work is done by the gas).
>
> The net work done during this cycle is represented by the gray rectangle BC$V_A V_B$. Since the area of this rectangle is less than the area under the red curve (see figure above), the work done in taking the system from A to B via state C (i.e., along AC and then CB) is clearly less than the work done in taking the system from A to B along the red curve.

Yet another way to go from state A to state B is to go along the arrows from A to D, and then from D to B.

> For the first part AD, we keep the gas pressure constant, and increase the volume by supplying thermal energy to the gas. Since the volume increases, $W > 0$ for this part (i.e., the work is done by the gas).
>
> For the second part DB, we keep the volume constant (by putting a wedge on the piston as before) and decrease the pressure by drawing thermal energy out of the system. So $W = 0$ for this part.

> The net work done during this cycle is represented by the rectangle DAV_AV_B. Since the area of this rectangle is greater than the area under the red curve (see figure above), the work done in taking the system from A to B via state D (i.e., along AD and then DB) is clearly greater than the work done in taking the system from A to B along the red curve.

One could discuss other examples of taking the system from A to B, but the three examples above are enough to highlight the key point:

> *A system can be taken from an initial state to a final state by an infinite number of processes. In general, the work done by the system and the thermal energy transfers will have different values for each of these processes.*

Sometimes, the word path dependent quantities is used to describe the property above, but we will avoid it because the term can be confusing (suggesting motion in space, whereas we are actually talking about motion in $P - V$ space).