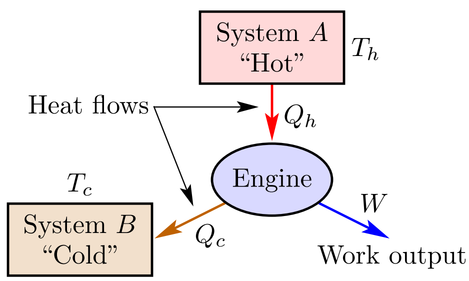
Reading assignment. Schroeder, section **4.2**.

0.1 Heat engines

We know from common experience that mechanical energy is eventually degraded to heat through friction and other losses. But the reverse never happens spontaneously, because of the second law of thermodynamics—the degraded state, in which the atoms of the materials whose surfaces made contact during the mechanical process undergo random thermal motion rather than systematic mechanical motion, has greater entropy.

The goal of a heat engine it to try to coax some useful work from thermal energy. Clearly, we can't just place a cylinder with a piston in contact with a gas and expect the piston to begin moving, because that would violate the second law, as we noted above. But it is possible to intervene in a heat-transfer process and extract some of the energy as useful work:



The idea is that the engine, which is supposed to be unchanged by the net process, absorbs some heat Q_h from a hot system and uses that to produce some useful work output W, while dumping a portion Q_c of the heat into a cold system. Here the terms "hot" and "cold" refer to the relative temperatures of systems A and B.

0.1.1 An upper bound to heat-engine performance

There are two laws that constrain the process. The first law of thermodynamics, conservation of energy, requires that

$$Q_h = Q_c + W\,. \tag{1}$$

Note that we're assuming all these quantities are positive, given the sense defined by the arrows in the figure.

The second law of thermodynamics, entropy maximization, requires that if the process is to proceed, the total entropy must increase. Assuming the work done is quasistatic, there will be no new entropy created in the mechanical process, so only the heat transfers change the entropy:

$$\Delta S_{\text{tot}} = \Delta S_h + \Delta S_c \geq 0\,, \tag{2}$$

where the inequality follows from the second law. Note again that the engine itself is unchanged by the process—it is merely a facilitator.

These two laws conspire to set limits on the performance of the system, and to determine what are those limits, we need a measure of the performance. Since the goal is the production of useful work, and the input to the process is Q_h, an appropriate definition is

$$\mathcal{E} = \frac{W}{Q_h}\,. \tag{3}$$

We might call this a *coefficient of performance*, or an *efficiency*. The heat output Q_c is waste heat, in the sense that it can't be used in this process in any way to improve its efficiency, though that does not preclude its use in other ways. Some of the waste heat from your automobile engine heats the car in winter, for example.

Since we're interested in obtaining upper limits on the performance, we'll suppose the heat transfers Q_h and Q_c occur quasistatically, so that

$$\Delta S_h = -\frac{Q_h}{T_h} \quad \text{and} \quad \Delta S_c = \frac{Q_c}{T_c}\,. \tag{4}$$

Also implicit in these expressions is the assumption that the hot and cold subsystems are actually reservoirs—they are sufficiently large that their temperatures remain fixed, even though we are removing or adding energy to them. It's straightforward to compute the entropy change via integration if the temperatures shift, but it's an unnecessary complication.

With those forms for the energy changes in mind, we can write the condition imposed by the second law as:

$$\frac{Q_c}{T_c} - \frac{Q_h}{T_h} \geq 0\,. \tag{5}$$

To obtain $\mathcal{E}$, we want to find the ratio W/Q_h, so we'll use the first law both to introduce W and to eliminate Q_c:

$$Q_c = Q_h - W\,. \tag{6}$$

Substituting this into the condition given by the second law gives

$$\frac{Q_h - W}{T_c} - \frac{Q_h}{T_h} \geq 0\,. \tag{7}$$

Now just solve that for W/Q_h, to get

$$\mathcal{E} = \frac{W}{Q_h} \leq 1 - \frac{T_c}{T_h}\,. \tag{8}$$

Thus, the second law gives us an upper bound to the performance of any heat engine. Any real engine will suffer from frictional losses, nonquasistatic processes and other imperfections that necessarily reduce its performance below this upper bound.

Some points to note:

- The second law requires that some heat Q_c be wasted in the process:

$$Q_c \geq Q_h \frac{T_c}{T_h} \,. \tag{9}$$

- When $T_c = T_h$, all of the heat Q_h must be wasted, and $\mathcal{E} \leq 0$.

- If we could make $T_c = 0$, then the upper bound on $\mathcal{E}$ becomes one. Of course, that's impossible, and even if it were possible, it would be impractical. We use heat reservoirs that are convenient, not ones that we have to take extreme measures to construct.

0.1.2 The Carnot cycle

Sadi Carnot invented an imaginary cyclic process that has an efficiency that equals the limit set by the second law. It is similar in its general features to familiar cyclic engines, so it serves as a useful benchmark against which real engines can be measured. The engine consists of a system containing a "working substance," such as a gas, that can absorb or release heat and can change some extensive variable, such as volume, in a way that can be harnessed to do work. A useful model is a gas in a cylinder with a piston, but there are many other possibilities. We'll describe the process in terms of a gas as the working substance.

The cycle consists of four steps, all of which take place quasistatically. As in the general discussion above, there are two subsystems, one of which has temperature T_h and serves as a source of heat for the engine; the other has temperature T_c, and serves as a sink for the waste heat. We'll assume the hot and cold subsystems are large reservoirs of thermal energy, so their temperatures are not affected by the heat transfers to and from the working substance.

1. The working substance, already at the temperature T_h of the hot reservoir, is placed in thermal contact with that reservoir. It then absorbs heat from the reservoir and expands isothermally (the reservoir keeps its temperature constant) while doing work against the piston. The volume increases, the pressure decreases, and the entropy increases by Q_h/T_h, the amount by which the entropy of the reservoir decreases.

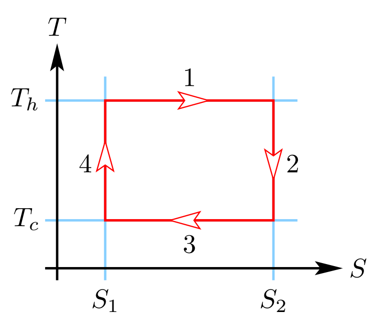
2. The working substance is disconnected from the hot reservoir and thermally isolated. It continues to expand, now adiabatically (no heat flow), doing additional work against the piston. The volume increases, the temperature and pressure decrease, and the entropy remains constant because of the lack of heat flow. The expansion is terminated when the temperature reaches that of the cold reservoir, T_c.

3. The working substance is placed in thermal contact with the cold reservoir at temperature T_c and compressed by the piston isothermally. The piston does work on the working substance, undoing some of the useful work done in the first two steps. The volume decreases, the pressure increases, and the entropy decreases as heat flows from the working substance into the cold reservoir. The step terminates when the entropy of the working substance has decreased to its initial value at the beginning of step 1, at which point the entropy change during the step is Q_c/T_c.

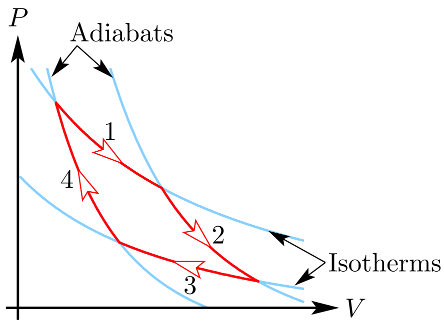
4. The working substance is disconnected from the cold reservoir and thermally isolated. It continues to be compressed, now adiabatically. The volume decreases, the temperature and pressure increase, and the entropy is unchanged. The piston continues to do work on the working substance, undoing still more of the useful work done in the first two steps. This step terminates when the temperature reaches that of the hot reservoir, T_h.

At the end of the cycle, the working substance is back in its initial state, with the same energy, entropy, volume, pressure, and temperature it had when the cycle started. That is, there has been no net change to the engine itself. What has happened is that heat Q_h has been removed from the hot reservoir, heat Q_c has been added to the cold reservoir, and some net beneficial work has been done against the piston.

Here's a graph of the cycle in the temperature *vs* entropy plane:



Here's the corresponding graph in the pressure *vs* volume plane:



Recall from an exercise we did long ago that adiabats are steeper than isotherms in the pressure *vs* volume diagram, because heat transfer in isothermal processes reduces pressure changes.

Note that there is no net change in the entropy or the energy $U(S, V, N)$ of the working substance, so the only effects are the heat transfers Q_h and Q_c to the reservoirs and the net work done by the working substance.
[EOC, Wed. 2/22/2006, #19]

Reading assignment. Schroeder, section **5.1**.

Exercise. Show that the efficiency of a Carnot engine equals the maximum permitted by the second law:

$$\mathcal{E} = \frac{W}{Q_h} = 1 - \frac{T_c}{T_h}\,. \tag{10}$$

Note that the point is to show that the Carnot engine actually achieves the maximum possible efficiency, not that it shares with all other heat engines the property of not exceeding that value.

There are a couple of additional interesting points to note regarding the Carnot cycle:

- Since the steps in the Carnot cycle are quasistatic, it's impractical to try to build a real engine based closely on it. In particular, the heat flows Q_h and Q_c take place between systems at the same temperature, which makes them infinitely slow. In a real engine, the working substance cannot have exactly the same temperature as either reservoir if heat is to flow at a reasonable rate.

- Since no new entropy is created in the quasistatic steps, the cycle is reversible.

  Question. What does the reverse process do?

  Answer: It takes work input and trnasfers energy from the cold reservoir to the hot reservoir. That makes it a refrigerator (or air conditioner or heat pump.)

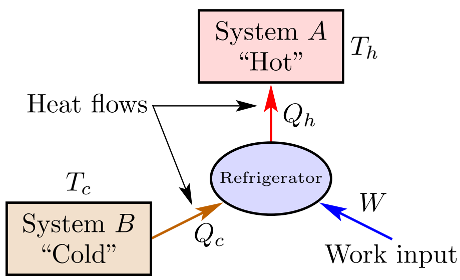
HW Problem. Schroeder problem 4.1, p. 124.

HW Problem. Schroeder problem 4.3, p. 124.

HW Problem. Schroeder problem 4.6, pp. 126–127.

0.1.3 Refrigerators

As was hinted at above, we can think of a refrigerator as a cyclic heat engine running in reverse. Indeed, the Carnot cycle run in reverse removes heat from the cold reservoir, dunps heat into the hot reservoir, and requires work input to accomplish the task. The generic diagram of a refrigeration process looks just like that of a heat engine, apart from reversal of all three energy flows:



Since all of the heat flows and the work flow are reversed relative to the heat engine, we'll reverse the sign conventions to make them all positive. The analysis of the process is much the same as for a heat entine, but we need a slightly different definition of performance:

$$\text{COP} = \frac{Q_c}{W}\,, \tag{15}$$

where "COP" stands for *coefficient of performance*. Here the useful result or benefit is the heat Q_c removed from the cold reservoir, and the energy input, or cost, is the work W required to power the refrigerator.

As was the case for a heat engine, the first and second laws of thermodynamics set an upper limit on the performance:

$$\begin{aligned} &\text{1st law:} \qquad && Q_h = W + Q_c \\ &\text{2nd law:} \qquad && \Delta S_{\text{tot}} = \Delta S_h + \Delta S_c = \frac{Q_h}{T_h} - \frac{Q_c}{T_c} \geq 0\,. \end{aligned} \tag{16}$$

From the first law and the definition of the coefficient of performance, we find

$$\text{COP} = \frac{Q_c}{Q_h - Q_c} = \frac{1}{(Q_h/Q_c) - 1}\,. \tag{17}$$

But the second law tells us that

$$\frac{Q_h}{Q_c} \geq \frac{T_h}{T_c}\,, \tag{18}$$

so the coefficient of performance must satisfy the inequality

$$\text{COP} \leq \frac{1}{(T_h/T_c) - 1} \qquad \text{(refrigerator)}\,. \tag{19}$$

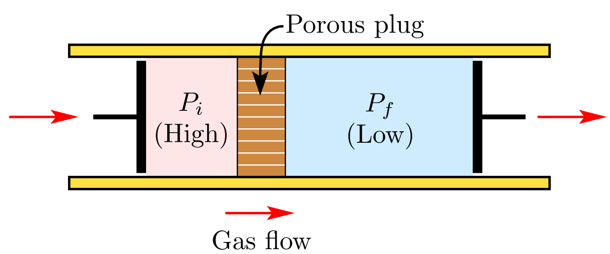
Notice that the best performance limit is achieved when $T_h = T_c$, that is, for the maximum value of T_c/T_h, rather than for the minimum of that ratio as we found for a heat engine.

HW Problem. Schroeder problem 4.14, p. 130.

Throttling process or Joule-Thomson process

[See Schroeder pp. 139–143] This is a process that is useful in refrigeration, particularly in liquefaction of gases, but it turns out also to be an interesting application of enthalpy, a quantity we encountered early on and will be encountering again shortly. You may be familiar with common cases in which expansion of a gas through a restricting valve causes the gas to cool. This happens, for example, when you let the air out of a tire, and on a cold day that can be quite painful for the finger operating the valve. You can let pressurized carbon dioxide out of a cartridge and find that it cools enough to solidify, forming dry-ice snow.

A simple analysis of the effect is based on a scheme in which constant pressure is maintained by pistons on each side of a flow-restricting plug:



Consider a portion V_i of the gas on the left passing through the plug and having volume V_f at pressure P_f afterward. The process is adiabatic (no heat flow), so the change in energy of the gas is due entirely to the work done by the pistons during the flow. The pressure is constant on both sides, so the work done by each piston is a simple PV product:

$$U_f - U_i = P_i V_i - P_f V_f\,, \tag{20}$$

the negative sign of the work of the piston on the right arising because that piston does negative work on the gas. This implies equality of the initial and final enthalpies:

$$U_f + P_f V_f = U_i + P_i V_i \quad \text{or} \quad H_f = H_i\,, \tag{21}$$

where we've used the definition of enthalpy in terms of energy:

$$H = U + PV\,. \tag{22}$$

Let's see what happens when we try this out on an ideal gas. Its energy is given by the equipartition theorem:

$$U = \frac{f}{2} NkT\,, \tag{23}$$

where f is the number of degrees of freedom, and its PV product is given by the ideal-gas law as

$$PV = NkT\,. \tag{24}$$

Therefore, its enthalpy is

$$H_{\text{ideal}} = \frac{f}{2} NkT + NkT = \left(\frac{f}{2} + 1\right) NkT\,. \tag{25}$$

Since H_{ideal} is proportional to T, the constancy of the enthalpy in a throttling process implies constancy of the temperature as well. That is, the effect vanishes for an ideal gas. Thus, if a throttling process is to change the temperature, that effect must originate in the nonideality of real gases. [EOC, Fri. 2/24/2006, #20]