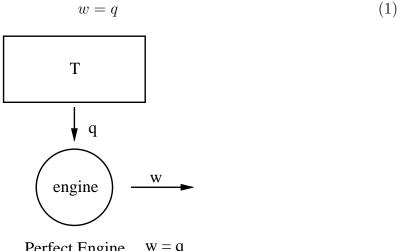
## CHAPTER 4: Engines

## Heat Engines

Heat engines have important technological importance. The basic idea is that one would like to extract heat from a heat reservoir, where that energy is spread randomly over a huge number of degrees of freedom, and convert it into work. By work we mean enrgy associated with a single degree of freedom connected with an external parameter of some outside device. Typically the engine goes through a cycle, returning to its initial state after having turned some heat into work. Think about the gasoline engine in your car. Ideally we would like a perfect engine that converts all the heat into useable work:



Perfect Engine  $\mathbf{w} = \mathbf{q}$ 

This obeys the first law of thermodynamics but it violates the second law. (Nothing's perfect.) From our previous discussions we know that work can be converted into heat in an irreversible process in which the distribution of systems over accessible states becomes more random so that entropy increases. One cannot expect to simply reverse the process and convert internal energy randomly distributed over all its degrees of freedom into work that changes one macroscopic degree of freedom. It's possible but fantastically improbable. It amounts to decreasing the number of accessible states, i.e., to decreasing the entropy. The second law of thermodynamics requires that the total entropy of the complete system (consisting of the heat engine, the outside device on which it does work, and the heat reservoir) be such that in a cycle

$$\Delta S \ge 0 \tag{2}$$

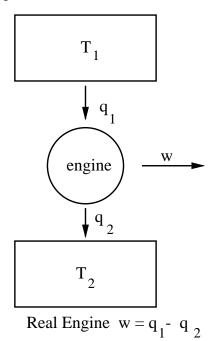
Now the heat engine itself returns to its previous state after a cycle is complete so its entropy is unchanged. The outside device on which work is done by changing an external parameter has no entropy change because we envision that it has an external parameter that changes without doing it at the expense of its other degrees of freedom. For example consider lifting a weight. So that leaves the heat reservoir from which heat has been extracted. So dQ < 0. But

$$dS = \frac{dQ}{T} \tag{3}$$

This implies that dS < 0 and that violates the second law of thermodynamics. In fact one way of stating the second law is to say

• It is impossible to construct a perfect heat engine.

(This statement is sometimes called Kelvin's formulation of the second law of thermodynamics.) We can make realizable heat engines that do not violate the second law by bringing in a second heat bath to absorb some heat. Since it absorbs heat, its entropy is increased. If it increases its entropy enough, it will ensure that the entire system has a net increase in entropy. Let's suppose that we have 2 reservoirs, a hotter one at temperature  $T_1$  from which heat is extracted and a cooler one at temperature  $T_2$  which absorbs some heat. In between a heat engine absorbs some heat  $q_1$  from the hotter reservoir, does some work and dumps some heat  $q_2$  into the cooler reservoir.



In this case the first law requires that in a cycle

$$q_1 = w + q_2 \tag{4}$$

After one cycle the engine and the device on which work is done are back where they started, so their entropy does not change. The net increase in entropy must come from the heat reservoirs:

$$\Delta S = \frac{(-q_1)}{T_1} + \frac{q_2}{T_2} \ge 0 \tag{5}$$

From (4)  $q_2 = q_1 - w$ . Plugging this into (5), we get

$$\frac{-q_1}{T_1} + \frac{q_1 - w}{T_2} \ge 0 \tag{6}$$

$$\frac{w}{T_2} \le q_1 \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{7}$$

The equals sign holds for quasi-static processes. We can rewrite this last equation as

$$\eta \equiv \frac{w}{q_1} \le q - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1} \tag{8}$$

where  $\eta = w/q_1$  is called the "efficiency" of the engine. For a perfect engine  $\eta = w/q_1 = 1$ . For a real engine  $\eta < 1$ :

$$\eta \equiv \frac{w}{q_1} = \frac{q_1 - q_2}{q_1} < 1 \tag{9}$$

since some heat does not get transformed into work but is dumped into another heat reservoir. The most efficient engine occurs for quasi–static processes where  $\Delta S = 0$ . From (9) this maximum efficiency is

$$\eta = \frac{T_1 - T_2}{T_1} \tag{10}$$

Furthermore any engines which operates between these two reservoirs in a quasi-static manner has this same maximum efficiency.

## Carnot Engine

Conceptually the simplest engine operating quasi-statically between 2 heat reservoirs is called a "Carnot engine." Let x denote the external parameter of the engine M; changes in this parameter give rise to the work performed by the engine. Let the engine initially be in a state where  $x = x_a$  and its temperature  $T = T_2$ , the temperature of the colder heat reservoir. The Carnot engine then goes through a cycle consisting of 4 steps, all performed quasi-statically. Let's label the macrostates of the engine by small letters a, b, c, and d.

- 1.  $a \to b$ : The engine is thermally insulated. Its external parameter is changed slowly until the engine temperature reaches  $T_1$ . Thus  $x_a \to x_b$  such that  $T_2 \to T_1$ .  $\Delta S = 0$  since the system is thermally isolated and the process is quasi-static. (One can think of a piston compressing gas in a thermally insulated cylinder.)
- 2.  $b \to c$ : The engine is now placed in thermal contact with the heat reservoir at temperature  $T_1$ . Its external parameter is changed further, the engine remaining at temperature  $T_1$  and absorbing some heat  $q_1$  from the reservoir. Thus  $x_b \to x_c$  such that  $q_1$  is absorbed by the engine. (The gas in the cylinder is allowed to expand while its temperature is maintained at  $T_1$ . It absorbs heat  $q_1$ .)

- 3.  $c \to d$ : The engine is again thermally insulated. Its external parameter is changed in such a direction that its temperature goes back to  $T_2$ . Thus  $x_c \to x_d$  such that  $T_1 \to T_2$ .  $\Delta S = 0$ . (The gas in the thermally insulated cylinder is allowed to expand until the gas temperature is  $T_2$ .)
- 4.  $d \to a$ : The engine is now placed in thermal contact with the heat reservoir at temperature  $T_2$ . Its external parameter is then changed until it returns to its initial value  $x_a$ , the engine remaining at temperaturee  $T_2$  and dumping some heat  $q_2$  into this reservoir. Thus  $x_d \to x_a$  and heat  $q_2$  is given off by the engine. (The gas is compressed while its temperature is maintained at  $T_2$ . It puts heat  $q_2$  into the reservoir.)

The engine is now back in its initial state and the cycle is completed. The amount of work done during a Carnot cycle is given by

$$w = \int_{a \to b \to c \to d \to a} p dV \tag{11}$$

This corresponds to the shaded area in the pV plot. Usually the cooler reservoir is just the air. Think of your car engine giving off heat to the radiator that in turn gives the heat to the air.

## Refrigerators

A refrigerator is a device which removes heat from a cooler reservoir and puts it in a hotter reservoir. A perfect refrigerator would do this heat transfer without affecting the environment in any other way, i.e., no work would need to be done. But a perfect refrigerator would violate the second law. The total entropy has to increase:

$$\Delta S = \frac{q}{T_1} + \frac{(-q)}{T_2} \ge 0 \tag{12}$$

or

$$q\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \ge 0\tag{13}$$

which is impossible since q>0 and  $T_1>T_2$ . Thus we can state the second law of thermodynamics as:

• It is impossible to make a perfect refrigerator.

This is known as the Clausius formulation of the second law. We are all familiar with this. We have to plug in our refrigerators in the kitchen. In fact about 95% of your electric bill due to the electricity gobbled up by your refrigerator. A real refrigerator requires that some work w be done to make it run. If it takes heat  $q_2$  from the cooler reservoir at temperature  $T_2$  and transfers heat  $q_1$  to the hotter reservoir at temperature  $T_1$ , then the first law requires that

$$q_2 = q_1 - w \tag{14}$$

So the heat absorbed from the colder reservoir is less than the heat given off to the hotter reservoir. The second law requires that

$$\Delta S = \frac{q_1}{T_1} + \frac{(-q_2)}{T_2} \ge 0 \tag{15}$$

or

$$\frac{q_2}{q_1} \le \frac{T_2}{T_1} \tag{16}$$

where the equals sign holds only for a refrigerator operating between two reservoirs quasistatically. One way to make a such a refrigerator would be to run the Carnot engine in reverse.