Appendix I
Abstract Heat Engines

In this Appendix we provide a concise description of classical thermodynamics as an abstract discipline.

Let us imagine that we can measure heat and work, that is, that we know how to associate these characteristics of physical processes with real numbers. Let heat be transformable into work and let work be transformable into heat, and let there exists a universal unit measure of both heat and work. At this point we introduce the concept of *energy* and consider work and heat as two possible forms of *energy passage*. For each pair of warm bodies, A and B, let us have a way to compare their heat and say either that “A is warmer than B” or that “B is warmer than A” or that “A and B are equally warm.” We assume that this relation is transitive, i.e., if “A is warmer than B” and “B is warmer than C,” then “A is warmer than C,” and if “A and B are equally warm” and “B and C are equally warm,” then “A and C are equally warm.”

In this way, we have begun to construct thermodynamics without the concept of temperature. We assume, however, that there is a relation order on the set of all heated bodies and that for any two of them we can say which one is warmer or that they are equally warm. Now we introduce the second law of thermodynamics:

> *Work cannot be produced without the passage of heat from a warmer body to a cooler one.*

Since the second law of thermodynamics is formulated as a negative statement, and since we believe that everything not forbidden is permitted, then from this law follows the principle of receiving work from heat:

> *It is possible to construct a machine that would receive heat from a warmer body, give heat to a cooler body, and produce work W>0.*

The simplest heat machine that produces work is shown in Fig.1a. There are two heat reservoirs 1 and 2, where 1 is warmer than 2. In accordance with the principle of receiving work from heat, it is possible to construct a heat engine that would take heat Q_1 from the hot reservoir, give heat Q_2 to the cool reservoir, and produce work W. The *first law of thermodynamics*, or the *law of conservation of energy*, formulates relations between the quantities Q_1, Q_2 and W:

$$W = Q_1 - Q_2. \tag{1}$$

In accordance with the second law of thermodynamics, work W can be produced only if $Q_2 > 0$, this means that only part of the heat taken from the hot reservoir turns into work. This restriction does not exist for turning work into heat. The entire work produced by a heat engine can be turned into an equal amount of heat.

The engine is called *reversible* if it can work both of the ways shown in Fig.1: as 1a and as 1b.

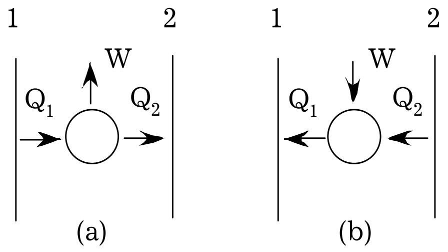

Fig. 1. Abstract heat engines. Vertical lines represent reservoirs of heat; reservoir 1 is hotter than 2. (a) Direct diagram: the engine takes heat Q_1 from reservoir 1, gives heat Q_2 to reservoir 2, and produces work W. (b) Reverse diagram: the engine receives work W from an external agent, takes heat Q_2 from the colder reservoir, and passes heat Q_1 to the hotter reservoir.

In other words, if the engine is reversible, we may take heat Q_2 from the cooler reservoir by spending work W and give it to the hotter reservoir, all in accord with the first law of thermodynamics, $Q_1 = W + Q_2$. The engine is called *non-reversible* if, after receiving work W from an external agent, we cannot take heat Q_2 from the colder reservoir and give heat Q_1 to the hotter one. We assume that the heat reservoirs are so large that the engines' functioning does not change their "temperature." As we do not yet have a measure for temperature, we will say that transferring heat from a hot reservoir to a cold one does not change the order on the set of heat reservoirs. We will call such reservoirs *unchangeable*. The following variable

$$\rho = \frac{Q_1 - Q_2}{Q_1} \tag{2}$$

is called the *coefficient of efficiency*; it shows what portion of the heat coming from the hot reservoir is turned into work. The following statement holds:

Statement 1. For two unchangeable heat reservoirs, one of which is hotter than the other, there is no engine with a coefficient of efficiency higher than that in the reversible engine.

Proof. Consider Fig. 2. Engine 1 is reversible and engine 2 is some other engine (not necessary reversible). Both engines receive heat Q_1 from the hot reservoir. The reversible engine produces work W_1, and the second engine produces work W_2 (see Fig.2a). Suppose $W_2 > W_1$. The reversible engine corresponds to the reversed diagram, as we show it in Fig.2b. A portion of the work produced by engine 2 is spent to return heat Q_1 (taken by engine 2) to the hotter reservoir by passing work W_1 to engine 1. Since $W_2 > W_1$, the additional work $W_2 - W_1$ is produced without transferring heat from a hotter body to a cooler one: in the end, we returned the heat taken but produced work $W_2 - W_1 > 0$. This is forbidden by the second law of thermodynamics. Therefore, our supposition of $W_2 > W_1$ is wrong, and

$$W_1 \geq W_2 \quad \blacksquare \qquad (3)$$

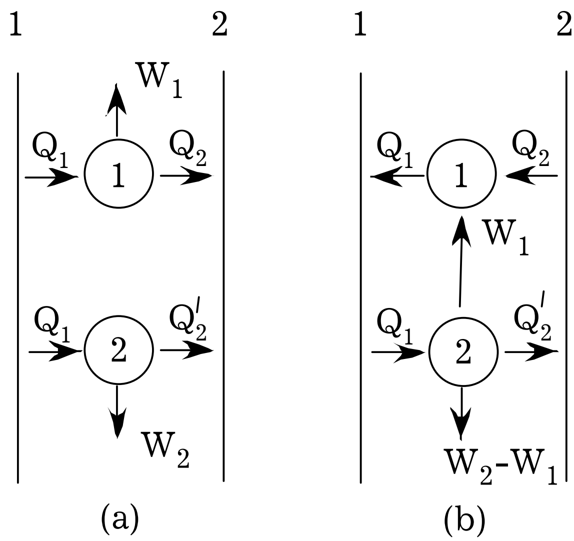

Fig. 2. Engine 1 is reversible; engine 2 may be either reversible or non-reversible.

Carnot's theorem. All reversible engines working between the same heat reservoirs have the same coefficient of efficiency.
Proof. Let both engines in Fig.2 be reversible. It follows from statement 1 that since engine 1 is reversible, $W_1 \geq W_2$, and since engine 2 is reversible, $W_2 \geq W_1$. Thus, $W_1 = W_2$ and

$$\frac{W_1}{Q_1} = \frac{W_2}{Q_1} \quad \blacksquare \qquad (4)$$

It follows from Carnot's theorem that, for a reversible engine, the coefficient of efficiency does not depend on the principle of its work nor on the fuel it consumes.

Let us now introduce the concept of *temperature*. Select one reservoir to be called *basic* and consider a set of other reservoirs, each of which is hotter than the basic one. Place a reversible engine between the basic reservoir and each of the others and take from them just as much heat as necessary for a reversible engine to release into the basic reservoir heat Q*. Heat Q* will be called the *unit of heat*. The quantity

$$T = \frac{Q}{Q*}, \tag{5}$$

where Q is taken from a given reservoir, will be called its *temperature*. The temperature of the basic reservoir is equal to 1 (Fig.3).

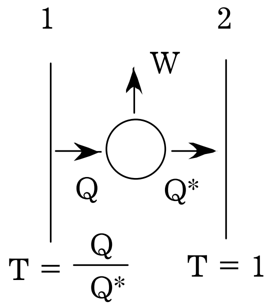

Fig. 3. Reservoir 2 is basic. Reservoir 1 is hotter than the basic reservoir. Q is the heat needing to be taken from reservoir 1 by a reversible engine to produce work *W* and release heat Q* to reservoir 2.

Statement 2. Reservoir 1 is hotter than reservoir 2, if and only if the temperature of reservoir 1 is higher than that of reservoir 2.

Proof.

(1) Necessity.

Let reservoir 1 be hotter than reservoir 2 and each engine, 1 and 2, release heat Q* into the basic reservoir (Fig. 4). Because engine 2 is reversible, diagram (a) in Fig. 4 can be transformed into diagram (b). Thus, the heat taken from the basic reservoir is equal to the heat returned to it. The work performed by the system in Fig. 4b is

$$W = W_1 - W_2 = (Q_1 - Q^*) - (Q_2 - Q^*) = Q_1 - Q_2. \quad (6)$$

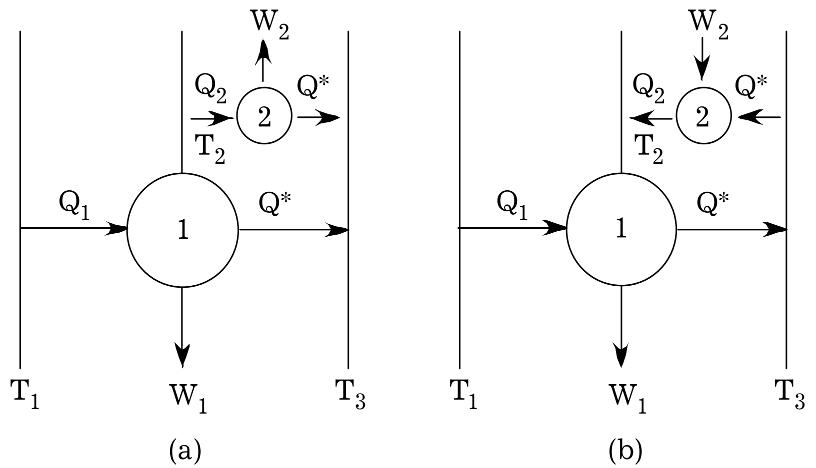

Fig. 4. Engines 1 and 2 are reversible. Reservoir 3 is basic.

Since the heat returned to the basic reservoir is exactly equal to the heat taken from it, the system can be considered as working between reservoirs 1 and 2, and since engines 1 and 2 are reversible, the whole system is also a reversible engine receiving heat Q_1 from reservoir 1 and returning heat Q_2 to reservoir 2. The coefficient of efficiency of a reversible engine is higher than zero, thus

$$W = Q_1 - Q_2 > 0, \quad (7)$$

hence

$$T_1 = \frac{Q_1}{Q^*} > \frac{Q_2}{Q^*} = T_2 \,. \quad (8)$$

(2) Sufficiency. Let $T_1 > T_2$. Then (8) holds, therefore $W = Q_1 - Q_2 > 0$, which, according to the second law of thermodynamics, is possible only when reservoir 1 is hotter than reservoir 2.

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It also follows from (8) that, for the reversible engine, the coefficient of efficiency is

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} . \qquad (9)$$

Since the coefficient of efficiency of the reversible engine is maximal under given conditions of functioning, then for any other engine working between reservoirs with temperature T_1 and T_2

$$\frac{Q_1 - Q_2}{Q_1} \leq \frac{T_1 - T_2}{T_1} . \qquad (10)$$

Suppose another reservoir is chosen as basic. The temperature of reservoirs 1 and 2 on the new scale are T_1' and T_2' respectively. It follows from (9) that

$$\frac{T_1 - T_2}{T_1} = \frac{T_1' - T_2'}{T_1'} \qquad (11)$$

or

$$\frac{T_2}{T_1} = \frac{T_2'}{T_1'} . \qquad (12)$$

Thus, the ratio of temperatures for a pair of objects is the same on any scale.

Note that a formulation of the second law of thermodynamics may be given by expression (10) or by the equivalent expression

$$\frac{Q_2}{T_2} - \frac{Q_1}{T_1} \geq 0 . \qquad (13)$$

The statements formulated above, including the formulation of the second law of thermodynamics given in the beginning of this Appendix, can be deduced from (10). It follows that $Q_2 > 0$, i.e., producing work is impossible without transferring heat from a hotter body to a cooler one.

Consider now some correlations necessary for constructing the model. Engine M is placed between reservoirs with temperatures T_1 and T_2, where $T_1 > T_2$. It receives heat Q_1 from the hotter reservoir and releases heat Q_2 into the cooler one. The work produced by M is

$$W_1 = Q_1 - Q_2. \tag{14}$$

In addition, a reversible engine is placed between the same reservoirs; it produces work

$$W_0 = Q_1 \frac{T_1 - T_2}{T_1}. \tag{15}$$

Theoretically, this work is the maximum possible for the given ratio of temperatures in the reservoirs. The quantity

$$\Delta W_1 = W_0 - W_1 \tag{16}$$

is called the *lost available work*. If engine M is non-reversible,

$$\Delta W_1 > 0. \tag{17}$$

The lost available work is the energy lost by a heat engine due to its imperfection. It is the additional work which M could produce if it were reversible. It follows from (16) that

$$\Delta W_1 = Q_1 \frac{T_1 - T_2}{T_1} - (Q_1 - Q_2) = Q_2 - \frac{T_2}{T_1} Q_1 = T_2 \left(\frac{Q_2}{T_2} - \frac{Q_1}{T_1} \right). \tag{18}$$

The quantity

$$\Delta H = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} \tag{19}$$

is called the system's *entropy change* as a result of producing work W_1. Therefore,

$$\Delta W_1 = T_2 \Delta \mathrm{H}. \tag{20}$$