Logic and thermodynamics: the heat-engine axiomatics of the second law

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We challenge the statement that the principle of Thomson and the principle of Clausius are equivalent. A logical mistake in the supposed textbook proof of their equivalency is indicated. On this account we refine the heat-engine axiomatics. We consider the energy exchange in the configuration comprised of two heat reservoirs and one mechanical device and show explicitly the domains banned by the laws of thermodynamics.

In the preface to the textbook[1] on thermodynamics Ryogo Kubo passed the following observation. "As in contrast to the atomic theory, thermodynamics does not find a support in our intuition. This is one of the reasons why students consider thermodynamics difficult for mastering and can not apply it to concrete problems." As a confirmation of his words we see[2] a confusion in the very foundations of the theory. There is an error in the axiomatics of phenomenological thermodynamics or, may be, imperfection, that moves over from one textbook to another for a century (see e.g. Ref. 3,4,5). This is the well-known proof by contradiction of that the principle of Thomson is equivalent to the principle of Clausius and vice versa. This theorem is mostly decorative and so does not prevent us from the proper conclusions. However, it may be just the reason of the difficulties in comprehending the whole structure of thermodynamics. We use it as a guide to make the formulation of the second law more coherent and unequivocal. The role of formal logic in constructing deductive theories is thus emphasized.

We consider the exchange of the energy in the ternary configuration comprised of the two thermostats h and c and one mechanical system m. The thermomechanical device that implements this exchange in a cycle is known as the heat engine. The first law restricts the values ΔE of the increments of the energy by the plane

$$\Delta E_h + \Delta E_m + \Delta E_c = 0\,. \tag{1}$$

The second law puts further restraints on the vector $(\Delta E_h, \Delta E_m, \Delta E_c)$. The principle of Thomson forbids the region in the plane (1) where

$$\Delta E_h \leq 0,\ \Delta E_m > 0,\ \Delta E_c \leq 0\,. \tag{2}$$

The principle of Clausius forbids in the plane (1) the ray

$$(\Delta E_h, 0, \Delta E_c):\ \Delta E_h > 0 \tag{3}$$

and thus ranks the bodies into cold c and hot h. The principles (2) and (3) do not specify the whole region banned by the second law. But they play a crucial role in constructing this region. As we see, these principles belong to different domains. So, they can not be equivalent.

Using the both principles we may prove[3] the following lemma:

$$\text{if } \Delta E_m > 0 \text{ then } \Delta E_c > 0\,. \tag{4}$$

Indeed, let $\Delta E_c = 0$. Then we have from Eq. (1) $\Delta E_h < 0$, that contradicts the Thomson's principle (2). Let $\Delta E_c < 0$. The Thomson's principle (2) does not forbid the process

$$\Delta E_h > 0,\ \Delta E_m > 0,\ \Delta E_c < 0\,. \tag{5}$$

It also allows a process

$$\Delta' E_h > 0,\ \Delta' E_m < 0,\ \Delta' E_c = 0\,. \tag{6}$$

Summing up (5) and (6) for $\Delta' E_m = -\Delta E_m$ we get

$$\Delta E_h + \Delta' E_h > 0,\ \Delta E_m + \Delta' E_m = 0,\ \Delta E_c + \Delta' E_c < 0\,. \tag{7}$$

The process (7) contradicts the Clausius' principle (3). That proves lemma (4).

To find the region allowed by thermodynamics we accept the postulate of *the existence of reversible processes* (r). It states that for each $\Delta E_h^{(r)}$ there exists $\Delta E_c^{(r)}$ such that we can find $\Delta' E_c^{(r)}$ and $\Delta' E_h^{(r)}$ complying with

$$\Delta E_h^{(r)} + \Delta' E_h^{(r)} = 0 \tag{8}$$

$$\Delta E_c^{(r)} + \Delta' E_c^{(r)} = 0\,. \tag{9}$$

The reverse process is unique that is easily proved using the Thomson's principle (2).

Proceeding from (4) and (8), (9) we may prove the Carno's theorem. It says that the efficiency of a reversible heat engine is greater or equal to the efficiency of any other heat engine. Below we give a more accurate proof of the Carno's theorem than it is usually done[1].

Consider the energy exchange in the ternary configuration according to Eq. (1). We want to compare (1) with the reversible process

$$\Delta E_h^{(r)} + \Delta E_m^{(r)} + \Delta E_c^{(r)} = 0 \tag{10}$$

under the condition

$$\Delta E_h = \Delta E_h^{(r)} \,. \tag{11}$$

To this end, we will carry out firstly (1) and then the process

$$\Delta' E_h^{(r)} + \Delta' E_m^{(r)} + \Delta' E_c^{(r)} = 0 \tag{12}$$

that is reverse to (10). Summing up Eq. (1) and Eq. (12) and using in it (11) and (8) we get

$$\Delta E_m + \Delta' E_m^{(r)} + \Delta E_c + \Delta' E_c^{(r)} = 0 \,. \tag{13}$$

By virtue of the Thomson's principle (2) we have from Eq. (13)

$$\Delta E_c + \Delta' E_c^{(r)} \geq 0 \,. \tag{14}$$

Excluding $\Delta' E_c^{(r)}$ from Eq. (14) and (9) gives

$$\Delta E_c - \Delta E_c^{(r)} \geq 0 \,. \tag{15}$$

Let $\Delta E_m^{(r)} > 0$. Then by the lemma (4) $\Delta E_c^{(r)} > 0$. Inequality (15) says that with the condition (11) the work made by the reversible heat engine is greater than the work done by the irreversible heat engine. Dividing (15) by $\Delta E_c^{(r)}$ and using in it tautologically (11) we get

$$-\frac{\Delta E_h}{\Delta E_h^{(r)}} + \frac{\Delta E_c}{\Delta E_c^{(r)}} \geq 0 \,. \tag{16}$$

Let $\Delta E_m^{(r)} < 0$. Then by the lemma (4) and (9) we have for reversible processes $\Delta E_c^{(r)} < 0$. In this case inequality (16) should be replaced by

$$\frac{\Delta E_h}{\Delta E_h^{(r)}} - \frac{\Delta E_c}{\Delta E_c^{(r)}} \geq 0 \,. \tag{17}$$

At last, we may unite (16) and (17) into the inequality

$$\frac{\Delta E_h}{|\Delta E_h^{(r)}|} + \frac{\Delta E_c}{|\Delta E_c^{(r)}|} \geq 0 \,. \tag{18}$$

Combine n irreversible and $n^{(r)}$ reversible heat engines such that

$$\frac{\Delta E_h}{\Delta E_h^{(r)}} = \frac{n^{(r)}}{n} \,. \tag{19}$$

Then we may deduce[3] (18) for a general case that does not obey the restriction (11). As you see, the proof of the Carno's theorem makes use of the Thomson's principle (2). It can also be proved using the Clausius' principle (3).

Let us take instead of (1) a reversible process (r_0). Then, reversing the processes, we may turn[1] (18) into equality. This equality can be written as

$$\frac{|\Delta E_h^{(0)}|}{|\Delta E_h^{(r)}|} = \frac{|\Delta E_c^{(0)}|}{|\Delta E_c^{(r)}|} \,. \tag{20}$$

Now we can define[1,3] an absolute temperature scale by the relations

$$|\Delta E_h^{(0)}| = \kappa\, \theta_h\,, \quad |\Delta E_c^{(0)}| = \kappa\, \theta_c \tag{21}$$

where $\kappa > 0$ is a constant. Substituting (20) and (21) into (18) gives

$$\frac{\Delta E_h}{\theta_h} + \frac{\Delta E_c}{\theta_c} \geq 0\,. \tag{22}$$

Taken together with Eq. (1), inequality (22) specifies the domain of the processes allowed by thermodynamics. This is a half-plane in the energy space $(\Delta E_h, \Delta E_m, \Delta E_c)$.

As we see from the above, the principle of Thomson and the principle of Clausius are not equivalent. However, there is a popular textbook proof[3,4,5] of their equivalence. In order to show explicitly the error in the supposed proof we must give both the verbal and logical formulation of these principles. The Thomson's principle states: One can not take heat from a body and totally convert it to work. The Clausius' principles states: "Heat cannot, of itself, pass from a colder to a hotter body." The equivalence is proved by contradiction (i.e. from the contrary). The two theorems are needed.

A: If the Thomson's principle is wrong then the Clausius' principle is wrong as well.

B: If the Clausius' principle is wrong then the Thomson's principle is wrong as well.

It is sufficient to analyze the supposed proof of the first theorem. It runs as follows.

1. Let the Thomson's principle be wrong.
2. Then we may take a heat from the cold body and convert it wholly to a work.
3. Next we may convert this work into the internal energy of the hot body.
4. The pure result of these operations is that heat was transferred from the cold body to the hot body.

That contradicts the Clausius' principle and hence the statement A is valid.

Here the error is in the step 3. To explicate it we formulate the Thomson's principle in logical terms. Let us define on the line $\Delta E + \Delta E_m = 0$ the Boolean function that describes the energy exchange between a termostat and a mechanical system:

$$I(\Delta E_m) \;=\; true \quad \text{for} \quad \Delta E_m \leq 0 \tag{23}$$

$$I(\Delta E_m) \;=\; false \quad \text{for} \quad \Delta E_m > 0\,. \tag{24}$$

This function just expresses the Thomson's principle. Negating it we get

$$\neg I(\Delta E_m) \;=\; false \quad \text{for} \quad \Delta E_m \leq 0 \tag{25}$$

$$\neg I(\Delta E_m) \;=\; true \quad \text{for} \quad \Delta E_m > 0\,. \tag{26}$$

This allows $\Delta E_m > 0$ and forbids $\Delta E_m \leq 0$. We made use (26) in step 2 and violated (25) in step 3. The origin of this mistake is in that the verbal formulation of the Thomson's principle says explicitly (24) and does not speak out (23). However, the latter is implicit as in an ellipsis or enthymeme. The literal understanding of the words gave rise to the error in the logical inference. This illustrates the significance of formal logic in constructing deductive theories.

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