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Generalized Kelvin Formulation of the Second Law of Thermodynamics

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Abstract

The Kelvin formulation of the second law of thermodynamics permits the following generalization: If the efficiency of a heat engine approaches unity, then the rejected work vanishes. This generalization allows deriving the behavior of a Carnot cycle near absolute zero of temperature. Also, the unattainability of absolute zero can be shown. In turn, these results allow deriving the behavior of the entropy near absolute zero, as has already been shown previously. The point of view is the phenomenological, macroscopic, and non-statistical one of classical thermodynamics.

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1. Introduction

Classical thermodynamics is a phenomenological, macroscopic, and non-statistical formalism derived from the laws of thermodynamics (and some additional assumptions). Some of the laws have several formulations or versions which are (more or less) equivalent to each other. One of the formulations of the second law is the Kelvin formulation. (See [1] for other formulations, e.g. Clausius and Carathéodory. However, we do not count in this context the axioms proposed by Lieb and Yngvason [1], as they constitute a formalism of their own, outside of classical thermodynamics.)

The Kelvin formulation of the second law is often also called Kelvin-Planck formulation, or Planck formulation. For sake of simplicity, we will refer to all of them as the Kelvin formulation (KSL). The wording that can be found for the KSL is not always identical. For example, [1] states that the KSL claims that "No process is possible, the sole result of which is that a body is cooled and work is done." On the other hand, [2] states that the KSL prohibits "a periodically (cyclically) working thermodynamic machine, which does nothing else but executing work per cycle, where a heat amount ΔQ is taken only from one single heat reservoir." We will not review all different wordings of the KSL. We take for granted that they are conceptually equivalent.

Some conventions concerning notation and terminology:

1. In order to denote an exchange of heat or work, some textbooks use the notations ΔQ and ΔW while others use the notations Q and W. We prefer the notations Q and W.
2. If a system accepts energy from its environment, then the energy exchange is positive (e.g., $Q > 0$ or $W > 0$). If a system rejects energy to its environment, then the energy exchange is negative (e.g., $Q < 0$ or $W < 0$).
3. We will often consider a thermodynamic system performing a cycle process. During a turn of the cycle, the system may exchange both heat Q and work W with its environment. The quantities Q, W are net quantities which, respectively, can be seen as the sum of amounts $Q_{\text{in}} \geq 0$, $W_{\text{in}} \geq 0$ which the system accepts from its environment and amounts $Q_{\text{out}} \leq 0$, $W_{\text{out}} \leq 0$ which the system rejects to its environment. Such a system will often be called a heat engine.

We will turn our attention to a generalization of the KSL: If the efficiency of a heat engine approaches 1, then its rejected net work vanishes. This generalized KSL will allow deriving the behavior of a Carnot cycle near absolute zero. Moreover, it will be shown that absolute zero is

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unattainable. From these results, the behavior of the Clausius entropy near absolute zero can be derived as well (as has already been shown in [3]).

The intention of this paper is not describing new phenomena but finding a minimal set of simple axioms (as prescribed by the principle of Occam's razor). The novelty can be summarized as follows: Contrary the KSL itself, its generalization allows deriving the above-mentioned statements; therefore, it could render unnecessary the traditional versions of the third law of thermodynamics. (See [4] for the third law.) Also, whereas the KSL is a verbal statement, its generalization is a mathematical statement.

The scope of this paper is the theory of classical thermodynamics. Also, only the necessary main line of reasoning is presented: On the one hand, given the fundamental subject of the paper, a great number of extra considerations would be possible. On the other hand, this would inflate the paper and restrict the possible readership. The author thinks it wise that extra considerations should be the subject of future papers.

2. Generalized Kelvin Formulation

The KSL permits the following generalization.

(Generalized Kelvin formulation). *For all thermodynamic cycle processes that transform accepted heat* $Q_{\text{in}} \geq 0$ *into rejected net work* $W \leq 0$ *with an efficiency* $\eta = |W|/|Q_{\text{in}}|$, *the following limit holds:* $\lim_{\eta \to 1} W = 0$.

If the KSL claims that no heat engine with $\eta = 1$ and $|W| > 0$ can be observed, then the generalized Kelvin formulation (GKSL) claims that there exist $\eta^* < 1$ and $|W^*| > 0$ such that no heat engine with $\eta \geq \eta^*$ can be observed, because the measuring equipment will be unable to detect any net work, $|W| < |W^*|$. (The values of η^* and $|W^*|$ may depend on the measuring equipment.) This means that the GKSL is more general and more comprehensive than the KSL.

Of course, the GKSL claims validity for all kinds of heat engine, not just reversible or quasistatic ones.

The continuous extension of the GKSL for $\eta = 1$ leads to $W = 0$ and $Q_{\text{in}} = 0$. This implies $1 = \eta = |W|/|Q_{\text{in}}| = 0/0$, and the equation $1 = 0/0$ amounts to a failure of the formalism. This motivates the following convention.

Convention 2.1. *No physical validity is attributed to the continuous extension of the GKSL for* $\eta = 1$.

In other words, above convention claims that $\eta = 1$ does not exist in the physical reality; this statement is identical to the KSL.

3. Carnot Cycle Near Absolute Zero

A Carnot cycle is a reversible thermodynamic cycle process operating between two different heat baths that are connected adiabatically. For a Carnot cycle, the following equations hold (see [2]):

$$|Q_{\text{h}}| = |W| + |Q_{\text{c}}|, \tag{1}$$

$$\eta = 1 - \frac{T_{\text{c}}}{T_{\text{h}}} = 1 - \frac{|Q_{\text{c}}|}{|Q_{\text{h}}|} = \frac{|W|}{|Q_{\text{h}}|}, \tag{2}$$

where $|Q_{\text{h}}|$ is the heat exchanged with the hot heat bath at the temperature T_{h}, $|Q_{\text{c}}|$ is the heat exchanged with the cold heat bath at the temperature T_{c}, $|W|$ denotes net work, and η denotes efficiency. (1) is a result of the first law of thermodynamics.

A Carnot cycle may operate as a heat engine or as a heat pump. If it is operating as a heat engine, then $Q_{\text{in}} = Q_{\text{h}}$ and $Q_{\text{out}} = Q_{\text{c}}$ hold, and the GKSL can be applied.

Theorem 3.1. *For a Carnot cycle, the following equations hold:*

$$\lim_{T_{\text{c}} \to 0} \eta = 1, \tag{3}$$

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$$\lim_{T_c \to 0} |W| = 0, \tag{4}$$

$$\lim_{T_c \to 0} |Q_h| = 0, \tag{5}$$

$$\lim_{T_c \to 0} |Q_c| = 0, \tag{6}$$

$$\lim_{T_c \to 0} \frac{|Q_c|}{T_c} = 0. \tag{7}$$

Proof. The equations to be proven are independent of whether the Carnot cycle operates as a heat engine or as a heat pump. We assume that it is operating as a heat engine. (3) is a consequence of (2). (4) is a consequence of (2) and the GKSL. (This can be shown as follows: From the GKSL we know that for any $\epsilon > 0$ there is a $\delta > 0$ such that $0 < |\eta - 1| < \delta$ implies $|W| < \epsilon$. Moreover, from (3) follows that for δ there is a $\delta^* > 0$ such that $0 < |T_c| < \delta^*$ implies $|\eta - 1| < \delta$ where $0 = |\eta - 1|$ can be excluded because of convention 2.1. A combination of these statements yields that for any $\epsilon > 0$ there is a $\delta^* > 0$ such that $0 < |T_c| < \delta^*$ implies $|W| < \epsilon$. This proves (4).) We now prove (5): (2) can be rearranged to $|Q_h| = |W|/\eta$. (5) is then proven by (3) and (4). We now prove (6): (1) can be rearranged to $|Q_c| = |Q_h| - |W|$. (6) is then proven by (4) and (5). We now prove (7): (2) can be rearranged to $|Q_c|/T_c = |Q_h|/T_h$. (7) is then proven by (5). □

4. Unattainability of Absolute Zero

There are several ways of defining temperature as a physical quantity. For example, temperature may be defined as a consequence of the existence of entropy (e.g., [1]). Instead, we will rely on the absolute thermodynamic temperature scale (ATTS) which uses the universal efficiency (2) of a Carnot cycle to define temperature as a physical quantity. The procedure of the ATTS is as follows [2]: One of the two temperatures of the Carnot cycle, for example T_h, is taken to be known and is kept fixed. The other temperature, e.g. T_c, is then defined through (2).

Theorem 4.1. *The absolute thermodynamic temperature scale is unable to define a temperature $T = 0$.*

Proof. We assume a Carnot cycle with $T_c = 0$, operating as a heat engine. (2) yields $\eta = 1$. However, convention 2.1 states that $\eta = 1$ has no physical validity. This means that the ATTS is unable to define a temperature $T = 0$. □

Remark 1 on theorem 4.1. *Other temperature scales may be able to define a temperature $T = 0$. We do not discuss them, since classical thermodynamics principally relies on the ATTS if KSL or GKSL are regarded as basic versions of the second law.*

Remark 2 on theorem 4.1. *A recent proof [5] of the Nernst theorem relies on the assumption that $T_c = 0$, $T_h > 0$, $Q_c = 0$, and $Q_h = 0$ are valid values for the ATTS. However, (2) then leads to $0 = 0/0$. In other words, [5] does not take into account the failure of the thermodynamic formalism at $T = 0$ described both in this paper and in [4].*

Corollary 4.2. *From the point of view of the ATTS, a temperature $T = 0$ is unattainable.*

Proof. According to theorem 4.1, a temperature $T = 0$ does not exist from the point of view of the ATTS. The unattainability is then a trivial consequence of the non-existence. □

Theorem 4.1 and corollary 4.2 can be seen as an alternative to the unattainability version of the third law by Nernst which may be expressed as the impossibility to reach absolute zero of temperature by a finite number of thermodynamic processes and in finite time [6].

The unattainability of $T = 0$ would lead to excessive usage of the notation $T \to 0$. The following convention [3] helps avoid this.

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Convention 4.3. *A mathematically motivated temperature* $T = 0$ *is introduced according to the following procedure: Every relation that is known to exist for* $T \to 0$ *is taken to be valid for* $T = 0$ *as well.*

Above convention 4.3 allows the construction of a state space with temperatures $T \geq 0$, where the surface $T = 0$ is a purely mathematical extension of physical relations existing for $T \to 0$.

5. Conclusion

The generalized Kelvin formulation allows deriving statements typically associated with traditional versions of the third law of thermodynamics. For the derivation of the entropic behavior near absolute zero, see section "Entropic version" of [3]. (See also section "Introduction" of [3], in particular the remarks concerning notation, terminology and methods.) Also, the generalized Kelvin formulation is a mathematical statement which facilitates its theoretical usage.

This paper has been conceived as a contribution to the theory of classical thermodynamics. Anything outside this scope has not been discussed. In particular, there has been no comparison with modern theories.

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