

Mathematical Kelvin Formulation of the Second Law of Thermodynamics

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Abstract

A mathematical Kelvin formulation of the second law of thermodynamics in the form of a limit is proposed: If the efficiency of a heat engine approaches unity, then the rejected work vanishes. This limit 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.

Keywords: second law; third law; thermodynamics; absolute zero; entropy

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.)

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] cites the KSL as follows: “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.
4. If a thermodynamic system performing a cycle process rejects net work $W \leq 0$, it is called a heat engine.

Traditionally, the KSL is a verbal statement. We will turn our attention to the KSL as a mathematical statement in the form of the following limit: If the efficiency $\eta = -W/Q_{\text{in}}$ of a heat engine approaches 1, then its rejected net work vanishes. This mathematical KSL will allow deriving the behavior of a Carnot cycle near absolute zero. Moreover, it will be shown that absolute zero is 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 to describe new phenomena but to find a minimal set of simple axioms, as prescribed by the principle of Ockham's razor. The novelty can be summarized as follows: The mathematical KSL allows deriving the above-mentioned statements; therefore, it could render unnecessary the traditional versions of the third law of thermodynamics. (See [4] for those traditional versions of the third law.)

The scope of this paper is the theory of classical thermodynamics. Moreover, for sake of conciseness, only the necessary main line of reasoning will be presented; extra considerations may be the subject of dedicated papers.

2. Mathematical Kelvin formulation

We suggest that the KSL can also be expressed as follows.

(Mathematical Kelvin formulation). *For any heat engine the following limit holds: $\lim_{\eta \rightarrow 1} W = 0$.*

The above mathematical Kelvin formulation (MKSL) claims validity for all kinds of heat engine, not only reversible or near-equilibrium ones.

The continuous extension of the MKSL 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. Therefore, we attribute no physical validity to this continuous extension. Likewise, a discontinuity with $W \rightarrow 0$, $Q_{\text{in}} \rightarrow 0$ as $\eta \rightarrow 1$ on the one hand and $W < 0$, $Q_{\text{in}} > 0$ for $\eta = 1$ on the other hand can be regarded as unphysical as well. This leads to the following conclusion.

Conclusion 2.1. *A heat engine with $\eta = 1$ does not exist.*

Above conclusion can be seen as identical to (or at least conceptually equivalent to) the traditional, verbal 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]):

$$W + Q_{\text{h}} + Q_{\text{c}} = 0, \quad (1)$$

$$\eta = 1 - \frac{T_{\text{c}}}{T_{\text{h}}} = 1 + \frac{Q_{\text{c}}}{Q_{\text{h}}} = -\frac{W}{Q_{\text{h}}}, \quad (2)$$

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

Any 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 MKSL can be applied.

Theorem 1. *For a Carnot cycle the following equations hold:*

$$\lim_{T_{\text{c}} \rightarrow 0} \eta = 1, \quad (3)$$

$$\lim_{T_{\text{c}} \rightarrow 0} W = 0, \quad (4)$$

$$\lim_{T_c \rightarrow 0} Q_h = 0, \quad (5)$$

$$\lim_{T_c \rightarrow 0} Q_c = 0, \quad (6)$$

$$\lim_{T_c \rightarrow 0} \frac{Q_c}{T_c} = 0. \quad (7)$$

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 (3), the MKSL, and conclusion 2.1. (This can be shown as follows: From the MKSL 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 conclusion 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). $\square$

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 2. *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, conclusion 2.1 states that a heat engine with $\eta = 1$ does not exist. $\square$

Remark 1 (on Theorem 2). *Other temperature scales may be able to define a temperature $T = 0$. We do not discuss them, since classical thermodynamics relies on the ATTS if KSL or MKSL are regarded as principal versions of the second law [2].*

Remark 2 (on Theorem 2). *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 1. *From the point of view of the ATTS, a temperature $T = 0$ is unattainable.*

Proof. According to Theorem 2, 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. $\square$

Theorem 2 and corollary 1 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 $T \rightarrow 0$. This can be avoided by a convention proposed in [3]: “A mathematically motivated temperature $T = 0$ is introduced according to the following procedure: Every relation that is known to exist for $T \rightarrow 0$ is taken to be valid for $T = 0$ as well.” This convention 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 $T \rightarrow 0$.

5. Conclusion

The mathematical 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 resulting theoretical formalism is relatively clear, simple, and rigorous.

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 the various other thermodynamic theories.

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