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Bounded energy exchange as an alternative to the third law of thermodynamics

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ABSTRACT

This paper introduces a postulate explicitly forbidding the extraction of an infinite amount of energy from a thermodynamic system. It also introduces the assumption that no measuring equipment is capable of detecting arbitrarily small energy exchanges. The Kelvin formulation of the second law is reinterpreted accordingly. Then statements related to both the unattainability version and the entropic version of the third law are derived. The value of any common thermodynamic potential of a one-component system at absolute zero of temperature is ascertained if some assumptions with regard to the state space can be made. The point of view is the phenomenological, macroscopic and non-statistical one of classical thermodynamics.

1. Introduction

The first law of thermodynamics states that the internal energy U of a thermodynamic system is a state variable. This means that the value of U at the end of a cycle is the same as at its beginning, $\oint \mathrm{d}U = 0$. A hypothetical cycle that results in an increased internal energy U after its completion, $\oint \mathrm{d}U > 0$, is called a perpetual motion machine of the first kind.

The Kelvin formulation of the second law of thermodynamics states that there can be no cycle whose sole effect is the extraction of heat Q from a single heat bath and its transformation into work W. Such a cycle would constitute a perpetual motion machine of the second kind.

However, there is no law of thermodynamics that explicitly forbids a process during which an infinite amount of energy is extracted from a thermodynamic system. This infinite amount of energy

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could be used to drive a perpetual motion machine of neither the first nor the second kind. Section 2 introduces a postulate explicitly forbidding such a process. This postulate is suggested as an alternative to the third law of thermodynamics. In Section 3 it will be shown that intrinsic limitations of the measuring equipment are not only an experimental concern but also need to be taken into account theoretically by classical thermodynamics when exploring temperatures T near absolute zero. For this purpose the assumption is introduced that no measuring equipment is capable of detecting arbitrarily small energy exchanges. This assumption leads to a reinterpretation of the second law. In the remaining part of Section 3 statements related to the unattainability version of the third law are derived. The unattainability version has been introduced by Nernst [1] and may be expressed as the impossibility to reach absolute zero of temperature by a finite number of thermodynamic processes and in finite time. In Section 4 statements related to the entropic version of the third law are derived. In statistical mechanics, the entropic version is related to the equation $S = k \ln W$ where a non-degenerate ground state would involve $W_0 = 1$ and therefore $S_0 = 0$. However, the point of view of this paper is the non-statistical one of classical thermodynamics. (To avoid a possible misconception: Classical thermodynamics is a self-contained formalism derived from the laws of thermodynamics. It is not identical to classical statistical mechanics.) Classical thermodynamics has several formulations for the entropic version, like:

(1) "$\Delta S \rightarrow 0$ for the entropy change of a reversible isothermal process if the temperature T approaches absolute zero" (Nernst [1]; originally restricted to the entropy change of chemical reactions).
(2) "The entropy of all chemically homogeneous systems of finite density in equilibrium approaches zero as $T \rightarrow 0$" (Planck [2]).
(3) "$S \rightarrow 0$ as $T \rightarrow 0$ for a perfect crystal" (Lewis and Randall [3]).
(4) "The partial derivatives of the entropy vanish as $T \rightarrow 0$ for a suitable set of state variables" (Cross and Eckstrom [4]).

Section 5 examines the results of the previous sections for the example of a thermodynamic system containing a pure substance. The value of any common thermodynamic potential at absolute zero of temperature is ascertained if some assumptions with regard to a set of state variables can be made.

Belgiorno [5] provides a fairly recent summary of most aspects concerning the third law. For a more detailed introduction to the third law, for a discussion of its status in current literature, and for a comprehensive list of literature concerning the third law, we refer the reader to [5]. Belgiorno discusses further conditions ensuring the validity of Nernst's formulation of the entropic version in [6]. Kox [7] analyzes the early history of the third law and the related confusion as to its correct formulation. There are some recent publications on the third law concerned with the problem of its failure to comply with black hole thermodynamics (e.g., [8,9]). Wreszinski and Abdalla [10] provide a formulation of the third law using the alternative approach to equilibrium thermodynamics described by Lieb and Yngvason in [11]. Klimenko [12] concerns himself mainly with the issue of teaching the third law, but he also proposes special types of the Carnot–Nernst cycle as perpetual motion machines of the third kind. Finally, there are some recent publications concerned with the emergence of the laws of thermodynamics from quantum considerations, either from a point of view of nonequilibrium quantum statistical mechanics [13] or from a point of view of (non-statistical) quantum thermodynamics [14]. (The third law is discussed in [14] but not in [13].)

There are several motivations for this paper, for example:

(1) The present absolute entropy scale relies on absolute zero of temperature as a reference, whereas the present absolute enthalpy scale relies on (more or less arbitrary) standard states and conditions [15]. This paper allows obtaining absolute enthalpy values which rely on absolute zero of temperature.
(2) It should not be necessary to postulate the behaviour of a physical quantity once this quantity has been properly defined. This strongly suggests that the definition of entropy as obtained from the Kelvin formulation should also allow ascertaining the behaviour of the entropy at absolute zero.
(3) The third law is often said to be less fundamental than the other laws (e.g., [7]) or to have a non definitively posed status (e.g., [5]). This justifies looking for alternatives. Also, entropy is often