A RIGOROUS DEFINITION OF ENTROPY WITHOUT THE CONCEPTS OF
HEAT AND OF EMPIRICAL TEMPERATURE

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EXTENDED ABSTRACT

Several methods for the definitions of thermodynamic temperature and entropy have been developed in the literature: three of these methods deserve a special attention.

The traditional method is based on the Kelvin-Plank statement of the second law, and employs the concepts of empirical temperature, heat, heat reservoir (or thermal reservoir). One of the best presentations of this method is due to Fermi [1]. A different approach was proposed by Carathéodory [2] and deepened or simplified by several other authors, such as P.T. Landsberg, H.A. Buchdahl, L.A. Turner, F.W. Saers [3-6]. Carathéodory’s approach is based on the concept of adiabatic accessibility, through which the existence of equivalence classes of mutually-adiabatically-accessible stable equilibrium states of a system can be established, together with an order relation between these classes. A recent contribution to the definition of entropy with an approach similar to that of Carathéodory is due to Lieb and Yngvason [7].

The third approach is that developed by the Keenan school of thermodynamics [8, 9]. This approach is based on the concept of stable equilibrium states and on a statement of the second law which asserts the existence and the uniqueness of a stable equilibrium state of any system, with given amounts of constituents and given values of the parameters and of the energy.

On the other hand, the Carathéodory-derived approaches are very abstract. Most of them, especially the most rigorous [7], focus on the conditions for establishing the existence of an entropy function, but do not define a simple operational method to associate entropy values with the states under exam. The approach of the Keenan School is an interesting attempt to reach logical rigor while keeping the operational character of the traditional method; in the form given in Ref. [9], it does not employ either the concept of heat or that of empirical temperature.

Recently, Beretta and Zanchini developed an improved version of the Keenan-school formulation of the foundations of thermodynamics [10, 11]. This approach, with some new refinements, is presented here. Further possible improvements, under study, are outlined.

The improvements already obtained, with respect to Ref. [9], are the following. The basic definitions of system, state, isolated system, separable system are stated more rigorously. The definition of entropy is given directly, without the intermediate step of availability. The assumptions (or postulates) are split so that each independent statement is a separate assumption. An important distinction between the definition of entropy difference (as well as of energy difference) between a pair of states of a closed system and that between a pair of states of an open system is pointed out: the latter is based on conventions on the entropy (energy) values of the elementary species in their reference states.

The domain of validity of the definition of entropy is that of validity of the assumptions, to be determined by further investigations. A general validity for all the states of every system is not claimed. On the other hand, no limitation to the potential domain of validity of the definition has yet been stated rigorously.