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LETTER TO THE EDITOR

An equivalent theorem of the Nernst theorem

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Abstract. It is proved that on the basis of the second law of thermodynamics, the Nernst theorem and the conclusion that the heat capacities tend to zero as the temperature approaches absolute zero can be derived from each other. In the process of the proof, it is not necessary to appeal to the unattainability of absolute zero. Therefore, the conclusion that the heat capacities tend to zero as the temperature approaches absolute zero is an equivalent theorem of the Nernst theorem.

In many thermodynamics books, it has been proved that it can be derived from the Nernst theorem that the heat capacities tend to zero as the temperature approaches absolute zero (Hsieh 1975, Kestin 1979), but it has not been proved that the former can be derived from the latter. It is even asserted in several books (e.g., Beattie and Oppenheim 1979) that we *cannot* derive the Nernst theorem from the conclusion that the heat capacities tend to zero as the temperature approaches absolute zero and from the second law of thermodynamics. Thus many people have mistakenly assumed that these are not equivalent theorems. In fact, both can be derived from each other without invoking the law of unattainability of absolute zero. In this letter we shall prove, on the basis of the second law of thermodynamics, that the Nernst theorem *can* be derived from the conclusion that the heat capacities tend to zero as the temperature approaches absolute zero. This will be helpful to readers in acquiring a deeper understanding of the third law of thermodynamics.

For a general thermodynamic system, the fundamental equation of thermodynamics may be expressed as

$$dU = T\,dS + \sum_i Y_i\,dy_i \tag{1}$$

where U is the internal energy of the system, S is the entropy of the system, T is the absolute temperature, y_i $(i = 1, 2, \ldots)$ are generalised coordinates, and Y_i are their corresponding generalised forces. From (1), one obtains

$$C_y = T(\partial S/\partial T)_y \tag{2}$$

where y represents all generalised coordinates. C_y is the heat capacity when y is not varied. From (2), the entropy of the system may be written as

$$S = S(T, y) = S(T_0, y) + \int_{T_0}^{T} (C_y/T)\,dT. \tag{3}$$

According to the conclusion that the heat capacities tend to zero as the temperature approaches absolute zero

$$\lim_{T\to 0} C_y = 0 \tag{4}$$

we have (Kestin 1979) that

$$C_y \leqslant AT^m \tag{5}$$

when T is appropriately low, where m is an appropriate positive constant and A is a function of y. Then we have

$$0 \leqslant \int_0^T (C_y/T)\,\mathrm{d}T \leqslant \int_0^T AT^{m-1}\,\mathrm{d}T = AT^m/m \tag{6}$$

so the integral $\int_0^T (C_y/T)\,\mathrm{d}T$ is convergent. Therefore, (3) can be written simply as (Wang 1955, Callen 1960):

$$S = S(0, y) + \int_0^T (C_y/T)\,\mathrm{d}T. \tag{7}$$

Now, the thermodynamic system is assumed to evolve along a quasistatic reversible adiabatic process. Then, y varies from y' to y''. Correspondingly, T varies from T_1 to T_2, whereas S does not vary. From (7), we have

$$S(0, y') + \int_0^{T_1} (C_y(y', T)/T)\,\mathrm{d}T = S(0, y'') + \int_0^{T_2} (C_y(y'', T)/T)\,\mathrm{d}T. \tag{8}$$

Then

$$S(0, y'') - S(0, y') = \int_0^{T_1} (C_y(y', T)/T)\,\mathrm{d}T - \int_0^{T_2} (C_y(y'', T)/T)\,\mathrm{d}T. \tag{9}$$

First assume that

$$S(0, y'') > S(0, y'). \tag{10}$$

Then we can find a positive T_1 such that the equation

$$\int_0^{T_1} (C_y(y', T)/T)\,\mathrm{d}T < S(0, y'') - S(0, y') \tag{11}$$

holds. Then the integral $\int_0^{T_2} (C_y(y'', T)/T)\,\mathrm{d}T$ would be negative which is a contradiction since C_y and T_2 must not be negative. Similarly we can show that the assumption $S(0, y'') < S(0, y')$ also leads to a contradiction. Consequently we must have $\Delta S \to 0$ as $T \to 0$ which is the Nernst theorem.

So far, we have proved that the Nernst theorem can be derived from the conclusion that the heat capacities tend to zero as the temperature approaches absolute zero. Because it has been widely proved that the latter can be derived from the former and because the law of unattainability of absolute zero is not used in the course of the two proofs, we may therefore well say that both the Nernst theorem and the conclusion that the heat capacities tend to zero as the temperature approaches absolute zero can be derived from each other, and it is thus clear that they are equivalent theorems.

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