

Nernst's postulate derived directly from the vanishing heat capacity at zero temperature

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Abstract. – We show that Nernst's original postulate follows directly from a vanishing heat capacity at zero temperature without further constraints. Thermodynamic stability of the system along with the independence of the other thermodynamic state variables ensures a sufficiently slow temperature approach to zero that the change of the entropy of the system vanishes at least as rapidly as the heat capacity.

Body. – Nernst's original postulate from 1907 states that the entropy change in any isothermal process approaches zero as the temperature approaches zero. This is the version of the postulate we will prove based only on the assumption that the heat capacity of the system vanishes in the same limit.

For a general thermodynamic system the fundamental equation of thermodynamics and the entropy differential may be expressed as

$$dU = T dS + \sum_i Y_i dy_i \quad (1)$$

and

$$dS = \left(\frac{\partial S}{\partial T} \right)_y dT + \sum_i \left(\frac{\partial S}{\partial y_i} \right)_{T, y_{j \neq i}} dy_i, \quad (2)$$

where U , S , T , y_i and Y_i ($i = 1, 2, \dots$) are, respectively, the internal energy, entropy, absolute temperature, generalized coordinates, and generalized forces of the system, while the unindexed subscript y represents all generalized coordinates. From eq. (1) one obtains [1–5]

$$\left(\frac{\partial S}{\partial U} \right)_y = \frac{1}{T}, \quad (3)$$

$$\left(\frac{\partial^2 S}{\partial U^2} \right)_y = -\frac{1}{T^2} \left(\frac{\partial T}{\partial U} \right)_y = -\frac{1}{T^2 C_y} < 0, \quad (4)$$

where C_y is the heat capacity when y is held constant. Since $(\partial^2 S/\partial U^2)_y < 0$ is the equilibrium stability condition of a general thermodynamic system, this implicitly requires that the heat capacity C_y is always positive. Equation (4) indicates that the curve of the relation between S and U when y remains constant, *i.e.* the curve $S_y(U)$, can only be concave.

Some thermodynamic systems can appear at negative absolute temperature, *e.g.* in connection with population inversion as in a laser. It follows from eq. (3) and the concavity of $S_y(U)$ that such negative absolute temperatures are hotter than any positive absolute temperature, while $T = +0\text{K}$ is the limit of low temperatures. It is worthwhile noticing that such an important conclusion is a direct deduction from thermodynamic stability and the first and second laws of thermodynamics, but not the third one. In the following we will not use negative temperatures, only the fact that $+0\text{K}$ is the lowest possible temperature.

Now we assume that a small reversible adiabatic cooling process is carried out by the change of the generalized coordinates from y' to y'' . The temperature change of the system in the process is $(\Delta T)_S$, and we get from eq. (2), with $\Delta S = 0$,

$$\sum_i \left(\frac{\partial S}{\partial y_i} \right)_{T, y_j \neq i} (\Delta y_i)_S = -C_y \frac{(\Delta T)_S}{T}, \quad (5)$$

where $(\Delta y_i)_S = y_i'' - y_i'$. Due to the conclusion above that no temperature can be colder than $+0\text{K}$, any reversible adiabatic cooling process which starts from a certain positive absolute temperature T cannot produce a temperature drop $-(\Delta T)_S$ larger than the starting temperature T . Consequently, $-(\Delta T)_S$ approaches zero at least as quickly as $T \rightarrow 0$, and in any reversible adiabatic cooling process $-(\Delta T)_S/T$ can only be a positive number less than or equal to unity. Now, since the heat capacities by assumption tend to zero as the temperature approaches absolute zero,

$$\lim_{T \rightarrow 0} C_y = 0, \quad (6)$$

one obtains

$$\lim_{T \rightarrow 0} \sum_i \left(\frac{\partial S}{\partial y_i} \right)_{T, y_j \neq i} (\Delta y_i)_S = 0 \quad (7)$$

from eq. (5).

It is worthwhile pointing out that when T is very small, so is $-(\Delta T)_S$, whereas $(\Delta y_i)_S$ need not be small. It may have a finite value which can be varied by controlling the exterior conditions, whether the temperature of the system is high or low [1,2]. In fact, this observation has been used extensively in practice. For example, when the relation between the principle of unattainability of absolute zero temperature and Nernst's postulate is discussed, it is emphasized in many thermodynamics textbooks [2-5] that no matter how low T is, one can make use of a reversible adiabatic process to lower the temperature of the system still further, *e.g.*, by varying the magnetic field of a paramagnetic system from H' to H'' , or, in general, y of a thermodynamic system can be varied from y' to y'' . Thus, since the variations $(\Delta y_i)_S$ are mutually independent (although related to $(\Delta T)_S$ through eq. (5) for a reversible adiabatic process), eq. (7) can only be satisfied if each of the terms in the sum vanishes separately, *i.e.*

$$\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial y_i} \right)_{T, y_j \neq i} = 0. \quad (8)$$

This statement is not limited to an adiabatic process which we used solely to illustrate the point that the $(\Delta y_i)_S$ need not approach zero even though C_y does, thus necessitating the vanishing

of each $\partial S/\partial y_i$. Consequently, the right-hand side of eq. (2) vanishes for any isothermal process in the limit of zero temperature, the first term because the process is isothermal, the second term due to eq. (8), and we have

$$\lim_{T \rightarrow 0} (\Delta S)_T = 0. \quad (9)$$

Thus it is proved that Nernst's original postulate can be derived from eq. (6) by deduction from only the first and second laws of thermodynamics. Note that the argument does not in any way rely on empirical data or experience, just mathematics.

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