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COMMENT

A comment on Nernst's theorem

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Abstract. It is shown by example that the condition $C_v \to 0$ as $T \to 0$ is not enough to establish Nernst's theorem.

In this comment an example is constructed which shows that the heat capacity C_v at constant volume can vanish as the absolute zero ($T=0$) is approached without the entropy of the system approaching a constant value (Nernst's theorem). This would appear to contradict a recent result (Yan and Chen 1988).

For simplicity we chose the ideal gas equation $pv = NkT$ for our system but the heat capacities C_v, C_p are not assumed to be constants. Integration of the Maxwell equation $(\partial S/\partial v)_T = (\partial p/\partial T)_v = Nk/v$ then gives

$$S(v, T) = Nk \ln[v/D(T)] \tag{1}$$

where $-Nk \ln D(T)$ is the 'constant' of integration. Consider two choices:

$$D(T) = \begin{cases} N[(\gamma-1)B/kT]^{1/(\gamma-1)} & (2) \\ (N/c)\exp(-kT/2b) & (3) \end{cases}$$

where B, b, c, γ are constants and $\gamma \equiv C_p/C_v$. Relation (2) leads to the ideal gas of constant heat capacity, for one has

$$S = Nk\left(\ln\frac{v}{N} + (\gamma-1)^{-1}\ln\frac{kT}{(\gamma-1)B}\right)$$

$$\mathrm{d}S = \frac{(\gamma-1)^{-1}Nk}{T}\,\mathrm{d}T + \frac{Nk}{V}\,\mathrm{d}v.$$

It follows from $(\partial U/\partial S)_v = T$ and Joule's law (U depends only on the temperature) that

$$U = (\gamma-1)^{-1}NkT.$$

Normally one takes $\gamma = \frac{5}{2}$. These are of course well known results.

Relation (3) leads similarly to

$$S = Nk\left(\ln\frac{cv}{N} + \frac{kT}{2b}\right)$$

$$\mathrm{d}S = \frac{Nk}{v}\,\mathrm{d}v + \frac{Nk^2}{2b}\,\mathrm{d}T$$

and hence

$$U = Nk^2T^2/4b.$$

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In this case

$$C_v/Nk = kT/2b$$

so that

$$S = Nk\ln(cv/N) + C_v.$$

Hence in the case (3) $C_v \to 0$ as $T \to 0$ (but C_p remains non-zero) while the entropy near $T = 0$ still depends on v in contradiction with Nernst's theorem (see also Landsberg 1961, p 199).

Equation (7) of Yan and Chen

$$S(T, v) = S(0, v) + \int_0^T (C_v/T)\,dT$$

is identically satisfied by our example, showing that such an equation cannot be made the basis of a proof that $C_v \to 0$ implies $\Delta S \to 0$.

The search for a proof that $C_v \to 0$ implies $\Delta S \to 0$ as $T \to 0$ goes back to Nernst. For a brief summary, see Simon (1951) who remarked 'that the attempt to derive the 3rd law from the 2nd plus the vanishing of the specific heats has not succeeded'. For some systems like Grüneisen-law solids (Klein and Glass 1958) or ideal quantum gases (Landsberg 1954) the proof that $C_v \to 0$ and $\Delta S \to 0$ as $T \to 0$ is, however, straightforward.

An alternative and more intuitive way of looking at this matter is to note the following. For unattainability of the absolute zero and also for Nernst's theorem the $S(x, T)$ diagram is as shown in figure 1, x being typically the volume. For a diagram such as figure 2 both theorems fail: the absolute zero can be attained adiabatically by

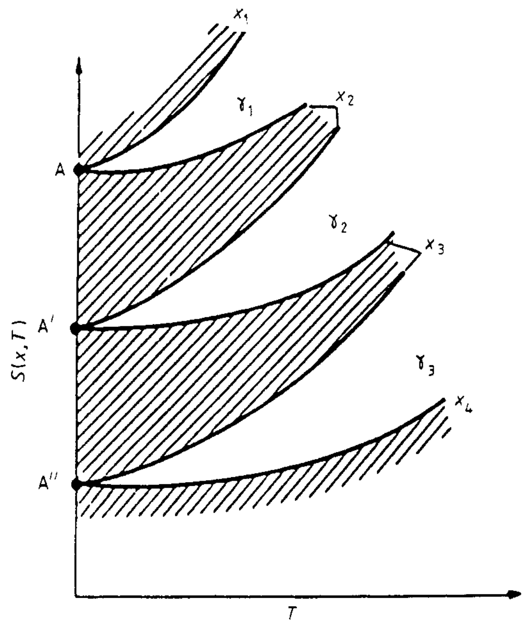

Figure 1. The unattainability theorem and Nernst's theorem are both fulfilled for the regions γ_1, γ_2, γ_3 delimited by the shaded areas and by the characteristic values x_1, x_2, x_3, x_4 of x.

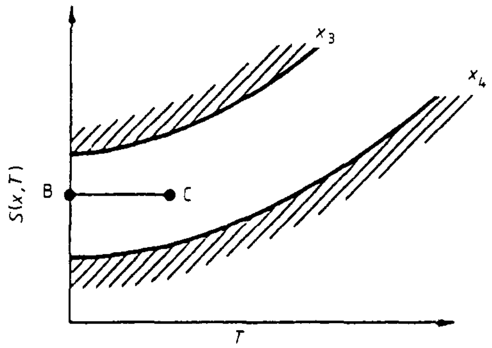

Figure 2. The two theorems are violated for this $S(x, T)$ diagram.

process CB, and also

$$\lim[S(x, T) - S(x', T)] \neq 0.$$

However, $C_x \equiv T(\partial S/\partial T)_x$ vanishes at $T=0$ in both cases. Hence, again, $C_v = 0$ at $T=0$ does not imply Nernst's theorem.

References

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