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A concise rebuttal on a concise proof of the equivalence of the Nernst theorem and the heat capacity statement of the third law of thermodynamics

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The interplay between adiabatic cooling and isothermal ordering is analyzed to rebut the proof of the equivalence of the Nernst theorem and the heat capacity statement of the third law presented by Su and Chen.

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Recently Su and Chen[1] addressed the relationship between the Nernst theorem and the vanishing of the specific heat and presented a "concise proof" of their equivalence. The issue had raised some confusion and clarification earlier.[2; 3; 4; 5; 6] In classical thermodynamics the Nernst theorem states that "the isotermal change of entropy $(\Delta S)_T$ vanishes as the temperature vanishes". It follows evidences extracted from chemical equilibrium, phase equilibrium and the vanishing of thermal expansion coefficients. Formally the theorem sets the vanishing of $(\partial S/\partial X)_T = (\partial Y/\partial T)_X = (\partial^2 A/\partial T\partial X)$, where X, Y are suitable mechanical parameters such as the pressure/volume or the magnetic field/magnetization, and A is a suitable thermodynamic potential like the free energy or the free enthalpy.

The vanishing of the specific heats is another kind of evidence in itself. It refers to the fact that the susceptibility $C_x/T = (\partial S/\partial T)_X = -(\partial^2 A/\partial T^2)$ has a ceil —ie does not become exceedingly large— as the temperature vanishes.

The domain of $(\partial S/\partial T)_X$ is restricted by stability: it must be positive. The domain of $(\partial S/\partial X)_T$ is not restricted by stability: it can be positive, negative or zero at any given temperature.

In their concise argument Su and Chen analyze the interplay between the isothermal change of entropy $(\Delta S)_T$, the adiabatic change of temperature $(\Delta T)_s$, and the iso-X change of entropy $(\Delta S)_X$.

The interplay between this three quantities is given by Euler's chain rule:

$$\left(\frac{\partial S}{\partial T}\right)_X \left(\frac{\partial T}{\partial X}\right)_S \left(\frac{\partial X}{\partial S}\right)_T = -1, \tag{1}$$

which is geometrically shown in figure 1.

The physical interpretation of figure 1 is of interest here. Let us suppose that E_1 is located at the lowest temperature ever achieved. In order to further cool the sample we need to peform adiabatic cooling, as noted by Su and Chen, but prior to that we need to reduce isothermically the entropy of the sample. The point is that $E_1 \to E_3$ is not possible through the $X = X_1$ line. Instead, the path $E_1 \to E_2 \to E_3$ is mandatory. From that the susceptibility is given as:

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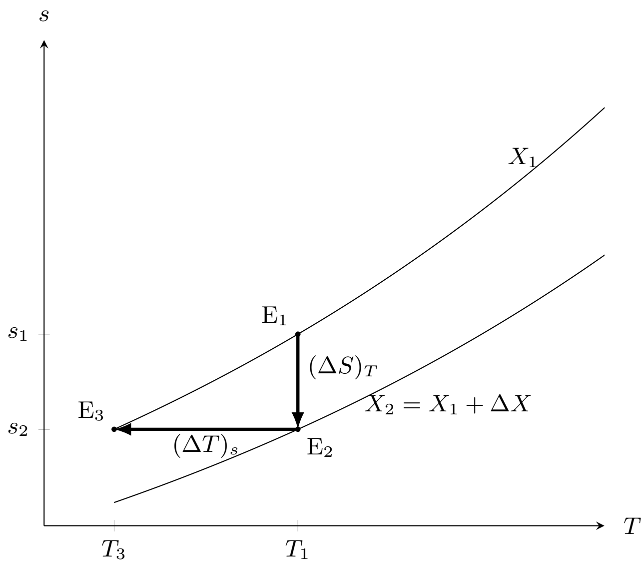

Figure 1 A two stroke process in which X is restored. First an isothermal decrease of the entropy $(\Delta S)_T$, followed by an adiabatic cooling $(\Delta T)_S$. The susceptibility $(\partial S/\partial T)_X$ (> 0) is given by the ratio $(\Delta S)_T/(\Delta T)_s$ when $\Delta X \to 0$. With the equilibrium state E_1 at the lowest available temperature T_1, this is the only way to step further into lower temperatures T_3.

$$\left(\frac{\partial S}{\partial T}\right)_X = \lim_{\Delta X\to 0}\frac{(\Delta S)_T}{(\Delta T)_s} = -\lim_{\Delta X\to 0}\frac{S(T,X+\Delta X)-S(T,X)}{T(S,X+\Delta X)-T(S,X)}. \tag{2}$$

Equation (2) is similar to Equation (7) by Su and Chen only that, C_x/T is expressed as $(\partial S/\partial T)_X$.

In Equation (2) the numerator vanishes as the temperature vanishes following the Nernst theorem. The denominator vanishes as the temperature vanishes as per the unattainability statement, which, in fact, follows from the Nernst theorem.

However, there is no way to elucidate which of the two in Equation (2) —$(\Delta T)_S$ and $(\Delta S)_T$— vanishes faster. With $C_x = T(\partial S/\partial T)_x = T(\Delta S)_T/(\Delta T)_s$, there is no way to elucidate whether heat capacities vanish or not.

In their argument Su and Chen set $-(\Delta T)_s < T$, which is correct, and make $(\Delta T)_S/T$ finite from which they get C_x vanishes. But the premise is only possible if $(\Delta T)_S$ vanishes as fast as T. No proof of that is given. Indeed no proof of that exists until further evidence —such as the vanishing of C_X— is introduced.

The bottom line is that in $S(T,X)$ the dependence on X is independent from the dependence on T. Therefore, the condition $\lim_{T\to 0}(\partial S/\partial X)_T = 0$ does not force any further condition on $\lim_{T\to 0}(\partial S/\partial T)_X$.[6; 7; 8]

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REFERENCES

[1] S. Su and J. Chen, A concise proof of the equivalence of the Nernst theorem and the heat capacity statement of the third law of thermodynamics, Modern Physics Letters A **37**, 2250246 (2022).
[2] Z. Yan and J. Chen, An equivalent theorem of the Nernst theorem, Journal of Physics A: Mathematical and General **21**, L707 (1988).
[3] P. T. Landsberg, A comment on Nernst's theorem, Journal of Physics A: Mathematical and General **22**, 139 (1989).
[4] I. Oppenheim, Comment on 'an equivalent theorem of the Nernst theorem', Journal of Physics A: Mathematical and General **22**, 143 (1989).
[5] A. J. Kox, Confusion and clarification: Albert Einstein and Walther Nernst's heat theorem, 1911–1916, Studies in History and Philosophy of Science Part B: Studies in History and Philosophy of Modern Physics **37**, 101 (2006).
[6] A. Y. Klimenko, Teaching the third law of thermodynamics, The Open Thermodynamics Journal **6**, 1 (2012).
[7] M. Planck, *Treatise on Thermodynamics* (Longmans, 1927 (Repub Dover 1990)).
[8] J. M. Martín-Olalla and A. Rey de Luna, Universal restrictions to the conversion of heat into work derived from the analysis of the Nernst theorem as a uniform limit, Journal of Physics A: Mathematical and General **36**, 10.1088/0305-4470/36/29/303 (2003).