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1989 J. Phys. A: Math. Gen. 22 143

(http://iopscience.iop.org/0305-4470/22/1/022)

J. Phys. A: Math. Gen. **22** (1989) 143–144. Printed in the UK

COMMENT

Comment on 'An equivalent theorem of the Nernst theorem'

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Received 3 August 1988

Abstract. In a letter entitled 'An equivalent theorem of the Nernst theorem', Yan and Chen purport to derive the third law of thermodynamics on the basis of the second law and the conclusion that heat capacities tend to zero as the temperature approaches absolute zero. The proof is faulty and the third law is an additional postulate in thermodynamics.

The argument presented by Yan and Chen (1988) is faulty and the equivalence of the Nernst theorem and the second law of thermodynamics with the postulate that heat capacities tend to zero as the temperature approaches absolute zero has not been established. Indeed, as stated in the book by Beattie and Oppenheim (1979), the Nernst theorem *cannot* be derived in this fashion.

We consider a simple closed, one-component, one-phase system and choose temperature, T, and pressure, p, as our independent variables. The change of the entropy in this system is given by

$$\mathrm{d}S = \left(\frac{C_p}{T}\right)\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p \tag{1}$$

where C_p is the heat capacity at constant pressure and

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p. \tag{2}$$

It follows from (1) that

$$S(T, p) = S(T_0, p) + \int_{T_0}^{T} \frac{C_p(T', p)}{T'}\,\mathrm{d}T'. \tag{3}$$

We consider a reversible adiabatic process from T_1, p' to T_2, p''. Thus

$$S(T_1, p') = S(T_2, p'') \tag{4}$$

and along the adiabatic path

$$\mathrm{d}p = \frac{C_p/T}{(\partial V/\partial T)_p}\,\mathrm{d}T. \tag{5}$$

We assume that the sign of the coefficient $(\partial V/\partial T)_p$ does not change during this process or during the temperature range from T_0 to T_1. Thus, since C_p is non-negative, if $(\partial V/\partial T)_p > 0$ and $T_2 > T_1$, then $p'' > p'$ and $S(T_0, p'') < S(T_0, p')$; if $(\partial V/\partial T)_p < 0$ and

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$T_2 > T_1$, then $p'' < p'$ and $S(T_0, p'') < S(T_0, p')$. Finally, if $(\partial V/\partial T)_p > 0$ and $T_2 < T_1$, then $p'' < p'$ and $S(T_0, p'') > S(T_0, p')$; if $(\partial V/\partial T)_p < 0$ and $T_2 < T_1$, then $p'' > p'$ and $S(T_0, p'') > S(T_0, p')$.

From (3) and (4), we obtain

$$S(T_0, p') + \int_{T_0}^{T_1} \frac{C_p(T, p')}{T} \, \mathrm{d}T = S(T_0, p'') + \int_{T_0}^{T_2} \frac{C_p(T, p'')}{T} \, \mathrm{d}T \tag{6}$$

and

$$S(T_0, p'') - S(T_0, p') = \int_{T_0}^{T_1} \frac{C_p(T, p')}{T} \, \mathrm{d}T - \int_{T_0}^{T_2} \frac{C_p(T, p'')}{T} \, \mathrm{d}T \tag{7}$$

which are equations (8) and (9) of Yan and Chen (1988) with $T_0 = 0$.

We note that a consequence of the third law which follows from (2) is that

$$\lim_{T \to 0} \left(\frac{\partial V}{\partial T} \right)_p = 0 \tag{8}$$

but this knowledge is unavailable to us at the moment.

For $T_2 > T_1$, $S(T_0, p'') < S(T_0, p')$ and there are no useful conclusions from (7). If $T_1 > T_2$, $S(T_0, p'') > S(T_0, p')$ (equation (10) of Yan and Chen). However, since $T_1 > T_2$, we cannot find a T_1 small enough such that

$$\int_0^{T_1} \frac{C_p(T, p')}{T} \, \mathrm{d}T < S(0, p'') - S(0, p')$$

(equation (11) of Yan and Chen). Thus, there is no contradiction inherent in (7) as $T_0 \to 0$ and one cannot show that $S(0, p') = S(0, p'')$.

The essential point missed in the argument of Yan and Chen is that p'' is not arbitrary; it is determined by T_1, T_2 and p'.

References

Beattie J A and Oppenheim I 1979 *Principles of Thermodynamics* (Amsterdam: Elsevier) p 235

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