Essence of the Third Law: The Delineation of Two Forms of Thermodynamics (*)(**).

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Summary. — The third law is generalized to the effect that for systems in internal thermodynamic equilibrium, either the entropy tends to zero with the temperature, implying a state of complete order, or the entropy tends to its maximum value as the temperature increases without limit, indicating a state of complete disorder.

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1. – The third law for conventional thermodynamics.

The third law, or Nernst's postulate, is stated conventionally as «the contribution to the entropy of a system by each aspect which is in internal thermodynamic equilibrium tends to zero at absolute zero» [1]. It is usually contended that the appreciation of the Nernst postulate had to await the discovery of quantum statistics, since classical statistics did not obey the postulate [2].

We shall state the third law in such a way that it incorporates the classical ideal gas. The entropy density of quantum statistics is, in energy units where Boltzmann's constant is unity,

\[ s(x) = x \ln \left( \frac{y + x}{x} \right) \pm y \ln \left( \frac{y + x}{y} \right), \]

where «+» and «−» signs refer to Bose-Einstein (BE) and Fermi-Dirac (FD) statistics, respectively. The number of quanta or particles in a given frequency interval is denoted by x. For BE statistics, y represents the number of oscillators in a

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given frequency interval per unit volume, while for FD statistics it represents the total number of states available. In the small-\(x\) limit, (1) reduces to

\[
(2) \quad s(x) = -x \ln \left( \frac{x}{y} \right).
\]

The entropy density, (2), satisfies the inequality

\[
(3) \quad s((1 - \lambda)x_1 + \lambda x_2) \geq (1 - \lambda)s(x_1) + \lambda s(x_2),
\]

where the parameter \(\lambda \in [0, 1]\). The inequality in (3) asserts that every point of the chord connecting the end points \(x_1\) and \(x_2\) lies below the curve. Such a function is said to be concave\[3\]. Moreover, since \(s(0) = 0\), we can choose one of the end points of the interval at the origin, say \(x_1 = 0\). Then the criterion of concavity reduces to\[4\]

\[
(4) \quad s(\lambda x) \geq \lambda s(x).
\]

Then, setting \(\lambda x = x_a\) and \((1 - \lambda)x = x_b\) such that \(x_a + x_b = x\), the sum of (4) and \(s((1 - \lambda)x) = (1 - \lambda) s(x)\) gives

\[
(5) \quad s(x_a) + s(x_b) \geq s(x_a + x_b),
\]

showing that the quantum statistical entropy is subadditive.

The same conclusion can be reached by the concavity criterion

\[
(6) \quad s''(x) < 0,
\]

where the prime denotes differentiation, and the third law

\[
(7) \quad s(0) = 0 \quad \text{for} \quad T = 0.
\]

The temperature is given by the second law

\[
(8) \quad s'(x) = \frac{\chi}{T},
\]

where \(\chi\) is the intensive variable conjugate to \(x\). Taken together (6) and (7) imply that \(s(x)/x\) is a decreasing function (theorem 127, p. 99 of ref.\[3\]). This means that

\[
x^2 \frac{d}{dx} \left( \frac{s(x)}{x} \right) = xs'(x) - s(x) \leq 0,
\]

or

\[
(9) \quad s(x)/x \geq s'(x).
\]

This is a sufficient condition that the entropy density satisfy (5) (theorem 103, p. 83 of ref.\[3\]). Hence,

\[
[\text{Concavity (6) + Third law (7) \Rightarrow Subadditivity (5)}]
\]

We can even do away with the third law, in the form (7), and show that subadditivity follows directly from the concavity of the entropy. The concavity of the