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On the Validity of a Global Thermodynamic Inequality

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The theorem of Tykodi[1] reads as follows:

Theorem. For any two equilibrium states (T_1, P_1), (T_2, P_2) of a fixed mass of a pure (one-component) fluid such that $P_1 = P_2 = P$ and such that in the equilibrium phase diagram in the T, P plane the straight line segment joining the states (T_1, P) and (T_2, P) does not intersect a two-phase coexistence line, it is always true that

$$V_1 - T_1(\partial V_1/\partial T_1)_p + T_2(\partial V_1/\partial T_1)_p > 0$$

or equivalently, when $(\partial V_1/\partial T_1)_p \neq 0$,

$$T_2 > T_1 - (1/\alpha_1) = T_1'$$

where $\alpha = (\partial V/\partial T)_p/V$ is the thermal expansion coefficient.

What is the physical significance of this inequality? It would imply that a thermodynamic system in state (T_1, V_1, P) cannot pass to another isobaric state (T_2, V_2, P) of the same phase unless $T_2 > T_1'$—a truly remarkable statement.

The inequality defines the locus (an isobar in the V, T plane) of allowable equilibrium states[2] that the system may pass to from its initial state (T_1, V_1, P). States with $T > T_1'$ are allowed while those with $T \leqslant T_1'$ are forbidden.

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[1] Xerox Corporation, Rochester, New York.

[2] The real or actual isobaric equilibrium states of the same phase that the system may attain must be a subset of the theoretically allowable states defined by the theorem.

Clearly, if the initial state is outside the range of allowable states, the theorem is *false* because the system would have to pass through forbidden states to reach the range of allowable states (an equilibrium state is connected to all other equilibrium states of the same phase). This situation occurs if $T_1 < T_1'$, or equivalently, if $\alpha_1 < 0$. There are examples of pure fluids with negative thermal expansion coefficients; a notable one is water between 0° and 4°C at atmospheric pressure.

It is well known that for an ideal gas, $\alpha = 1/T$. Thus, for an ideal gas, $T_1' = 0$ and the inequality holds. For a real fluid, the theorem is *true* if $0 < \alpha \leqslant 1/T$ since $T_1' \leqslant 0$ for this case (we ignore from consideration those nonclassical systems capable of exhibiting negative absolute temperatures). Although the theorem holds under these conditions and is applicable to many real liquids, it contains no informational content. It is known that the range of allowable states is above absolute zero; the bound provided by the theorem does not improve our knowledge of the system.

The most interesting case obtains when $\alpha > 1/T$. Under these conditions, the initial state is within the range of allowable states ($T_1 > T_1'$) and the theorem places a positive lower bound ($T_1' > 0$) on the minimum temperature that the system may attain without changing phase.[3] Unfortunately, a proof of the theorem for this case has not been found.

In summary, the theorem is false if $\alpha < 0$; it is true, but possesses no informational content, if $0 < \alpha \leqslant 1/T$. It is also trivially true if $\alpha = 0$. Only when $\alpha > 1/T$ does the theorem potentially provide new information about the fluid in question; however, no proof for the theorem has been found for this case. A cursory examination of real gases that obey a van der Waals equation of state indicate that the condition $\alpha \geqslant 1/T$ is satisfied.

REFERENCE

1. R. J. Tykodi, *J. Stat. Phys.* 3:417 (1971).

[3] The best bound is, of course, the maximum value of T'. If the theorem is valid, the maximum value of T' must be less than or equal to the temperature where the isobar intersects the two-phase coexistence line in the VT plane.