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# Questions and Answers

## A GLOBAL THERMODYNAMIC INEQUALITY

In the course of writing a monograph on nonequilibrium thermodynamics, I found it necessary to consider the following theorem in ordinary, equilibrium thermodynamics[1]:

**Theorem:** For any two equilibrium states $(T_\alpha, P_\alpha)$, $(T_\beta, P_\beta)$ of a fixed mass of a pure (one-component) fluid such that $P_\alpha = P_\beta \equiv P$ and such that in the equilibrium phase diagram in the $T$, $P$ plane the straight-line segment joining the states $(T_\alpha, P)$ and $(T_\beta, P)$ does not intersect a two-phase coexistence line, it is always true that

$$V_\alpha - T_\alpha(\partial V_\alpha/\partial T_\alpha)_P + T_\beta(\partial V_\alpha/\partial T_\alpha)_P > 0$$

or, equivalently, that

$$T_\beta(\partial V_\alpha/\partial T_\alpha)_P - \mu_\alpha C_P(\alpha) > 0$$

where $\mu$ is the Joule–Thomson coefficient, $\mu \equiv (\partial T/\partial P)_H$.

The familiar inequalities of equilibrium thermodynamics ($C_V > 0$, etc.) deal with the local, in-the-small, properties (curvature, etc.) of appropriate thermodynamic surfaces; the inequality in the above theorem, however, deals with the global, in-the-large, features (convexity, etc.) of an appropriate thermodynamic surface. In the time since I first came across this theorem, I have been unable either to prove it or to disprove it.

I therefore wish to call to the attention of the readers of this journal the above theorem and to leave it as a challenge for them:

1. Prove or disprove the theorem.

2. If the theorem can be proved to be true, can it be generalized by dropping one or both of the restrictive conditions?

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[1] R. J. Tykodi, *Thermodynamics of Steady State*, The Macmillan Co., New York, 1967, pp. 59–61, 168.