Some similar results have been reported for binary systems. In his analysis of critical lines predicted by van der Waals' equation, van Konynenburg (1968, p. 44) has shown that critical points can be computed in binary mixtures at unstable points. Heidemann and Mandhane (1973) have calculated free energy of mixing curves for binary liquid-liquid mixtures described by the NRTL equation that show critical points occurring where neighboring points are unstable.

NOTATION

C_v = heat capacity at constant volume
G^E = excess Gibbs free energy
m = $n + 2$
n = number of components
N = total moles
N_j = moles of j
P = pressure
R = gas constant
$\underline{S}$ = total entropy
T = temperature
$\underline{U}$ = total internal energy
$\underline{V}$ = total volume
x_j = mole fraction substance j
$y^{(k)}$ = kth order Legendre transform

Greek Letters

α = parameter in Equation (1)
μ_j = chemical potential of j

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Reply

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Dr. Heidemann raises an interesting point. The key sentences are those which precede Equation (21) ". . . one can state that the necessary and sufficient criterion of stability is

$$y^{(m-2)}_{(m-1)(m-1)} > 0 \qquad (21)$$

In other words, if any $y^{(m-2)}_{(m-1)(m-1)}$ is positive, then all $y^{(k-1)}_{kk}$ ($k = 1, \ldots, m-1$) are positive and the system is stable."

Taken out of context, the statement is incorrect. In the discussion preceding the sentences in question, we try to make the following points:

1. On p. 1201, "Only stable states are amenable to experimental study." Thus, we position ourselves in a *stable* region and, by perturbing the system, we attempt to locate the boundaries where the system becomes unstable.

2. In stable regions, for a n-component system,

$$y^{(k-1)}_{kk} > 0, \quad k = 1, \quad \ldots, \quad n+1$$

This result is our Equation (19) and Dr. Heidemann's Equation (14).

3. As one searches for the boundaries of the stable system, we state that the *first* criterion to be violated is $y^{(n)}_{(n+1)(n+1)}$, that is, when this derivative becomes zero, the system has reached the limit of stability.

4. Finally, we claim that if the system is unstable, then by inference, it is not amenable to further study.

In the ternary-system examples given by Dr. Heidemann (Figures 1 and 2), if we begin the search for the limit of stability by starting in a stable region, then it is clear that if we move in any direction, the system first becomes unstable when $y^{(3)}_{44}$ becomes negative.

Thus, the sentence in question should have been stated more correctly as: "Generalizing, when starting from a region of known stability, one can state that the necessary and sufficient criterion of the limit of stability is

$$y^{(m-2)}_{(m-1)(m-1)} = 0 \qquad (21)''$$