LITERATURE CITED

Bartotin, J. N., and D. Thomas, "Kinetic and electron microscope studies dealing with an artificial peroxidase membrane," *J. Histochem. Cytochem.*, **22**, 1048 (1974).

Broun, G., D. Thomas, G. Gellf, D. Domurado, A. M. Berjonneau, and C. Guillon, "New methods of crosslinking enzyme molecules into a water insoluble matrix: properties after insolubilization," *Biotechnol. Bioeng.*, **15**, 359 (1973).

Goldman, R., L. Goldstein, and E. Katchalski, "Water-insoluble enzyme derivatives and artificial enzyme membranes" in *Biochemical Aspects of Reactions on Solid Supports,* George R. Stark (ed.), Academic Press, New York and London (1971).

Gryskiewicz, J., "Insoluble Enzymes," *Folia Biologica.*, **19**, 119 (1971).

Ryu, D. Y., R. Fuchs, and A. E. Humphrey, "Scale-up Method for Fermentation Processes based on Oxygen Transfer Rate," *Biotechnol. Bioeng. Symp.*, **4**, 427 (1973).

Thomas, D., C. Bourdillon, G. Broun, and J. P. Kernevez, "Kinetic behavior of enzymes immobilized in artificial membranes: inhibition and reversibility effects," *Biochem.*, **13**, 2995 (1974).

Topiwala, H. H., and G. Hamer, "A Study of Gas Transfer in Fermenters," *Biotechnol. Bioeng. Symp.*, **4**, 547 (1973).

Weetall, H. H., "Immobilized Enzymes Corning Glass Compendium," Corning Glass Works, Corning, New York 14830.

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The Criteria for Thermodynamic Stability

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Beegle, Modell, and Reid (1974b), in their recent discussion of the use of Legendre transforms to establish thermodynamic stability, have made an erroneous statement. The error is contained in the following sentences quoted from the paper.

". . . 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 $y^{(m-2)}_{(m-1)(m-1)}$ is positive, then all y^{k-1}_{kk} ($k = 1, \ldots, m-1$) are positive and the system is stable. The condition at which the system reaches the limit of stability is the one at which $y^{(m-2)}_{(m-1)(m-1)}$ becomes zero."

However,

1. The condition stated is not sufficient to assure stability; that is, the second sentence is not always true.

2. It is possible to have $y^{(m-2)}_{(m-1)(m-1)} = 0$ at points which do not lie on the limit of stability. While it is true that this condition is satisfied at all points which lie on the limit of stability, the converse is not true.

A COUNTER-EXAMPLE

A ternary liquid-liquid equilibrium problem will be analyzed at this point to illustrate that (21) is not sufficient to establish stability. The excess Gibbs free energy is taken to be

$$\frac{G^E}{RT} = \alpha(x_A x_B + x_A x_C + x_B x_C) \qquad (1)$$

According to Tisza (1951, 1961, 1966) and to Beegle et al. (1974b), at stable points four inequalities must be satisfied. The internal energy is used for y^0. That is,

$$y^0 = \underline{U}(\underline{S}, \underline{V}, N_A, N_B, N_C) \qquad (2)$$

Then, at stable points (see Beegle et al. (1974a) for mechanics of handling the Legendre transforms)

$$y^0{}_{11} = \frac{T}{C_v} > 0 \qquad (3)$$

$$y^1{}_{22} = -\left(\frac{\partial P}{\partial V}\right)_{T,N_A,N_B,N_C} > 0 \qquad (4)$$

$$y^2{}_{33} = \left(\frac{\partial \mu_A}{\partial N_A}\right)_{T,P,N_B,N_C} > 0 \qquad (5)$$

and

$$y^3{}_{44} = \left(\frac{\partial \mu_B}{\partial N_B}\right)_{T,P,\mu_A,N_C} > 0 \qquad (6)$$

In the absence of other information, it is presumed that (3) and (4) are satisfied. For (5) and (6) we find, respectively, that

$$\frac{N}{RT} y^2{}_{33} = \frac{1 - x_A}{x_A} - 2\alpha[(1 - x_A)^2 - x_B x_C] \qquad (7)$$

and

$$\frac{N}{RT} y^3{}_{44} = \frac{1 - x_B}{x_B} - 2\alpha[(1 - x_B)^2 - x_A x_C] - \frac{[-1 + \alpha x_C + 2\alpha(x_A x_B - x_C{}^2)]^2}{\frac{N}{RT} y^2{}_{33}} \qquad (8)$$

Equation (8) is a specific instance of the "generalized derivative operator" introduced by Beegle et al. (1974b). That is,

$$y^{(k-1)}_{kk} = y^{(k-2)}_{kk} - (y^{(k-2)}_{k(k-1)})^2 / y^{k-2}_{(k-1)(k-1)} \qquad (9)$$

which in this case becomes

$$y^3{}_{44} = \left(\frac{\partial \mu_B}{\partial N_B}\right)_{T,P,N_A,N_C} - \frac{\left(\frac{\partial \mu_A}{\partial N_B}\right)^2_{T,P,N_A,N_C}}{y^2{}_{33}} \qquad (10)$$

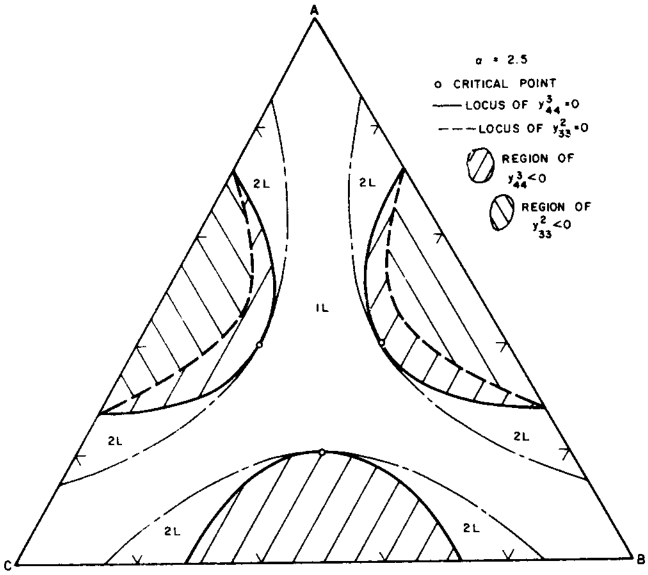

Fig. 1. Regions of instability and phase boundaries in the system described by Equation (1); $\alpha = 2.5$.

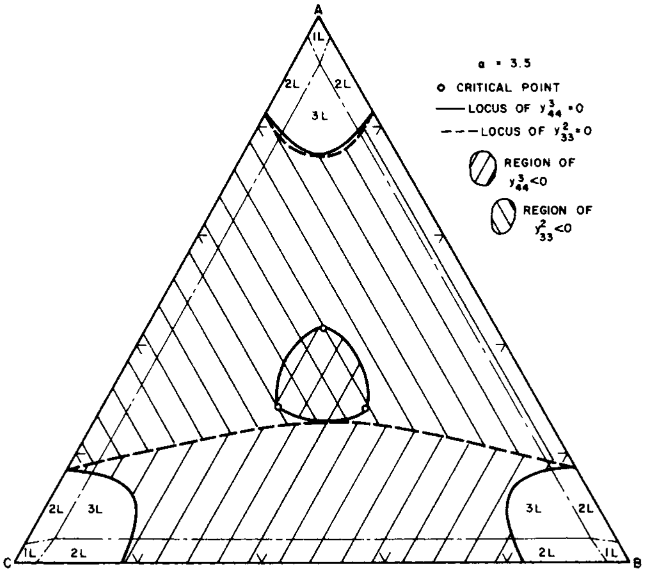

Fig. 2. Regions of instability and phase boundaries in the system described by Equation (1); $\alpha = 3.5$.

It can be seen that any point at which $y^2{}_{33}$ becomes zero will be a point of discontinuity in $y^3{}_{44}$, across which $y^3{}_{44}$ must change sign.

The phase diagram and the loci $y^2{}_{33} = 0$ and $y^3{}_{44} = 0$ when $\alpha = 2.5$ have been plotted in Figure 1. The phase diagram contains three separate binodal curves. Along the locus $y^2{}_{33} = 0$, $y^3{}_{44}$ has a discontinuity, changing from negative to positive. There is, therefore, a large region which is unstable to infinitesimal perturbations, as indicated by $y^2{}_{33} < 0$, in which $y^3{}_{44}$ is positive. According to Beegle et al. (1974b) there should be no such region. If one checked only criterion (21), one would conclude that the system is stable in a large region of unstable points.

It could be pointed out that the determinant

$$y^3{}_{44} \cdot y^2{}_{33} = \begin{vmatrix} \left(\frac{\partial \mu_A}{\partial N_A}\right)_{T,P,N_B,N_C} & \left(\frac{\partial \mu_A}{\partial N_B}\right)_{T,P,N_A,N_C} \\ \left(\frac{\partial \mu_B}{\partial N_A}\right)_{T,P,N_B,N_C} & \left(\frac{\partial \mu_B}{\partial N_B}\right)_{T,P,N_A,N_C} \end{vmatrix} \tag{11}$$

does not exhibit discontinuities and does not change sign inside the region of instability in Figure 1. It was this determinant that was recommended by Gibbs (1875, p. 132) for use in determining the limits of stability, rather than the equivalent of $y^3{}_{44}$. Apparently in anticipation of the kind of discontinuities observed in Figure 1, Gibbs comments ". . . it is possible that the denominator in the fraction may vanish as well as the numerator for an infinitesimal change of phase in which the quantities indicated are constant." However, it should not be concluded that the sign of $y^3{}_{44} \cdot y^2{}_{33}$ is alone sufficient to determine stability. Continuing with the ternary system described by Equation (1), we take $\alpha = 3.5$. The phase diagram and the loci $y^2{}_{33} = 0$ and $y^3{}_{44} = 0$ have been plotted in Figure 2. The phase diagram exhibits three separate regions of two-phase equilibrium and a triangular region of three liquid phases in equilibrium. As before $y^3{}_{44}$ has discontinuities along $y^2{}_{33} = 0$ changing from negative to positive. There is quite a large region of unstable points at which $y^3{}_{44} > 0$ and $y^2{}_{33} < 0$. In this case, however, there is also a locus of points $y^3{}_{44} = 0$ which lies completely inside the region $y^2{}_{33} < 0$. At all the points inside this roughly triangular locus the product $y^3{}_{44} \cdot y^2{}_{33}$ is positive. Yet all these points are unstable.

Furthermore, all the points lying on this roughly triangular locus obey $y^3{}_{44} = 0$ yet they are not at the limit of stability.

CORRECTED CONCLUSIONS

The correct conclusions to be drawn from the generalized analysis of stability presented by Tisza (1966) are a good deal more slack than those presented by Beegle et al. (1974b). These could be stated as follows:

I. The necessary and sufficient criterion of stability in an n component system is that

$$y_{kk}^{(k-1)} > 0; \quad k = 1, \ldots, n + 1 \tag{12}$$

II. All points on the limit of stability obey

$$y^{(n)}_{(n+1)(n+1)} = 0 \tag{13}$$

IMPLICATIONS IN THE COMPUTATION OF CRITICAL POINTS

In a three-component system, critical points, in general, lie at the intersections of $y^3{}_{44} = 0$ and $y^3{}_{444} = 0$ (Tisza, 1966, p. 159, or equivalently, Gibbs, 1875, p. 131). With y^0 as defined by (2),

$$y^3{}_{444} = \left(\frac{\partial^2 \mu_B}{\partial N_B{}^2}\right)_{T,P,\mu_A,N_C} \tag{14}$$

This result has been used to compute critical points (plait points) in the liquid-liquid equilibrium system of Figures 1 and 2. In Figure 1, the computed points lie at the tops of the three binodal curves, as expected. In Figure 2, however, there are three points satisfying $y^3{}_{44} = 0$ and $y^3{}_{444} = 0$ which fall at unstable points.

The possibility that spurious critical points may exist should be taken into account by anyone attempting to compute plait points in liquid-liquid equilibrium systems. From the conclusions reported by Beegle et al. (1974b), one would infer that such spurious solutions could not occur.

Heidemann and Mandhane (1975) have presented a number of ternary liquid-liquid equilibrium diagrams in which spurious critical points have been found.

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

LITERATURE CITED

Beegle, B. L., M. Modell, and R. C. Reid, "Legendre Transforms and Their Application in Thermodynamics," *AIChE J.*, **20**, 1194 (1974).
———., "Thermodynamic Stability Criterion of Pure Substances and Mixtures," *ibid.*, 1200 (1974).
Gibbs, J. W., "On the Equilibrium of Heterogeneous Substances," in *Trans. Conn. Acad. III*, 108 (1876), as reprinted, *The Scientific Papers of J. Willard Gibbs, Volume One, Thermodynamics*, Dover, New York (1961).
Heidemann, R. A., and J. M. Mandhane, "Some Properties of the NRTL Equation in Correlating Liquid-Liquid Equilibrium Data," *Chem. Eng. Sci.*, **28**, 1213 (1973).
———., "Ternary Liquid-Liquid Equilibria: The van Laar Equation," *ibid.*, **30**, 425 (1975).
Tisza, Laszlo, "On the General Theory of Phase Transitions," in *Phase Transformations in Solids*, R. Smoluchowski, J. E. Mayer, and W. A. Weyl (eds.), Wiley, New York (1951).
———., "The Thermodynamics of Phase Equilibrium," *Annals Physics*, **13**, 1 (1961).
———., *Generalized Thermodynamics*, M.I.T. Press, Cambridge, Mass. (1966).
van Konynenburg, P., "Critical Lines and Phase Equilibria in Binary Mixtures," Ph.D. thesis, Univ. California, Los Angeles (1968).

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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

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

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

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