$y^{(j)}$ = jth Legendre transform of the Fundamental Equation $= f(\xi_1, \ldots, \xi_j, x_{j+1}, \ldots, x_m)$

$y_k{}^{(j)}$ = first-order partial derivative of the jth Legendre transform with respect to x_k (if $k > j$) or ξ_k (if $k \leq j$)

$y^{(j)}_{ik}$ = second-order partial derivative of $y^{(j)}$ with respect to either $x_i (i > j)$ or $\xi_i (i \leq j)$ and $x_k (k > j)$ or $\xi_k (k \leq j)$

μ_j = chemical potential of component j $\equiv (\partial \underline{U}/\partial N_j)_{\underline{S},\underline{V},N_1,\ldots[N_j]\ldots,N_n}$

ξ_k = $(\partial y^{(0)}/\partial x_k)_{x_1,\ldots[x_k]\ldots,x_m}$ or $(\partial y^{(j)}/\partial x_k)_{\xi_1,\ldots,\xi_j,x_{j+1},\ldots[x_k]\ldots,x_m}$ if $k > j$

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Thermodynamic Stability Criterion for Pure Substances and Mixtures

Criteria are derived to specify the limit of stability for pure material and multicomponent thermodynamic systems. Through the use of Legendre transforms, the criteria may be expressed in a very simple form that only involves the determination of positiveness of a single second-order partial derivative of a potential function. Alternate and equivalent criteria are shown to result from a simple reordering of the independent variables in the Fundamental Equation of Gibbs. Certain criteria that are often stated as necessary conditions of stability (for example, $C_v > 0$) are shown to be insufficient for specifying the *limit* of stability; that is, a system will always become unstable for other reasons before C_v can attain a negative value.

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SCOPE

Thermodynamic systems are often categorized as being stable or unstable. The latter, by definition, cannot exist and must undergo a change to one or more stable phases. Of interest here are the criteria (or criterion) which one may use to track a stable system as it approaches an unstable state, the cross-over condition being defined as the limit of stability.

The basic concept is that an isolated system in stable equilibrium possesses the maximum possible entropy or, equivalently, the least energy (at constant entropy). By a series expansion around the state variables, inequalities can be developed to indicate whether or not a system is indeed in stable equilibrium or, more importantly, under what conditions would a given system be expected to reach the stability limit.

These inequalities are developed in their general form and use is made of Legendre transform theory to simplify the resulting inequalities.

CONCLUSIONS AND SIGNIFICANCE

For a n-component system, it is shown that a single criterion sufficies to define the stability limit. This criterion is

$$y^{(n)}_{(n+1)(n+1)} \begin{cases} > 0 & \text{(stable systems)} \\ = 0 & \text{(at the limit of stability)} \end{cases}$$

Here, $y^{(n)}$ is the nth Legendre transform and $y^{(n)}_{(n+1)(n+1)}$ represents the second-order partial derivative of $y^{(n)}$ with respect to the $n + 1$ variable (see Beegle et al., 1974). For a pure component system ($n = 1$), the energy is a function of the entropy, volume, and mass. Depending upon the ordering of these variables, six equivalent criteria can be written from the relation given above (see Table 1). The most common of these is $-(\partial P/\partial \underline{V})_{T,N} > 0$. It is shown that other cited criteria (for example, $C_v > 0$), although necessary for stable states, are not sufficient criteria to determine the limit of stability.

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Applying the criterion to binary and ternary systems, one again finds very simple inequalities to employ in testing stability. Again there result multiple and equivalent criteria depending upon the ordering of the variables of entropy, volume, and mole numbers (see Tables 2 and 3). It is shown that multicomponent systems have wider domains of instability than pure components.

Finally, generalized determinant inequalities are formulated so that the stability criterion shown above may be written in terms of other Legendre transforms if available data suggest that derivatives of these transforms could be more readily obtained.

Critical states are not discussed; they are the subject of a subsequent paper.

Thermodynamic systems can be broadly classified as being either stable or unstable. However, only stable systems exist and are amenable to experimental study. By the very definition, unstable systems will spontaneously change to form one or more different, stable systems.

As state variables such as temperature, pressure, composition, etc. vary, it is important to possess criteria that can be used to judge when a given stable system might become unstable. Although several thermodynamic texts introduce such criteria (Prigogine and Defay, 1954; Callen, 1960; Münster, 1970; Modell and Reid, 1974; Rowlinson, 1969), none present a general treatment of the subject and, in some cases, the criteria given are too restrictive.

In the present paper we derive simple yet necessary and sufficient criteria for stability. The criteria are illustrated for pure components, binary, and multicomponent systems. Reference is made to the first paper of this series (Beegle et al., 1974) wherein some aspects of Legendre transform theory were developed.

STABILITY CONCEPTS—A SIMPLE EXAMPLE

To focus on a particularly simple example, consider a subcooled, single-phase pure liquid in an isothermal environment (see Figure 1.) As the pressure is reduced to the saturation pressure (b), one might expect boiling to result. Usually this event does occur and vapor at (c) appears. However, if the liquid is reasonably free of nucleation motes and the container is made from an ideal smooth surface, we can superheat the liquid by passing into the dome toward (d). Reducing the pressure still further, we find experimentally that there is a limit to how far we can lower the pressure before a spontaneous phase change occurs. Often, however, we can attain very high *negative* pressures before the transition appears. The path from (b) to (d) is termed *metastable* indicating there exists a more stable phase (that is, vapor) but, with respect to small perturbations on the system, no significant change results. Although the lowest attainable pressure depends on our skill as experimentalists, we will show that there does exist a true thermodynamic limit where even the smallest further reduction in pressure leads to a phase change. We call this condition the *limit of intrinsic stability;* on Figure 1, it is shown schematically at (e).

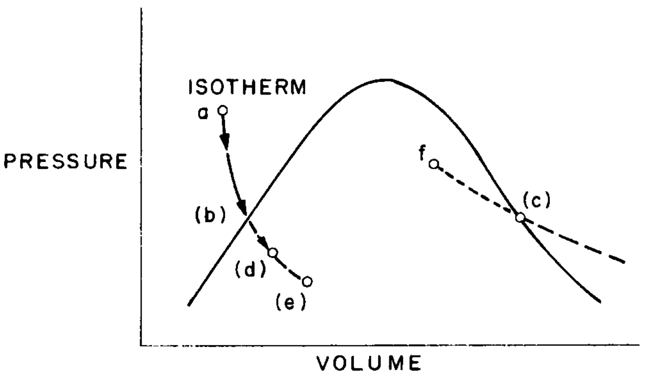

Fig. 1. Illustration of superheated or supercooled metastable states.

The point to be emphasized in this simple example is that the liquid phase is intrinsically stable in the domain from (a) through (b) and (d) up to (e). At (e), at least one of the stability criteria is violated.

Similar reasoning could be invoked for an isothermal compression of saturated vapor at (c) to some intrinsic limit at (f) where even a slight increase in pressure would lead to the disappearance of the vapor phase.

GENERAL CRITERIA OF EQUILIBRIUM AND STABILITY

Either the entropy or energy representation may be employed to express the general criteria (Gibbs, 1876, 1878; Modell and Reid, 1974). Both are completely equivalent. We choose the latter since derivatives in the energy system are more commonly employed in classical thermodynamics. For a system in a stable equilibrium state at constant total entropy, volume, and mass, the total internal energy should be a minimum. Alternatively, any small perturbation should result in an increase in total internal energy. For such small perturbations, $\underline{U}$ can be expanded in a Taylor series

$$\Delta \underline{U} = \delta \underline{U} + \delta^2 \underline{U} + \ldots > 0 \qquad (1)$$

For equilibrium to exist,

$$\delta \underline{U} = 0 \qquad (2)$$

and for the system to be stable

$$\delta^p \underline{U} > 0 \qquad (3)$$

where $\delta^p \underline{U}$ is the lowest nonvanishing variation. The constraints on Equation (1) are that, for all variations, the total entropy, volume, and mass be unchanged.

The Fundamental Equation of thermodynamics may be expressed as

$$\underline{U} = U(\underline{S}, \underline{V}, N_1, \ldots, N_n) \qquad (4)$$

but since this implies some particular ordering of terms, we will use, instead, the subscripted variables x_1, x_2, ... where any ordering is allowed. Also, since we shall employ Legendre transforms in the treatment, then, to allow ready reference to the previous paper (Beegle et al., 1974), we shall substitute $y^{(0)}$, for $\underline{U}$. Then Equations (1) through (4) become

$$\left.\begin{array}{l} \Delta y^{(0)} = \delta y^{(0)} + \delta^2 y^{(0)} + \ldots > 0 \\ \delta y^{(0)} = 0 \\ \delta^p y^{(0)} > 0 \\ y^{(0)} = f(x_1, \ldots, x_m) \end{array}\right\} \qquad (5)$$

The equilibrium equality, Equation (2), is not pertinent to the present development. It is most useful to formulate criteria of equilibrium for systems containing semipermeable membranes, or where phase and chemical reaction equilibria are being studied (Modell and Reid, 1974). Of more interest here is the stability inequality, Equation (3). Except at critical points, only second-order terms need be employed. (At critical points, as shown in a subsequent paper, the second-order variation is zero and higher-order terms must be considered to delineate stability.) The second-order variation may be expanded around the state variables:

$$\delta^2 y^{(0)} = K \sum_{i=1}^{m} \sum_{j=1}^{m} y_{ij}^{(0)} \delta x_i \delta x_j > 0 \qquad (6)$$

where K is a positive numerical constant and will be dropped from the subsequent treatment which evaluates only the sign of $\delta^2 y^{(0)}$. For a stable system, $\delta^2 y^{(0)}$ is positive; for an unstable system, it is negative. Thus, the limit of intrinsic stability is the point at which $\delta^2 y^{(0)}$ becomes zero.

Since the variations δx_i and δx_j may be either positive or negative, it is more convenient to rearrange the summations in a sum-of-squares form. As indicated in Appendix I,* the result is

$$\sum_{i=1}^{m} \sum_{j=1}^{m} y_{ij}^{(0)} \delta x_i \delta x_j = \sum_{k=1}^{m} \frac{\mathcal{D}_k}{\mathcal{D}_{k-1}} \delta Z_k^2 > 0 \qquad (7)$$

with

$$\delta Z_k = \sum_{j=k}^{m} \frac{\mathcal{G}_{kkj}}{\mathcal{D}_k} \delta x_j \qquad (8)$$

and

$$\mathcal{D}_k = \begin{vmatrix} y_{11}^{(0)} & y_{12}^{(0)} & \cdots & y_{1k}^{(0)} \\ y_{21}^{(0)} & y_{22}^{(0)} & \cdots & y_{2k}^{(0)} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ y_{k1}^{(0)} & y_{k2}^{(0)} & \cdots & y_{kk}^{(0)} \end{vmatrix} \qquad (9)$$

$$\mathcal{G}_{kij} = \begin{vmatrix} y_{11} & y_{12} & \cdots & y_{1,k-1} & y_{1j} \\ y_{21} & y_{22} & \cdots & y_{2,k-1} & y_{2,j} \\ \cdot & \cdot & & \cdot & \cdot \\ \cdot & \cdot & & \cdot & \cdot \\ y_{k-1,1} & y_{k-1,2} & \cdots & y_{k-1,k-1} & y_{k-1,j} \\ y_{i1} & y_{i2} & \cdots & y_{i,k-1} & y_{ij} \end{vmatrix} \quad i, j \geqq k \qquad (10)$$

$\mathcal{D}_k$ is a k by k principal subdeterminant of the matrix of coefficients of the quadratic. $\mathcal{G}_{kij}$ is $\mathcal{D}_k$ with all $y_{kr}^{(0)}$ terms in the kth row replaced by $y_{ir}^{(0)}$ and all $y_{rk}^{(0)}$ terms in the kth column replaced by $y_{rj}^{(0)}$. (r is any integer between 1 and k.)

Equation (7) can be greatly simplified with the use of Legendre transforms. As shown in the first paper of this set,° the ratio of matrices $\mathcal{D}_k/\mathcal{D}_{k-1}$ can be expressed as

$$\mathcal{D}_k/\mathcal{D}_{k-1} = y_{kk}^{(k-1)} \qquad (11)$$

where $y^{(k-1)}$ is the $(k-1)$ Legendre transform of $y^{(0)}$ into $(\xi_1, \ldots, \xi_{k-1}, x_k, \ldots, x_m)$ space. In a similar manner,°°

$$\mathcal{G}_{kkj}/\mathcal{D}_k = y_{kj}^{(k)} \quad j > k \qquad (12)$$

and

$$\mathcal{G}_{kkk}/\mathcal{D}_k = 1 \qquad (13)$$

As an illustrative example, employing the Fundamental Equation, Equation (4), choose a pure material where $m = n + 2 = 3$. Let $\underline{S} = x_1$, $\underline{V} = x_2$, and $N = x_3$. Then, from Equations (6), (7), (8), (11), and (12), (dropping the positive constant K),

$$\delta^2 y^{(0)} = \mathcal{D}_1 \delta Z_1^2 + (\mathcal{D}_2/\mathcal{D}_1) \delta Z_2^2 + (\mathcal{D}_3/\mathcal{D}_2) \delta Z_3^2 \qquad (14)$$

where

$$\mathcal{D}_1 = y_{11}^{(0)} = U_{SS}$$

$$\mathcal{D}_2/\mathcal{D}_1 = y_{22}^{(1)} = A_{VV}$$

$$\mathcal{D}_3/\mathcal{D}_2 = y_{33}^{(2)} = G_{NN}$$

$$\begin{aligned} \delta Z_1 &= (\mathcal{G}_{111}/\mathcal{D}_1) \delta x_1 + (\mathcal{G}_{112}/\mathcal{D}_1) \delta x_2 \\ &\quad + (\mathcal{G}_{113}/\mathcal{D}_1) \delta x_3 \\ &= \delta x_1 + y_{12}^{(1)} \delta x_2 + y_{13}^{(1)} \delta x_3 \\ &= \delta \underline{S} + A_{TV} \delta \underline{V} + A_{TN} \delta N \end{aligned}$$

$$\begin{aligned} \delta Z_2 &= (\mathcal{G}_{222}/\mathcal{D}_2) \delta x_2 + (\mathcal{G}_{223}/\mathcal{D}_3) \delta x_3 \\ &= \delta x_2 + y_{23}^{(2)} \delta x_3 \\ &= \delta \underline{V} + G_{PN} \delta N \end{aligned}$$

$$\delta Z_3 = (\mathcal{G}_{333}/\mathcal{D}_3) \delta x_3 = \delta x_3 = \delta N$$

Thus, for a pure material,

$$\begin{aligned} \delta^2 y^{(0)} &= U_{SS} [\delta \underline{S} + A_{TV} \delta \underline{V} + A_{TN} \delta N]^2 \\ &\quad + A_{VV} [\delta \underline{V} + G_{PN} \delta N]^2 + G_{NN} (\delta N)^2 \end{aligned} \qquad (15)$$

The criterion for stable equilibrium may then be expressed either as Equations (7) and (8), or by their equivalent,

$$\sum_{k=1}^{m} y_{kk}^{(k-1)} \delta Z_k^2 > 0 \qquad (16)$$

$$\delta Z_k = \delta x_k + \sum_{j=k+1}^{m} y_{kj}^{(k)} \delta x_j \qquad (17)$$

An important simplification remains to be carried out for Equation (16). Consider the last term in the sum, that is, $y_{mm}^{(m-1)} \delta Z_m^2$. The partial Legendre transform $y^{(m-1)}$ is a function of $(\xi_1, \xi_2, \ldots, \xi_{m-1}, x_m)$. Since

$$y_{mm}^{(m-1)} = \left(\frac{\partial^2 y^{(m-1)}}{\partial x_m^2} \right)_{\xi_1, \ldots, \xi_{m-1}} = \left(\frac{\partial \xi_m}{\partial x_m} \right)_{\xi_1, \ldots, \xi_{m-1}} \qquad (18)$$

then $y_{mm}^{(m-1)}$ must be zero since, by specifying $(m-1)$ intensive variables $(\xi_1, \ldots, \xi_{m-1})$, all other intensive variables in a system are fixed. That is, since the second derivative itself is a derivative of an intensive property with respect to an extensive property at constant $(m-1)$ intensive variables, then it must be identically zero. Thus the upper limit on the sum in Equation (17) should be $(m-1)$, not m.

The final result may be stated concisely: for a stable system

$$y_{kk}^{(k-1)} > 0 \quad k = 1, \ldots, m-1 \qquad (19)$$

The limit of intrinsic stability is defined by the condition at which any one of these second-order partial derivatives becomes zero.

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* Appendices I and II have been deposited as Document No. 02493 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., N. Y., N. Y. 10017 and may be obtained for $1.50 for microfiche or $5.00 for photocopies.

° Beegle et al., 1974, Equations (31) and (35).

°° *ibid.*, Equations (32) and (35).

A NECESSARY AND SUFFICIENT CRITERION OF STABILITY

If the generalized derivative operator introduced in Appendix II of Beegle et al. (1974) is employed to reduce $y_{kk}^{(k-1)}$, then

$$y_{kk}^{(k-1)} = y_{kk}^{(k-2)} - (y_{k(k-1)}^{(k-2)})^2 / y_{(k-1)(k-1)}^{(k-2)} \tag{20}$$

From the stability criteria, Equation (19), both $y_{kk}^{(k-1)}$ as well as $y_{(k-1)(k-1)}^{(k-2)}$ must be positive. It is then clear from Equation (20) that $y_{kk}^{(k-2)}$ must also be positive. It may also be noted that $y_{kk}^{(k-2)}$ would have been the coefficient of δZ_k if the ordering of variables x_{k-1} and x_k were to have been reversed. Thus, it is reasonable to expect no unusual behavior from this term as either $y_{kk}^{(k-1)}$ or $y_{(k-1)(k-1)}^{(k-2)}$ is reduced to simulate a system that is approaching the limit of intrinsic stability. An important, logical conclusion may then be drawn. Suppose $y_{(k-1)(k-1)}^{(k-2)}$ decreases toward zero. Equation (20) then indicates that as $y_{(k-1)(k-1)}^{(k-2)}$ decreases, before it can reach the value zero, $y_{kk}^{(k-1)}$ becomes negative. Thus the positive nature of $y_{kk}^{(k-1)}$ is always violated before that of $y_{(k-1)(k-1)}^{(k-2)}$. Generalizing, one can state that the necessary and sufficient criterion of stability is

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

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

The criterion for the limit of stability, Equation (21), may be expressed in several alternate ways. By definition,

$$\begin{aligned} y_{(m-1)(m-1)}^{(m-2)} &\equiv \left(\frac{\partial^2 y^{(m-2)}}{\partial x^2{}_{m-1}} \right)_{\xi_1,\ldots,\xi_{m-2},x_m} \\ &= \left(\frac{\partial \xi_{m-1}}{\partial x_{m-1}} \right)_{\xi_1,\ldots,\xi_{m-2},x_m} \end{aligned} \tag{22}$$

Or, from Equation (11), Equation (21) is equivalent to

$$\mathcal{D}_{m-1} > 0 \tag{23}$$

with $\mathcal{D}_k$ defined by Equation (9). Finally, a most useful and general expression for Equation (21) is that

$$\mathcal{L}_i > 0 \quad 0 \leqq i \leqq m-2 \tag{24}$$

where $\mathcal{L}_i$ is a determinant defined as

$$\mathcal{L}_i \equiv \begin{vmatrix} y_{(i+1)(i+1)}^{(i)} & y_{(i+1)(i+2)}^{(i)} & \cdots & y_{(i+1)(m-1)}^{(i)} \\ y_{(i+2)(i+1)}^{(i)} & y_{(i+2)(i+2)}^{(i)} & \cdots & y_{(i+2)(m-1)}^{(i)} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ y_{(m-1)(i+1)}^{(i)} & y_{(m-1)(i+2)}^{(i)} & \cdots & y_{(m-1)(m-1)}^{(i)} \end{vmatrix} \tag{25}$$

For any i and j between 0 and $m - 2$, $\mathcal{L}_i/\mathcal{L}_j$ is a positive constant and therefore any single $\mathcal{L}_i$ can be used to test stability.

TABLE 1. EQUIVALENT STABILITY CRITERIA FOR A PURE MATERIAL

Ordering of (x_1, x_2, x_3)	Stability criterion
$(\underline{S}, \underline{V}, N)$	$A_{VV} = -(\partial P/\partial \underline{V})_{T,N} > 0$
$(\underline{S}, N, \underline{V})$	$A_{NN} = (\partial \mu/\partial N)_{T,\underline{V}} > 0$
$(\underline{V}, \underline{S}, N)$	$H_{SS} = (\partial T/\partial \underline{S})_{P,N} > 0$
$(\underline{V}, N, \underline{S})$	$H_{NN} = (\partial \mu/\partial N)_{P,\underline{S}} > 0$
$(N, \underline{S}, \underline{V})$	$U'_{SS} = (\partial T/\partial \underline{S})_{\mu,\underline{V}} > 0$
$(N, \underline{V}, \underline{S})$	$U'_{VV} = -(\partial P/\partial \underline{V})_{\mu,\underline{S}} > 0$

Note: Following the convention introduced by Beegle et al. (1974), potential functions in which one mole number is transformed to a chemical potential are denoted by a prime, those in which two mole numbers are transformed are denoted by a double prime, etc. Thus, $\underline{U}' = f(\underline{S}, \underline{V}, \mu_1, N_2, \ldots, N_n)$.

APPLICATIONS TO THERMODYNAMIC SYSTEMS

Pure Substances

In this case, Equation (4) reduces to

$$\underline{U} = \underline{U}(\underline{S}, \underline{V}, N) = U(x_1, x_2, x_3) \tag{26}$$

To apply the criterion of stability, Equation (24), one must first choose the ordering of $\underline{S}$, $\underline{V}$, and N. For example, if $\underline{S} = x_1$, $\underline{V} = x_2$, $N = x_3$, then $y^{(0)} = \underline{U}$, $y^{(1)} = \underline{A}$, and $n = 3$. Only two forms of Equation (24) are possible, that is, when $i = 0$ and $i = 1$.

$\underline{i = 0}$

$$\mathcal{L}_0 = \begin{vmatrix} U_{SS}\, U_{SV} \\ U_{VS}\, U_{VV} \end{vmatrix} > 0 \tag{27}$$

$\underline{i = 1}$

$$\mathcal{L}_1 = A_{VV} > 0 \tag{28}$$

Equations (27) and (28) are completely equivalent criteria.

Usually, however, the $(m - 2)$ transform criterion [that is, Equation (21) or (28)] is employed to delineate the stability criterion. Thus,

$$A_{VV} = \left(\frac{\partial^2 \underline{A}}{\partial \underline{V}^2} \right)_{T,N} = -\left(\frac{\partial P}{\partial \underline{V}} \right)_{T,N} = -\frac{1}{N} \left(\frac{\partial P}{\partial V} \right)_T > 0 \tag{29}$$

Equation (29) expresses the well-known fact that, for stable systems of pure materials, the pressure increases as the volume decreases if the system is constrained to be isothermal and of constant mass.

Yet even Equations (27) and (28) are not unique ways to express the stability criterion for pure materials. Different ordering of the x_1, x_2, x_3 (that is, $\underline{S}$, $\underline{V}$, N) set produces equivalent criteria. In fact, there are six equivalent forms of Equation (21), and these are listed in Table 1. If a pure-component system were to reach the limit of intrinsic stability, all of these criteria would be violated (that is, equal zero) simultaneously, for example at points (e) and (f) in Figure 1.

The criteria shown in Table 1 indicate that when a system is stable, all $y_{kk}^{(k-1)}$ must be positive. In the pure component case, the only other positive term is $y_{11}^{(0)}$ (U_{SS}, U_{VV}, or U_{NN}). For example, $U_{SS} = (\partial^2 \underline{U}/\partial \underline{S}^2)_{\underline{V},N} = (\partial T/\partial \underline{S})_{\underline{V},N} = T/NC_v > 0$. C_v is then positive. As noted previously, but repeated again for reemphasis, U_{SS} never attains a zero or negative value as the system becomes unstable since higher-order criteria (Table 1) approach zero values before lower order terms.

TABLE 2. STABILITY CRITERIA FOR BINARY SYSTEMS OF A AND B

Ordering of (x_1, x_2, x_3, x_4)	Stability criteria
$(\underline{S}, \underline{V}, N_A, N_B)$	$G_{AA} = \left(\dfrac{\partial \mu_A}{\partial N_A}\right)_{T,P,N_B} > 0$
$(\underline{S}, N_A, \underline{V}, N_B)$	$A'_{VV} = -\left(\dfrac{\partial P}{\partial \underline{V}}\right)_{T,\mu_A,N_B} > 0$
$(\underline{S}, N_A, N_B, \underline{V})$	$A'_{BB} = \left(\dfrac{\partial \mu_B}{\partial N_B}\right)_{T,\mu_A,\underline{V}} > 0$
$(\underline{V}, N_A, \underline{S}, N_B)$	$H'_{SS} = \left(\dfrac{\partial T}{\partial \underline{S}}\right)_{P,\mu_A,N_B} > 0$
$(\underline{V}, N_A, N_B, \underline{S})$	$H'_{BB} = \left(\dfrac{\partial \mu_B}{\partial N_B}\right)_{P,\mu_A,\underline{S}} > 0$
$(N_A, N_B, \underline{S}, \underline{V})$	$U''_{SS} = \left(\dfrac{\partial T}{\partial \underline{S}}\right)_{\mu_A,\mu_B,\underline{V}} > 0$
$(N_A, N_B, \underline{V}, \underline{S})$	$U''_{VV} = -\left(\dfrac{\partial P}{\partial \underline{V}}\right)_{\mu_A,\mu_B,\underline{S}} > 0$

where $\underline{A}' = f(T, \underline{V}, \mu_A, N_B)$
$\underline{H}' = f(\underline{S}, P, \mu_A, N_B)$
$\underline{U}'' = f(\underline{S}, \underline{V}, \mu_A, \mu_B)$

Note: Any ordering of (x_1, x_2, x_3, x_4) which differs only in the arrangement of the first two variables and/or in the ordering of N_A, N_B are not shown in this table.

Binary Systems

For a system composed of A and B,

$$\underline{U} = \underline{U}(\underline{S}, \underline{V}, N_A, N_B) \qquad (30)$$

Choosing the $(x_1, \ldots, x_4)$ ordering as given in Equation (30), then the stability limit criterion is simply

$$y_{33}^{(2)} = G_{AA} = \left(\frac{\partial^2 \underline{G}}{\partial {N_A}^2}\right)_{T,P,N_B} > 0 \qquad (31)$$

Or, in a more common form,

$$\left(\frac{\partial \mu_A}{\partial N_A}\right)_{T,P,N_B} > 0 \qquad (32)$$

Different stability criteria may be determined if the ordering of the independent variables in Equation (30) is changed. These are shown in Table 2. As for pure component systems, *all* the criteria are identical, and if a system should reach the limit of intrinsic stability, *all* are violated simultaneously.

The binary stability criterion, Equation (31) [or Equation (32) or any of the forms in Table 2] may not always be particularly convenient to use. For example, P-V-T data or correlations are normally expressed in a pressure explicit equation of state, that is,

$$P = f(\underline{V}, T, N_A, N_B) \qquad (33)$$

In this case, criteria employing the Helmholtz free energy are more desirable. With Equations (24) and (25) and for $i = 1$, $y^{(1)} = \underline{A}$, $x_1 = \underline{S}$, $x_2 = \underline{V}$, $x_3 = N_A$, $x_4 = N_B$,

$$\mathcal{L}_1 = \begin{vmatrix} y_{22}^{(1)} & y_{23}^{(1)} \\ y_{32}^{(1)} & y_{33}^{(1)} \end{vmatrix} = \begin{vmatrix} A_{VV} & A_{VA} \\ A_{VA} & A_{AA} \end{vmatrix} > 0 \qquad (34)$$

where

$$A_V = (\partial \underline{A}/\partial \underline{V})_{T,N} = -P \quad \text{and}$$
$$A_{VV} = (\partial^2 \underline{A}/\partial \underline{V}^2)_{T,N} = -(\partial P/\partial \underline{V})_{T,N}$$
$$A_{VA} = (\partial^2 \underline{A}/\partial \underline{V} \partial N_A) = -(\partial P/\partial N_A)_{T,\underline{V},N_B}$$

and

$$A_{AA} = (\partial^2 \underline{A}/\partial {N_A}^2)_{T,\underline{V},N_B} = (\partial \mu_A/\partial N_A)_{T,\underline{V},N_B}$$
$$= \int_{(\underline{V})}^{\infty} \left(\frac{\partial^2 P}{\partial {N_A}^2}\right)_{T,\underline{V},N_B} d\underline{V} + \frac{RT}{N_A} \qquad (35)$$

Thus all the A_{ij} derivatives may be found given an equation of state of the form shown in Equation (33). [Equation (35) is derived in Appendix II.*]

A binary system becomes unstable over a larger domain than a pure component, that is, Equation (34) is more restrictive than the pure-material criterion, Equation (29). This may be illustrated on Figure 2 where pressure is plotted as a function of specific volume. Equation (33) is assumed to be given by the Redlich-Kwong equation of state (Redlich and Kwong, 1949). The isotherms intersect the curve encompassing the unstable domain (the spinoidal curve) with finite negative slopes. Clearly Equation (29) is not the first criterion to be violated as this binary becomes unstable.

Ternary Systems

The final example illustrated here is a ternary system of A, B, and C. Extrapolation to multicomponent systems is readily accomplished.

For the system to be stable, with $m = 5$, Equation (21) indicates that

$$y_{44}^{(3)} > 0 \qquad (36)$$

or if one should desire to express this criterion using derivatives of the Helmholtz free energy, then with Equation (25), $i = 1$,

$$\mathcal{L}_1 = \begin{vmatrix} A_{VV} & A_{VA} & A_{VB} \\ A_{AV} & A_{AA} & A_{AB} \\ A_{BV} & A_{BA} & A_{BB} \end{vmatrix} > 0 \qquad (37)$$

The second-order derivatives were defined earlier and may be readily determined with a pressure explicit equation of state (see also Appendix II for A_{AA}, A_{BB}, and $A_{AB} = A_{BA}$).

The form of Equation (36) or Equation (37) will, of course, change depending on the ordering of the variables $\underline{S}$, $\underline{V}$, N_A, N_B, and N_C. We show in Table 3 some of the equivalent forms. To expand slightly on this point, consider the first form in Table 3. The $y^{(3)}$ Legendre transform may be expressed as (Beegle et al., 1974),

$$y^{(3)} = \underline{G}' = f(T, P, \mu_A, N_B, N_C) = \underline{U} - T\underline{S} + P\underline{V} - \mu_A N_A \tag{38}$$

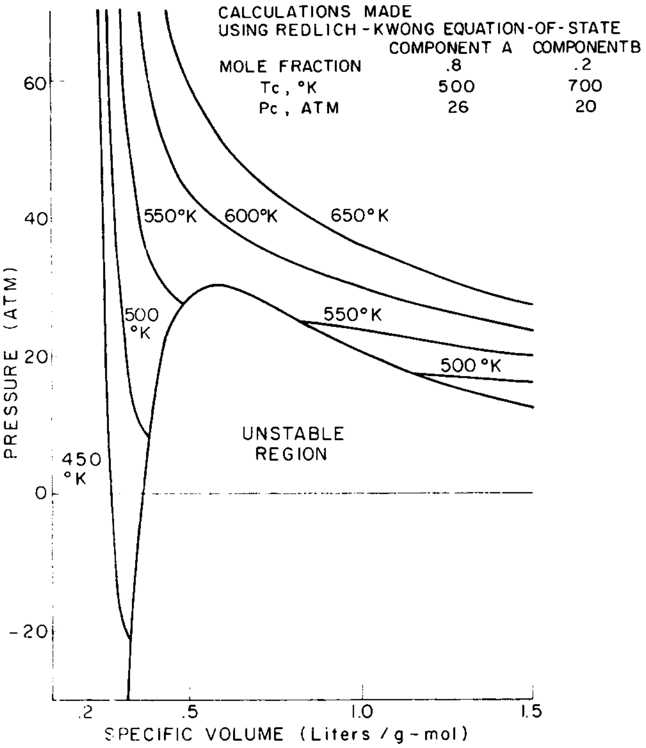

Fig. 2. Unstable region for a binary mixture.

$$dy^{(3)} = d\underline{G}' = -\underline{S}dT + \underline{V}dP - N_A d\mu_A + \mu_B dN_B + \mu_C dN_C$$

$$\left(\frac{\partial y^{(3)}}{\partial x_4}\right)_{\xi_1,\xi_2,\xi_3,x_5} = \left(\frac{\partial \underline{G}'}{\partial N_B}\right)_{T,P,\mu_A,N_C} = G_B' = \mu_B$$

and

$$\left(\frac{\partial^2 y^{(3)}}{\partial x_4^2}\right)_{\xi_1,\xi_2,\xi_3,x_5} = \left(\frac{\partial^2 \underline{G}'}{\partial N_B^2}\right)_{T,P,\mu_A,N_C} = G'_{BB} = \left(\frac{\partial \mu_B}{\partial N_B}\right)_{T,P,\mu_A,N_C} \tag{39}$$

A ternary *P-V-T* plot for a given ternary will be similar to that shown on Figure 2 though the unstable region is now even larger than shown for the binary.

CONCLUDING REMARKS

In this paper we have developed the criterion of stability that is applicable for both pure materials and multicomponent systems. The development utilized Legendre transform theory described in the first paper of this set (Beegle, et al., 1974). It was demonstrated that the criterion of stability could be expressed very simply in terms of a single second-order partial derivative [Equation (21)] of a Legendre transform of the $(m - 2)$ order, m being the number of independent variables. Two other significant results were that: the necessary and sufficient stability criterion could be expressed in various ways depending on the ordering of the independent variables (see Tables 1, 2, 3); and that alternate and equivalent criteria could be developed with lower-order Legendre transforms [Equation (24)] so that pressure explicit equations of state may be readily employed to delineate the limits of intrinsic stability. Note that although an equation of state may fit well thermodynamic data outside the multiphase domain, it may not accurately describe the behavior of real systems in the domain of metastable states unless fitted to adequate experimental data in this domain.

Table 3. Stability Criterion for Ternary Systems of *A*, *B*, *C*

Ordering of $(x_1, x_2, x_3, x_4, x_5)$	Stability criterion
$(\underline{S}, \underline{V}, N_A, N_B, N_C)$	$G'_{BB} = \left(\frac{\partial \mu_B}{\partial N_B}\right)_{T,P,\mu_A,N_C} > 0$
$(\underline{S}, N_A, N_B, \underline{V}, N_C)$	$A''_{VV} = -\left(\frac{\partial P}{\partial V}\right)_{T,\mu_A,\mu_B,N_C} > 0$
$(\underline{S}, N_A, N_B, N_C, \underline{V})$	$A''_{CC} = \left(\frac{\partial \mu_C}{\partial N_C}\right)_{T,\mu_A,\mu_B,\underline{V}} > 0$
$(\underline{V}, N_A, N_B, \underline{S}, N_C)$	$H''_{SS} = \left(\frac{\partial T}{\partial \underline{S}}\right)_{P,\mu_A,\mu_B,N_C} > 0$
$(\underline{V}, N_A, N_B, N_C, \underline{S})$	$H''_{CC} = \left(\frac{\partial \mu_C}{\partial N_C}\right)_{P,\mu_A,\mu_B,\underline{S}} > 0$
$(N_A, N_B, N_C, \underline{S}, \underline{V})$	$U'''_{SS} = \left(\frac{\partial T}{\partial \underline{S}}\right)_{\mu_A,\mu_B,\mu_C,\underline{V}} > 0$
$(N_A, N_B, N_C, \underline{V}, \underline{S})$	$U'''_{VV} = -\left(\frac{\partial P}{\partial \underline{V}}\right)_{\mu_A,\mu_B,\mu_C,\underline{S}} > 0$

where $\underline{G}' = f(T, P, \mu_A, N_B, N_C)$
$\underline{A}'' = f(T, \underline{V}, \mu_A, \mu_B, N_C)$
$\underline{H}'' = f(\underline{S}, P, \mu_A, \mu_B, N_C)$
$\underline{U}''' = f(\underline{S}, \underline{V}, \mu_A, \mu_B, \mu_C)$

Note: Any ordering of $(x_1, x_2, x_3, x_4, x_5)$ which differs only in the arrangement of the first three variables and/or in the ordering of N_A, N_B, N_C are not shown in this table.

In a subsequent paper, the critical point condition will be discussed and the results of the first two papers illustrated with real systems, that is, the spinoidal and critical points of pure components and mixtures will be determined using typical equations of state.

NOTATION

$\underline{A}$ = total Helmholtz free energy
$\mathcal{G}_{ijk}$ = determinant defined in Equation (10)
$\mathcal{D}_k$ = determinant defined in Equation (9)
$\underline{G}$ = total Gibbs free energy
$\underline{H}$ = total enthalpy
$\mathcal{L}_j$ = determinant defined in Equation (25)
N_j = moles of j
P = pressure
R = gas constant
$\underline{S}$ = total entropy
T = temperature
$\underline{U}$ = total energy
$\underline{V}$ = total volume
x_j = extensive independent variable
$y^{(k)}$ = kth order Legendre transform
Z_k = extensive parameter defined in Equation (8)

Greek Letters

μ_j = chemical potential of j
ξ_j = intensive independent variable that is the conjugate coordinate of x_j

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Charged Membrane Ultrafiltration of Inorganic Ions in Single and Multi-Salt Systems

An experimental study of the ultrafiltration of several ionic inorganic solutes, using a negatively-charged membrane, is detailed. Both single salt and multi-salt systems are investigated in a continuous flow, thin channel unit, with an average transmembrane pressure difference of 2.76×10^5 N/m^2 and a channel Reynolds number of 2800. The solute rejection is predictable to some extent in terms of Donnan ion exclusion theory, and the water flux is dictated by the combined effects of osmotic pressure and membrane-cation interaction.

In the single salt experiments, the anion rejections can be related to the inlet (feed) concentration by power functions of the form: rejection $= 1 - K\,C_i^a$, in which $0 < a < 1.0$. The power a is 0.4 for chloride salts, 0.25 for monovalent oxyanion salts, and 0.1 for divalent oxyanion salts, but a is independent of the cation present (Na^+, Ca^{2+}, or La^{3+}). The constant K is generally a function of both the anion (except in the case of SO_4^{2-}, HPO_4^{2-}, and CrO_4^{2-}) and the cation, being determined by such factors as ion charge density and membrane-cation interaction. The membrane resistance to water flux is found to depend on cation charge and cation radius. For systems containing two or more salts, the presence of a divalent anion decreases the rejection of the monovalent anion. For multi-salt systems, a rejection of Ca^{2+} plus Mg^{2+} of 0.82 and a water flux of 12.9×10^{-4} cm/s (27.2 gal/ft^2-day) are achieved at a transmembrane pressure difference of 4.10×10^5 N/m^2 (4.1 atm), indicating that the process has considerable potential for industrial water softening.

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SCOPE

Ultrafiltration is a pressure-activated membrane process and is generally carried out at low pressures of about 10^5 to 10^6 N/m^2. Ultrafiltration with conventional uncharged anisotropic membranes has been used primarily for the separation of modest molecular weight organic solutes, organic macromolecules, and colloids from