L = length of column
M = quantity of adsorbent
N = total number of adsorbable species present in solution
n = index of time elapsed
P_l = defined in Equation (26)
P_s = defined in Equation (33)
q_i = solid phase concentration of species i
q_{i0} = solid phase concentration in equilibrium with c_{i0}
q_{si} = solid interphase concentration of species i
r = separation factor
T = throughput parameter
t = time
u = flow rate
x_i = dimensionless liquid phase concentration
x_{si} = dimensionless liquid interphase concentration for species i
y_i = dimensionless solid phase concentration for species i
y_{si} = dimensionless solid interphase concentration for species i
Z = dimensionless distance variable
z = distance from column inlet

Greek Letters

ϵ = void fraction of fixed bed
θ = dimensionless time variable
Λ_i = partition coefficient of species i
ρ = bulk density of carbon in column
ξ_i^l = dimensionless liquid phase mass transfer coefficient of species i defined in Equation (6)
ξ_i^s = dimensionless solid phase mass transfer coefficient of species i defined in Equation (7)
ϕ_i = parameter defined as ξ_i^s/ξ_i^l
χ = internal porosity of carbon
χ'_{pore_i} = defined by Equation (57)

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Manuscript received August 30, 1976; revision received January 13, and accepted January 14, 1977.

Limiting Criteria for Intrinsically Stable Equilibrium in Multiphase, Multicomponent Systems

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Necessary and sufficient conditions for intrinsically stable equilibrium in a multiphase, multicomponent body are developed with interfacial effects taken into full account. There is a limiting criterion for intrinsic stability that must be satisfied within every phase, and there is another limiting criterion that must be satisfied on every phase interface. The limits of intrinsic stability for a multiphase, multicomponent body are defined by the failure either of the first criterion within one of the phases or of the second criterion on one of the phase interfaces.

SCOPE

An equilibrium state is stable if it persists following a disturbance. It is intrinsically stable if it persists following a very small disturbance. The prior literature has been concerned with the necessary and sufficient condi-

tions for an intrinsically stable equilibrium within a single phase.

This discussion develops the necessary and sufficient conditions as well as the limiting criteria for an intrinsically stable equilibrium within a multicomponent, multiphase system. Interfacial effects are taken fully into account by including the mass, momentum, energy, and entropy associated with all of the phase interfaces.

Applications are suggested but not developed in detail.

CONCLUSIONS AND SIGNIFICANCE

There are two limiting criteria that must be satisfied for an intrinsically stable equilibrium in a multicomponent, multiphase system: Equations (73) or (74) within every phase and Equations (75) or (76) on every phase interface. The limits of intrinsic stability for a multiphase, multicomponent body are defined by the violation either of Equation (73) within one of the phases or of Equation (75) on one of the phase interfaces.

Although Equation (75) appears to fail at the collapse point of a relatively insoluble monolayer, it is probably unreasonable to expect direct experimental verification of these criteria for intrinsic stability. The most appropriate use of these criteria would be in predicting the limits of intrinsic stability, given equations of state for every phase and for every phase interface.

The temperature at which water vaporizes at atmospheric pressure depends upon the circumstances. In the presence of a powder or boiling chips which favor the formation of large bubbles, we find that it boils at very nearly 100°C. In a very clean, smooth glass container, it is possible to superheat water somewhat above 100°C before boiling occurs. As an extreme example, Dufour (1861) has superheated water suspended in oil to 178°C.

In each of these experiments we have a relatively isolated body whose form, below some limiting temperature, remains stable when subjected to the random disturbances that are always present in real experiments. But at this limiting temperature (or above), the original form of the body is unstable to all disturbances, no matter how small.

I define equilibrium to be achieved by a body when the Clausius-Duhem inequality becomes an equality. Let us assume that a body initially at equilibrium is momentarily disturbed. If, after the disturbance ceases, the body returns to very nearly its original state, we say that the equilibrium is stable. If, instead, the body evolves into a distinctly different state, we refer to the equilibrium as being unstable. An equilibrium may be unstable to relatively large disturbances but stable when subjected to small disturbances. We will say that an equilibrium is intrinsically stable if the conditions for equilibrium are not immediately violated by the imposition of small disturbances, so small that mass transfer to, from, and across the phase interfaces are unaffected. A supersaturated salt solution is intrinsically stable, although it may be unstable to macroscopic transients such as those imposed by scraping a glass stirring rod across the wall of the beaker containing the solution.

Necessary and sufficient conditions for an intrinsically stable equilibrium of a single-phase, multicomponent body have been discussed previously[*] (Gibbs, 1948; Tisza, 1951; Prigogine and Defay, 1954; Denbigh, 1955; Haase, 1956; Callen, 1960; Rowlinson, 1969; Münster, 1970; Beegle, Modell, and Reid, 1974; Modell and Reid, 1974). Slattery (1972) considered a multiphase, multicomponent body but neglected all interfacial effects.

Beegle, Modell, and Reid (1974) have pointed out that for a single-phase multicomponent body, a particular one of these conditions will fail before all the others. This is the limiting criterion for intrinsic stability. The failure of this condition defines the limits of intrinsic stability for the body.

In the followng sections, I develop necessary and sufficient conditions for an intrinsically stable equilibrium in an isolated, multiphase, multicomponent body totally enclosed by fixed, impermeable, adiabatic walls. Interfacial effects are taken into account by including the mass, momentum, energy, and entropy associated with all of the phase interfaces.

CONSTRAINTS ON ISOLATED BODY

There are constraints imposed upon an isolated, multiphase, multicomponent body by the mass balances for the individual species, by Euler's first law, by the energy balance, and by the Clausius-Duhem inequality. In examining the consequences of these constraints, I will make the following assumptions:

1. By isolated, I mean that the body is totally enclosed by fixed, impermeable, adiabatic walls and that the sum of all the forces acting on the body is zero.
2. In order to account for interfacial effects, I will allow mass, momentum, energy, and entropy to be associated with all of the internal phase interfaces.

In the sections that immediately follow, after stating these constraints in more detail, I will use the transport theorem (Appendix A) to rearrange them in a more convenient form.

MASS BALANCE FOR SPECIES A

The mass balance for each species A requires that the time rate of change of a mass of A within the body be equal to the rate at which the mass of A is produced by chemical reactions:

$$\frac{d}{dt}\left[\int_R \rho_{(A)}\,dV + \int_\Sigma \rho_{(A)}^{(\sigma)}\,dA\right] = \int_R \sum_{j=1}^{J} r_{(A,j)}\,dV + \int_\Sigma \sum_{k=1}^{K} r_{(A,k)}^{(\sigma)}\,dA \quad (1)$$

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[*] With the exception of Slattery (1972), all of these writers have discussed the necessary and sufficient conditions for the achievement of a stable state of rest (stable equilibrium state). A stable state of rest is defined to have a corresponding entropy that is greater than the entropy associated with any other possible state of rest. For example, Gibbs (1948) (see also Coleman and Noll, 1960) restricted his comparisons to all states of rest that a body might achieve with a fixed volume and internal energy.

Here dV indicates that a volume integration is to be performed over the region R occupied by the body, and dA denotes that an area integration is to be performed over all of the internal phase interfaces Σ. The mass density of species A within a phase is denoted by $\rho_{(A)}$; it is a piecewise continuous function of position in R. The mass density of A on a phase interface is signified by $\overset{(\sigma)}{\rho}_{(A)}$; it is a piecewise continuous function of position on Σ. By $r_{(A,j)}$ is meant the rate at which mass of species A is produced per unit volume by the homogeneous chemical reaction j ($j = 1, 2, \ldots, J$); $\overset{(\sigma)}{r}_{(A,k)}$ is the rate at which mass of species A is produced per unit area by the heterogeneous chemical reaction k ($k = 1, 2, \ldots, K$). After an application of the transport theorem (Appendix A),* Equation (1) takes the form

$$\int_R \left\{ \frac{\partial \rho_{(A)}}{\partial t} + \operatorname{div} [\rho_{(A)} \mathbf{v}_{(A)}] - \sum_{j=1}^{J} r_{(A,j)} \right\} dV$$

$$+ \int_\Sigma \left\{ \frac{\partial \overset{(\sigma)}{\rho}_{(A)}}{\partial t} - \nabla_{(\sigma)} \overset{(\sigma)}{\rho}_{(A)} \cdot \mathbf{u} + \operatorname{div}_{(\sigma)} [\overset{(\sigma)}{\rho}_{(A)} \overset{(\sigma)}{\mathbf{v}}_{(A)}] \right.$$

$$\left. - \sum_{k=1}^{K} \overset{(\sigma)}{r}_{(A,k)} + [\, \rho_{(A)} [\mathbf{v}_{(A)} \cdot \boldsymbol{\xi} - v^{(\sigma)}_{(\xi)}]\,] \right\} dA = 0 \quad (2)$$

It is understood here that when $\partial/\partial t$ is applied to a quantity associated with R, position in R is held constant. When $\partial/\partial t$ is applied to a quantity associated with Σ, the surface coordinates (Slattery, 1974) denoting position on Σ are fixed. $v^{(\sigma)}_{(\xi)} \equiv \mathbf{v}^{(\sigma)} \cdot \boldsymbol{\xi} = \mathbf{u} \cdot \boldsymbol{\xi}$ is the speed of displacement of the interface. On that portion of Σ separating phases i and j, I will use as shorthand notation

$$[Q\, \boldsymbol{\xi}] \equiv Q^{(i)} \boldsymbol{\xi}^{(i)} + Q^{(j)} \boldsymbol{\xi}^{(j)} \quad (3)$$

where $Q^{(i)}$ is evaluated within phase i in the limit as Σ is approached, and $\boldsymbol{\xi}^{(i)}$ is the unit normal to Σ pointing into phase i.

Since this is an isolated body, there is no mass transfer at the bounding surfaces of R. In other words, at the fixed bounding surfaces of R, the normal component of the velocity of an individual species is zero. Under these conditions, the divergence theorem requires

$$\int_R \operatorname{div} (\rho_{(A)} \mathbf{v}_{(A)})\, dV = - \int_\Sigma [\, \rho_{(A)} \mathbf{v}_{(A)} \cdot \boldsymbol{\xi}\,]\, dA \quad (4)$$

Similarly, since there is no mass transfer between Σ and the fixed bounding surfaces of R, the surface divergence theorem (Appendix A)* tells us that

$$\int_\Sigma \operatorname{div}_{(\sigma)} [\overset{(\sigma)}{\rho}_{(A)} \overset{(\sigma)}{\mathbf{v}}_{(A)}]\, dA = - \int_\Sigma 2\, H\, \overset{(\sigma)}{\rho}_{(A)} \overset{(\sigma)}{\mathbf{v}}_{(A)} \cdot \boldsymbol{\xi}\, dA \quad (5)$$

Let us introduce the j^{th} homogeneous reaction coordinate $\psi_{(j)}$ by defining for all $A, B = 1, 2, \ldots, N$

$$\frac{\partial \psi_{(j)}}{\partial t} \equiv \frac{r_{(A,j)}}{M_{(A)}\, \nu_{(A,j)}} = \frac{r_{(B,j)}}{M_{(B)}\, \nu_{(B,j)}} \quad (6)$$

The right side of this equation represents a normalized rate of production of moles of species A by the homogeneous chemical reaction j at a fixed point in space. The stoichiometric coefficient is taken to be a positive number for a species consumed in the reaction. In much the same manner, we can introduce the k^{th} heterogeneous reaction coordinate $\overset{(\sigma)}{\psi}_{(k)}$ by defining for all $A, B = 1, 2, \ldots, N$

$$\frac{\partial \overset{(\sigma)}{\psi}_{(k)}}{\partial t} - \nabla_{(\sigma)} \overset{(\sigma)}{\psi}_{(k)} \cdot \mathbf{u} \equiv \frac{\overset{(\sigma)}{r}_{(A,k)}}{M_{(A)}\, \overset{(\sigma)}{\nu}_{(A,k)}} = \frac{\overset{(\sigma)}{r}_{(B,k)}}{M_{(B)}\, \overset{(\sigma)}{\nu}_{(B,k)}} \quad (7)$$

On the right side of this equation we have a normalized rate of production of moles of species A by the heterogeneous chemical reaction k at a point fixed on the surface in such a way that its only motion is normal to the interface; $\overset{(\sigma)}{\nu}_{(A,k)}$ is the stoichiometric coefficient for species A in the heterogeneous chemical reaction k.

In view of Equations (4) through (7), we may express Equation (2) as

$$Z_A \equiv \int_R \frac{\partial}{\partial t} \left[\rho_{(A)} - \sum_{j=1}^{J} M_{(A)}\, \nu_{(A,j)}\, \psi_{(j)} \right] dV$$

$$+ \int_\Sigma \left\{ \frac{\partial}{\partial t} \left[\overset{(\sigma)}{\rho}_{(A)} - \sum_{k=1}^{K} M_{(A)}\, \overset{(\sigma)}{\nu}_{(A,k)}\, \overset{(\sigma)}{\psi}_{(k)} \right] \right.$$

$$- \nabla_{(\sigma)} \left[\overset{(\sigma)}{\rho}_{(A)} - \sum_{k=1}^{K} M_{(A)}\, \overset{(\sigma)}{\nu}_{(A,k)}\, \overset{(\sigma)}{\psi}_{(k)} \right] \cdot \mathbf{u}$$

$$\left. - 2\, H\, \overset{(\sigma)}{\rho}_{(A)} \overset{(\sigma)}{\mathbf{v}}_{(A)} \cdot \boldsymbol{\xi} - [\, \rho_{(A)}\, v^{(\sigma)}_{(\xi)}\,] \right\} dA = 0 \quad (8)$$

Here H is the mean curvature (McConnell, 1957) of Σ.

Euler's First Law

Since this body is isolated, the sum of the forces exerted upon the body is zero. Euler's first law requires that the time rate of change of the momentum of the body must be zero:

$$\frac{d}{dt} \left[\int_R \rho\, \mathbf{v}\, dV + \int_\Sigma \rho^{(\sigma)}\, \mathbf{v}^{(\sigma)}\, dA \right] = 0 \quad (9)$$

Here $\mathbf{v}$ is the mass averaged velocity within a phase. An application of the transport theorem (Appendix A)* yields

$$\mathbf{Z}_m \equiv \int_R \frac{\partial (\rho \mathbf{v})}{\partial t}\, dV$$

$$+ \int_\Sigma \left\{ \frac{\partial (\rho^{(\sigma)}\, \mathbf{v}^{(\sigma)})}{\partial t} - \nabla_{(\sigma)} [\rho^{(\sigma)}\, \mathbf{v}^{(\sigma)}] \cdot \mathbf{u} \right.$$

$$\left. - \rho^{(\sigma)}\, [\mathbf{B} \cdot \mathbf{v}^{(\sigma)}]\, v^{(\sigma)}_{(\xi)} - [\, \rho\, \mathbf{v}\, v^{(\sigma)}_{(\xi)}\,] \right\} dA = 0 \quad (10)$$

In arriving at this result, I have used both Green's transformation (Slattery, 1972) and the surface divergence theorem (Appendix A).* I have also recognized that $\mathbf{v}$ and $\mathbf{v}^{(\sigma)}$ must be zero at the surface bounding R.

ENERGY BALANCE

The contact forces acting at the boundary of this isolated body do no work, since the boundary is fixed in space. The boundary is adiabatic, which I interpret as meaning that there is neither contact energy transmission nor radiant energy transmission with the surroundings. I will neglect the possibility of radiant energy transmission within the body. This means that the time rate of change of the internal energy of the body is the result only of work done by the inertial forces and the body forces:

$$\frac{d}{dt} \left[\int_R \rho\, \hat{U}\, dV + \int_\Sigma \rho^{(\sigma)}\, \hat{U}^{(\sigma)}\, dA \right]$$

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* Supplementary material has been deposited as Document No. 02964 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 440 Park Ave. South, New York, N.Y. 10016 and may be obtained for $3.00 for microfiche or $5.00 for photocopies.

$$= \int_R \left[-\rho \mathbf{v} \cdot \frac{d_{(\mathbf{v})} \mathbf{v}}{dt} + \sum_{A=1}^{N} \rho_{(A)} \mathbf{v}_{(A)} \cdot \mathbf{b}_{(A)} \right] dV + \int_\Sigma \left[-\rho^{(\sigma)} \mathbf{v}^{(\sigma)} \cdot \frac{d_{(\mathbf{v}^{(\sigma)})} \mathbf{v}^{(\sigma)}}{dt} + \sum_{A=1}^{N} \rho^{(\sigma)}_{(A)} \mathbf{v}^{(\sigma)}_{(A)} \cdot \mathbf{b}^{(\sigma)}_{(A)} \right] dA \quad (11)$$

Here $\hat{U}$ is the internal energy per unit mass within a phase; $\hat{U}^{(\sigma)}$ is the internal energy per unit mass on a phase interface; $d_{(\mathbf{v})}/dt$ denotes a derivative with respect to time following a point within a phase that moves with the mass averaged velocity $\mathbf{v}$; $d_{[\mathbf{v}^{(\sigma)}]}/dt$ denotes a derivative with respect to time following a point in the interface that moves with the mass averaged surface velocity $\mathbf{v}^{(\sigma)}$.

I show in Appendix B* that, after an application of the transport theorem, Equation (11) may be rearranged in the form

$$\begin{aligned} Z_e \equiv & \int_R \frac{\partial}{\partial t} \left[\check{E} - \sum_{A=1}^{N} \sum_{j=1}^{J} \phi_{(A)} M_{(A)} \nu_{(A,j)} \psi_{(j)} \right] dV \\ & + \int_\Sigma \left\{ \frac{\partial}{\partial t} \left[\overline{E}^{(\sigma)} - \sum_{A=1}^{N} \sum_{k=1}^{K} \phi^{(\sigma)}_{(A)} M_{(A)} \nu^{(\sigma)}_{(A,k)} \psi^{(\sigma)}_{(k)} \right] \right. \\ & - \nabla_{(\sigma)} \left[\overline{E}^{(\sigma)} - \sum_{A=1}^{N} \sum_{k=1}^{K} \phi^{(\sigma)}_{(A)} M_{(A)} \nu^{(\sigma)}_{(A,k)} \psi^{(\sigma)}_{(k)} \right] \cdot \mathbf{u} \\ & + \sum_{A=1}^{N} \sum_{k=1}^{K} [\rho^{(\sigma)}_{(A)} - M_{(A)} \nu^{(\sigma)}_{(A,k)} \phi^{(\sigma)}_{(k)}] \\ & \left[-\frac{\partial \phi^{(\sigma)}_{(A)}}{\partial t} + \nabla_{(\sigma)} \phi^{(\sigma)}_{(A)} \cdot \mathbf{u} \right] - 2H \left[\overline{E}^{(\sigma)} v^{(\sigma)}_{(\xi)} + \sum_{A=1}^{N} \rho^{(\sigma)}_{(A)} \phi^{(\sigma)}_{(A)} (\mathbf{v}^{(\sigma)}_{(A)} \cdot \boldsymbol{\xi} - v^{(\sigma)}_{(\xi)}) \right] \\ & - \left[\check{E} v^{(\sigma)}_{(\xi)} + \sum_{A=1}^{N} \rho_{(A)} (\phi_{(A)} - \phi^{(\sigma)}_{(A)}) (\mathbf{v}_{(A)} \cdot \boldsymbol{\xi} - v^{(\sigma)}_{(\xi)}) + \frac{1}{2} \rho (v^2 - v^{(\sigma)2}) \right. \\ & \left. \left. (\mathbf{v} \cdot \boldsymbol{\xi} - v^{(\sigma)}_{(\xi)}) \right] \right\} dA = 0 \end{aligned} \quad (12)$$

where

$$\check{E} \equiv \rho \left(\hat{U} + \frac{1}{2} v^2 \right) + \sum_{A=1}^{N} \rho_{(A)} \phi_{(A)} \quad (13)$$

is the total energy per unit volume associated with each phase, and

$$\overline{E}^{(\sigma)} \equiv \rho^{(\sigma)} \left[\hat{U}^{(\sigma)} + \frac{1}{2} v^{(\sigma)2} \right] + \sum_{A=1}^{N} \rho^{(\sigma)}_{(A)} \phi^{(\sigma)}_{(A)} \quad (14)$$

is the total energy per unit area associated with the interface. I have assumed here that the body forces are representable in terms of potentials:

$$\mathbf{b}_{(A)} = -\nabla \phi_{(A)} \quad (15)$$

$$\mathbf{b}^{(\sigma)}_{(A)} = -\nabla \phi^{(\sigma)}_{(A)} \quad (16)$$

We refer to $\phi_{(A)}$ and $\phi^{(\sigma)}_{(A)}$ as the potential energies per unit mass attributable to the body forces $\mathbf{b}_{(A)}$ and $\mathbf{b}^{(\sigma)}_{(A)}$, respectively.

CLAUSIUS-DUHEM INEQUALITY

For this isolated body, the Clausius-Duhem inequality (second law of thermodynamics) says that the time rate of change of the body's entropy must be greater than or equal to zero:

$$\frac{d}{dt} \left[\int_R \check{S} \, dV + \int_\Sigma \overline{S}^{(\sigma)} \, dA \right] \geqq 0 \quad (17)$$

Applying the transport theorem (Appendix A)* as well as the divergence theorem, we find that this may also be written as

$$\int_R \frac{\partial \check{S}}{\partial t} dV + \int_\Sigma \left\{ \frac{\partial \overline{S}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \overline{S}^{(\sigma)} \cdot \mathbf{u} - 2H \overline{S}^{(\sigma)} v^{(\sigma)}_{(\xi)} - [\check{S} v^{(\sigma)}_{(\xi)}] \right\} dA \geqq 0 \quad (18)$$

Equilibrium is attained when the Clausius-Duhem inequality becomes an equality. If equilibrium is reached by our isolated body at some time t_e, Equation (17) requires

at $t = t_e$:

$$\frac{d}{dt} \left[\int_R \check{S} \, dV + \int_\Sigma \overline{S}^{(\sigma)} \, dA \right] = 0 \quad (19)$$

This together with (17) implies that we should also expect

at $t = t_e$:

$$\frac{d^2}{dt^2} \left[\int_R \check{S} \, dV + \int_\Sigma \overline{S}^{(\sigma)} \, dA \right] \equiv \lim_{t \to t_e} \frac{1}{t_e - t} \left\{ \frac{d}{dt} \left[\int_R \check{S} \, dV + \int_\Sigma \overline{S}^{(\sigma)} \right] \Bigg|_{t_e} - \frac{d}{dt} \left[\int_R \check{S} \, dV + \int_\Sigma \overline{S}^{(\sigma)} \, dA \right] \Bigg|_t \right\} < 0 \quad (20)$$

Equations (19) and (20) tell us that, as an isolated body approaches equilibrium, its entropy approaches a local maximum as a function of time.

IMPLICATIONS OF EQUATION (19)

If equilibrium is to be achieved by the isolated multicomponent body considered here, Equation (19) must be satisfied within the constraints imposed by the mass balance for each species Equation (8), by Euler's first law Equation (10), and by the energy balance Equation (12). Let us recognize these constraints with Lagrangian multipliers:

$$\frac{d}{dt} \left[\int_R \check{S} \, dV + \int_\Sigma \overline{S}^{(\sigma)} \, dA \right] = \int_R \frac{\partial \check{S}}{\partial t} dV$$

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* See footnote on p. 277.

$$+\int_{\Sigma}\left\{\frac{\partial\overline{S}^{(\sigma)}}{\partial t}-\nabla_{(\sigma)}\overline{S}^{(\sigma)}\cdot\mathbf{u}-2H\overline{S}^{(\sigma)}v^{(\sigma)}_{(\xi)}-[\check{S}\,v^{(\sigma)}_{(\xi)}]\right\}dA+\sum_{A=1}^{N}\lambda_A Z_A+\boldsymbol{\lambda}_m\cdot\mathbf{Z}_m+\lambda_e Z_e=0 \quad (21)$$

Here λ_A $(A = 1, 2, \ldots, N)$ and λ_e are constants or Lagrangian multipliers; λ_m is a constant spatial vector, the components of which are Lagrangian multipliers.

Let us assume that at each point within a phase the functional dependence of the Helmholtz free energy per unit volume $\check{A}$ may be described by the caloric equation of state

$$\check{A}\equiv\check{U}-T\check{S}$$

$$=\check{A}\,(T,\rho_{(1)},\rho_{(2)},\ldots,\rho_{(N)}) \quad (22)$$

Differentiating with respect to time, we have

$$\frac{\partial\check{S}}{\partial t}=\frac{1}{T}\frac{\partial\check{U}}{\partial t}-\sum_{A=1}^{N}\frac{\mu_{(A)}}{T}\frac{\partial\rho_{(A)}}{\partial t} \quad (23)$$

where

$$\mu_{(A)}\equiv\left[\frac{\partial\check{A}}{\partial\rho_{(A)}}\right]_{T,\,\rho_{(B)}\,(B\neq A)} \quad (24)$$

is the chemical potential of species A on a mass basis. (The difference between the chemical potential defined on a mass basis and the chemical potential defined on a molar basis is described by Slattery, 1972.)

In a similar manner, let us assume that at each point on the interface the functional dependence of the Helmholtz free energy per unit area $\overline{A}^{(\sigma)}$ may be described by the surface caloric equation of state

$$\overline{A}^{(\sigma)}\equiv\overline{U}^{(\sigma)}-T^{(\sigma)}\overline{S}^{(\sigma)}$$

$$=\overline{A}^{(\sigma)}(T^{(\sigma)},\rho^{(\sigma)}_{(1)},\rho^{(\sigma)}_{(2)},\ldots,\rho^{(\sigma)}_{(N)}) \quad (25)$$

This implies that

$$\frac{\partial\overline{S}^{(\sigma)}}{\partial t}=\frac{1}{T^{(\sigma)}}\frac{\partial\overline{U}^{(\sigma)}}{\partial t}-\sum_{A=1}^{N}\frac{\mu^{(\sigma)}_{(A)}}{T^{(\sigma)}}\frac{\partial\rho^{(\sigma)}_{(A)}}{\partial t} \quad (26)$$

where

$$\mu^{(\sigma)}_{(A)}\equiv\left[\frac{\partial\overline{A}^{(\sigma)}}{\partial\rho^{(\sigma)}_{(A)}}\right]_{T^{(\sigma)},\rho^{(\sigma)}_{(B)}\,(B\neq A)} \quad (27)$$

is the surface chemical potential of species A on a mass basis.

Taking the derivative with respect to time of Equations (13) and (14), we find

$$\frac{\partial\check{E}}{\partial t}=\frac{\partial\check{U}}{\partial t}+\rho\mathbf{v}\cdot\frac{\partial\mathbf{v}}{\partial t}+\frac{1}{2}v^2\frac{\partial\rho}{\partial t}+\sum_{A=1}^{N}\phi_{(A)}\frac{\partial\rho_{(A)}}{\partial t} \quad (28)$$

and

$$\frac{\partial\overline{E}^{(\sigma)}}{\partial t}=\frac{\partial\overline{U}^{(\sigma)}}{\partial t}+\rho^{(\sigma)}\mathbf{v}^{(\sigma)}\cdot\frac{\partial\mathbf{v}^{(\sigma)}}{\partial t}+\frac{1}{2}v^{(\sigma)2}\frac{\partial\rho^{(\sigma)}}{\partial t}+\sum_{A=1}^{N}\phi^{(\sigma)}_{(A)}\frac{\partial\rho^{(\sigma)}_{(A)}}{\partial t}+\sum_{A=1}^{N}\rho^{(\sigma)}_{(A)}\frac{\partial\phi^{(\sigma)}_{(A)}}{\partial t} \quad (29)$$

where we have again assumed that the potentials $\phi_{(A)}$ and $\phi^{(\sigma)}_{(A)}$ are independent of time. After rearranging Equation (21) with the help of Equations (23), (26), (28), and (29), we can say that at equilibrium

$$\int_R\left\{\left(\frac{1}{T}+\lambda_e\right)\frac{\partial\check{U}}{\partial t}+\sum_{A=1}^{N}\left[-\frac{\mu_{(A)}}{T}+\lambda_{(A)}+\boldsymbol{\lambda}_m\cdot\mathbf{v}+\lambda_e\frac{1}{2}v^2+\lambda_e\phi_{(A)}\right]\frac{\partial\rho_{(A)}}{\partial t}\right.$$

$$-\sum_{j=1}^{J}\sum_{A=1}^{N}[\lambda_{(A)}M_{(A)}\nu_{(A,j)}+\lambda_e\phi_{(A)}M_{(A)}\nu_{(A,j)}]\frac{\partial\psi_{(j)}}{\partial t}$$

$$\left.+\rho(\boldsymbol{\lambda}_m+\lambda_e\mathbf{v})\cdot\frac{\partial\mathbf{v}}{\partial t}\right\}dV$$

$$+\int_{\Sigma}\left\{\left[\frac{1}{T^{(\sigma)}}+\lambda_e\right]\left[\frac{\partial\overline{U}^{(\sigma)}}{\partial t}-\nabla_{(\sigma)}\overline{U}^{(\sigma)}\cdot\mathbf{u}\right]\right.$$

$$+\sum_{A=1}^{N}\left[-\frac{\mu^{(\sigma)}_{(A)}}{T^{(\sigma)}}+\lambda_{(A)}+\boldsymbol{\lambda}_m\cdot\mathbf{v}^{(\sigma)}+\lambda_e\frac{1}{2}v^{(\sigma)2}+\lambda_e\phi^{(\sigma)}_{(A)}\right]\cdot\left[\frac{\partial\rho^{(\sigma)}_{(A)}}{\partial t}-\nabla_{(\sigma)}\rho^{(\sigma)}_{(A)}\cdot\mathbf{u}\right]$$

$$-\sum_{k=1}^{K}\sum_{A=1}^{N}[\lambda_{(A)}M_{(A)}\nu^{(\sigma)}_{(A,k)}+\lambda_e\phi^{(\sigma)}_{(A)}M_{(A)}\nu^{(\sigma)}_{(A,k)}]\left[\frac{\partial\psi^{(\sigma)}_{(k)}}{\partial t}-\nabla_{(\sigma)}\psi^{(\sigma)}_{(k)}\cdot\mathbf{u}\right]$$

$$\left.+\rho^{(\sigma)}[\boldsymbol{\lambda}_m+\lambda_e\mathbf{v}^{(\sigma)}]\cdot\left[\frac{\partial\mathbf{v}^{(\sigma)}}{\partial t}-\nabla_{(\sigma)}\mathbf{v}^{(\sigma)}\cdot\mathbf{u}\right]\right\}dA$$

$$+\int_{\Sigma}\left\{2Hv^{(\sigma)}_{(\xi)}\left[\left(\frac{1}{T^{(\sigma)}}+\lambda_e\right)\overline{U}^{(\sigma)}-\frac{\gamma}{T^{(\sigma)}}-\sum_{A=1}^{N}\frac{\mu^{(\sigma)}_{(A)}\rho^{(\sigma)}_{(A)}}{T^{(\sigma)}}+\lambda_e\frac{1}{2}\rho^{(\sigma)}v^{(\sigma)2}\right]\right.$$

$$-2H\sum_{A=1}^{N}\rho^{(\sigma)}_{(A)}[\lambda_{(A)}+\lambda_e\phi^{(\sigma)}_{(A)}]\mathbf{v}^{(\sigma)}_{(A)}\cdot\boldsymbol{\xi}$$

$$-[\boldsymbol{\lambda}_m\cdot\mathbf{B}\cdot\mathbf{v}^{(\sigma)}]\rho^{(\sigma)}v^{(\sigma)}_{(\xi)}$$

$$+\left[\!\!\left[\left(-\frac{\check{U}}{T}-\frac{P}{T}+\sum_{A=1}^{N}\frac{\mu_{(A)}\rho_{(A)}}{T}-\lambda_e\check{U}-\lambda_e\frac{1}{2}\rho v^2\right.\right.\right.$$

$$- \lambda_e \sum_{A=1}^{N} \rho_{(A)}\, \phi_{(A)} - \sum_{A=1}^{N} \lambda_{(A)}\, \rho_{(A)} - \rho \boldsymbol{\lambda}_m \cdot \mathbf{v} \Big]\, v_{(\xi)}^{(\sigma)}$$

$$- \lambda_e \sum_{A=1}^{N} \rho_{(A)} \left(\phi_{(A)} - \phi_{(A)}^{(\sigma)}\right) \left(\mathbf{v}_{(A)} \cdot \boldsymbol{\xi} - v_{(\xi)}^{(\sigma)}\right)$$

$$- \lambda_e \frac{1}{2} \rho \left(v^2 - v^{(\sigma)2}\right) \left(\mathbf{v} \cdot \boldsymbol{\xi} - v_{(\xi)}^{(\sigma)}\right) \Big] \Big\} \; dA = 0 \tag{30}$$

In arriving at this particular form, I have used both the Euler equation (Slattery, 1972)

$$\hat{A} = - P \hat{V} + \sum_{B=1}^{N} \mu_{(B)}\, \omega_{(B)} \tag{31}$$

and the surface Euler equation*

$$\hat{A}^{(\sigma)} = \gamma \hat{\mathcal{A}} + \sum_{B=1}^{N} \mu_{(B)}^{(\sigma)}\, \omega_{(B)}^{(\sigma)} \tag{32}$$

in which

$$P \equiv - \left(\frac{\partial \hat{A}}{\partial \hat{V}}\right)_{T,\, \omega_{(B)}} \tag{33}$$

is the thermodynamic pressure (Slattery, 1972)

$$\gamma \equiv \left(\frac{\partial \hat{A}^{(\sigma)}}{\partial \hat{\mathcal{A}}}\right)_{T^{(\sigma)},\, \omega_{(B)}^{(\sigma)}} \tag{34}$$

is the thermodynamic interfacial tension, and $\hat{\mathcal{A}}$ is the interfacial area per unit mass.

In order that Equation (30) be satisfied at equilibrium, it is sufficient that all velocities be zero and that all intensive quantities are independent of time. But this is not necessary.

If this equilibrium is intrinsically stable, Equation (30) will not be immediately violated by the imposition of arbitrary or random transients so small that mass transfer across the phase interfaces is unaffected. Equivalently, if this equilibrium is intrinsically stable, Equation (30) must be satisfied to the first perturbation of an arbitrary disturbance. This implies that the integrands for the integrations over R and Σ in Equation (30) (or their first perturbations) are zero everywhere. For an intrinsically stable equilibrium

$$\frac{1}{T} + \lambda_e = 0 \tag{35}$$

$$- \frac{\mu_{(A)}}{T} + \lambda_{(A)} + \boldsymbol{\lambda}_m \cdot \mathbf{v} + \lambda_e \frac{1}{2} v^2 + \lambda_e \phi_{(A)} = 0 \tag{36}$$

$$\sum_{A=1}^{N} \left[\lambda_{(A)}\, M_{(A)}\, \nu_{(A,j)} + \lambda_e\, \phi_{(A)}\, M_{(A)}\, \nu_{(A,j)}\right] = 0 \tag{37}$$

$$\boldsymbol{\lambda}_m + \lambda_e \mathbf{v} = 0 \tag{38}$$

$$\frac{1}{T^{(\sigma)}} + \lambda_e = 0 \tag{39}$$

$$- \frac{\mu_{(A)}^{(\sigma)}}{T^{(\sigma)}} + \lambda_{(A)} + \boldsymbol{\lambda}_m \cdot \mathbf{v}^{(\sigma)} + \lambda_e \frac{1}{2} v^{(\sigma)2} + \lambda_e\, \phi_{(A)}^{(\sigma)} = 0 \tag{40}$$

$$\sum_{A=1}^{N} \left[\lambda_{(A)}\, M_{(A)}\, \nu_{(A,k)}^{(\sigma)} + \lambda_e\, \phi_{(A)}^{(\sigma)}\, M_{(A)}\, \nu_{(A,k)}^{(\sigma)}\right] = 0 \tag{41}$$

$$\boldsymbol{\lambda}_m + \lambda_e \mathbf{v}^{(\sigma)} = 0 \tag{42}$$

and the integrand for the second surface integral on the left of Equation (30) is zero. Equations (35) and (39) say

$$T = T^{(\sigma)} = - \frac{1}{\lambda_e} = \text{a constant} \tag{43}$$

From Equations (38) and (42), we have

$$\mathbf{v} = \mathbf{v}^{(\sigma)} = - \frac{\boldsymbol{\lambda}_m}{\lambda_e} = 0 \tag{44}$$

when we remember that the boundaries of the system are stationary and impermeable. Equations (36) and (40) tell us that

$$\mu_{(A)} + \phi_{(A)} = \mu_{(A)}^{(\sigma)} + \phi_{(A)}^{(\sigma)} = \lambda_{(A)}\, T = \text{a constant} \tag{45}$$

We see from Equations (37) and (41) that

$$\sum_{A=1}^{N} \mu_{(A)}\, M_{(A)}\, \nu_{(A,j)} = 0 \tag{46}$$

and

$$\sum_{A=1}^{N} \mu_{(A)}^{(\sigma)}\, M_{(A)}\, \nu_{(A,k)}^{(\sigma)} = 0 \tag{47}$$

In view of Equations (43) through (45), the integrand for the second surface integral on the left of Equation (30) reduces to

$$- 2H \sum_{A=1}^{N} \frac{\mu_{(A)}^{(\sigma)}\, \rho_{(A)}^{(\sigma)}}{T^{(\sigma)}} \left[\mathbf{v}_{(A)}^{(\sigma)} \cdot \boldsymbol{\xi} - v_{(\xi)}^{(\sigma)}\right]$$

$$+ \sum_{A=1}^{N} \Big\lfloor \frac{1}{T} \left(\phi_{(A)} - \phi_{(A)}^{(\sigma)}\right) \left(\mathbf{v}_{(A)} \cdot \boldsymbol{\xi} - v_{(\xi)}^{(\sigma)}\right) \Big] = 0 \tag{48}$$

Since the surface chemical potentials $\mu_{(A)}^{(\sigma)}$ and the potential energies $\phi_{(A)}$ and $\phi_{(A)}^{(\sigma)}$ are arbitrary, this in turn implies that for an intrinsically stable equilibrium, there can be no mass transfer to, from, or across the phase interfaces:

$$\text{at} \quad \Sigma : \mathbf{v}_{(A)} \cdot \boldsymbol{\xi} - v_{(\xi)}^{(\sigma)} = \mathbf{v}_{(A)}^{(\sigma)} \cdot \boldsymbol{\xi} - v_{(\xi)}^{(\sigma)} = 0 \tag{49}$$

This is consistent with but not implied by our original statement that the random transients are too small to immediately affect mass transfer at the phase interfaces.

To summarize, Equations (43) through (47) and (49) define necessary conditions for an intrinsically stable equilibrium in an isolated body. We can not say that they are sufficient, since we have not as yet examined the implications of Equation (20).

IMPLICATIONS OF EQUATION (20)

For equilibrium to be achieved by the isolated multicomponent body considered here, Equation (20) must also be satisfied within the constraints imposed by the mass balance for each species Equation (8), by Euler's first law Equation (10), and by the energy balance Equation (12). A convenient way of recognizing these constraints is to evaluate the second derivative on the left of Equation (20) by differentiating the left side of Equation (30). After some rearrangement explained in Appen-

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* Equation (32) can be derived from Equation (25) in much the same manner as Equation (31) follows from Equation (22) (Slattery, 1972).

dix C,* we find that Equation (20) requires

$$\int_R \left\{ \left(\frac{\partial T}{\partial \check{S}}\right)_{\rho_{(C)}} \left(\frac{\partial \check{S}}{\partial t}\right)^2 + \sum_{A=1}^{N} \frac{2}{T} \left(\frac{\partial \mu_{(A)}}{\partial \check{S}}\right)_{\rho_{(C)}} \frac{\partial \check{S}}{\partial t} \frac{\partial \rho_{(A)}}{\partial t} + \sum_{A=1}^{N} \sum_{B=1}^{N} \frac{1}{T} \left[\frac{\partial \mu_{(A)}}{\partial \rho_{(B)}}\right]_{\check{S},\rho_{(C)}\ (C \neq B)} \frac{\partial \rho_{(A)}}{\partial t} \frac{\partial \rho_{(B)}}{\partial t} + \frac{\rho}{T} \frac{\partial \mathbf{v}}{\partial t} \cdot \frac{\partial \mathbf{v}}{\partial t} \right\} dV$$

$$+ \int_\Sigma \left\{ \frac{1}{T^{(\sigma)}} \left[\frac{\partial T^{(\sigma)}}{\partial \overline{S}^{(\sigma)}}\right]_{\rho^{(\sigma)}_{(C)}} \left[\frac{\partial \overline{S}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \overline{S}^{(\sigma)} \cdot \mathbf{u}\right]^2 \right.$$

$$+ \sum_{A=1}^{N} \frac{2}{T^{(\sigma)}} \left[\frac{\partial \overset{(\sigma)}{\mu}_{(A)}}{\partial \overline{S}^{(\sigma)}}\right]_{\rho^{(\sigma)}_{(C)}} \left[\frac{\partial \overline{S}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \overline{S}^{(\sigma)} \cdot \mathbf{u}\right] \left[\frac{\partial \rho_{(A)}}{\partial t} - \nabla_{(\sigma)} \overset{(\sigma)}{\rho}_{(A)} \cdot \mathbf{u}\right]$$

$$+ \sum_{A=1}^{N} \sum_{B=1}^{N} \frac{1}{T^{(\sigma)}} \left[\frac{\partial \overset{(\sigma)}{\mu}_{(A)}}{\partial \rho^{(\sigma)}_{(B)}}\right]_{\overline{S}^{(\sigma)},\rho^{(\sigma)}_{(C)}\ (C \neq B)} \left[\frac{\partial \overset{(\sigma)}{\rho}_{(A)}}{\partial t} - \nabla_{(\sigma)} \overset{(\sigma)}{\rho}_{(A)} \cdot \mathbf{u}\right]$$

$$\left. \left[\frac{\partial \overset{(\sigma)}{\rho}_{(B)}}{\partial t} - \nabla_{(\sigma)} \overset{(\sigma)}{\rho}_{(B)} \cdot \mathbf{u}\right] \right\} dA > 0 \quad (50)$$

If an equilibrium is intrinsically stable, Equation (50) will not be immediately violated by the imposition of arbitrary or random transients so small that mass transfer across the phase interfaces is unaffected. Equivalently, if this equilibrium is intrinsically stable, Equation (50) must be satisfied to the second perturbation of an arbitrary disturbance.

For a single-phase system, the first integral on the left of Equation (50) must be greater than zero. Since the dimensions of the system are arbitrary, this implies

$$\frac{1}{T}\left(\frac{\partial T}{\partial \check{S}}\right)_{\rho_{(C)}} \left(\frac{\partial \check{S}}{\partial t}\right)^2 + \sum_{A=1}^{N} \frac{2}{T} \left[\frac{\partial \mu_{(A)}}{\partial \check{S}}\right]_{\rho_{(C)}} \frac{\partial \check{S}}{\partial t} \frac{\partial \rho_{(A)}}{\partial t} + \sum_{A=1}^{N} \sum_{B=1}^{N} \frac{1}{T} \left[\frac{\partial \mu_{(A)}}{\partial \rho_{(B)}}\right]_{\check{S},\rho_{(C)}\ (C \neq B)} \frac{\partial \rho_{(A)}}{\partial t} \frac{\partial \rho_{(B)}}{\partial t} + \frac{\rho}{T} \left(\left| \frac{\partial \mathbf{v}}{\partial t} \right| \right)^2 > 0 \quad (51)$$

Consider now the vector space whose elements are ordered sets of $N + 2$, real valued functions of time and position (as the field of scalars, we take all real valued functions of time and position with the usual rules for addition and multiplication of functions); this is a generalization of the vector space of $N + 2$-tuples of real numbers (Halmos, 1958). Let $\mathbf{x}$ be an element of this vector space:

$$\mathbf{x} \equiv \left[\frac{\partial \check{S}}{\partial t}, \frac{\partial \rho_{(1)}}{\partial t}, \ldots, \frac{\partial \rho_{(N)}}{\partial t}, \left| \frac{\partial \mathbf{v}}{\partial t} \right| \right] \quad (52)$$

In these terms, Equation (51) may be written as

$$(\mathbf{x}, \mathbf{S}\,\mathbf{x}) > 0 \quad (53)$$

where $(\mathbf{x}, \mathbf{S}\,\mathbf{x})$ represents an inner produce of the vectors $\mathbf{x}$ and $\mathbf{S}\,\mathbf{x}$ of this vector space. Here, $\mathbf{S}$ is a transformation of the vector space into itself. If we take

$$\begin{aligned} \boldsymbol{\Upsilon}_1 &\equiv (1, 0, \ldots, 0) \\ \boldsymbol{\Upsilon}_2 &\equiv (0, 1, 0, \ldots, 0) \\ &\ \ \vdots \\ \boldsymbol{\Upsilon}_{n+2} &\equiv (0, \ldots, 0, 1) \end{aligned} \quad (54)$$

as a basis for this vector space, then the elements of the matrix of the transformation $\mathbf{S}$ with respect to this basis are (Halmos, 1958)

$$S_{11} \equiv \frac{1}{T}\left(\frac{\partial T}{\partial \check{S}}\right)_{\rho_{(C)}} \quad (55)$$

$$S_{1,1+A} \equiv S_{1+A,1} \equiv \frac{1}{T}\left[\frac{\partial \mu_{(A)}}{\partial \check{S}}\right]_{\rho_{(C)}} \quad \text{for} \quad A = 1, 2, \ldots, N \quad (56)$$

$$S_{1+A,\,1+B} = S_{1+B,\,1+A} \equiv \frac{1}{T}\left[\frac{\partial \mu_{(A)}}{\partial \rho_{(B)}}\right]_{\check{S},\rho_{(C)}\ (C \neq B)} \quad \text{for} \quad A, B = 1, 2, \ldots, N \quad (57)$$

$$S_{N+2,R} \equiv S_{R,N+2} \equiv 0 \quad \text{for} \quad R = 1, 2, \ldots, N + 1 \quad (58)$$

$$S_{N+2,\,N+2} \equiv \frac{\rho}{T} \quad (59)$$

In writing (57), I have observed that (Slattery, 1972)

$$\left[\frac{\partial \mu_{(A)}}{\partial \rho_{(B)}}\right]_{T,\rho_{(C)}\ (C \neq B)} = \left[\frac{\partial \mu_{(B)}}{\partial \rho_{(A)}}\right]_{T,\rho_{(C)}\ (C \neq A)} \quad (60)$$

Notice that $\mathbf{S}$ is symmetric.

Since Equation (50) applies to every multiphase body, not only the surface integral on the left of Equation (50) is greater than zero but also the integrand of this surface integral is greater than zero everywhere on Σ:

$$\frac{1}{T^{(\sigma)}} \left[\frac{\partial T^{(\sigma)}}{\partial \overline{S}^{(\sigma)}}\right]_{\rho^{(\sigma)}_{(C)}} \left[\frac{\partial \overline{S}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \overline{S}^{(\sigma)} \cdot \mathbf{u}\right]^2$$

$$+ \sum_{A=1}^{N} \frac{2}{T^{(\sigma)}} \left[\frac{\partial \overset{(\sigma)}{\mu}_{(A)}}{\partial \overline{S}^{(\sigma)}}\right]_{\rho^{(\sigma)}_{(C)}} \left[\frac{\partial \overline{S}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)} \overline{S}^{(\sigma)} \cdot \mathbf{u}\right] \left[\frac{\partial \overset{(\sigma)}{\rho}_{(A)}}{\partial t} - \nabla_{(\sigma)} \overset{(\sigma)}{\rho}_{(A)} \cdot \mathbf{u}\right]$$

$$+ \sum_{A=1}^{N} \sum_{B=1}^{N} \frac{1}{T^{(\sigma)}} \left[\frac{\partial \overset{(\sigma)}{\mu}_{(A)}}{\partial \rho^{(\sigma)}_{(B)}}\right]_{\overline{S}^{(\sigma)},\rho^{(\sigma)}_{(C)}\ (C \neq B)}$$

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* See footnote on p. 277.

$$\left[\frac{\partial \rho_{(A)}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)}\, \rho_{(A)}^{(\sigma)} \cdot \mathbf{u}\right]\left[\frac{\partial \rho_{(B)}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)}\, \rho_{(B)}^{(\sigma)} \cdot \mathbf{u}\right] > 0 \qquad (61)$$

The vector space elements are ordered sets of $N + 1$, real valued functions of time and position on the dividing surface Σ (as the field of scalars, we take all real valued functions of time and position on Σ with the usual rules for addition and multiplication of functions) is a generalization of the vector space of $N + 1$-tuples of real numbers (Halmos, 1958). If

$$\mathbf{x}^{(\sigma)} \equiv \left(\left\{ \frac{\partial \overline{S}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)}\, \overline{S}^{(\sigma)} \cdot \mathbf{u} \right\}, \left\{ \frac{\partial \rho_{(1)}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)}\, \rho_{(1)}^{(\sigma)} \cdot \mathbf{u} \right\}, \ldots, \left\{ \frac{\partial \rho_{(N)}^{(\sigma)}}{\partial t} - \nabla_{(\sigma)}\, \rho_{(N)}^{(\sigma)} \cdot \mathbf{u} \right\} \right) \qquad (62)$$

is an element of this vector space, Equation (61) may be written as

$$[\mathbf{x}^{(\sigma)}, \mathbf{S}^{(\sigma)}\, \mathbf{x}^{(\sigma)}] > 0 \qquad (63)$$

where $[\mathbf{x}^{(\sigma)}, \mathbf{S}^{(\sigma)}\, \mathbf{x}^{(\sigma)}]$ represents an inner product of the vectors $\mathbf{x}^{(\sigma)}$ and $\mathbf{S}^{(\sigma)}\, \mathbf{x}^{(\sigma)}$ of this vector space. Here $\mathbf{S}^{(\sigma)}$ is a transformation of the vector space into itself. If we take

$$\begin{aligned} \gamma_1^{(\sigma)} &\equiv (1, 0, \ldots, 0) \\ \gamma_2^{(\sigma)} &\equiv (0, 1, 0, \ldots, 0) \\ &\;\;\vdots \\ \gamma_{N+1}^{(\sigma)} &\equiv (0, \ldots, 0, 1) \end{aligned} \qquad (64)$$

as a basis for this vector space, the elements of the matrix of the transformation $\mathbf{S}^{(\sigma)}$ with respect to this basis are (Halmos, 1958)

$$S_{11}^{(\sigma)} \equiv \frac{1}{T^{(\sigma)}} \left[\frac{\partial T^{(\sigma)}}{\partial S^{(\sigma)}}\right]_{\rho_{(C)}^{(\sigma)}} \qquad (65)$$

$$S_{1,1+A}^{(\sigma)} \equiv S_{1+A,1}^{(\sigma)} \equiv \frac{1}{T^{(\sigma)}} \left[\frac{\partial \mu_{(A)}^{(\sigma)}}{\partial S^{(\sigma)}}\right]_{\rho_{(C)}^{(\sigma)}}$$

$$\text{for} \quad A = 1, 2, \ldots, N \qquad (66)$$

$$S_{1+A,1+B}^{(\sigma)} = S_{1+B,1+A}^{(\sigma)} \equiv \frac{1}{T^{(\sigma)}} \left[\frac{\partial \mu_{(A)}^{(\sigma)}}{\partial \rho_{(B)}^{(\sigma)}}\right]_{\overline{S}^{(\sigma)}, \rho_{(C)}^{(\sigma)}\ (C \neq B)}$$

$$\text{for} \quad A, B = 1, 2, \ldots, N \qquad (67)$$

In writing Equation (67), I have observed that

$$\left[\frac{\partial \mu_{(A)}^{(\sigma)}}{\partial \rho_{(B)}^{(\sigma)}}\right]_{\overline{S}^{(\sigma)}, \rho_{(C)}^{(\sigma)}\ (C \neq B)} = \left[\frac{\partial \mu_{(B)}^{(\sigma)}}{\partial \rho_{(A)}^{(\sigma)}}\right]_{\overline{S}^{(\sigma)}, \rho_{(C)}^{(\sigma)}\ (C \neq A)} \qquad (68)$$

Note that, like $\mathbf{S}$, $\mathbf{S}^{(\sigma)}$ is also symmetric.

There are two conclusions that should be drawn from this discussion:

1. For an intrinsically stable equilibrium, Equation (53) must hold at each point within a phase, where $\mathbf{S}$ is the self-adjoint transformation whose matrix with respect to the basis Equations (54) is defined by Equations (55) through (59). This means that $\mathbf{S}$ is a positive transformation (Halmos, 1958). In order that $\mathbf{S}$ be positive, it is necessary and sufficient that the principal minors of the determinant of $\mathbf{S}$ all be greater than zero (Halmos, 1958). (If we cross out rows and columns bearing the same numbers in the matrix of $\mathbf{S}$, the remaining small matrix is still positive and so is its determinant. The determinants found in this manner are the principal minors of the determinant of $\mathbf{S}$.) These are constraints that must be satisfied by any caloric equations of state taking the form of Equation (22) at those conditions capable of supporting an intrinsically stable equilibrium.

2. For an intrinsically stable equilibrium, Equation (63) must be satisfied at each point on the dividing surface Σ, where $\mathbf{S}^{(\sigma)}$ is the self-adjoint transformation whose matrix with respect to the basis Equations (64) is defined by Equations (65) through (67). We conclude that $\mathbf{S}^{(\sigma)}$ is also positive. The necessary and sufficient conditions for $\mathbf{S}^{(\sigma)}$ to be positive are that the principal minors of the determinant of $\mathbf{S}^{(\sigma)}$ all be greater than zero. These are constraints that must be satisfied by any surface caloric equation of state taking the form of Equation (25) at those conditions capable of supporting an intrinsically stable equilibrium.

LIMITING CRITERIA FOR INTRINSICALLY STABLE EQUILIBRIUM

The tensor $\mathbf{S}$ is symmetric. Consequently, there is a basis for the vector space whose elements are ordered sets of $N + 2$, real valued functions of time and position with respect to which the matrix of $\mathbf{S}$ assumes a diagonal form (Birkhoff and MacLane, 1953; Halmos, 1958). The entries on the diagonal are known as the proper or characteristic values of the transformation. Without constructing the specific forms for these proper values, there are three interesting conclusions that we can draw:

1. At those conditions capable of supporting an intrinsically stable equilibrium, the caloric equation of state must be such that the determinant of $\mathbf{S}$ as well as the proper values of $\mathbf{S}$ must all be greater than zero.

2. At those conditions capable of supporting an intrinsically stable equilibrium, there are no more than $N + 2$ independent constraints upon the caloric equation of state (for example, the $N + 2$ proper values of $\mathbf{S}$).

As soon as any one of the proper values of $\mathbf{S}$ goes to zero, det $\mathbf{S}$ goes to zero. Therefore, the limiting criterion for an intrinsically stable equilibrium is det $\mathbf{S} > 0$. But we can be more specific. As shown in Appendix D,* each succeeding proper value is more critical in defining the limits of intrinsic stability for a particular caloric equation of state. This leads us to our third conclusion.

3. The limiting criterion for an intrinsically stable equilibrium with a particular caloric equation of state is

$$\frac{\det \mathbf{S}}{D_n} = \frac{\rho}{T} \frac{D_{N+1}}{D_N} > 0 \qquad (69)$$

with the determinants D_k defined by

$$D_k \equiv \begin{vmatrix} S_{11} & \ldots & S_{1k} \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ S_{k1} & \ldots & S_{kk} \end{vmatrix} \qquad (70)$$

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* See footnote on p. 277.

This has been recognized previously by Modell and Reid (1974) (see also Beegle, Modell, and Reid, 1974).

The tensor $\mathbf{S}^{(\sigma)}$ is also symmetric. There is a basis for the vector space whose elements are ordered sets of $N + 1$, real valued functions of time and position on the dividing surface Σ with respect to which the matrix of $\mathbf{S}^{(\sigma)}$ assumes a diagonal form (Birkhoff and MacLane, 1953; Halmos, 1958). By analogy with our discussion of $\mathbf{S}$, we can make three similar statements about the surface caloric equation of state:

4. At those conditions capable of supporting an intrinsically stable equilibrium, the surface caloric equation of state must be such that the determinant of $\mathbf{S}^{(\sigma)}$ as well as the proper values of $\mathbf{S}^{(\sigma)}$ must all be greater than zero.
5. At those conditions capable of supporting an intrinsically stable equilibrium, there are no more than $N + 1$ independent constraints upon the surface caloric equation of state [for example, the $N + 1$ proper values of $\mathbf{S}^{(\sigma)}$].
6. The limiting criterion for an intrinsically stable equilibrium with a particular surface caloric equation of state is

$$\frac{\det \mathbf{S}^{(\sigma)}}{D^{(\sigma)}_{N}} = \frac{D^{(\sigma)}_{N+1}}{D^{(\sigma)}_{N}} > 0 \tag{71}$$

with the determinants of $D^{(\sigma)}_{k}$ defined by

$$D^{(\sigma)}_{k} \equiv \begin{vmatrix} S^{(\sigma)}_{11} & \ldots & S^{(\sigma)}_{1k} \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ S^{(\sigma)}_{k1} & \ldots & S^{(\sigma)}_{kk} \end{vmatrix} \tag{72}$$

The implications of Equations (69) and (71) for one- and two-component systems are detailed in Appendix E.* More generally, in a multicomponent system, Equation (69) implies that the limiting criterion for an intrinsically stable equilibrium with a particular caloric equation of state is†

$$\begin{aligned} \frac{\det \mathbf{S}}{D_N} &= \frac{\rho}{T}\,\frac{D_{N+1}}{D_N} \\ &= \frac{\rho}{T^2}\left[\frac{\partial \mu_{(N)}}{\partial \rho_{(N)}}\right]_{T,\mu_{(k)}\ (k\neq N)} \\ &= \frac{1}{T^2\omega_{(N)}}\left[\frac{\partial P}{\partial \rho_{(N)}}\right]_{T,\mu_{(k)}\ (k\neq N)} > 0 \end{aligned} \tag{73}$$

where N may refer to any one of the N species, since the ordering of terms in defining $\mathbf{S}$ is arbitrary. For this same reason, an equivalent stability criterion is

$$\frac{\rho}{T^2}\left(\frac{\partial T}{\partial \check{S}}\right)_{\mu_{(k)}} = \frac{1}{T^2\,\hat{S}}\left(\frac{\partial P}{\partial \check{S}}\right)_{\mu_{(k)}} > 0 \tag{74}$$

Equation (71) requires that, in a multicomponent svstem, the limiting criterion for an intrinsically stable equilibrium with a particular surface caloric equation of state is†

$$\begin{aligned} \frac{\det \mathbf{S}^{(\sigma)}}{D^{(\sigma)}_{N}} &= \frac{D^{(\sigma)}_{N+1}}{D^{(\sigma)}_{N}} \\ &= \frac{1}{T^{(\sigma)}}\left[\frac{\partial \mu^{(\sigma)}_{(N)}}{\partial \rho^{(\sigma)}_{(N)}}\right]_{T^{(\sigma)},\mu^{(\sigma)}_{(k)}\ (k\neq N)} \\ &= -\frac{1}{T^{(\sigma)}\,\rho^{(\sigma)}_{(N)}}\left[\frac{\partial \gamma}{\partial \rho^{(\sigma)}_{(N)}}\right]_{T^{(\sigma)},\mu^{(\sigma)}_{(k)}\ (k\neq N)} > 0 \end{aligned} \tag{75}$$

where again N may refer to any one of the N species, since the ordering of terms in defining $\mathbf{S}^{(\sigma)}$ is also arbitrary. An equivalent limiting stability criterion is

$$\frac{1}{T^{(\sigma)}}\left[\frac{\partial T^{(\sigma)}}{\partial \overline{S}^{(\sigma)}}\right]_{\mu^{(\sigma)}_{(k)}} = -\frac{1}{T^{(\sigma)}\,\overline{S}^{(\sigma)}}\left[\frac{\partial \gamma}{\partial \overline{S}^{(\sigma)}}\right]_{\mu^{(\sigma)}_{(k)}} > 0 \tag{76}$$

SUMMARY

We have assumed that Equation (22) describes the form of the caloric equation of state within a phase and that Equation (25) denotes the form of the surface caloric equation of state on a phase interface. With these assumtions, we find that, in order for a multiphase, multicomponent system to exist in an intrinsically stable equilibrium state, Equation (73) must be satisfied within every phase and Equation (75) must be satisfied on every phase interface. The limits of intrinsically stable equilibrium are defined by the failure of Equation (73) within one of the phases or by the failure of Equation (75) on one of the phase interfaces.

Consider a relatively insoluble material spread as a monolayer over a portion of a liquid-gas interface bounded by movable barriers. As the spread film is slowly compressed, the interfacial tension γ decreases as the surface mass density $\rho^{(\sigma)}_{(N)}$ of the insoluble material increases in accord with Equation (75). Note that if the compression takes place sufficiently slowly, we would expect the surface chemical potentials $\mu^{(\sigma)}_{(k)}$ ($k = 1, 2, \ldots, N - 1$) of the other species present to remain fixed at the values of their chemical potentials in the adjoining phases. But there is a minimum value of the interfacial tension that can be achieved in this way by compression of the monolayer. If further compression is attempted, the monolayer collapses, and the spread material is forced out of the monolayer into the adjacent liquid phase (Gaines, 1966). This collapse point appears to correspond to a limit of intrinsic stability for the multiphase system at which Equation (75) is violated on that portion of the liquid-gas interface within the barriers.

The interpretation of experimental observations in terms of the limiting criteria for intrinsic stability involves a certain amount of speculation. Although it seems likely, we cannot be certain that, in the experiment described above, Equation (75) is violated on the interface within the barriers before Equation (73) fails within the adjacent liquid phase. It is perhaps safe to say only that the experimentally observed collapse point occurs within the neighborhood of the limit of intrinsic stability.

It is more appropriate to look forward to using Equations (73) and (75) in predicting the limits of intrinsic stability in multiphase, multicomponent systems. In addition to the collapse point of a monolayer, one might consider the limiting conditions at which phase transitions occur in monolayers (Gaines, 1966), the limiting conditions under which a macroemulsion is transformed into a micellar solution (or microemulsion) (Gerbacia and Rosano, 1973), and the limiting conditions for the multiple phase transitions that can be observed upon the addition

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* See footnote on p. 277.

† In going from the first to the second lines of Equations (73) and (75), I have employed an expression for the second derivative of a second Lengendre transform given by Beegle, Modell, and Reid (1974) [see Equations (31) and (35)]. This same relationship has been used in proceeding from the third to the fourth lines of Equations (E4) and (E12) and from the first to the second lines of Equations (E6) and (E14).

of a mixed surfactant system to a two-phase mixture of crude oil and brine (Robbins, 1976). In studies of organic-brine-mixed surfactant systems, interfacial tension displays a distinct minimum as a function of concentration (Cayias et al. 1976; Wilson et al., 1976). In the absence of contrary evidence, one might speculate that the minimum interfacial tension occurs within the immediate neighborhood of a limit of intrinsic stability. This speculation may be supported by the observation of Healy et al. (1976) that very low interfacial tensions were accompanied by a phase transition.

NOTATION

$\hat{A}$ = Helmholtz free energy per unit mass within a phase

$\check{A}$ = Helmholtz free energy per unit volume within a phase

$\hat{A}^{(\sigma)}$ = Helmholtz free energy per unit mass within a phase interface

$\overline{A}^{(\sigma)}$ = Helmholtz free energy per unit area within a phase interface

$\hat{\mathcal{A}}$ = area per unit mass in a phase interface

$\mathbf{B}$ = second groundform tangential tensor field (McConnell, 1957)

$\mathbf{b}_{(A)}$ = body force per unit mass acting on species A within a phase

$\mathbf{b}_{(A)}^{(\sigma)}$ = body force per unit mass acting on species A within a phase interface

C = closed curve bounding Σ

dA = denotes that an area integration is to be performed

D_K = defined by Equation (70)

$D_K^{(\sigma)}$ = defined by Equation (72)

ds = indicates that a line integration is to be performed

dV = indicates that a volume integration is to be performed

$\check{E}$ = defined by Equation (13)

$\overline{E}^{(\sigma)}$ = defined by Equation (14)

H = mean curvature of the phase interface (McConnell, 1957)

$M_{(A)}$ = molecular weight of species A

R = region occupied by multiphase, multicomponent body

$r_{(A,j)}$ = rate at which mass of species A is produced per unit volume by the homogeneous chemical reaction j ($j = 1, 2, \ldots, J$)

$r_{(A,j)}^{(\sigma)}$ = rate at which mass of species A is produced per unit area by the heterogeneous chemical reaction k ($k = 1, 2, \ldots, K$)

S = entropy per unit volume within a phase

$\mathbf{S}$ = transformation whose matrix with respect to the basis Equation (54) is defined by Equations (55) through (59)

$\overline{S}^{(\sigma)}$ = entropy per unit area on a phase interface

$\mathbf{S}^{(\sigma)}$ = transformation whose matrix with respect to the basis Equations (64) is defined by Equations (65) through (67)

S_{ij} = elements of the matrix of $\mathbf{S}$ defined by Equations (55) through (59)

$S_{ij}^{(\sigma)}$ = elements of the matrix of $\mathbf{S}$ defined by Equations (65) through (67)

T = temperature within a phase

t = time

t_e = time at which equilibrium is attained

$T^{(\sigma)}$ = temperature within a phase interface

$\mathbf{u}$ = velocity of a point on the surface with a fixed set of surface coordinates (Slattery, 1974)

$\hat{U}$ = internal energy per unit mass within a phase

$\hat{U}^{(\sigma)}$ = internal energy per unit mass on a phase interface

$\hat{V}$ = volume per unit mass within a phase

$\mathbf{v}^{(\sigma)}$ = mass-averaged velocity in an interface

$v_{(\xi)}^{(\sigma)}$ = speed of displacement of interface

$$v_{(\xi)}^{(\sigma)} \equiv \mathbf{v}^{(\sigma)} \cdot \boldsymbol{\xi} = \mathbf{u} \cdot \boldsymbol{\xi}$$

$\mathbf{v}_{(A)}$ = velocity of species A within a phase

$\mathbf{v}_{(A)}^{(\sigma)}$ = velocity of species A in a phase interphase

$\mathbf{x}$ = defined by Equation (52)

$\mathbf{x}^{(\sigma)}$ = defined by Equation (62)

Z_A = defined by Equation (8)

Z_e = defined by Equation (12)

$\mathbf{Z}_m$ = defined by Equation (10)

Greek Letters

γ = interfacial tension, defined by Equation (34)

$\boldsymbol{\gamma}_k$ = defined by Equations (54)

$\boldsymbol{\gamma}_k^{(\sigma)}$ = defined by Equations (64)

λ_A, λ_e = Lagrangian multipliers

$\boldsymbol{\lambda}_m$ = constant spatial vector, the components of which are Lagrangian multipliers

$\mu_{(A)}$ = chemical potential on a mass basis within a phase, defined by Equation (24)

$\mu_{(A)}^{(\sigma)}$ = chemical potential on a mass basis within a phase interface, defined by Equation (27)

$\boldsymbol{\mu}$ = unit normal to a closed curve bounding Σ that is both tangent to Σ and outwardly directed with respect to Σ

$\nu_{(A,j)}$ = stoichiometric coefficient for species A in the homogeneous chemical reaction j. This is taken to be a positive number for a species consumed in the reaction.

$\nu_{(A,k)}^{(\sigma)}$ = stoichiometric coefficient for species A in the heterogeneous chemical reaction k. This is taken to be a positive number for a species consumed in the reaction.

$\boldsymbol{\xi}$ = unit normal to the phase interface (see Appendix A)

$\boldsymbol{\xi}^{(i)}$ = unit normal to Σ pointing into phase i

ρ = total mass density within a phase

$\rho^{(\sigma)}$ = total mass density on a phase interface

$\rho_{(A)}$ = mass density of species A within a phase

$\rho_{(A)}^{(\sigma)}$ = mass density of species A on a phase interface

Σ = collection of phase interfaces within the multiphase, multicomponent body

$\phi_{(A)}$ = potential energy per unit mass attributable to $\mathbf{b}_{(A)}$

$\phi_{(A)}^{(\sigma)}$ = potential energy per unit mass attributable to $\mathbf{b}_{(A)}^{(\sigma)}$

$\psi_{(j)}$ = j^{th} homogeneous reaction coordinate defined by Equation (6)

$\psi_{(k)}^{(\sigma)}$ = k^{th} heterogeneous reaction coordinate defined by Equation (7)

$\omega_{(A)}$ = mass fraction of species A within a phase

$\omega_{(A)}^{(\sigma)}$ = mass fraction of species A within a phase interface

Other

$\partial/\partial t$ = derivative with respect to time. When applied to a quantity associated with R, position in R is held constant. When applied to a quantity associated with Σ, the surface coordinates (Slattery, 1974) denoting position on Σ are fixed.

$d_{(\mathbf{v})}/dt$ = derivative with respect to time following a point within a phase that moves with the mass averaged velocity $\mathbf{v}$

$d_{[\mathbf{v}^{(\sigma)}]}/dt$ = derivative with respect to time following a point in the interface that moves with the mass averaged velocity $\mathbf{v}^{(\sigma)}$

∇ = gradient

$\nabla_{(\sigma)}$ = surface gradient operation (Slattery, 1974)

div = divergence

$\text{div}_{(\sigma)}$ = surface gradient operation (Slattery, 1974)

det = determinant

[ ] = shorthand notation defined by Equation (3)

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Manuscript received July 20, and accepted December 10, 1976.

The Relation Between the Reaction Mechanism and the Stoichiometric Behavior of Chemical Reactions

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The need to describe stoichiometric behavior of complex chemical reactions by independent reactions was first recognized by Gibbs (1876, 1961) in his work on heterogenous chemical equilibria. Since then, several authors have attacked the problem to find the independent reactions or the number of them from basic knowledge of the composition of the components and their reaction tendencies (Jouguet, 1921; Defay, 1931; Brinkley, 1946; Prigo-