NONUNIQUENESS OF EQUILIBRIA IN CLOSED REACTING SYSTEMS

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Abstract—While the equilibrium point in an *ideal* closed reacting system is unique and globally stable, it is shown herein that *nonideal* systems can have multiple equilibria and that more than one of these can be stable. The simplest kind of nonideality, exemplified by strictly regular solutions, can lead to large jumps in the equilibrium concentrations with only small parameter changes, in analogy to behavior known for open systems.

1. INTRODUCTION

A deeper understanding of both the transient and equilibrium behavior of chemically-reacting systems is important in many disciplines, ranging from chemical reaction engineering to theoretical biology. Despite the numerous analyses devoted to either open or closed and uniform or nonuniform systems (see Refs. [1–5]), our knowledge of general reacting systems is still inadequate in many respects. The equilibrium behavior of closed, *ideal* systems has been most thoroughly studied, both with respect to existence and uniqueness of thermodynamic equilibria and with respect to the relationship between kinetic and thermodynamic equilibria. Such systems have a unique thermodynamic equilibrium point and if the kinetics are modelled by mass action rate laws the kinetic and thermodynamic equilibrium points coincide [6–8]. However, ideal systems comprise a very limited class of solution behavior and as Eckert[9] has recently emphasized, chemical reactions in nonideal systems are important in many instances. Unfortunately the range of nonideal behavior is so wide and gives rise to such a diversity of descriptions that a general analysis is out of the question; case by case studies are required. Our purpose here is to study one special class of nonideal systems with a view toward discovering what may be expected in general. We shall focus primarily on the question of multiplicity of equilibria in these systems.

When analyzing systems with many components and reactions for multiple equilibria, it is useful to describe the system from a more abstract point of view. In the following section we introduce the necessary concepts and terminology for a modern treatment of kinetics and equilibria, along with the basic definitions of stability. Section 3, which contains the majority of the new results, deals with the equilibria in binary and ternary reacting systems.†

Although the emphasis throughout the third section is on equilibrium systems, it is important to determine whether the equilibrium solutions can in fact be obtained as the asymptotic limit as $t \to \infty$ of an appropriate initial

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†After submitting this manuscript, we received a preprint of a paper by Caram H. and Scriven L. E., *Chem. Engng Sci.* 1976 **31** 163, which treats a binary reacting system using several different models of nonideality, among them the one used here.

value problem. To answer this in complete generality is beyond the scope of this paper, but one aspect is discussed in the concluding section.

2. PRELIMINARIES ON KINETICS, EQUILIBRIA AND PHASE STABILITY

(a) Kinetics and equilibria

To provide a common framework for the analyses in the following section, it is necessary to adopt terminology and definitions that apply for any number of components and reactions. Our terminology will follow that in [6, 10–12]. For simplicity, we first restrict attention to closed, uniform systems at constant temperature and pressure.

Suppose that in a single-phase system containing N chemical species $\mathscr{A}_i$ there are $r \leq N - 1$ independent reactions, written as

$$\sum_{i=1}^{N} \nu_{ij} \mathscr{A}_i = 0 \quad j = 1, \ldots r. \tag{1}$$

With each reaction is associated a rate function $\bar{R}_j(c)$ that relates the intrinsic rate of reaction to the composition variables $c_1, \ldots, c_N$. The time evolution of the mixture's composition is given by the solution of the kinetic equations

$$\frac{d\mathbf{n}}{dt} = V \underline{\nu} \bar{R}(c). \tag{2}$$

Because

$$V = V(\mathbf{n}) = \sum_{i=1}^{N} v_i(\mathbf{n}) n_i,$$

this equation can be written

$$\frac{1}{V(\mathbf{n})} \frac{d\mathbf{n}}{dt} = \underline{\nu} \bar{R}(\mathbf{n}/V(n)) \equiv \underline{\nu} \mathbf{R}(\mathbf{n}) \tag{3}$$

where $\mathbf{R}(\mathbf{n})$ is homogeneous of degree zero in $\mathbf{n}$. Throughout we assume that the Jacobian $\partial \mathbf{R}/\partial \mathbf{n}$ has rank r everywhere in the nonnegative orthant R_N^+ of the N-dimensional composition space. Any physically-meaningful solution of (3) must also lie in R_N^+.

Since there are only r independent reactions, the rank $\rho(\underset{\sim}{\nu})$ of the stoichiometric matrix $\underset{\sim}{\nu}$ is r and the null space of $\underset{\sim}{\nu}^T$ has dimension $N - r$. If $\{\Omega_j\}$, $j = 1, \ldots N - r$, is a basis for the null space of $\underset{\sim}{\nu}^T$, the $N - r$ quantities $\langle \Omega_j, n \rangle$ are invariant under (3). The equations

$$\langle \Omega_j, n - n^0 \rangle = 0 \quad j = 1, \ldots N - r \quad (4)$$

define an inhomogeneous linear manifold whose intersection with R_N^+ will be called the *reaction simplex* $\Omega(n^0)$ through the point n^0. All points of a fixed simplex are equivalent by virtue of belonging to the same coset of the subspace defined by $\langle \Omega_j, n \rangle = 0$, $j = 1, \ldots N - r$. All possible simplices are generated by varying the initial composition n^0. Without loss of generality, the $N - r$ vectors Ω_j that are normal to a simplex can be so chosen that each quantity $\langle \Omega_j, n \rangle$ is nonnegative, and each represents either the total mass or one of the $N - r - 1$ linear combinations of species that is conserved.

If we require that

$$\sum_j \nu_{ij} R_j(n_1, \ldots \overset{i}{0}, \ldots n_N) \geq 0 \quad i = 1, \ldots N \quad (5)$$

then the composition vector of any closed uniform system is confined to the simplex in which it begins. By the law of definite proportions[13], the composition change in the jth reaction can be characterized by an extent ξ_j and the set $\{\xi_j\}$, $j = 1, \ldots r$ can serve as a set of coordinates in Ω. All composition changes are then expressible in the form

$$n(t) - n^0 = \underset{\sim}{\nu} \xi(t). \quad (6)$$

A composition $n^* \epsilon R_N^+$ at which $\nu R(n^*) = 0$ is called a steady state composition or a point of *kinetic equilibrium*. Because $\rho(\underset{\sim}{\nu}) = r$, kinetic equilibrium requires that $R_j(n^*) = 0$, $j = 1, \ldots r$. By virtue of the assumption that $\rho(\partial R / \partial n) = r$, the implicit function theorem implies that the system of equations $R = 0$ defines an $N - r$ dimensional submanifold of R_N^+[14]. We call this manifold the kinetic equilibrium manifold KE. At a fixed n^0, the kinetic equilibrium points lie in the intersection of KE and $\Omega(n^0)$ and thus are given by

$$\{n^* \epsilon R_N^+ | n^* \epsilon KE \cap \Omega(n^0)\} \quad (7)$$

or alternatively, by

$$\{n^* \epsilon R_N^+ | n^* = n^0 + \underset{\sim}{\nu} \xi^* ; \bar{R}_j(\xi^*, n^0) = 0, \quad j = 1, \ldots r\}.$$

(In the latter description $R_j(\xi, n^0) : R_j(n) | \Omega(n^0)$ is the restriction of $R_j(n)$ to $\Omega(n^0)$.) It is well known[15] that these sets are nonempty provided the R_j are Lipschitzian. Whether or not they contain more than one point is the subject of the following section.

According to the classical definition, a *thermodynamic equilibrium point* in a single phase reacting system is a point at which the affinity

$$A_j = - \sum_{i=1}^N \nu_{ij} \mu_i \quad j = 1, \ldots r \quad (8)$$

of each of the reactions vanishes[13]. In view of the definition $\mu_i \equiv (\partial G / \partial n_i)_{T,P,n_j}$, the condition for equilibrium can be written

$$A = - \underset{\sim}{\nu}^T \mu = - \underset{\sim}{\nu}^T \frac{\partial G}{\partial n} = 0. \quad (9)$$

If $\partial G / \partial n$ is resolved into components orthogonal and parallel to Ω, then (9) can be written

$$\underset{\sim}{\nu}^T \left(\frac{\partial G}{\partial n} \right)^\perp + \underset{\sim}{\nu}^T \left(\frac{\partial G}{\partial n} \right)^\parallel = 0. \quad (10)$$

Since $\underset{\sim}{\nu}^T$ annihilates vectors orthogonal to Ω, this reduces to

$$\underset{\sim}{\nu}^T \left(\frac{\partial G}{\partial n} \right)^\parallel = 0 \quad (11)$$

and therefore equilibrium points coincide with the critical points of $G | \Omega$ for any n^0.

In any open set of R_N^+ in which the Jacobian $\partial A / \partial n$ has rank $s \leq r$, the equations $A = 0$ define an $N - s$ dimensional submanifold TE, called the thermodynamic equilibrium manifold. For any fixed n^0, the set of points

$$\{n^* \epsilon R_N^+ | n^* \epsilon TE \cap \Omega(n^0)\} \quad (12)$$

are the thermodynamic equilibrium points compatible with n^0. The following argument shows that this set is nonempty.

Any equilibrium point $n^* = n^0 + \underset{\sim}{\nu} \xi^*$ must satisfy

$$\frac{\partial \tilde{G}}{\partial \xi}(\xi^*, n^0) \equiv \frac{\partial}{\partial n}(G | \Omega(n^0))|_{n^*} = 0. \quad (13)$$

The simplex $\Omega(n^0)$ is closed and bounded and G is a smooth function throughout $\Omega(n^0)$; therefore it achieves its maximum and minimum on $\Omega(n^0)$. The chemical potential μ_i can always be written[13]

$$\mu_i = \mu_i^0(T, P) + RT \ln \gamma_i(n) x_i = \frac{\partial G}{\partial n_i} \quad (14)$$

where $\gamma_i(n) \to \text{constant} > 0$ as $n_i \to 0$. Accordingly, $\partial G / \partial n_i \to -\infty$ as $n_i \to 0$ and $G | \Omega(n^0)$ has no critical points on the boundary. This implies that there exists at least one thermodynamic equilibrium point in the interior of $\Omega(n^0)$ and that this point is at a local minimum of $G | \Omega(n^0)$. Moreover, there is only one such point if the Jacobian

$$\frac{\partial \tilde{A}}{\partial \xi} \equiv \frac{\partial (A | \Omega(n^0))}{\partial n} = - \underset{\sim}{\nu}^T \frac{\partial^2 G}{\partial n \partial n} \underset{\sim}{\nu} = - \frac{\partial^2 G}{\partial \xi \partial \xi} \quad (15)$$

is positive definite throughout $\Omega(n^0)$. Clearly $\rho(\partial \tilde{A} / \partial \xi)$ is independent of n^0, but because the activity coefficients γ_i depend on molecular parameters that characterize the interactions between species, $\rho(\partial \tilde{A} / \partial \xi)$ will indirectly depend on these parameters. Several specific systems are studied in the following section.

Thus far we have distinguished between kinetic and

thermodynamic equilibria. However, if the class of admissible dynamical processes is restricted *a priori* to those for which $dG/dt \leq 0$, with equality only at kinetic equilibria, then all interior kinetic equilibria for which $\rho(\partial R/\partial n) = r$ are also thermodynamic equilibria[5, 10, 11]. We have assumed $\rho(\partial R/\partial n) = r$ throughout $R_N{}^+$ and therefore every interior point of kinetic equilibrium is a point of thermodynamic equilibrium. This precludes the occurrence of any so-called false equilibria, at which $R = 0$ but $A \neq 0$, in the interior of $\Omega(n^0)$ but does not prevent their occurrence on the boundary of the simplex. If the latter occur they are inaccessible from the interior of the simplex.

In addition to providing a relationship between the two kinds of equilibria, the postulate that $dG/dt \leq 0$ places restrictions on the constitutive relations for the affinity and reaction rate. Since

$$\frac{dG}{dt} = \frac{d}{dt}\langle \mu, n \rangle = -V(n)\langle A, R \rangle \leq 0, \qquad (16)$$

it is necessary that $\langle A, R \rangle \geq 0$ for all n reachable from an initial composition n^0. It will be evident that the constitutive relations used in the following section satisfy this restriction.

(b) *Conditions for phase stability*

The question of uniqueness of thermodynamic or kinetic equilibria goes hand in hand with the question of phase stability. A homogeneous phase can persist only if all random, non-uniform concentration disturbances decay in time and this is certainly impossible if there exists more than one equilibrium point. At constant T and P, an equilibrium state is thermodynamically stable if

$$\left\langle \zeta, \frac{\partial^2 G}{\partial n \partial n} \zeta \right\rangle > 0 \qquad (17)$$

for all ζ compatible with the constraints, with the exception of the neutral displacement $\zeta = \lambda n$, $\lambda > 0$[16]. In a nonreacting system, the necessary and sufficient condition for stability at all compositions is that the Hessian $\partial^2 G/\partial n \partial n$ be positive semidefinite and of rank $N - 1$ throughout $R_N{}^+$. Under these conditions, it follows from (15) that the thermodynamic equilibrium point is unique, and according to a theorem of Duhem and Jouguet[13], it is necessarily stable. This is the case, for example, in ideal systems.

In the general case, a necessary but not sufficient condition for multiple thermodynamic equilibria is that the phase be unstable with respect to diffusion at some compositions. This in turn requires that $\partial^2 G/\partial n \partial n$ have one or more negative eigenvalues in some region of composition space. A mixture brought into an unstable region by manipulating the compositions or external parameters can restore stability either by changing the composition via reaction or by separating into two more phases, provided the latter is allowed by the phase rule. When m phases are possible, minimization of the total free energy subject to the constraint that the total mole

vector

$$n = \sum_{j=1}^{m} n^j$$

satisfies (6) leads to the equilibrium conditions

$$n_i^* = n_i^0 + \sum_k \nu_{ik}\xi_k^*$$

$$\mu_i^1 = \mu_i^2 = \cdots \mu_i^m \quad i = 1, \ldots N \qquad (18)$$

$$A_q = -\sum_i \mu_i \nu_{i_q} \quad q = 1, \ldots r.$$

For fixed m, the uniqueness and stability of equilibrium points is governed by the Jacobian of the equations at (18). One can show that the m-phase system has a unique, stable equilibrium point provided that each of the m phases is stable to disturbances that lie parallel to the reaction simplex. Unfortunately one cannot determine m *a priori*; when the Hessian of the free energy has one or more negative eigenvalues in some region of composition space each value of m consistent with the phase rule must be checked for existence of a solution.

3. MULTIPLE EQUILIBRIA IN NONIDEAL SYSTEMS

(a) *Free energy in a binary regular solution*

Analysis of nonideal systems is complicated by the fact that the dependence of the activity coefficients on composition must be known. Here we consider the simplest class of nonideal systems, those described by the so-called strictly regular solution model[17]. These are characterized by the fact that the components have equal molar volumes but the intermolecular forces are no longer equal, as in ideal solutions. To a first approximation, the excess (or nonideal) entropy of mixing is zero and the internal energy change due to mixing is equal to the free energy change. If one writes

$$G = G_{IDEAL} + G_{EXCESS} \equiv G_I + G_E \qquad (19)$$

then, by a straightforward extension of Lewis and Randall's[18] derivation for the binary case, one finds that

$$G_E = \chi n \sum_{\substack{i=1 \\ j>i}}^{N} (2\epsilon_{ij} - \epsilon_{ii} - \epsilon_{jj})x_i x_j = n\sum_{i \leq j} \omega_{ij}x_i$$

$$= \sum_{i \leq j} \omega_{ij}\frac{n_i n_j}{n}. \qquad (20)$$

Here ϵ_{ij} is the interaction energy between i and j (assumed negative) and χ is a parameter that depends on the model used for the liquid state. It involves Avagadro's number and either the coordination number of the lattice or the radial distribution function. The constants

$$\omega_{ij} \equiv \chi(2\epsilon_{ij} - (\epsilon_{ii} + \epsilon_{jj})). \qquad (21)$$

provide a measure of the nonideality of the solution. Generally it happens that $\omega_{ij} > 0$ since ϵ_{ij} is less negative than $(\epsilon_{ii} + \epsilon_{jj})/2$[18].

The composition dependence of the activity coefficients $\gamma_k(n)$ is obtained from (20) by noting that

$$RT \ln \gamma_k(n) = \frac{\partial G_E}{\partial n_k} = \sum_{i \leq j} \omega_{ij}[\delta_{ik}x_j + \delta_{jk}x_i - x_ix_j]. \quad (22)$$

From this one finds that in binary systems, which we study first, the chemical potentials are given by

$$\mu_1 = \mu_1^0(T, P) + RT \ln x_1 + RT\omega(1 - x_1)^2$$

$$\mu_2 = \mu_2^0(T, P) + RT \ln (1 - x_1) + RT\omega x_1^2 \quad (23)$$

where $\omega \equiv \omega_{12}/RT$. The total free energy is

$$G = \sum_{i=1}^{2} n_i\mu_i = (n_1\mu_1^0 + n_2\mu_2^0)$$

$$+ RT(n_1 \ln x_1 + n_2 \ln (1 - x_1)) + RT\omega n x_1(1 - x_1) \quad (24)$$

and therefore the Hessian of G is

$$\frac{\partial^2 G}{\partial \mathbf{n} \partial \mathbf{n}} = -\frac{RT}{n}\begin{bmatrix} \dfrac{x_1 - 1}{x_1} + 2\omega(1 - x_1)^2 & 1 - 2\omega x_1(1 - x_1) \\ 1 - 2\omega x_1(1 - x_1) & \dfrac{-x_1}{1 - x_1} + 2\omega x_1^2 \end{bmatrix}. \quad (25)$$

This Hessian is singular for all x_1 and has rank zero along the spinodal curve[13]

$$\omega = \frac{1}{2x_1(1 - x_1)}. \quad (26)$$

Since the maximum of $x_1(1 - x_1)$ for $x_1 \epsilon [0, 1]$ is 4, the minimum ω on the spinodal is $\omega = 2$; for $\omega < 2$, the Hessian has rank 1 for all $x_1 \epsilon [0, 1]$ and the binary system is stable with respect to diffusion. It follows that the equilibrium point in any closed binary reacting mixture is unique if $\omega < 2$.

(b) *First-order reaction in a binary system*

Consider a binary mixture of $\mathcal{A}$ and $\mathcal{B}$ that react according to the first-order mechanism

$$\mathcal{A} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathcal{B}. \quad (27)$$

We assume that the kinetics can be derived from transition state theory[19, 20] and therefore the rate is given by

$$R = R_f - R_r = k_f \, e^{-(\mu^+ - \mu_1^0)/RT}\gamma_1 x_1$$

$$- k_r \, e^{-(\mu^+ - \mu_2^0)/RT}\gamma_1 x_2, \quad (28)$$

where μ^+ is the internal portion of the chemical potential of the activated complex. Here and hereafter species $\mathcal{A}$ is denoted by "1" and species $\mathcal{B}$ by "2". Since the volume and total moles remain constant, the mass balance equation for $\mathcal{A}$ is

$$\frac{dx_1}{dt} = -R. \quad (29)$$

By using (22) and rescaling time, this can be written

$$\frac{dx_1}{dt} = \frac{-k_f}{k_r}e^{-(\mu_2^0 - \mu_1^0)/RT} \, e^{\omega(1 - x_1)^2}x_1 + e^{\omega x_1^2}(1 - x_1). \quad (30)$$

Kinetic equilibrium obtains when

$$\frac{k_f}{k_r}e^{-(\mu_2^0 - \mu_1^0)/RT} = \frac{e^{\omega x_1^2}(1 - x_1)}{e^{\omega(1 - x_1)^2}x_1} \quad (31)$$

whereas thermodynamic equilibrium exists when

$$-A = \mu_2 - \mu_1 = 0 = (\mu_2^0 - \mu_1^0) + RT \ln (\gamma_2 x_2/\gamma_1 x_1)$$

or

$$e^{-(\mu_2^0 - \mu_1^0)/RT} = \frac{e^{\omega x_1^2}(1 - x_1)}{e^{\omega(1 - x_1)^2}x_1}. \quad (32)$$

Consequently, the two are equivalent if and only if

$$\frac{k_f}{k_r} = 1, \quad (33)$$

i.e. microscopic reversibility must hold. We assume hereafter that it does, and define the equilibrium constant for the reaction as

$$K = e^{-(\mu_2^0 - \mu_1^0)/RT}. \quad (34)$$

Equation (31) can be rearranged to yield

$$x_1 = \frac{1}{1 + K \, e^{\omega(1 - 2x_1)}} \equiv f(x_1). \quad (35)$$

The qualitative behavior of f is sketched in Fig. 1 for a case in which three roots exist. A double root exists whenever $x_1 = f(x_1)$ and $f'(x_1) = 1$, and from these equations one gets a relation between ω and x_1

$$\omega = \frac{1}{2x_1(1 - x_1)} \quad (36)$$

This locus coincides with the locus along which the Hessian of G has rank zero (see 26), as it must for any binary system.

If we use (36) to eliminate x_1 from (35), the result is a relation between K and ω that must hold on the locus of
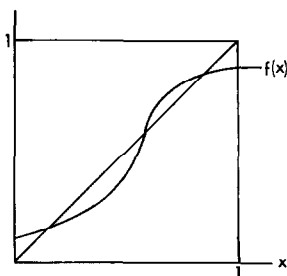

Fig. 1. Graph of the equilibrium function defined by eqn (35).

two equilibrium points:

$$K = e^{\pm\omega\sqrt{(1-2/\omega)}}\left(\frac{1 \mp \sqrt{(1-2/\omega)}}{1 \pm \sqrt{(1-2/\omega)}}\right). \qquad (37)$$

Because both K and ω contain the temperature, we rewrite the foregoing equation in terms of

$$\frac{\ln K}{\omega} = \frac{\mu_1^0 - \mu_2^0}{\omega_{12}} \equiv \frac{\Delta\mu}{\omega_{12}}. \qquad (38)$$

This ratio contains only parameters that characterize $\mathcal{A}$, $\mathcal{B}$ and their interactions, namely, the free energies of the pure components and the interaction energy. From (37) one finds that

$$\frac{\Delta\mu}{\omega_{12}} = \pm\left\{\sqrt{(1-2/\omega)} + \frac{1}{\omega}\ln\left(\frac{2}{\omega(1+\sqrt{(1-2/\omega)})^2}\right)\right\}. \qquad (39)$$

Some elementary analysis of this equation shows that the region of three solutions in the ω vs $\Delta\mu/\omega_{12}$ plane is confined to the strip $|\Delta\mu/\omega_{12}| < 1$; this region is shown in Fig. 2. One concludes that three equilibria are possible only if the $\mathcal{A} - \mathcal{B}$ interactions are sufficiently strong compared to the difference in pure component free energies and then only at a sufficiently low temperature.

In the symmetric case $\Delta\mu = 0$, three solutions exist for all $\omega \geq 2$, that is, for all temperatures below the consolute temperature. Thus instability with respect to diffusion is *necessary and sufficient* for multiple equilibria in this case. However, when $|\Delta\mu| > 0$, the condition $\omega \geq 2$ is no longer sufficient to have three solutions. This can be seen from Fig. 2 but is more graphic if we plot the equilibrium mole fractions x_1 computed from (35) vs ω^{-1}, as in Fig. 3. Here the symmetric solid curve is the spinodal curve; below this curve a nonreacting binary mixture is unstable. The curves on which the reaction equilibria lie are shown for several values of $\Delta\mu$. When $\Delta\mu = 0$ the locus consists of the vertical line $x_1 = 1/2$ and the symmetric parabolic dashed line tangent to the spinodal at $\omega^{-1} = 1/2$. The latter corresponds to the usual coexistence curve for a nonreacting mixture, so that when $\Delta\mu = 0$ there are two equilibria that are stable to all disturbances.

As $\Delta\mu$ increases from 0 the symmetric locus splits into two disjoint branches at (1/2, 1/2) and one equilibrium point lies outside the coexistence curve, one lies between the spinodal and the coexistence curves, and one lies within the spinodal region. The curve for $\Delta\mu/\omega_{12} = 1/4$ is
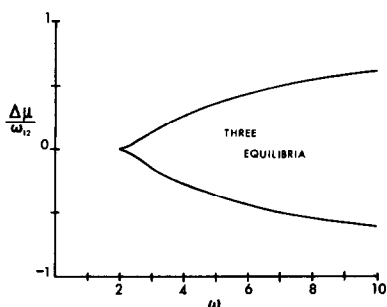
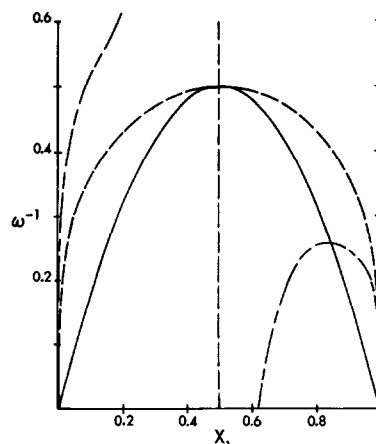Fig. 2. The $\omega - \Delta\mu/\omega_{12}$ plane for the reaction $\mathcal{A} \rightleftharpoons \mathcal{B}$.

Fig. 3. The $x_1 - \omega^{-1}$ plane for several values of $\Delta\mu/\omega_{12}$. Solid line: spinodal, dashed line ----: $\Delta\mu = 0$, broken line ———: $\Delta\mu/\omega_{12} = 1/4$.

shown in Fig. 3; the corresponding curve for $\Delta\mu/\omega_{12} = -1/4$ is the mirror image across $x_1 = 1/2$ of this curve. The fact that the locus of equilibria consists of two branches has an interesting consequence for the behavior of the system as T is varied. Suppose that $\Delta\mu/\omega_{12} = 1/4$ and that initially one can prepare a mixture whose equilibrium composition lies on the curve between the spinodal and coexistence curves. If fluctuations are small or diffusion very slow, the system can be held on this curve as T is increased, until the two equilibria with largest x_1 coalesce on the spinodal. At this temperature a sharp jump in concentration to the other branch would occur and thereafter the system would progress along the branch that lies outside the coexistence. Such hard bifurcations are analogous to those that exist in open systems that have multiple steady states[4]. What is different here is the fact that the transition from high x_1 to low x_1 is irreversible; the system can never return to the high x_1 branch as the temperature is lowered.

(c) *Ternary systems*

At constant T and P, ternary systems in which two independent reactions occur can only exist in one phase. While their analysis is more difficult in view of the wide range of ternary behavior possible, nothing essentially different from the binary case arises. However, when there is a single reaction, there is one degree of freedom and new possibilities arise. If one species is nonreacting, the analysis is very similar to that already done, even when the inert species interacts differently with each of the reacting species. Therefore, we restrict our attention to a reversible, bimolecular reaction that involves the three species $\mathcal{A}$, $\mathcal{B}$ and $\mathcal{C}$. We again assume that the regular solution model describes the mixture and from (22) find that

$$RT \ln \gamma_1 = \omega_{12}x_2^2 + \omega_{13}x_3^2 + (\omega_{12} - \omega_{23} + \omega_{13})x_2x_3$$

$$RT \ln \gamma_2 = \omega_{12}x_1^2 + \omega_{23}x_3^2 + (\omega_{12} + \omega_{23} - \omega_{13})x_1x_3$$

$$RT \ln \gamma_3 = \omega_{13}x_1^2 + \omega_{23}x_2^2 + (\omega_{13} + \omega_{23} - \omega_{12})x_1x_2. \qquad (40)$$

where the subscripts 1, 2 and 3 denote the species $\mathcal{A}$, $\mathcal{B}$
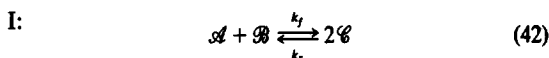
and $\mathscr{C}$, respectively. Any kinetic or equilibrium equation that results from using these general expressions is difficult to analyze in any generality, so we consider the special case in which $\mathscr{A} - \mathscr{C}$ and $\mathscr{B} - \mathscr{C}$ interactions are ideal but $\mathscr{A} - \mathscr{B}$ interactions are nonideal. In this case $\omega_{12} \neq 0$, $\omega_{13} = \omega_{23} = 0$, and (40) reduces to

$$\ln \gamma_1 = \omega x_2(x_2 + x_3) = \omega x_2(1 - x_1)$$

$$\ln \gamma_2 = \omega x_1(x_1 + x_3) = \omega x_1(1 - x_2)$$
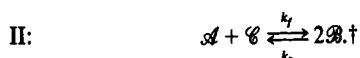
$$\ln \gamma_3 = - \omega x_1 x_2 \qquad (41)$$

where

$$\omega \equiv \omega_{12}/RT.$$

Given these limitations on the interactions between $\mathscr{A}$, $\mathscr{B}$ and $\mathscr{C}$, there are essentially only two distinct types of bimolecular reactions that involve all three species, viz.

I:
$$\mathscr{A} + \mathscr{B} \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2\mathscr{C} \qquad (42)$$

and

II:
$$\mathscr{A} + \mathscr{C} \underset{k_r}{\overset{k_f}{\rightleftarrows}} 2\mathscr{B}.\dagger$$

For I we suppose that

$$-\frac{\mathrm{d}n_1}{\mathrm{d}t} = -\frac{\mathrm{d}n_2}{\mathrm{d}t} = \frac{1}{2}\frac{\mathrm{d}n_3}{\mathrm{d}t} = k_f \gamma_1 \gamma_2 x_1 x_2 - k_r(\gamma_3 x_3)^2 \qquad (43)$$

and for II

$$-\frac{\mathrm{d}n_1}{\mathrm{d}t} = -\frac{\mathrm{d}n_3}{\mathrm{d}t} = \frac{1}{2}\frac{\mathrm{d}n_2}{\mathrm{d}t}$$

$$= k_f \gamma_1 \gamma_3 x_1 x_3 - k_r(\gamma_2 x_2)^2.$$

Kinetic equilibria for these reactions satisfy

$$K = \frac{k_f}{k_r} = \begin{cases} \dfrac{(\gamma_3 x_3)^2}{\gamma_1 \gamma_2 x_1 x_2}: & \text{I} \\[4mm] \dfrac{(\gamma_2 x_2)^2}{\gamma_1 \gamma_3 x_1 x_3}: & \text{II,} \end{cases} \qquad (44)$$

and these are identical with the thermodynamic equilibria provided

$$\ln K \equiv \begin{cases} (\mu_1^0 + \mu_2^0 - 2\mu_3^0)/RT : \text{I} \\ (\mu_1^0 + \mu_3^0 - 2\mu_2^0)/RT : \text{II} \end{cases} \qquad (45)$$

In view of (41), (44) can be rewritten

$$K = \begin{cases} e^{-\omega(x_1+x_2)} \dfrac{x_3^2}{x_1 x_2}: & \text{I} \\[4mm] e^{\omega(2x_1-x_2)} \dfrac{x_2^2}{x_1 x_3}: & \text{II} \end{cases} \qquad (46)$$

---

†A reaction of the type $\mathscr{A} + \mathscr{B} \rightleftharpoons \mathscr{C} + \mathscr{B}$ can be regarded as first order in all kinetic and equilibrium considerations simply by redefining the time scale. The simpler case in which only the forward reaction is bimolecular is not treated here.

and to determine when multiple solutions of these equations can exist, we must first find the reaction simplex $\Omega(\mathbf{n}^0)$ for each case. In either case $\Omega(\mathbf{n}^0)$ is the straight line that lies at the intersection of the planes

$$\langle \mathbf{\Omega}_1, \mathbf{n} - \mathbf{n}^0 \rangle = 0$$

$$\langle \mathbf{\Omega}_2, \mathbf{n} - \mathbf{n}^0 \rangle = 0. \qquad (47)$$

The stoichiometric matrix in each case is

$$\underset{\sim}{\boldsymbol{\nu}}^T = \begin{cases} (-1, & -1, & 2): & \text{I} \\ (-1, & 2, & -1): & \text{II} \end{cases} \qquad (48)$$

and it follows that in both cases

$$\mathbf{\Omega}_1 = (1, 1, 1)$$

$$\mathbf{\Omega}_2 = (M_1, M_2, M_3). \qquad (49)$$

However, it is necessary that $M_3 = \frac{1}{2}(M_1 + M_2)$ in case I whereas $M_2 = \frac{1}{2}(M_1 + M_3)$ in case II. From (47) and (49) one finds that

$$\Omega(\mathbf{n}^0) = \begin{cases} x_1 - x_2 = x_1^0 - x_2^0: & \text{I} \\ x_1 - x_3 = x_1^0 - x_3^0: & \text{II} \end{cases} \qquad (50)$$

We are now in a position to analyze (46) in detail.
Consider case I first and define

$$u = x_1 + x_2, \quad u \in [0, 1]$$

$$v = x_1 - x_2, \quad v \in [-1, 1]. \qquad (51)$$

It follows that equilibria must satisfy

$$K(u^2 - v^2) = 4(1 - u)^2 \, e^{-\omega u} \qquad (52)$$

where v is fixed by the initial composition. A sketch of the left- and right-hand sides of (52) shows that when $\omega > 0$ there exists exactly one root $u \in [0, 1]$ whenever $v \in [-1, 1]$ and $K > 0$. Therefore the equilibrium point is unique in such cases. However, if $\omega < 0$ and sufficiently large in magnitude, there can exist three roots for a range of K values.

The loci of equilibrium points found from (52) for a fixed $\omega < 0$ and several values of K are shown in Fig. 4(a). It is evident from this figure that whether or not multiple equilibria exist depends on both K and $\mathbf{n}^0$ (or v). The boundary of the region in the $\omega - K$ plane in which there are three solutions is found as follows. A multiple root exists whenever the reaction simplex $v = \text{constant}$ is tangent to the equilibrium locus; this requires that $\mathrm{d}v/\mathrm{d}u = 0$. On the boundary of the three solution region the curvature must also vanish at the point of tangency and thus the boundary can be found by solving

$$v^2 = u^2 - \frac{4}{K}(1 - u)^2 \, e^{-\omega u} \equiv f(u)$$

$$\frac{\mathrm{d}v}{\mathrm{d}u} = 2u + (u^2 - f(u))\left(\omega + \frac{2}{1 - u}\right) = 0$$

$$\frac{\mathrm{d}^2 v}{\mathrm{d}u^2} = 2 + 2\omega u + \frac{4u}{1 - u} + 2\left(\frac{u^2 - f(u)}{(1 - u)^2}\right) = 0. \qquad (53)$$
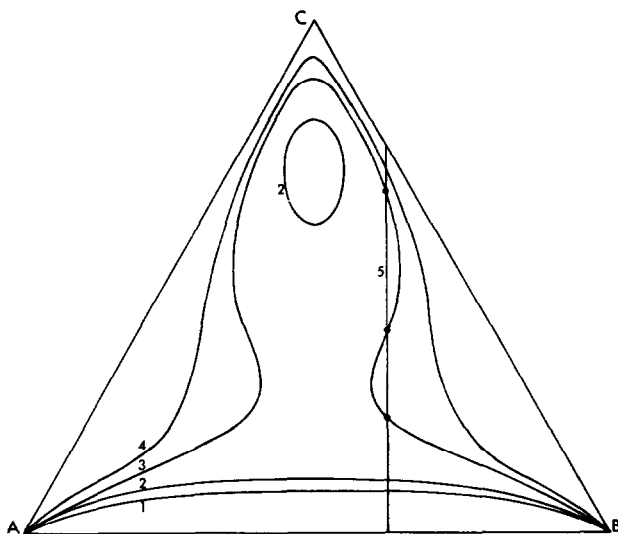
Fig. 4(a). The equilibrium loci (1–4) and a reaction simplex (5) for the reaction $\mathscr{A} + \mathscr{B} \rightleftharpoons 2\mathscr{C}$. (1) $K = 325$, (2) $K = 490$, (3) $K = 870$, (4) $K = 1250$, $\omega = -10$ throughout.
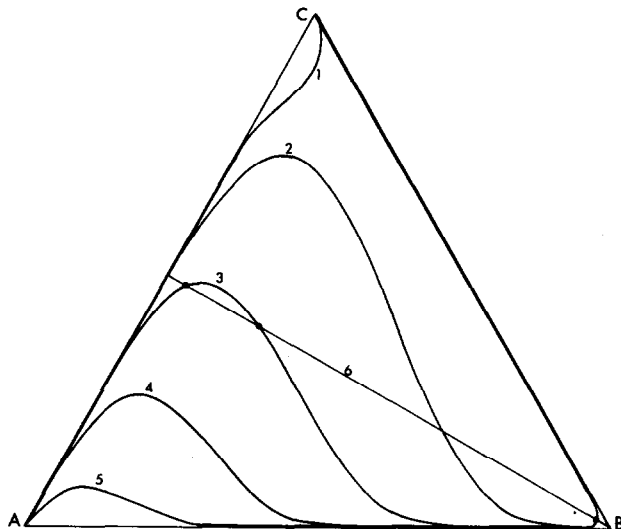
Fig. 4(b). The equilibrium loci (1–5) and a reaction simplex (6) for the reaction $\mathscr{A} + \mathscr{C} \rightleftharpoons 2\mathscr{B}$. (1) $K = 10^{-1}$, (2) $K = 10^{0}$, (3) $K = 10^{2}$, (4) $K = 10^{4}$, (5) $K = 10^{6}$, $\omega = 10$ throughout.

After rearrangement and simplification these reduce to

$$v^2 = f(u)$$

$$v^2 = 1 + \omega u (1 - u)^2$$

$$\omega^2 u^3 - (2\omega^2 + 3\omega)u^2 + (\omega^2 + 2\omega)u + (\omega + 2) = 0. \tag{54}$$

It is necessary that $v^2 \geq 0$ and from the second and third equations of (54) one finds that there are no solutions for any $K > 0$ if $\omega > -8$. At $\omega = -8$, $u = 1/2$ and $\log K = 2.347$; this point marks the cusp of the boundary of the three solution region shown in Fig. 5. For $\omega < -8$ one can compute the roots $u \in (0, 1)$ of the third equation, check whether $v^2 \geq 0$ in the second equation, and calculate the corresponding K from the first equation. Within the region of three solutions one can distinguish between cases where the equilibrium locus is a single continuous curve and those for which it consists of two disjoint

curves. The dashed line through the region of three solutions delineates these cases: above this line the equilibrium locus is the single "bishop-shaped" curve while below it the locus consists of an ellipse and a parabolic curve that runs between $x_1 = 1$ and $x_2 = 1$.

A similar analysis can be done for case II. Now one defines

$$u = x_1 + x_3$$

$$v = x_1 - x_3 \tag{55}$$

so the equilibrium relation can be written

$$K = \frac{-4(1 - u)^2}{u^2 - v^2} e^{\omega(2u + v - 1)}. \tag{56}$$

If $\omega \leq 0$ there exists a unique root for any $K > 0$. When $K = 0$ the unique solution is $u = 1$, i.e. $x_2 \equiv 0$, and
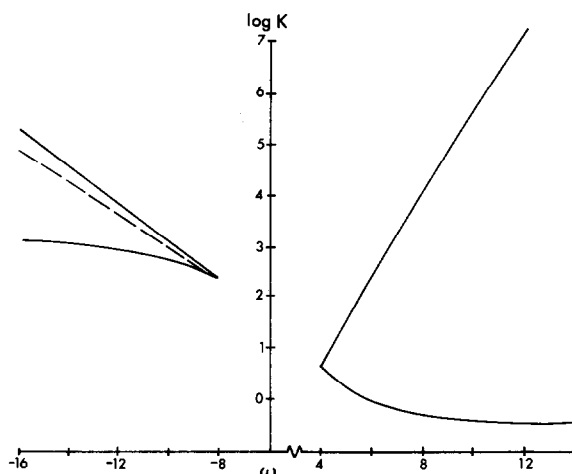
Fig. 5. The ω-log K plane for both $\mathcal{A} + \mathcal{B} \rightleftharpoons 2\mathcal{C}$ and $\mathcal{A} + \mathcal{C} \rightleftharpoons 2\mathcal{B}$. Multiple solutions for the former lie to the left of $\omega = -8$ in the wedge-shaped region. Multiple solutions for the latter lie to the right of $\omega = 4$.

by continuity the solution is unique for all ω whenever K is sufficiently small. Moreover, if ω is sufficiently small the solution is unique for all $K \geq 0$. Finally, when K is sufficiently large the solution is also unique for all ω. Only within a restricted range of K and ω are there three equilibrium points. The graphs of the equilibrium loci for a fixed ω within the three-solution region are shown in Fig. 4(b).

The boundary of the three solution region again corresponds to points at which the equilibrium curve is tangent to the reaction simplex and has zero curvature there. This leads to the three equations

$$f(u, v) = 0$$

$$f_u(u, v) = 0$$

$$f_{uu}(u, v) = 0 \tag{57}$$

for the boundary and after rearrangement and simplification these read

$$K = \frac{4(1-u)^2}{u^2 - v^2} e^{\omega(2u+v-1)}$$

$$\omega = \frac{u - v^2}{(1-u)(u^2 - v^2)}$$

$$v^4 + (2u - 3u^2 - 1)v^2 + 2u^3 - u^2 = 0. \tag{58}$$

These are solved as follows. For a fixed $u \in (0, 1)$, the last equation can be solved for v^2 and the results checked to ensure that $-1 \leq v \leq 1$. For such v's, the first two equations give the ω and K values on the boundary of the three-solution region. The result is the curve shown in Fig. 5. The solution is unique outside the solid curve in the right-half plane.

According to earlier discussion, three equilibrium points can exist only if $\rho(\partial^2 G/\partial n \partial n) < N - 1$ for some compositions in $\Omega(n^0)$. In this ternary system the spinodal is the curve along which the Hessian of G has rank one; from (41) one finds that this curve satisfies the equation

$$\omega^2 x_1 x_2 x_3 = 2\omega x_1 x_2 - 1 = 0. \tag{59}$$

After eliminating x_2 and solving one gets

$$x_3 = \frac{\omega^2 x_1(1-x_1) - 2\omega x_1 \pm \sqrt{[(2\omega x_1 + \omega^2 x_1(1-x_1))^2 - 4\omega^2 x_1]}}{2\omega^2 x_1} \tag{60}$$

and from this it follows that there are no solutions for which all x_i's are between zero and one, and consequently, no spinodal, when $-8 < \omega < 2$. Outside this range a spinodal always exists and the locus is a closed curve for $\omega < -8$ and a parabolic curve through $x_3 = 0$ for $\omega > 2$. A representative of each case is shown in Fig. 6(a) and 6(b) respectively, along with some equilibrium curves and a reaction simplex.

In Fig. 6(a) it is noteworthy that whenever three solutions exist, two are always stable with respect to small amplitude nonuniform disturbances while the intermediate solution always lies within the spinodal and consequently is unstable. This happens for all the (ω, K) values that were examined but we have not proven that the two extreme solutions are always stable. Moreover, it also appears that the points at which a multiple solution exist always lie on the spinodal but again this has not been proven. Recall that this was the case for the binary system treated in the preceding.

In contrast to the foregoing, when the non-ideal interactions are between a reactant and a product it can happen that for certain initial conditions only one of three equilibrium points lies outside the spinodal and hence is stable with respect to diffusion (Fig. 6b). For either case I or case II, the equilibrium point is unique (and necessarily stable) whenever the entire reaction simplex lies outside the spinodal region. This is a sufficient, but not necessary, condition for uniqueness, as one can see from the fact that some simplexes pass through the spinodal but yet the equilibrium point is unique.

Because the ternary systems studied here can have up to three equilibrium points, bifurcation or branching of these equilibria can occur as parameters that characterize the system are varied. For instance, in case I one obtains the bifurcation diagram shown in Fig. 7(a) when ω and K
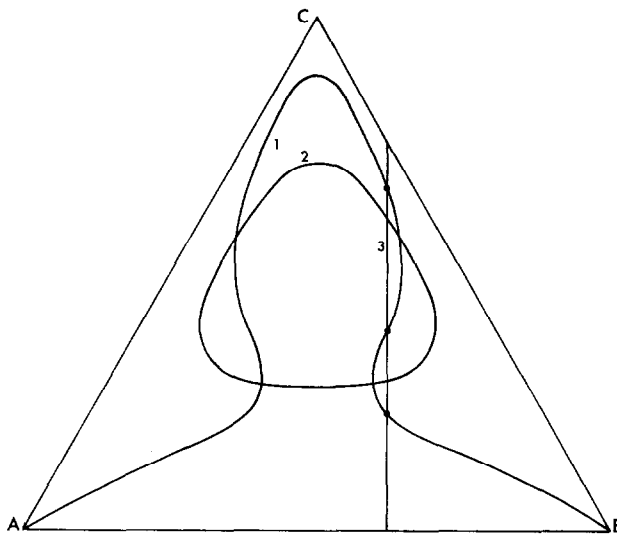
Fig. 6(a). The equilibrium curve (1), the spinodal curve (2) and a reaction simplex (3) for the reaction $\mathscr{A} + \mathscr{B} \rightleftharpoons 2\mathscr{C}$ at
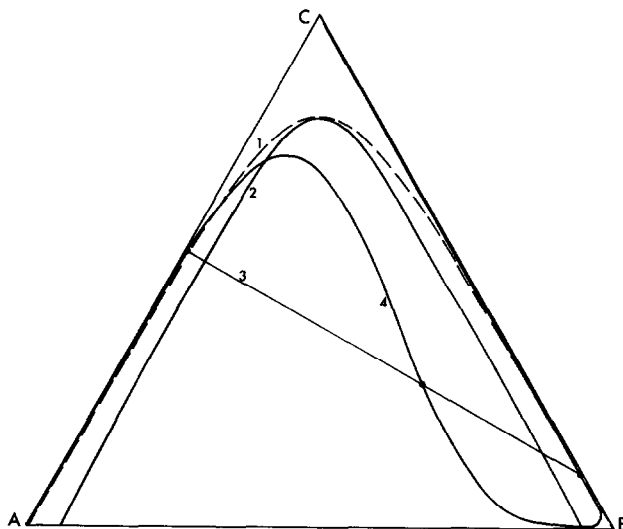$\omega = -10, K = 870$.

Fig. 6(b). The coexistance curve (1), the spinodal curve (2), a reaction simplex (3), and the equilibrium curve (4) for
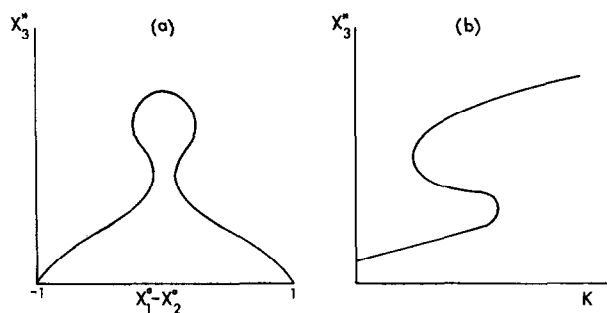$\mathscr{A} + \mathscr{C} \rightleftharpoons 2\mathscr{B}$ at $\omega = 10, K = 1$.

Fig. 7. The bifurcation curves showing the equilibrium mole fraction of x_3 vs (a) the difference in initial mole fraction
between $\mathscr{A}$ and $\mathscr{B}$, and (b) the equilibrium constant K.

lie in the three-solution region and the difference $x_1^0 - x_2^0$ in the initial mole fractions of $\mathscr{A}$ and $\mathscr{B}$ is regarded as the bifurcation parameter. When $x_1^0 - x_2^0$ is near -1, there is only one equilibrium point, at intermediate values of $x_1^0 - x_2^0$ there are three equilibrium points, and when $x_1^0 - x_2^0$ is near 1 the equilibrium point is again unique. One could as well regard K as the bifurcation parameter for appropriate ω and one would get a bifurcation diagram like that shown in Fig. 7(b). In either case it is clear that there exists more than one branch of equilibrium points

within some range of the bifurcation parameter, just as in the binary system treated earlier.

There is however one difference between binary systems and ternary systems with one reaction of type I or II. According to a thermodynamic analysis, spatially nonuniform solutions corresponding to a phase separation are impossible in a binary system. By contrast, a ternary system can undergo a phase separation for appropriate K and ω values. To see this, note that the concentrations in a multiphase system must satisfy (18). The last of these three equations gives the equilibrium locus already computed for both case I and case II. Since at most two phases can coexist, the second set of equations at (18) reduces to

$$\mu_i^1 = \mu_i^2 \quad i = 1, 2, 3 \tag{61}$$

and these give the coexistance locus. These have been solved for $\omega = 10$ and the result is shown as the dashed curve in Fig. 6(b). One finds that the tie lines connecting phases in equilibrium are horizontal lines $x_3 = $ constant.

Any multiphase equilibrium must satisfy all these equations and therefore is possible only if the equilibrium locus intersects the coexistance curve at opposite ends of a tie line and the reaction simplex determined by the first equation of (18) intersects the tie line. This is not the case for the (K, ω) values of $(1, 10)$ shown in Fig. 6(b). However, as K increases above 1 the intersection of the equilibrium and coexistance curves near $x_2 = 1$ moves slowly toward $x_2 = 1$ while the corresponding intersection near the line $x_2 = 0$ moves rapidly toward $x_1 = 1$. One can show that at any fixed ω, there is a K such that the intersections lie at opposite ends of a tie line and if the initial conditions are properly chosen a phase separation results. Thus there is a curve through the three-solution region of the $\omega - K$ plane on which the thermodynamic analysis predicts a two-phase equilibrium.

4. DISCUSSION

That even the very simplest form of nonideality readily leads to multiple equilibria in closed reacting systems suggests that their occurrence may be widespread, particularly under the high temperatures and pressure of many batch reactions. Accordingly, the possibility of their existence should be checked in any computation of equilibria[21]. The branching of equilibrium solutions as parameters of the system are varied points up the fact that slight changes in some parameters can often lead to abrupt changes in the equilibrium concentrations. These bifurcation diagrams for *equilibrium points* are completely analogous to those found for the *nonequilibrium steady states* of some open reacting systems (see, e.g. [4]), and in this respect, closed systems are no different than open systems. The major difference lies in the fact that time-periodic solutions are impossible in closed systems, by virtue of the postulate that $dG/dt \le 0$ for any spontaneous process that occurs at constant temperature and pressure. Another difference arises from the fact that spatially non-uniform solutions are static; they require no expenditure of free energy for their maintenance, in

contrast to the dynamic nonuniform solutions that can occur away from equilibrium.

Heretofore the analysis has been strictly thermodynamic and for many purposes this is adequate, but whenever more than one equilibrium points exists one is led to ask what the domain of attraction of each of the uniform solutions is and whether or not spatially nonuniform solutions other than those predicted by thermodynamics are possible. To answer either of these questions one must formulate the appropriate initial value problem for the continuity equation for each species and postulate constitutive relations for the diffusion fluxes. When near equilibrium and when gradients are small, one usually assumes that the flux is proportional to the gradient of the chemical potential;

$$\mathbf{j} = \underline{L}\nabla\mu = \underline{L}\frac{\partial\mu}{\partial\mathbf{c}}\nabla\mathbf{c} = \underline{L}\frac{\partial^2 G}{\partial\mathbf{c}\partial\mathbf{c}}\nabla\mathbf{c}. \tag{62}$$

After eliminating the linear dependence between both the fluxes j_i and the gradients $\nabla\mu_i$ one can write

$$\frac{\partial c}{\partial t} = \nabla \cdot \underline{D}\nabla c + \bar{\underline{R}}(c) \tag{63}$$

where all vectors now have $n - 1$ components. In ideal solutions $\mathbf{D}$ has only real positive eigenvalues[22] and any equilibrium point is asymptotically stable as a solution to (63). If one assumes that the constitutive relation (62) is valid arbitrarily far from equilibrium then for *monomolecular* reactions in an ideal system, the equilibrium point is globally asymptotically stable. Thus nonuniform steady states are impossible in ideal systems. Even when the mixture is nonideal and the reaction simplex passes through the two-phase region, one can still prove, using (62) in (63), that any equilibrium point that lies outside the spinodal is asymptotically stable. This is consistent with the thermodynamic analysis.

Inside the spinodal $\partial^2 G/\partial\mathbf{c}\partial\mathbf{c}$ has one or more negative eigenvalues and the simple linear relation given by (62) is inadequate. For any compositions inside the spinodal the free energy decreases when the components separate and as a result, diffusion steepens the concentration gradients rather than smoothing them out. Were (62) used in (63), one would predict that the gradients become arbitrarily steep; this is physically impossible and accordingly, the constitutive relation for the diffusion flux must be modified. One approach that has been used successfully in binary nonreacting systems is due to Cahn and Hilliard[23] and Cahn[24]. In this approach one recognizes that the strictly local formulation for the free energy applies only in a spatially uniform system. When gradients are large, the strictly local formulation accounts for only a part of the total free energy and additional terms proportional to the local nonuniformity of the concentration field become important. Consideration of these terms leads to the following relation between concentration gradients and the flux in a binary system[23]

$$\mathbf{j} = -L_1\frac{\partial^2 G}{\partial c^2}\nabla c + 2L_2\nabla\nabla^2 c. \tag{64}$$

This relation retains only the first order term of an expansion of G about the uniform state; higher order terms that lead to nonlinear diffusion equations are neglected *a priori*. Using this constitutive equation, Cahn has been able to predict some of the structural features observed in glasses that decompose by a spinodal mechanism.

As a first step toward studying the dynamical behavior of reacting systems in which the initial concentration distribution passes through the spinodal region, one could extend the Cahn–Hilliard approach to ternary systems and study the solutions of the resulting pair of coupled equations. This in itself is a formidable task. Moreover, if the constitutive equations for the free energy include non-local contributions, the strictly local formulation of reaction rates no longer applies and non-local terms appear in the rate expressions. This calls for a complete reformulation of all constitutive equations.

NOTATION

$\mathcal{A}_i$ chemical species
A_j affinity of the jth reaction; $j = 1, \ldots r$
$\mathbf{A}$ $(A_1, \ldots A_r)^T$
c_j molar concentration of jth species; $j = 1, \ldots N$
$\mathbf{c}$ $(c_1, \ldots c_N)^T$
$\underset{\sim}{D}$ matrix of diffusion coefficients
$f(x_1)$ equilibrium function for the binary reaction
$f(u, v)$ equilibrium function for the ternary reaction $\mathcal{A} + \mathcal{C} \rightleftharpoons 2\mathcal{B}$
G Gibbs free energy
$\bar{G}$ restriction of G to the reaction simplex
K equilibrium constant
k_r, k_f kinetic constants
N number of chemical species
n total number of moles $\left(= \sum_i n_i \right)$
n_i moles of species i
$\mathbf{n}$ $(n_1, \ldots n_N)^T$
$\mathbf{n}^0$ initial composition
$\mathbf{n}'$ steady state (kinetic equilibrium point)
$\mathbf{n}^*$ thermodynamic equilibrium point
P pressure
R gas constant
$\bar{\mathbf{R}}(\mathbf{c})$ reaction rate vector in molar concentration units
$\mathbf{R}(\mathbf{n})$ reaction rate vector
R_N^+ positive orthant of N dimensional Euclidean space
$\bar{\mathbf{R}}$ restriction of $\mathbf{R}(\mathbf{n})$ to $\Omega(\mathbf{n}^0)$
T absolute temperature

t time
v_i molar volume of ith species
V volume of mixture
x_i mole fraction of ith species

Greek symbols
γ_i activity coefficient of ith species
δ_{jk} Kronecker delta
ϵ_{ij} interaction energy between i and j
ζ displacement from equilibrium
μ_i chemical potential of ith species
μ $(\mu_1, \ldots \mu_N)^T$
$\underset{\sim}{\nu}$ matrix of stoichiometric coefficients
ξ_j extent of jth reaction
ξ $(\xi_1, \ldots \xi_r)$
ρ rank of $\underset{\sim}{\nu}$
χ parameter in eqn (20)
Ω_i basis vector for the null space of $\underset{\sim}{\nu}^T$
$\Omega(\mathbf{n}^0)$ reaction simplex through $\mathbf{n}^0$
ω_{ij} parameter defined by (21)
ω ω_{12}/RT

REFERENCES

[1] Aris R., *Chem. Engng Sci.* 1969 **24** 149.
[2] Othmer H. G. and Scriven L. E., *Ind. Engng Chem. Fundl.* 1969 **8** 302.
[3] Prigogine I. and Lefever R., *J. Chem. Phys.* 1968 **48** 1695.
[4] Othmer H. G., *Math. Biosci.* 1975 **24** 87.
[5] Oster G. F. and Perelson A. S., *Arch. Rat. Mech. Anal.* 1974 **55** 230.
[6] Aris R., *Arch. Rat. Mech. Anal.* 1965 **19** 81.
[7] Aris R., *Arch. Rat. Mech. Anal.* 1968 **27** 356.
[8] Shear D. B., *J. Chem. Phys.* 1968 **48** 4144.
[9] Eckert C. A., *Ind. Engng. Chem.* 1967 **59** 20.
[10] Bowen R. M., *J. Chem. Phys.* 1968 **49** 1625.
[11] Krambeck F. J., *Arch. Rat. Mech. Anal.* 1970 **38** 317.
[12] Gavalas G. R., *Nonlinear Differential Equations of Chemically Reacting Systems.* Springer-Verlag 1968.
[13] Prigogine I. and DeFay R., *Chemical Thermodynamics.* Longmans 1954.
[14] Fleming W. H., *Functions of Several Variables.* Addison-Wesley 1965.
[15] Wei J., *J. Chem. Phys.* 1962 **36** 1578.
[16] Callen H. B., *Thermodynamics.* Wiley 1960.
[17] Guggenheim E. A., *Mixtures.* Oxford 1952.
[18] Lewis G. N. and Randall M., *Thermodynamics.* McGraw-Hill 1961.
[19] Glasstone S., Laidler K. and Eyring H., *Theory of Rate Processes.* McGraw-Hill, New York 1941.
[20] Moelwyn-Hughes E. A., *The Chemical Statics and Kinetics of Solutions.* Academic Press, New York 1971.
[21] vanZeggeren F. and Storey S. H., *The Computation of Chemical Equilibria.* Cambridge 1970.
[22] Kirkaldy J. S., Weichert D. and Zia-UL-Haq, *Can. J. Phys.* 1963 **41** 2166.
[23] Cahn J. W. and Hilliard J. E., *J. Chem. Phys.* 1959 **31** 688.
[24] Cahn J. W., *J. Chem. Phys.* 1965 **42** 93.