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Limitation on Composition Change during the Isothermal Mass-Transfer Processes in Systems with Limited Miscibility

Liao-Ping Cheng and Carl C. Gryte*

Department of Chemical Engineering and Applied Chemistry, Columbia University, New York, New York 10027

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Introduction

Phase separation by spinodal decomposition is most conveniently observed in systems that are subject to abrupt changes in temperature.[1–4] There are, however, important instances wherein isothermal systems are subject to externally controlled concentration gradients: evaporation of solvent from a multicomponent polymeric solution[5] or immersion of a similar solution in a nonsolvent.[6–9] In these examples, phase separation is controlled by isothermal mass transfer. This paper unambiguously demonstrates that, for systems at the spinodal composition, all isothermal mass-transfer fluxes are zero. Thus, even if an isothermal system uniformly at a spinodal composition is seeded with particles at some other composition, mixing of this separated phase would not be observable through any mechanism that depends on the conventional equations of diffusional mass transfer.

Flux Equations

The diffusional fluxes that describe the mass transfer of each species can be derived from nonequilibrium thermodynamics as long as basic assumptions are satisfied: (a) within the system "local equilibrium" properties can be assumed, and fluctuation in the intensive properties is negligible; (b) diffusional mass transfer, even with strong concentration gradients, is sufficiently slow so that fluxes are directly proportional to forces; (c) in order to avoid the complication due to the non-Fickian diffusional phenomena often associated with concentrated or glassy polymeric systems, the time scale of mass transfer is assumed sufficiently long with respect to polymeric relaxation times.

Consider an $r + 1$ component system undergoes mass transfer. There are only r independent diffusional flows,[10] since one of the components is selected as the reference component and all other diffusional flows are determined by their velocities relative to the reference component. The phenomenological expressions for these diffusional fluxes are given by[10,11]

$$-J_i = \sum_k L_{ik} \nabla \mu_k \qquad (i, k = 1, 2, ..., r) \tag{1}$$

where J_i is the diffusional flux, L_{ik} is the phenomenological coefficient which satisfies Onsager's relation, i.e., $L_{ik} = L_{ki}$, and μ_k is the chemical potential of component k. Since temperature and pressure are kept constant during the mass-transfer process, μ_k depends only on concentration.

Limitation on Isothermal Diffusion

For convenience, the molality defined by Kurata[12] will be used. Selecting one of the components in the system as the reference, the molality of component i, m_i, is defined as the number of moles of component i per unit mass of the reference component. The molality of the reference component is then the reciprocal of its molecular weight. Therefore, the chemical potential of component i, μ_i, of an $r + 1$ component system at constant temperature and pressure is a function of $m_1, m_2, ..., m_r$ only. $\nabla \mu_i$ in eq 1 can be expressed in terms of $\partial \mu_i / \partial m_j$ and $\partial m_j / \partial x_i$ by using chain rule and the result is given by

$$\nabla \mu_i = \sum_k \frac{\partial \mu_i}{\partial m_k} \nabla m_k \qquad (i, k = 1, 2, ..., r) \tag{2}$$

Substitution of eq 2 into eq 1 and collecting the terms containing ∇m_k gives in matrix form

$$[-\mathbf{J}] = [\Delta][\nabla \mathbf{m}] \tag{3}$$

In the above equation, $[-\mathbf{J}]$ is the transpose of matrix $(-J_1, -J_2, ..., -J_r)$, $[\nabla \mathbf{m}]$ is the transpose of matrix $(\nabla m_1, \nabla m_2, ..., \nabla m_r)$, and $[\Delta]$ is given by

$$[\Delta] = \begin{bmatrix} \sum_k L_{1k} \frac{\partial \mu_k}{\partial m_1} & \sum_k L_{1k} \frac{\partial \mu_k}{\partial m_2} & \cdots & \sum_k L_{1k} \frac{\partial \mu_k}{\partial m_r} \\ \sum_k L_{2k} \frac{\partial \mu_k}{\partial m_1} & \sum_k L_{2k} \frac{\partial \mu_k}{\partial m_2} & \cdots & \sum_k L_{2k} \frac{\partial \mu_k}{\partial m_r} \\ \cdots & \cdots & \cdots & \cdots \\ \sum_k L_{ik} \frac{\partial \mu_k}{\partial m_1} & \sum_k L_{ik} \frac{\partial \mu_k}{\partial m_2} & \cdots & \sum_k L_{ik} \frac{\partial \mu_k}{\partial m_r} \\ \cdots & \cdots & \cdots & \cdots \\ \sum_k L_{rk} \frac{\partial \mu_k}{\partial m_1} & \sum_k L_{rk} \frac{\partial \mu_k}{\partial m_2} & \cdots & \sum_k L_{rk} \frac{\partial \mu_k}{\partial m_r} \end{bmatrix} \tag{4}$$

$[\Delta]$ can be shown to be equivalent to the product of the matrices given in eq 5

$$[\Delta] = \begin{bmatrix} L_{11} & L_{12} & \cdots & L_{1r} \\ L_{21} & L_{22} & \cdots & L_{2r} \\ \cdots & \cdots & \cdots & \cdots \\ L_{i1} & L_{i2} & \cdots & L_{ir} \\ \cdots & \cdots & \cdots & \cdots \\ L_{r1} & L_{r2} & \cdots & L_{rr} \end{bmatrix} \times \begin{bmatrix} \frac{\partial \mu_1}{\partial m_1} & \frac{\partial \mu_1}{\partial m_2} & \cdots & \frac{\partial \mu_1}{\partial m_r} \\ \frac{\partial \mu_2}{\partial m_1} & \frac{\partial \mu_2}{\partial m_2} & \cdots & \frac{\partial \mu_2}{\partial m_r} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_i}{\partial m_1} & \frac{\partial \mu_i}{\partial m_2} & \cdots & \frac{\partial \mu_i}{\partial m_r} \\ \cdots & \cdots & \cdots & \cdots \\ \frac{\partial \mu_r}{\partial m_1} & \frac{\partial \mu_r}{\partial m_2} & \cdots & \frac{\partial \mu_r}{\partial m_r} \end{bmatrix} = [\mathbf{L}][\mathbf{M}] \tag{5}$$

where $[\mathbf{L}]$ is the matrix containing only L_{ij} terms, and $[\mathbf{L}]$ satisfies Onsager's condition such that its determinant is ≥ 0. $[\mathbf{M}]$ is the matrix composed of $\partial \mu_i / \partial m_j$ terms. By using Cramer's rule,[13] variables ∇m_i can be expressed in

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terms of J_i, L_{ij}, and $\mu_i/\partial m_j$

$$\nabla m_i = \frac{\begin{vmatrix} \sum_k L_{1k}\frac{\partial \mu_k}{\partial m_1} & \sum_k L_{1k}\frac{\partial \mu_k}{\partial m_2} & \dots & -J_1 & \dots & \sum_k L_{1k}\frac{\partial \mu_k}{\partial m_r} \\ \sum_k L_{2k}\frac{\partial \mu_k}{\partial m_1} & \sum_k L_{2k}\frac{\partial \mu_k}{\partial m_2} & \dots & -J_2 & \dots & \sum_k L_{2k}\frac{\partial \mu_k}{\partial m_r} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \sum_k L_{ik}\frac{\partial \mu_k}{\partial m_1} & \sum_k L_{ik}\frac{\partial \mu_k}{\partial m_2} & \dots & -J_i & \dots & \sum_k L_{ik}\frac{\partial \mu_k}{\partial m_r} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \sum_k L_{rk}\frac{\partial \mu_k}{\partial m_1} & \sum_k L_{rk}\frac{\partial \mu_k}{\partial m_2} & \dots & -J_r & \dots & \sum_k L_{rk}\frac{\partial \mu_k}{\partial m_r} \end{vmatrix}}{|\Delta|}$$

$$\nabla m_i = \frac{|\mathbf{Q}|}{|\mathbf{L}|\cdot|\mathbf{M}|} \qquad (6)$$

where the ith column of the determinant in the numerator of eq 6 has been replaced by $(-J_1, -J_2, ..., -J_r)$ and $|\mathbf{Q}|$ is the determinant representing this numerator. From eq 5, the determinant of $[\Delta]$ is equal to the product of the determinant of matrices $[\mathbf{L}]$ and $[\mathbf{M}]$. The solution of eq 6 depends on the value of the denominator. In general, $|\Delta|$ is not equal to zero and a solution of ∇m_i exists. If, however, the determinant $|\mathbf{L}|$ or $|\mathbf{M}|$ equals zero and if ∇m_i is to retain its physical meaning (i.e., ∇m_i be finite), then the determinant in the numerator, $|\mathbf{Q}|$, of eq 6 must also be zero. The only possible condition that ensures $|\mathbf{Q}|$ be zero for all ∇m_i $(i = 1, 2, ..., r)$ is when all diffusional fluxes, J_i $(i = 1, ..., r)$, are zero. Although there are other conditions which also make $|\mathbf{Q}|$ equal zero, it is unlikely that any one of these conditions satisfies $|\mathbf{Q}|$ equals zero for all ∇m_i $(i = 1, ..., r)$. Therefore, it is plausible to propose that a nondiffusion condition is the single solution to the problem where $|\Delta| = 0$ occurs. Since Onsager dictates that $|\mathbf{L}|$ is generally greater than zero, the condition that $|\Delta|$ equals zero occurs only if $|\mathbf{M}|$ equals zero. In fact, $|\mathbf{M}| = 0$ is the generalized expression for the locus of the spinodal composition in a multicomponent system.[12] It is thus clear that if the set m_1, m_2, ..., m_r in some local region of an isothermal system approaches the coordinates of the spinodal compositions, all diffusional fluxes in the system at that composition are identically zero regardless of the composition in the other parts of the system. Thus, the spinodal is an absolute barrier to isothermal mass transfer.

Discussion

If a stable initial composition outside the spinodal envelope is subject to external concentration boundary conditions (as in the examples of solvent evaporation or immersion precipitation), there will be some circumstances under which the system may be forced to approach the spinodal. The conclusions derived from eq 6 dictate that in such instances the spinodal is an absolute barrier to isothermal mass transfer. All isothermal fluxes approach zero as the spinodal composition is approached.

At the critical region, the conditions for the binodal and the spinodal coincide and phase stability criteria depend upon third- and fourth-order terms in the free energy expansion.[12] This coincidence however does not invalidate the general conclusions concerning the application of eq 6 even to the critical region. At states removed from the critical point, the influence of the spinodal on the transport equations is not dependent on the ultimate equilibrium state of the system and thus does not depend on characteristics of the tie line. In those circumstances wherein an isothermal system crosses a binodal as a result of compositional change, phase separation can only occur by the combination of nucleation and growth. Spinodal decomposition[14] cannot be observed in such systems.

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