Analysis of Single-Stage Nonequilibrium Separation Process Problems

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Equations constituting the nonequilibrium rate-based separation process problem involving binary and ternary mixtures were analyzed. Multiplicity occurring in the nonequilibrium stage resulted from multiplicity taking place in the equilibrium calculations at the interface. This is achieved by demonstrating a one-to-one correspondence between the bulk and interface compositions in a nonequilibrium stage. The analysis of the film model for the mass-transfer problem where the fluxes are obtained using the Maxwell-Stefan equations showed solution uniqueness for this equation set. It also showed that the imposition of the mass-transfer equations does nothing to cause additional multiplicities.

Introduction

The following sections deal with the previous work done on solution multiplicity and the nonequilibrium model.

Solution Multiplicities in Equilibrium Separation Processes

Solution uniqueness for separation-process problems has been investigated by many workers, both from a numerical and an analytical standpoint. In 1974 Shewchuk found multiple solutions to a distillation problem, involving ethanol, benzene, and water. Unfortunately, his results were never published. The first published results were those of Magnussen et al. (1979). These multiplicities were confirmed numerically by various workers, including Kovach and Seider (1987), Venkataraman and Lucia (1988), Rovaglio and Doherty (1990), and Gani and Jorgensen (1994).

There have been various attempts to explain the cause(s) for the existence of solution multiplicities, and these attempts have resulted in several articles (Rosenbrock, 1960, 1962; Doherty and Perkins, 1982; Lucia, 1986, Sridhar and Lucia, 1989, 1990; Bekiaris et al., 1993, 1994; Lucia and Li, 1992; Sridhar, 1996, 1997).

Of these the most relevant to this work is that of Lucia (1986), where the single-stage problem involving homogeneous mixtures was analyzed for various specifications. It was shown that for some specifications, a unique solution was admitted by a single-stage problem involving a homogeneous mixture. However, this work involved the equilibrium model where the bulk phases in a separator were at equilibrium with each other. Analysis involving problems where bulk-phase equilibrium is absent is nonexistent. In this work we consider single-stage process problems where we use the rate-based nonequilibrium model originally developed by Krishnamurthy and Taylor (1985) and show that such a problem would admit a unique steady-state solution. In addition, we show that the Maxwell-Stefan equations when applied to the film model also admit a unique steady-state solution, thereby demonstrating that in separation process problems involving mass-transfer models the imposition of the rate equations does not cause additional multiplicity.

Single-Equilibrium-Stage Analysis

Lucia (1986) provided a rigorous analysis of the single-equilibrium-stage problem, where the specifications of temperature pressure (TP), heat-duty pressure (QP), and total vapor-flow pressure (VP) were rigorously analyzed. First the TP problem was analyzed and shown to have a unique steady-state solution. Then the next two (QP and VP) specifications were shown to have unique solutions, as it was demonstrated that there was a one-to-one correspondence between each of these specifications and the TP specification.

The TP problem was posed as a Gibbs free-energy minimization problem subject to linear mass-balance constraints. Then the convexity arguments were used to demonstrate that the Gibbs function was a convex function on the convex set

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defined by mass-balance constraints when the mixture was homogeneous. The Gibbs-Duhem equation was then used to provide some null-space arguments, and it was shown that the solution set had only one member. Details of the various steps and arguments can be obtained from Lucia (1986).

While this was the first rigorous analysis of the TP flash problem, we believe that the problem could be solved in an alternate fashion. The equations involved are the material-balance equations for c components

$$f_i - l_i - v_i = 0 \tag{1}$$

and the c phase equilibrium equations

$$\mu_i^l - \mu_i^v = 0. \tag{2}$$

The variables involved are liquid and vapor mol numbers l_i and v_i, $i = 1, 2, \ldots c$.

Considering all the equations together as $F(x) = 0$, the Jacobian matrix F' will be equal to

$$F' = \begin{bmatrix} -I & -I \\ \nabla^2 G^L & -\nabla^2 G^V \end{bmatrix}, \tag{3}$$

which is always nonsingular for homogeneous mixtures. The blocks $\nabla^2 G^L$ and $\nabla^2 G^V$ represent the Hessian matrices for the Gibbs free-energy functions for the liquid and vapor phases. Since the matrix $(\nabla^2 G^L + \nabla^2 G^V)$ is nonsingular for homogeneous mixtures, the Jacobian matrix F' is always nonsingular, and the single-stage homogeneous TP problem would admit a unique steady-state solution. While we have posed this problem in terms of the liquid and vapor mol numbers, the uniqueness results hold even if it is posed in terms of liquid and vapor phase mol fractions, as there is a one-to-one correspondence between the two formulations. The proof for this one-to-one correspondence is rather simple and is represented in the Appendix.

Brief Description of the Nonequilibrium model

In this section, we provide a brief description of the rate-based nonequilibrium model. The rate-based nonequilibrium model, originally developed by Krishnamurthy and Taylor (1985), was found to provide excellent simulation results for vapor−liquid separation process problems, as confirmed by Fair (1987), Seader (1988), Sivasubramanian and Boston (1988), and Ryan et al. (1994). Lao and Taylor (1994) have extended this work to multiple liquid-phase problems, while Sridhar and Torres (1998) have incorporated a rigorous stability analysis in these problems.

While mass and energy balance and phase-equilibrium relationships are found in equilibrium models, the difference between the equilibrium and nonequilibrium models lies in way in which the equations are used. In equilibrium problems, the balance equations are written for the stage as a whole, and the phases that exit the stage are in equilibrium with each other. For the nonequilibrium problem, on the other hand, the material and energy balance equations are written for each phase, allowing for mass and energy transfer across the boundaries. The temperature, pressure, and chemical potential are equal across the interface. It is shown by Krishnamurthy and Taylor (1985) that the addition of the material balance equations for both the phases results in the same material balance equation that one uses in the equilibrium-stage problem.

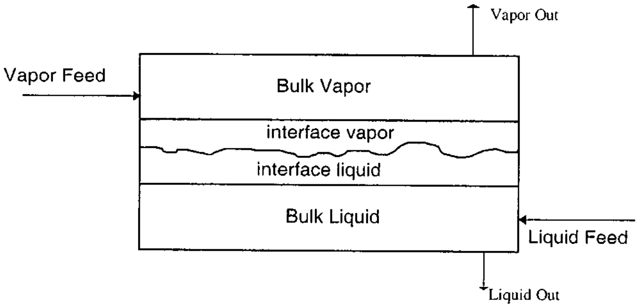

Figure 1. Single-stage nonequilibrium separation process.

Sridhar and Torres (1998) were able to combine a numerical implementation of the tangent plane criterion, as provided by Michelsen (1982), with the nonequilibrium model, and were able to solve problems involving two and three liquid phases. In that work, they demonstrated (in the problem involving toluene, *n*-propanol, and water) that the tangent plane criterion when combined with the nonequilibrium model, actually obtained the correct number of phases (two), while the equilibrium model incorrectly predicted three liquid phases. In the case of the problem involving nitromethane, 1-hexanol, and water, they were able to show that both equilibrium and nonequilibrium models correctly predicted three liquid phases.

Single-Stage Nonequilibrium TP Problem

In this section, we present the equations that constitute the single-stage nonequilibrium TP problem (Figure 1), where the specification is the temperature and pressure. The equations that constitute these problems include the material balance equations, the transfer-rate equations, and the interface equilibrium equations. The material balance equations are written for each of the two phases as

$$VY_i^V - F^V Z_i^V + N_i^V a = 0 \tag{4}$$

for the vapor phase, and

$$LX_i^L - F^L Z_i^L - N_i^L a = 0 \tag{5}$$

for the liquid phase. In Eq. 5, N represents the mass-transfer flux, a the interfacial area, F the feed, L the total liquid flow, while V represents the total vapor flow.

The transfer-rate equations for the vapor phase can be written as

$$N_i^V - N_i^V Y_i^V - J_i^V = 0, \tag{6}$$

while the transfer-rate equations for the liquid phase can be written as

$$N_i^L - N_i^L X_i^L - J_i^L = 0. \tag{7}$$

The diffusive fluxes $[J]$ can be obtained by multiplying the interface mass-transfer coefficients with the composition gradient as

$$J_i^V = \sum_{k=1}^{c-1} K_{ik}^V \left(Y_K^I - Y_K^V \right) \tag{8}$$

for the vapor, phase, and

$$J_i^L = \sum_{k=1}^{c-1} K_{ik}^L \left(X_K^V - X_K^I \right) \tag{9}$$

for the liquid phase. The mass-transfer coefficients $[K]$ can be obtained through a general solution of the Maxwell-Stefan equations as shown by Krishna (1977).

In addition, we have the phase-equilibrium equation at the interface as

$$\mu_i^{L,I} - \mu_i^{V,I} = 0, \tag{10}$$

and the interface material-balance equations

$$N_i^V + N_i^L = 0. \tag{11}$$

We also use the summation equations for the interface mol fractions

$$\sum_{i=1}^{c} X_i^I - 1 = 0 \tag{12}$$

and

$$\sum_{i=1}^{c} Y_i^I - 1 = 0. \tag{13}$$

These are the main equations that constitute the single-stage nonequilibrium model. The number of variables in the problem are the $2c-2$ bulk vapor and liquid phase compositions, $2c$ interface liquid and vapor mol fractions, the $2c$ liquid and vapor molar fluxes, and the liquid and vapor flow rates (2). The total number of variables is $6c$. The equations are the 2 summation equations, the c interface material-balance equations, the c interface phase-equilibrium equations, the $2c$ transfer-rate equations, and the $2c-2$ bulk-phase material-balance equations. The number of equations is also $6c$, and the problem is deterministic.

The main questions addressed in this article are

- Since the equilibrium-stage model admits a unique steady-state solution, is the solution for the nonequilibrium problem also unique, and if so why?
- Will the imposition of the transfer-rate equations on the equilibrium problem, which is in essence the nonequilibrium model, cause any additional multiplicity?

The answers to these questions are addressed in the next few sections. First, a one-to-one correspondence is shown between the equilibrium and nonequilibrium problems. This is achieved by showing a one-to-one correspondence between the bulk-phase compositions and the interface equilibrium compositions. Then we analyze the Maxwell-Stefan equations to show that when they are applied to the film model, a unique solution is obtained, thereby guaranteeing that the imposition of the transfer-rate equations do not in any way cause additional multiplicities.

Analysis of the Binary Single-Stage Nonequilibrium Problem

Consider a binary mixture of composition $[X_1 \;\; X_2]$. In order to investigate the problem of solution multiplicity for a single-stage problem, one strategy would be to show that if for every single-stage equilibrium problem formulation there would be only one nonequilibrium single-stage problem formulation. Since the equilibrium-stage problem has a unique steady-state solution, the nonequilibrium problem can have a unique steady-state solution if and only if there is a one-to-one correspondence between the two problems. One strategy to demonstrate this one-to-one correspondence would be to show that for every bulk-phase composition, there would be only one interface composition, all other conditions being same.

For a binary nonequilibrium problem, let $[X_1^b X_2^b]$ represent the bulk liquid-phase composition and $[Y_1^b Y_2^b]$ the bulk vapor-phase compositions. Let the corresponding interface compositions be $[X_1^i X_2^i]$ and $[Y_1^i Y_2^i]$. In order for a one-to-one correspondence to exist between the bulk and interface compositions, the Jacobian matrix

$$J = \begin{bmatrix} \dfrac{\partial X_1^b}{\partial X_1^i} & \dfrac{\partial X_1^b}{\partial Y_1^i} \\ \dfrac{\partial Y_1^b}{\partial X_1^i} & \dfrac{\partial Y_1^b}{\partial Y_1^i} \end{bmatrix} \tag{14}$$

must be nonsingular.

The expressions for the partial derivatives in the Jacobian matrix can be obtained by considering all the equations that constitute the nonequilibrium single-stage problem. These equations are the liquid material-balance equation,

$$LX_1^b - F^L Z_1^L + N_1^L a = 0, \tag{15}$$

the vapor material-balance equation,

$$VY_1^b - F^V Z_1^V + N_1^V a = 0, \tag{16}$$

the transfer-rate equation for the liquid phase,

$$N_1^L - N_t^L X_1^b - C_1\left(X_1^b - X_1^i \right) = 0, \tag{17}$$

the transfer-rate equation for the vapor phase,

$$N_1^V - N_t^V Y_1^b - C_2\left(Y_1^I - Y_1^b \right) = 0, \tag{18}$$

and the interface equilibrium equation

$$Y_1^i = K_1 X_1^i. \tag{19}$$

Substituting for N_1^L in Eq. 6 using the material-balance equations, we take

$$-\frac{L}{a}X_1^b+\frac{F^L}{a}Z_1^L-N_t^L X_1^b-C_1\left(X_1^b-X_1^i\right)=0 \tag{20}$$

and

$$-\frac{V}{a}Y_1^b+\frac{F^v}{a}Z_1^v-N_t^v Y_1^b-C_2\left(Y_1^i-Y_1^b\right)=0. \tag{21}$$

These equations can be rearranged as

$$\left(-\frac{L}{a}-N_t^L-C_1\right)X_1^b+\frac{F_L}{a}Z_1^L+C_1X_1^i=0 \tag{22}$$

and

$$\left(-\frac{V}{a}-N_t^V+C_2\right)Y_1^b+\frac{F_v}{a}Z_1^v-C_2Y_1^i=0. \tag{23}$$

This can be written in a concise form as

$$AX_1^b+\frac{F^L}{a}Z_1^L+C_1X_1^i=0 \tag{24}$$

and

$$BY_1^b+\frac{F_v}{a}Z_1^v-C_2Y_1^i=0. \tag{25}$$

The diagonal terms for the Jacobian matrix J can be written as

$$\frac{\partial X_1^b}{\partial X_1^i}=-\frac{C_1}{A} \tag{26}$$

and

$$\frac{\partial Y_1^b}{\partial Y_1^i}=\frac{C_2}{B}. \tag{27}$$

The Jacobian matrix J will thus be

$$J=\begin{bmatrix} -\dfrac{C_1}{A} & 0 \\ 0 & \dfrac{C_2}{B} \end{bmatrix}, \tag{28}$$

which is nonsingular. This will guarantee a one-to-one correspondence between the bulk and the interface compositions. The main motivation for writing Eq. 28 in the form shown is the fact that although most mass-transfer coefficients do depend on composition, this composition dependence is weak and that the coefficients are fairly constant over a wide range of compositions. The effect of the composition on the mass transfer is felt in the composition gradient, which multiplies the coefficient, rather than in the coefficients themselves. However, even if the mass-transfer coefficients are not weakly dependent on the compositions, the structure of the Jacobian matrix J will not be affected. The form will still be diagonal. The reason for this is the fact that there is an interaction only between the Y^i and Y^b, the interface, and bulk vapor-phase compositions, and X^i and X^b, the interface, and bulk liquid-phase compositions. Consequently, the nondiagonal terms will always be 0. There is no interaction between X^b and Y^i, and Y^b and X^i because the liquid-phase mass-transfer coefficients do not depend on the vapor-phase compositions and vice versa. The matrix will therefore always be diagonal. Furthermore, any changes in the coefficients as a result of composition changes will be dominated by the values of the coefficients themselves, and the diagonal terms will never be 0. The matrix will thus always be nonsingular.

The use of the equation $Y_1=K_1X_1$ is internal to the equilibrium problem, and therefore does not directly figure in this analysis. Incorrect use of this equation to obtain the cross terms will lead to a trivially singular Jacobian for any value of the diagonal terms, as shown. The matrix

$$J'=\begin{bmatrix} \dfrac{\partial X_1^b}{\partial X_1^i} & \dfrac{\partial X_1^b}{K_1\partial X_1^i} \\ \dfrac{K_1\partial Y_1^b}{\partial Y_1^i} & \dfrac{\partial Y_1^b}{\partial Y_1^i} \end{bmatrix} \tag{29}$$

is singular for all values of the diagonal terms, even for a simple ideal case when the *k*-values do not depend on the composition.

Extension to Multicomponent Systems

The extension of this analysis to multicomponent systems is quite straightforward. The corresponding Jacobian matrix J will be

$$J=\left[\begin{array}{c|c} \dfrac{\partial X_j^b}{\partial X_k^i} & \dfrac{\partial X_j^b}{\partial Y_k^i} \\ \hdashline \dfrac{\partial Y_j^b}{\partial X_k^i} & \dfrac{\partial Y_j^b}{\partial Y_k^i} \end{array}\right], \tag{30}$$

where $k=1,\ \ldots,\ c-1$ and $j=1,\ \ldots,\ c-1$. As an illustration, the Jacobian matrix J for a three-component case will be

$$J=\begin{bmatrix} \dfrac{\partial X_1^b}{\partial X_1^i} & \dfrac{\partial X_1^b}{\partial X_2^i} & \dfrac{\partial X_1^b}{\partial Y_1^i} & \dfrac{\partial X_j^b}{\partial Y_2^i} \\ \dfrac{\partial X_2^b}{\partial X_1^i} & \dfrac{\partial X_2^b}{\partial X_2^i} & \dfrac{\partial X_2^b}{\partial Y_1^i} & \dfrac{\partial X_2^b}{\partial Y_2^i} \\ \dfrac{\partial Y_1^b}{\partial X_1^i} & \dfrac{\partial Y_1^b}{\partial X_2^i} & \dfrac{\partial Y_1^b}{\partial Y_1^i} & \dfrac{\partial Y_1^b}{\partial Y_2^i} \\ \dfrac{\partial Y_2^b}{\partial X_1^i} & \dfrac{\partial Y_2^b}{\partial X_2^i} & \dfrac{\partial Y_2^b}{\partial Y_1^i} & \dfrac{\partial Y_2^b}{\partial Y_2^i} \end{bmatrix}. \tag{31}$$

The corresponding equations (Eqs. 24 and 25) for a multicomponent case will be

$$AX_k^b + \frac{F^L}{a} Z_k^L + C_k X_k^i = 0 \tag{32}$$

and

$$BY_K^b + \frac{F^v}{a} Z_k^v - C_k Y_K^i = 0, \tag{33}$$

where k is the component index from 1 to c.

For a multicomponent problem, as the composition dependence of the mass-transfer coefficients is weak, the nondiagonal terms of the Jacobian will be close to 0 and the diagonal terms will be as $-C_K/A_K$ and C_K/B_k. Consequently, the Jacobian J is nonsingular and there is a one-to-one correspondence between the bulk and the interface compositions in the multicomponent case as well. Even if the condition of the weak dependence of the coefficients on the composition is relaxed, the matrix will be diagonally dominant, as the values of the coefficients will be larger than any changes that can take place as a result of perturbations in composition, and the nonsingularity condition will still hold.

For homogeneous mixtures, the TP problem will yield a unique steady-state solution (see Lucia, 1986). This implies that if one takes a heterogeneous problem and obtains multiple solutions the solutions must collapse onto one another at a singular point that is in the heterogeneous region; see Lucia (1986) and Sridhar (1990). We will try to do the same for the nonequilibrium single-stage problem.

Consider a single-stage example involving the mixture ethanol, benzene, and water at a temperature of 335.75 K and an overall composition of (0.05, 0.67, 0.28). The nonequilibrium model yields two vapor–liquid solutions, which are shown in Tables 1 and 2. *x*-Bulk-1 and *x*-interface-1 represent the bulk and interface vapor phases, while *x*-bulk-2 and *x*-interface-2 represent the bulk and interface liquid phases. Both the solutions lie in the heterogeneous region and are found to approach each other even more in the heterogeneous region. Therefore the singular point in the nonequilibrium problem from which multiplicities arise lies in the heterogeneous region. This implies that a nonequilibrium single-stage problem involving homogeneous mixtures would admit a unique steady-state solution.

Table 1. Vapor–Liquid Solution 1

x-Bulk-1	0.0533	0.7286	0.2179
x-Bulk-2	0.01192	0.0110	0.9769
x-Interface-1	0.0530	0.7300	0.2169
x-Interface-2	0.0119	0.0100	0.9781
Flux1-2	3.96×10^{-6}	5.511×10^{-5}	9.9228×10^{-6}
Flux2-1	-3.96×10^{-6}	5.511×10^{-5}	9.9228×10^{-6}

Table 2. Vapor–Liquid Solution 2

x-Bulk-1	0.0758	0.5318	0.3923
x-Bulk-2	0.0084	0.8925	0.098
x-Interface-1	0.0759	0.5310	0.3931
x-Interface-2	0.0083	0.8936	0.0981
Flux1-2	3.59×10^{-6}	1.12×10^{-6}	1.68×10^{-5}
Flux2-1	-3.59×10^{-6}	-1.12×10^{-6}	-1.68×10^{-5}

Analysis of the Maxwell-Stefan Equations When Applied to the Film Model for Binary Mass Transfer

In this section, we analyze the expression for the diffusion flux N_1 in a binary mass-transfer problem involving the use of a film model. In their book Taylor and Krishna (1993) derived the expression for the molar fluxes N_1 and N_2, applying the Maxwell-Stefan equations for a film model. They develop the expression for N_1 as

$$N_1 = C_t \beta_0 \frac{\phi}{(e^{\phi} - 1)} \Delta x, \tag{34}$$

where C_t is the molar density, $\phi = (N_1 + N_2)/(C_t D/1)$, 1 the film thickness, D the fick diffusion coefficient, and β_0 the appropriate bootstrap coefficient. In this section, we analyze the number of solutions admitted by this equation. We discuss two cases, the first involving the equimolar counterdiffusion $(N_1 + N_2 = 0)$ and the second when $N_1 + N_2 \neq 0$. Since the Maxwell-Stefan equations as applied to a film model are used for staged separations, solution uniqueness for these equations will demonstrate that multiplicities cannot be caused by the imposition of the mass-transfer equations in single-stage separation process problems involving binary mixtures.

Case 1. $N_1 + N_2 = 0$.

$$N_1 = C_1 k \Delta x. \tag{35}$$

For a given composition gradient N_1 is fixed and unique trivially.

Case 2. $N_1 + N_2 \neq 0$. We start with the equation

$$N_1 = C_t \beta_0 \frac{\phi}{(e^{\phi} - 1)} \Delta x. \tag{36}$$

Let $C_t \beta_0 \Delta x = P$ and $C_t D/1 = \beta$

Then

$$N_1 = P \frac{\phi}{(e^{\phi} - 1)} \tag{37}$$

and

$$\phi = \frac{N_1 + N_2}{\beta}. \tag{38}$$

The equation for N_1 can then be written as

$$F(N_1) = N_1 - P \frac{(N_1 + N_2)/\beta}{\exp[(N_1 + N_2)/\beta] - 1} = 0. \tag{39}$$

Multiplicity is obtained only if the derivative

$$\frac{\partial F}{\partial N_1} = 0. \tag{40}$$

This is a straighforward differentiation that will yield

$$\frac{\partial F}{\partial N_1}=1-\frac{P}{\beta\left[\exp\left(N_1+N_2\right)/\beta-1\right]}+\frac{P\left(N_1+N_2\right)\exp\left[\left(N_1+N_2\right)/\beta\right]}{\beta^2\left[\exp\left(N_1+N_2\right)/\beta-1\right]^2}=0. \quad (41)$$

Let $\exp\left(N_1+N_2\right)/\beta-1=Z$. Then

$$1-\frac{P}{\beta Z}+\frac{P\left(N_1+N_2\right)\left(Z+1\right)}{\beta^2 Z^2}=0, \quad (42)$$

which implies that

$$\left(\beta Z\right)^2-\left(\beta Z\right)P+p\left(Z+1\right)\left(N_1+N_2\right)=0. \quad (43)$$

Since $\beta Z \ll 1$, $(\beta Z)^2 \approx 0$, and this term can be neglected.

Consequently, the preceding equation can be reduced to

$$-\left(\beta Z\right)+\left(Z+1\right)\left(N_1+N_2\right)=0. \quad (44)$$

Dividing throughout by β and recognizing that $\left(N_1+N_2\right)/\beta = \ln\left(Z+1\right)$, we have

$$-\left(Z\right)+\left(Z+1\right)\ln\left(Z+1\right)=0. \quad (45)$$

The only real root is $Z=1$, which is inadmissible since this case deals with $\left(N_1+N_2\right)\neq 0$. Therefore $\partial F/\partial N_1 \neq 0$, and consequently the equation

$$F\left(N_1\right)=N_1-P\frac{\left(N_1+N_2\right)/\beta}{\exp\left[\left(N_1+N_2\right)/\beta\right]-1}=0 \quad (46)$$

admits a unique solution.

Extension to Ternary Systems

In order to extend this analysis to ternary systems, we consider (as we did for binary systems) two cases, the first being equimolar counterdiffusion, while the second is the more general case where the sum of the three fluxes does not add up to 0. In either case, the equation one should analyze is equation 8.3.24 in the book by Taylor and Krishna (1993). This equation is

$$N=C_t\beta_0 K_0 \Xi_0(\Delta y), \quad (47)$$

where C_t is the molar density, K is the matrix of mass-transfer coefficients, β_0 the boostrap coefficients, and Ξ_0 is given by Eq. 49.

Case 1: Equimolar Counter-Diffusion. As shown by Taylor and Krishna (1993) for equimolar counterdiffusion, the matrix Ξ_0 can be well approximated by the identity matrix. Consequently, the flux is uniquely defined for a given concentration gradient.

Case 2: ($N_1+N_2+N_3\neq 0$). Let $C_t\beta_0 K_0\Delta y$ (in Eq. 47) be equal to the vector $\{w\}$, which is independent of the flux N. Then we can write

$$N=\Xi_0 w. \quad (48)$$

The analytical expression for matrix Ξ_0 is

$$\Xi_0=\left[\Phi\right]\left[\exp\left(\Phi\right)-1\right]^{-1}, \quad (49)$$

where Φ is the square matrix of mass-transfer rate factors of order $n-1$, n being the number of components and I is the identity matrix.

The terms of Φ (defined by Taylor and Krishna, 1993) are given by

$$\Phi_{ii}=\frac{N_i}{\left(C_t D_{in}/l\right)}+\sum_{\substack{k=1\\ i\neq k}}^{n}\frac{N_k}{\left(C_t D_{in}\right)/l} \quad (50)$$

and

$$\Phi_{ij}=\frac{N_i}{\left(C_t D_{ij}/l\right)}-\frac{N_i}{\left(C_t D_{in}/l\right)}. \quad (51)$$

Expanding $[\exp(\Phi)-\mathrm{I}]$ in a Taylor series, we take

$$\left[\exp\left(\Phi\right)-I\right]=\Phi+\left\{\Phi^2/2!\right\}+\left\{\Phi^3/3!\right\}+\cdots \quad (52)$$

Truncating after the first two terms, the matrix Ξ_0 reduces to

$$\Xi_0=\left[I+\left(\Phi/2\right)\right]^{-1}. \quad (53)$$

Consequently, we have

$$F\left(N\right)=\left(I+\Phi/2\right)\left(N\right)-w=0. \quad (54)$$

For a three-component system, the matrix Φ can be written as

$$\Phi=\begin{bmatrix}\Phi_{11} & \Phi_{12}\\ \Phi_{21} & \Phi_{22}\end{bmatrix}. \quad (55)$$

Consequently, the vector $(I+\phi/2)(N)$ will be equal to

$$\left(I+\phi/2\right)\left(N\right)=\begin{bmatrix}F_1\left(N\right)\\ F_2\left(N\right)\end{bmatrix}\begin{bmatrix}N_1+\phi_{11}N_1/2+\Phi_{12}N_2/2\\ N_2+\phi_{21}N_1/2+\Phi_{22}N_2/2\end{bmatrix}. \quad (56)$$

The Jacobian matrix for this set of equations $F'(N)$ can be written for a three-component system as

$$F'\left(N\right)=\begin{bmatrix}\dfrac{\partial F_1}{\partial N_1} & \dfrac{\partial F_1}{\partial N_2}\\[2ex] \dfrac{\partial F_2}{\partial N_1} & \dfrac{\partial F_2}{\partial N_2}\end{bmatrix}. \quad (57)$$

In order to obtain the expressions for the various derivatives, we use the expressions for the four terms in the matrix Φ. These expressions are derived in Taylor and Krishna (1993, p. 166). They are

$$\Phi_{11} = \frac{N_1}{C_t K_{13}} + \frac{N_2}{C_t K_{12}} + \frac{N_3}{C_t K_{13}} \tag{58}$$

$$\Phi_{22} = \frac{N_1}{C_t K_{12}} + \frac{N_2}{C_t K_{23}} + \frac{N_3}{C_t K_{23}} \tag{59}$$

$$\Phi_{12} = -N_1\left(\frac{1}{C_t K_{12}} - \frac{1}{C_t K_{13}}\right) \tag{60}$$

$$\Phi_{21} = -N_2\left(\frac{1}{C_t K_{12}} - \frac{1}{C_t K_{23}}\right). \tag{61}$$

By simple partial differentiation we can obtain the various terms of the Jacobian matrix F' as

$$\frac{\partial F_1}{\partial N_1} = 1 + \Phi_{11}/2 + \frac{N_1}{2}\left(\frac{\partial \Phi_{11}}{\partial N_1}\right) + \frac{N_2}{2}\left(\frac{\partial \Phi_{12}}{\partial N_1}\right) \tag{62}$$

$$\frac{\partial F_2}{\partial N_2} = 1 + \Phi_{22}/2 + \frac{N_2}{2}\left(\frac{\partial \Phi_{22}}{\partial N_2}\right) + \frac{N_1}{2}\left(\frac{\partial \Phi_{21}}{\partial N_2}\right) \tag{63}$$

$$\frac{\partial F_1}{\partial N_2} = (\Phi_{12}/2) + \frac{N_1}{2}\left(\frac{\partial \Phi_{11}}{\partial N_2}\right) + \frac{N_2}{2}\left(\frac{\partial \Phi_{12}}{\partial N_2}\right) \tag{64}$$

$$\frac{\partial F_2}{\partial N_1} = (\Phi_{21}/2) + \frac{N_2}{2}\left(\frac{\partial \Phi_{22}}{\partial N_1}\right) + \frac{N_1}{2}\left(\frac{\partial \Phi_{21}}{\partial N_1}\right). \tag{65}$$

Substituting Eqs. 58–61 in Eqs. 62–65 and recognizing that $(N_1 + N_2 + N_3) = N_t$, we get

$$\frac{\partial F_1}{\partial N_1} = 1 + \frac{(N_1 + N_t)}{2 C_t K_{13}} \tag{66}$$

$$\frac{\partial F_2}{\partial N_2} = 1 + \frac{(N_2 + N_t)}{2 C_t K_{23}} \tag{67}$$

$$\frac{\partial F_1}{\partial N_2} = \frac{N_1}{2 C_t K_{13}} \tag{68}$$

$$\frac{\partial F_2}{\partial N_1} = \frac{N_2}{2 C_t K_{23}}. \tag{69}$$

Using these expressions, we can calculate the determinant of the Jacobain F' as

$$D = \left(\frac{\partial F_1}{\partial N_1}\right)\left(\frac{\partial F_1}{\partial N_2}\right)\left(\frac{\partial F_2}{\partial N_1}\right)\left(\frac{\partial F_2}{\partial N_2}\right) = 1 + \frac{(N_2 + N_t)}{2 C_t K_{23}} + \frac{(N_1 + N_t)}{2 C_t K_{13}} + \frac{N_t (N_1 + N_2)}{4 C_t^2 K_{23} K_{13}} + \frac{N_t^2}{4 C_t^2 K_{23} K_{13}} + \frac{N_1 N_2}{4 C_t^2 K_{23} K_{13}}. \tag{70}$$

Since the fluxes (N) are usually small numbers, (10^{-5}–10^{-6}), the unity term dominates the sum of all the other terms and the determinant is nonzero. This implies that the Maxwell-Stefan equations when applied to the film model will yield a unique solution even in the absence of equimolar counterdiffusion, and the imposition of the mass-transfer rate equations will in no way contribute to additional multiplicities in a nonequilibrium separation process problem.

Conclusions

The main results obtained from this research are that there is a one-to-one correspondence between the bulk and the interface compositions in a nonequilibrium single-stage problem and that the imposition of the mass-transfer equations does in no way add to the multiplicity. This implies that all the multiplicity/uniqueness results in the equilibrium problem will carry over to the nonequilibrium case, and for a single-stage problem, the multiplicity in the nonequilibrium stage separation process is a result of the tendency of the mixture to exhibit a second liquid phase as in the equilibrium single-stage problem.

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Notation

a = interfacial area
f = feed mol number
G = Gibbs free energy
J = diffusive flux
K = mass-transfer coefficient, K-value
l = liquid mol number
N = molar flux
v = vapor mol number
x = liquid mol fraction
y = vapor mol fraction
z = feed mol fraction
μ = chemical potential

Subscripts and Superscripts

i, j, k = component index
b = bulk phase
i = interface
L, V = phase index representing liquid, vapor

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Appendix

In this Appendix we show a one-to-one correspondence between the formulations of liquid-phase mol numbers (l_1, l_2, l_3, $\ldots$, l_c) and the total flow rate combined with the $c-1$ mol fractions (L, x_1, x_2, x_3, $\ldots$, x_{c-1}) for a c-component mixture. This is done by demonstrating that the Jacobian matrix for the map between the two formulations is nonsingular. The Jacobian matrix for this map, a $c \times c$ matrix, is

$$J_M = \begin{bmatrix} x_1 & \\ x_2 & \\ \cdot & [LI] \\ \cdot & \\ \cdot & \\ x_c & -L\ -L\ -L\ -L \cdots -L \end{bmatrix}, \tag{A1}$$

whose determinant is $(-L)^{c-1}$, and I represents the identity matrix. Since the liquid flow L is never zero, the determinant of the Jacobian is nonzero and the matrix is nonsingular, guaranteeing a one-to-one correspondence between the two formulations.

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