On measurement of thermal diffusion coefficients in multicomponent mixtures

Kjetil B. Haugen\(^a\) and Abbas Firoozabadi\(^b\)

Department of Chemical Engineering, Mason Lab, Yale University, New Haven, Connecticut 06520-8286

(Received 19 August 2004; accepted 13 October 2004; published online 15 December 2004)

We investigate the steady-state separation of the individual components of an incompressible multicomponent liquid mixture in a narrow two-dimensional thermogravitational column. Analytic working equations for measuring thermal diffusion coefficients analogous to the existing equations for a binary mixture are derived. Similar to the binary results, we find that when compositional variation has negligible effect on fluid density and vertical diffusive flux can be ignored, molecular diffusion does not affect steady-state separation. However, when compositional effects on density are taken into account, molecular diffusion does affect the bulk convective flow and the steady-state separation of the components. There may be also two distinct trends in the velocity and separation profiles. With one or more negative thermal diffusion coefficients, there may be more than one convection cell resulting in oscillatory behavior of separation. The working equations presented can be used to measure thermal diffusion coefficients of multicomponent mixtures. Such measurements have not yet been reported in the literature. © 2005 American Institute of Physics. [DOI: 10.1063/1.1829033]

I. INTRODUCTION

Thermal diffusion has been studied extensively to provide understanding of separation processes and molecular interactions. These studies have been mainly limited to two-component mixtures. The molecular flux by thermal diffusion is proportional to the thermal gradient and the thermal diffusion coefficient. To our knowledge, thermal diffusion coefficients have not been measured in mixtures of three or more components, except measurements for only one of the components in a ternary mixture.\(^1\) Binary coefficient measurements may not, in general, provide ternary coefficients.

The two basic approaches for measuring thermal diffusion coefficients in binary mixtures are the thermogravitational column\(^2,3\) and the optical methods.\(^4\) Simple diffusion cells have also been used in the past. On the whole, the measurements from thermogravitational columns (of both rectangular and circular cross sections), diffusion cells, and optical methods are in agreement when the less dense species goes to the hot side. There has been no measurement of thermal diffusion coefficients in a thermogravitational column with a rectangular cross section when the less dense species goes to the cold side.

This work centers on the derivation of working equations in a thermogravitational column. The widely used expression for the thermal diffusion coefficient of binary liquids in a thermogravitational column is from the work of Furry–Jones–Onsager (FJO).\(^5\) Marcoux and Charrier–Mojtabi\(^6\) present the extension to ternary mixtures. The work in Refs. 5 and 6 assumes that the effect of compositional variation on density is negligible. Ecenarro et al.\(^7\) have included the effect of compositional dependency of the density in the derivations for a binary mixture. However, there is no discussion that there may be different velocity profiles and separation behaviors with positive and negative thermal diffusion ratios.

In this paper, we derive working equations for thermal diffusion coefficients for multicomponent mixtures. We consider any combination of positive and negative thermal diffusion ratios in our derivations. Depending on the sign and magnitude of a general parameter that will be defined in the paper, there may exist two different solutions to the problem; one for the positive parameter (positive thermal diffusion ratio in a binary) and one for the negative parameter.

In this work, similar to the work of FJO, we consider a two-dimensional column of height \(h\) and width \(L.\) All walls are impermeable, no-slip boundaries, and the vertical walls are maintained at constant but different temperatures (see Fig. 1). As a result, there is a horizontal thermal gradient in the fluid mixture. Because the conductivity of the fluid is assumed high, the gradient is a constant \(T_x = \Delta T/L.\) The aspect ratio of the column is small \(L/h \ll 1,\) and except at the top and bottom ends of the column, the bulk flow is strictly vertical. The fluid is also considered incompressible and the flow Newtonian. As a consequence of incompressibility and zero horizontal bulk velocity, the continuity implies that the vertical velocity component in the column only varies horizontally. This is also true for the corresponding stream function.

II. DIFFUSIVE FLUX

When there is no pressure diffusion, the diffusive flux of each component in the fluid mixture is driven by thermal and compositional gradients. While there is a general agreement...
on the form of the thermal diffusion term for binary mixtures, there has been discussion in literature on how this term should be extended in multicomponent mixtures.\textsuperscript{9} However, the proposed formulations provide proportionality to the thermal gradient. We first employ a general flux expression which encompasses various formulations

\[
\vec{J}_i = -\rho \sum_{j=1}^{n-1} D_{ij}^m \vec{\omega}_j + D_{Ti}^m \vec{\nabla}T.
\]

Here, \(\rho\) is the mass density, \(D_{ij}^m\) is the mass-based Fickian diffusion coefficient which in general differs from the mole-based diffusion coefficient, \(\omega_j\) is the weight fraction of component \(j\), \(D_{Ti}^m\) is the thermal diffusion coefficient of component \(i\), and \(T\) is the temperature. The above expression is valid for \(n\)-component mixtures, but because \(\sum_{j=1}^{n-1} J_i = 0\), there are only \(n-1\) independent fluxes (\(i=1,...,n-1\)). In general, the Fickian and thermal diffusion coefficients are functions of composition, temperature, and pressure. However, for a given experiment we assume the thermal, compositional and barometric variations to be small, and we treat these coefficients as averaged constants. This is a good assumption provided the mixture is far enough from the critical point for the coefficients to exhibit only weak thermal, compositional and barometric dependences.\textsuperscript{10} Note that in Eq. (1), the thermal diffusion flux is expressed as \(-\rho D_{Ti}^m \vec{\nabla}T\). In the literature, most authors use \(+\rho D_{Ti}^m \vec{\nabla}T\). In our formulation, a positive \(D_{Ti}^m\) indicates that the component segregates to the cold side in a binary. However, to make our results comparable with the literature, we will later define the thermal diffusion ratio in such a way that for a positive value, the component will segregate to the hot side in a binary.

\section*{III. MASS BALANCE}

The expression for mass balance of each component is given by

\[
\rho \frac{D \omega_i}{D t} = -\vec{\nabla} \cdot \vec{J}_i.
\]

At steady state, the time derivative \(\partial \omega_i / \partial t\) vanishes. Also, there is neither vertical temperature gradient nor horizontal velocity component. Combining Eq. (1) for diffusive flux with Eq. (2), we find the steady-state mass balance for each component in the fluid mixture

\[
- \frac{\partial \psi}{\partial x} \frac{\partial \omega_i}{\partial z} = \left( \sum_{j=1}^{n-1} D_{ij}^m \vec{\nabla}^2 \omega_j + D_{Ti}^m \frac{\partial^2 T}{\partial x^2} \right).
\]

In the above expression, we have invoked the Oberbeck-Boussinesq approximation assuming that the mass density \(\rho\) is constant except in the buoyancy term, and expressed the vertical velocity component in terms of the stream function \(\psi\). We integrate Eq. (3) along the \(x\) axis and make the additional assumption that the vertical composition gradients are constant\textsuperscript{9}

\[
- \psi \frac{\partial \omega_i}{\partial z} = \left( \sum_{j=1}^{n-1} D_{ij}^m \frac{\partial \omega_j}{\partial x} + D_{Ti}^m \frac{\partial T}{\partial x} \right).
\]

Note that Eq. (4) represents a balance between vertical convection and horizontal diffusion and that the constant of integration is zero because the horizontal diffusive flux and the stream function vanish at the impermeable vertical walls (see Fig. 2). Using the Dirac vector notation

\[
\begin{align*}
|v| &= [v_1,v_2,v_3,...,v_{n-1}],
|\vec{v}| &= [v_1,v_2,v_3,...,v_{n-1}]^T,
\end{align*}
\]

we express mass balance for all the components in the matrix form

\[
- \psi \frac{\partial \omega}{\partial z} = D^m \frac{\partial \omega}{\partial x} + \frac{\partial T}{\partial x} |D^m_T|,
\]

where \(D^m\) is the matrix of the mass-based Fickian diffusion coefficients \(D^m_{ij}\).

\section*{IV. NET VERTICAL FLUX}

The total flux of component \(i\) in the column is the sum of diffusive and convective contributions. The net vertical flux \(j_{iz}\) is found by integrating the vertical component across a horizontal cross section

\[
j_{iz} = -\rho \int_{-L/2}^{L/2} \omega_i \frac{\partial \psi}{\partial x} + \sum_{j=1}^{n-1} D^m_{ij} \frac{\partial \omega_j}{\partial z} dx,
\]
where the vertical velocity component is again expressed in terms of the stream function $\psi$. Integrating the first term by parts and noticing that the boundary terms vanish because the stream function is zero at the walls (see Fig. 2), we write the net vertical flux of each component in a matrix form

$$
|j_z| = \rho \int_{-L/2}^{L/2} \left( \psi \frac{\partial \omega}{\partial x} - D^m \frac{\partial \omega}{\partial z} \right) dx.
$$

(8)

We now solve Eq. (6) for the horizontal compositional gradient, assuming the diffusion matrix $D^m$ to be nonsingular. Then, we substitute the result into the equation above. Recall that the thermal and vertical compositional gradients are assumed independent of $x$. The only $x$-dependent variable is therefore the stream function. Thus, the expression for the net vertical flux reduces to

$$
|j_z| = -\rho \left( K(D^m)^{-1} \frac{\partial \omega}{\partial z} - H(D^m)^{-1} D^m_T \right)
+ LD^m \frac{\partial \omega}{\partial z}.
$$

(9)

where we have introduced two new constants $H$ and $K$

$$
H = -\frac{\Delta T}{L} \int_{-L/2}^{L/2} \psi dx, \quad K = \int_{-L/2}^{L/2} \psi^2 dx.
$$

(10)

The constant $H$ represents the tendency of the mixture to separate. This separation tendency depends both on the horizontal temperature gradient and on the stream function, i.e., on the convective bulk flow. The constant $K$ represents the mixing effect of convection and depends solely on the stream function. The last term of Eq. (9) also contributes to the mixing.

At steady state there is no net vertical flux through any cross section. Setting Eq. (9) equal to zero we find the following set of $n-1$ first-order, linear differential equations:

$$
[KI + L(D^m)^2] \frac{\partial \omega}{\partial z} = H[D^m_T].
$$

(11)

Here, I is the identity matrix. We solve the above set of equations for the vertical composition gradients by matrix inversion. The separation of each component is then readily found by integrating the result along the column

$$
\frac{\Delta \omega}{h} = H[KI + L(D^m)^2]^{-1} |D^m_T|.
$$

(12)

The above expression relates the separation of each component to the thermal diffusion coefficients in a multicomponent mixture. To the best of our knowledge such an expression has only been derived for binary\(^5\) and ternary mixtures.\(^6\) The binary result is readily obtained from Eq. (12) by choosing $D^m$ to be a scalar. Similarly, the ternary result is obtained when $D^m$ is a two-by-two matrix. For a binary mixture, the spacing of the column is chosen such that the vertical mass transport is dominated by convection,\(^5,8\) allowing the effect of vertical diffusive flux to be ignored. Making the same approximation for our multicomponent mixture will reduce the matrix equation Eq. (11) to a vector equation. The steady-state separation of each component then simplifies to

$$
\frac{\Delta \omega}{h} = D^m_T \frac{H}{K}.
$$

(13)

In the remainder of this paper we will use the simplified separation expression given by Eq. (13). However, for a multicomponent mixture it might be impossible to find a single spacing where the vertical diffusion of each component is negligible while allowing for measurable separations of all components at the same time. The results obtained from Eq. (13) should therefore always be verified by Eq. (12) which takes vertical molecular diffusive flux into account.

V. THE STREAM FUNCTION

Equations (12) and (13) are expressed in terms of the constants $K$ and $H$. Both constants relate to the stream function $\psi$ of the bulk flow, and the next step is to find an expression for $\psi$. We assume the bulk flow in the open column to be governed by the Navier-Stokes equation,

$$
\rho \frac{D\vec{v}}{Dt} = -\nabla P + \rho g + \mu \nabla^2 \vec{v}.
$$

(14)

In order to eliminate the pressure gradient, we take the curl of Eq. (14) and apply the Oberbeck-Boussinesq approximation mentioned above. This results in a differential relationship between the stream function $\psi$ and horizontal density variation

$$
\mu \frac{\partial^4 \psi}{\partial x^4} = -g \frac{\partial \rho}{\partial x}.
$$

(15)

Density is assumed to vary linearly with temperature and composition, i.e.,

$$
\rho = \rho_0 \left[1 - \beta(T - T_0) - \sum_{i=1}^{n-1} \gamma_i (\omega_i - \omega_{0i}) \right].
$$

(16)

Making use of the algebraic vector notation introduced in Eq. (5), we write the combined expression from Eqs. (15) and (16) as

$$
\mu \frac{\partial^4 \psi}{\partial x^4} = \rho_0 g \left( \beta T + \gamma \frac{\partial \omega}{\partial x} \right).
$$

(17)

Solving Eq. (6) for the horizontal compositional gradients and substituting the result into the above equation, we arrive at the differential equation for the stream function

$$
\frac{\partial^4 \psi}{\partial x^4} = \rho_0 g \left( \frac{\beta \Delta T}{L} - \frac{\Delta T}{L} \left( \gamma(D^m)^{-1} D^m_T \right) \right)
- \psi \left( \gamma(D^m)^{-1} \frac{\partial \omega}{\partial z} \right),
$$

(18)

where we have replaced the horizontal temperature gradient by its constant value $\Delta T/L$. Let us introduce the dimensionless variables $\tilde{x}$ and $\tilde{\psi}:

$$
\tilde{x} = \frac{L}{2} \tilde{x}, \quad \tilde{\psi} = \frac{\rho_0 g \beta \Delta T}{2 \mu} \left( \frac{L}{2} \right)^3 \tilde{\psi}.
$$

(19)

Then, Eq. (18) transforms into the dimensionless form
\[
\frac{\partial^4 \psi}{\partial x^4} = 1 - S - R \psi,
\]
where \( R \) and \( S \) are two dimensionless parameters related to the compositional effect on density, often referred to as the forgotten effect,\(^7\)
\[
R = \frac{\rho g}{\mu} \left( \frac{L}{2} \right)^4 \left( \gamma (D^m)^{-1} \right) \left( \frac{\partial \omega}{\partial z} \right),
\]
\[
S = \beta^{-1} \left( \gamma (D^m)^{-1} \right) \left( \frac{\partial \omega}{\partial z} \right),
\]
The impermeable, no-slip boundary conditions require the stream function itself and its first derivative to vanish at the walls (\( x = \pm 1 \)). Equation (20) has the same form as that of a binary mixture.\(^7\) The only difference as we extend the theory to a multicomponent mixture is in the definition of the dimensionless parameters \( R \) and \( S \).

VI. FURRY-JONES-ONSAGER (FJO) EXPRESSION

When only the thermal expansion is taken into account, the compositional expansion factors \( \gamma_i \) all vanish, and the parameters \( R \) and \( S \) become zero. The dimensionless stream function can then be found by solving Eq. (20) with \( R = S = 0 \),
\[
\bar{\psi} = \frac{1}{2} \left( x^2 - 1 \right)^2.
\]
Now that the stream function is known, the expressions for the two constants \( H \) and \( K \) are found by nondimensionalizing and evaluating the integrals given by Eq. (10)
\[
H = \frac{\rho_0 \gamma T^2 L^3}{6 \mu}, \quad K = \frac{\rho_0 \gamma^2 T^2 L^7}{9 \mu^2}.
\]
The separation of each component in the mixture is found by substituting the expressions for the constants \( H \) and \( K \) into Eq. (13),
\[
\frac{\Delta \omega_i}{\omega} = - \frac{504 \mu D_T^m}{\rho_0 \gamma T L^4}.
\]
The stream function and thus the steady-state separation of each component in the column are related only to the dimensions of the column, the average properties of the bulk fluid, and the thermal diffusion coefficient for that component. In other words, there is no dependency on the Fickian diffusion coefficients \( D_{ij}^m \) as long as vertical diffusive flux is ignored. In a binary mixture, the thermal diffusion coefficient is defined in terms of the thermal diffusion ratio \( \alpha_T \),
\[
D_T^m = \frac{D^m \alpha_T (1 - \omega)}{T}.
\]
The introduction of the minus sign is intended to make our results comparable to the literature. Combining Eqs. (24) and (25), we obtain the well known expression for separation of components in an ideal binary FJO column\(^8\)
\[
\frac{\Delta \omega}{\omega} = \frac{504 \mu D_T^m (1 - \omega)}{\rho_0 \gamma T L^4}.
\]
The index "0" denotes average values.

VII. THE FORGOTTEN EFFECT

When compositional effects on density variation are taken into account, the two parameters \( R \) and \( S \) are nonzero. The solution to Eq. (20) is in this general case given by
\[
\bar{\psi} = \frac{1 - S}{4 \eta^4} \left[ 1 - \frac{\sin \eta (1 + \bar{x}) \cos \eta (1 - \bar{x})}{\sin 2 \eta + \sinh 2 \eta} - \frac{\sin (1 + \bar{x}) \cosh (1 - \bar{x})}{\sin 2 \eta + \sinh 2 \eta} - \frac{\sin (1 - \bar{x}) \cosh (1 + \bar{x})}{\sin 2 \eta + \sinh 2 \eta} - \frac{\sin (1 - \bar{x}) \cosh (1 + \bar{x})}{\sin 2 \eta + \sinh 2 \eta} \right],
\]
where the parameter \( \eta \) is given by \( R = 4 \eta^4 \). The corresponding constants \( H \) and \( K \) are found by nondimensionalizing and evaluating the integrals given by Eq. (10)
\[
H = \frac{(1 - S) \rho_0 \gamma \beta \Delta T^2 L^3}{2 \mu \eta},
\]
\[
F(\eta) = \frac{1 - \frac{\cosh 2 \eta - \cos 2 \eta}{\sin 2 \eta + \sin 2 \eta}}{\frac{1}{4 \eta} \frac{\sin 2 \eta + \sin 2 \eta}{\sin 2 \eta + \sin 2 \eta}}.
\]
\[
G(\eta) = \frac{1 - \frac{5 \cosh 2 \eta - \cos 2 \eta}{\sin 2 \eta + \sin 2 \eta}}{\frac{5 \cosh 2 \eta - \cos 2 \eta}{\sin 2 \eta + \sin 2 \eta}}.
\]
The above constants are consistent with the results for a binary mixture reported in Ref. 7. Of course, the stream function from Eq. (27) and the constants from Eqs. (28) will reduce to the FJO values in the limit as \( \eta \to 0 \). The separation of each component in the mixture is found by substituting the above expressions for the constants \( K \) and \( H \) into Eq. (13)
\[
\frac{\Delta \omega_i}{\omega} = - \frac{2^6 \mu D_T^m \eta^4 F(\eta)}{(1 - S) \rho_0 \gamma T L^4 G(\eta)}.
\]
From Eq. (21a), we can see that \( R \) and thus \( \eta \) only depend on known or measurable quantities. However, this is not true for the definition of \( S \), Eq. (21b) since it contains the thermal diffusion coefficients which we want to find and thus must treat as unknowns. As a first step, we combine Eqs. (13) and (21b),
\[
S = \frac{K}{\bar{\gamma} \left( \gamma (D^m)^{-1} \right) \left( \frac{\partial \omega}{\partial z} \right)}.
\]
Since the constants \( H \) and \( K \) are known except for the influence of \( S \), we now have an equation in one unknown which we can solve quite easily. Combining Eqs. (28) and (30), we arrive at
The above equation can be simplified further by using the definition of $R=\eta^4$ given by Eq. (21a),

$$S = \frac{(S-1)G(\eta)}{F(\eta)} = -\frac{G(\eta)}{F(\eta) - G(\eta)}.$$ (32)

Conclusively, in the case where mass transport of each component along the column is dominated by convection, both parameters $R$ and $S$ can be expressed explicitly in terms of a common parameter $\eta$. Substituting Eq. (32) into Eq. (29) and nondimensionalizing the separation with respect to the ideal value found in Eq. (24) yields,

$$\frac{\Delta \bar{\omega}_i}{h} = \frac{8}{63} \frac{\eta^4}{G(\eta)} \left( F(\eta) - G(\eta) \right).$$ (33)

The above equation expresses the relative importance of the forgotten effect on the separation in the column. It approaches unity in the limit $R, S, \eta \to 0$ and behaves like

$$\frac{8}{63R^{1/4}}$$ (34)

for large positive $R$ values.

Figure 3 illustrates the dimensionless vertical velocity profile $\bar{\omega} = -\partial \bar{\psi}/\partial \bar{x}$, for increasing $R>0$. This corresponds to the case where the net effect of thermal diffusion is to bring the lighter components to the hot side and the heavier components to the cold side of the column. As a consequence, the variations in density caused by thermal expansion is enhanced by the horizontal compositional gradient. The enhancement is stronger at the walls and as the compositional influence on density increases, convection tends to be isolated to a boundary layer at the walls. Since this is the part of the fluid where species composition is farther from the average, separation increases with $R$.

Of course Eq. (27) through Eq. (33) are all valid also for negative values of $R$. However, in this case, $\eta$ is a complex number, a fact that complicates the physical interpretation of the mathematical results. It is more convenient to introduce a new variable $\phi$ defined by $\phi^4 = -R$. Expressing the stream function Eq. (27) and the separation Eq. (33) in terms of $\phi$ leads to

$$\hat{\psi} = -S \left[ \frac{\sin \phi \cosh(\phi x) + \sinh \phi \cos(\phi x)}{\sin \phi \cosh \phi + \sinh \phi \cos \phi} \right] - 1$$ (35)

$$\Delta \bar{\omega}_i = -\frac{2\phi^4}{63} \frac{F(\phi) - G(\phi)}{G(\phi)}.$$ (36)

where the functions $F(\phi)$ and $G(\phi)$ are given by

$$F(\phi) = 1 - \frac{2}{\phi} \frac{\sin \phi \cosh \phi + \sinh \phi \cos \phi}{\phi \sin \phi \cosh \phi + \sinh \phi \cos \phi}$$ (37a)

$$G(\phi) = 1 - \frac{5}{2\phi} \frac{\sin \phi \sinh \phi}{\sin \phi \cosh \phi + \sinh \phi \cos \phi} + \frac{1}{2(\sin \phi \cosh \phi + \sinh \phi \cos \phi)^2}.$$ (37b)

Again, the above expression approaches unity as $\phi \to 0$. In the opposite limit, $\phi \to \infty$, one can show that Eq. (36) can be approximated by

$$\frac{\Delta \bar{\omega}_i}{h} = -\frac{2R}{63} \frac{1}{3 + 2 \sin[2(-R)^{1/4}]}.$$ (38)

Figure 4 illustrates the vertical velocity profile $\bar{\omega}$ for decreasing $R<0$. This corresponds to the case where the net effect of thermal diffusion is to bring the heavier components to the hot side and the lighter components to the cold side of the column. As a consequence, the variations in density caused by thermal expansion is opposed by the horizontal compositional gradient. The effect is stronger at the walls. As long as the compositional influence on density is weaker than its thermal counterpart, the net tendency is to isolate convection of the fluid to the central part of the column. Since this is the part of the fluid where species composition is closer to the average, we expect separation to decrease with decreasing $R$ within this domain. However, as soon as the compositional influence on density becomes stronger than its thermal
counterpart, the number of convection cells in the column starts to increase. At each point, thermal and compositional expansion compete to determine whether the bulk fluid moves upward or downward. The left half of Fig. 5 shows how separation in the column varies with $R$. We see that negative $R$ causes an oscillatory behavior that is not observed for positive $R$. The reason is that for negative $R$ the convective flow in the column may split into more than one cell in the horizontal direction. We can easily determine when the number of cells is about to increase. If there is to exist more than one cell, there must be both upward and downward motion in each half of the column. This implies that the vertical velocity field must have more than one extremum. In the limiting case, one extremum must be located at each wall, i.e.,

$$\frac{\partial^2 \psi}{\partial x^2} \bigg|_{x = \pm 1} = 0. \quad (39)$$

From Eq. (35) we conclude that the criterion is simply

$$\tan \phi = \tanh \phi. \quad (40)$$

Seemingly, $\phi=0$ is a solution. However, in this case the full expression for the second derivative of $\psi$ is a fraction where the numerator and the denominator are both zero. The limit exists and is nonzero, implying that $\phi=0$ is not a valid solution. This is expected since, $\phi=0$ corresponds to the ideal case with no compositional effect on density (see Fig. 6). To arrive at an exact analytical expression we assume $\tanh \phi \approx 1$ which is a good approximation for $\phi>3$. Thus, we conclude that the criteria for generating another convection cell are given by

$$\tan \phi = 1 \Rightarrow \phi = \frac{\pi}{4} + k \pi, \quad k=1,2,3,..... \quad (41)$$

Note that $\phi=\pi/4$ is not a valid solution. This is because in the first quadrant $\tan \phi$ always grows faster than $\tanh \phi$ and the two cannot be equal (except when $\phi=0$, a possibility we have already identified as a false solution). Figure 7 shows the vertical velocity profile in the column as the number of cells is about to increase to two and three. Interestingly, the mixing in the column proves to very efficient as this is about to happen, and Eq. (41) also corresponds to separations close to local minima (see Figs. 5 and 8). Another interesting ob-
servation is that the local maxima of the separation in the column is located at $\phi$ values between the ones given by Eq. (40), i.e., at
\[
\phi = \frac{3\pi}{4} + k\pi, \quad k = 1, 2, 3, \ldots
\] (42)

It is important to recognize that neglecting molecular diffusive transport along the column places a restriction on the range of $R$ values where the above derivations are valid. The asymptotic expressions Eqs. (34) and (38) indicate that the separation in the column becomes infinite in the limits $R \rightarrow \pm \infty$. This is clearly a nonphysical result. When the absolute value of $R$ becomes sufficiently large, the bulk velocity field no longer dominates the species transport in the column. Consequently, longitudinal diffusion can no longer be ignored.

VIII. CONCLUSIONS

We have derived working equations to be used in the measurement of thermal diffusion coefficients for multicomponent mixtures. In the past, the focus has been on binary mixtures with no reported measurements for ternary- and higher-component mixtures. Multicomponent thermal diffusion coefficients may not be estimated from binary data.10 The essence of our new derivations is presented in the following.

(1) Eq. (24) provides the general expression that relates the component segregation to the thermal diffusion coefficients at steady state. The same expression can be used irrespective of the sign of thermal diffusion coefficients. The main assumptions in the derivation of Eq. (24) are (a) negligible effect of composition variation on density, and (b) negligible effect of vertical molecular diffusion. In case molecular diffusion affects the vertical segregation, Eq. (12) provides the working relationship.

(2) For some binary mixtures and multicomponent fluids, the effect of compositional variation on density can be significant. In this case we use a parameter $R$ defined by Eq. (21a). For positive $R$ values, the shape of the vertical velocity profile alters to the extent that velocity variations can occur mainly close to the wall. As a result, the segregation increases with increasing $R$.

(3) When $R$ becomes negative, subtleties develop in the vertical velocity and separation profiles. With decreasing $R$, first there is a decrease in segregation, then an increase, followed by oscillatory behavior. The oscillatory behavior is due to the increase in the number of convection cells. The possibility of having more than one convection cell for negative $R$ is the first report of its kind in the literature. In this work, we have assumed that the cells extend through the whole vertical domain. Another possibility is more than one cell in the vertical direction. Such a possibility may increase mixing and result in very little separation.

The working equations for separation when $R$ is positive is given by Eq. (33). For negative $R$, the separation is presented by Eq. (36). Both expressions give the ratio of separation with the compositional variation of density to the case when this effect is neglected.

ACKNOWLEDGMENT

This work was supported by a Yale University Fellowship to K.H. and by the member companies of the Reservoir Engineering Research Institute (RERI) in Palo Alto, California.

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