Transient separation of multicomponent liquid mixtures in thermogravitational columns

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The transient separation of the individual components in a multicomponent liquid mixture in a thermogravitational column can be used to determine the thermal and molecular diffusion coefficients. Two models of the transient behavior are developed. First, a classical model where density only depends on temperature. Second, a general model where the compositional effect on density is also taken into account. Diffusion coefficients can be determined by fitting experimental data to either model. The procedure is demonstrated for a ternary liquid mixture. The results reveal that the classical model is very unreliable even though composition variation only contributes to the total buoyancy by one-third. Diffusion coefficients can be obtained reliably from the general model provided the experimental noise does not exceed ±1% of steady-state separation. This level of accuracy in composition measurements is achievable. © 2007 American Institute of Physics. [DOI: 10.1063/1.2794043]

I. INTRODUCTION

The thermogravitational column (TGC) was invented by Clusius and Dickel in 1938. They filled the space between two concentric cylinders with a gas and heated the inner cylinder. The horizontal temperature gradient introduced convective flow and due to thermal diffusion, the ascending and descending portions of the gas had different compositions. Clusius and Dickel observed a significant separation of the components of the gas and suggested that the technique could be used for component and isotope separation. Using thermal diffusion to separate isotopes had been suggested by Chapman twenty years earlier. However, no appreciable separation was measured until Clusius and Dickel realized that the isotope separation may be greatly enhanced by convection. In 1939, Furry et al. developed a theory for isotope separation in a thermogravitational column. The Furry-Jones-Onsager (FJO) theory laid the grounds for measuring thermal diffusion coefficients in gases.

The thermogravitational column can separate components in a gas very effectively. As an example, Clusius and Dickel increased the concentration of oxygen in air from 21% to 85%. The temperature difference between the cylinders was about 600 °C. Of course, such high temperature differences are unlikely in liquids and the components are separated by a few percent at the most. An interest to use the thermogravitational column to measure thermal diffusion coefficients in liquids emerged with the development of equipment capable of measuring such small variations in concentration. In 1962, Horne and Bearman extended the FJO theory to liquids in cylindrical TGCs. Ecenarro et al. realized that the derivations by Horne and Bearman can be simplified when the gap between the cylinders is much smaller than the two radii. Horne and Bearman, and Ecenarro et al. improved the FJO theory by allowing density to be a function of both temperature and composition. In the work by Furry et al., the effect of composition was ignored and is thus often referred to as the forgotten effect.

Traditionally, the thermogravitational column has only been used to determine thermal diffusion coefficients of binary mixtures from steady-state separations. Recently, the simplified Horne-Bearman theory introduced by Ecenarro et al. has been extended to ternary and multicomponent mixtures. Molecular diffusion coefficients do not affect steady-state separations, and obtaining them from component separation in a thermogravitational column requires transient measurements. In 1951, Majumdar presented an exact solution to the transient separation problem for binary gases. He used his theory to obtain the thermal diffusion ratio for oxygen in air from transient measurements made by Clusius and Dickel. Later on, the transient problem has also been solved for binary liquid mixtures.

The purpose of this work is to show how molecular and thermal diffusion coefficients of multicomponent liquid mixtures can be obtained from transient component separation data in a thermogravitational column. First, we develop a classical model, i.e., density is assumed to vary only with temperature. Second, we generalize the model by taking the composition dependence of density into account. Third, we show how diagonal and off-diagonal molecular diffusion coefficients and thermal diffusion coefficients can be obtained from fitting the general model to experimental data. Finally, we illustrate our approach with a ternary example.

II. THERMOGRAVITATIONAL COLUMN

There are two ways of designing a TGC for the purpose of measuring diffusion coefficients. First, one can construct a rectangular slab of height $h$, width $L$, and depth $d$. The aspect
respective. The radii are chosen such that $L \leq h$ and $L \leq d$. Second, one can make a hollow cylinder of inner and outer radii, $r_1$ and $r_2$, respectively. The radii $r_1$ and $r_2$ and the column height $h$ are much greater than the gap $L=r_2-r_1$ between the cylinder walls. Regardless of design, a horizontal temperature gradient is introduced across the width/gap by maintaining the vertical walls at constant but different temperatures. Due to the chosen aspect ratios, the resulting convective flow is strictly vertical. Under the above assumptions, the mathematical analyses of the cylindrical and rectangular columns reduce to the same two-dimensional problem (see Fig. 1). Although a TGC can be used to measure diffusion coefficients of both liquids and gases, this work focuses on liquids.

III. MASS TRANSPORT

In general, the total mass flux of the components in a multicomponent mixture is given by

$$\mathbf{J} = - \rho \mathbf{D} (\nabla \omega) + |D_T| \nabla T + |D_p| \nabla P - |\omega| \mathbf{v}.$$  \hspace{1cm} (1)

Here, $|\mathbf{J}|$ is a column vector of the total mass fluxes, $\rho$ is the mixture density, $\mathbf{D}$ is the diffusion coefficient matrix, $|\nabla \omega|$ is a column vector of the mass fraction gradients, $|D_T|$ is the thermal diffusion coefficient column vector, $T$ is temperature, $|D_p|$ is the pressure diffusion coefficient column vector, $P$ is pressure, $|\omega|$ is a column vector of the mass fractions, and $\mathbf{v}$ is bulk velocity. The first three terms are due to diffusion, while the last term accounts for convective mass transport. In this work, we use mass-averaged velocity as reference, and all diffusion coefficients are therefore mass based.

In a thermogravitational column, a number of simplifications can be made in the general flux expression in Eq. (1). Due to the short column height, pressure diffusion can be neglected for mixtures not too close to their critical points. As mentioned in the previous section, column design only allows for vertical flow. Assuming the two-dimensional flow to be incompressible, we can express the velocity field by a stream function $\psi$. From continuity, it follows that the velocity field and thus the stream function can only vary horizontally. In liquids, thermal conductivity is high and we can assume that the temperature gradient immediately assumes its steady-state value $T_c = \Delta T / L$. The total vertical and horizontal mass fluxes in a multicomponent mixture in a thermogravitational column are, therefore,

$$|J_z| = - \rho \left( D \frac{\partial \omega}{\partial z} + |\omega| \frac{\partial \psi}{\partial x} \right),$$  \hspace{1cm} (2a)

$$|J_x| = - \rho \left( D \frac{\partial \omega}{\partial x} + |D_T| \Delta T / L \right).$$  \hspace{1cm} (2b)

From continuum mechanics, we know that mass conservation is given by

$$\frac{\partial}{\partial t} (\rho |\omega|) = - (\nabla \cdot \mathbf{J}),$$  \hspace{1cm} (3)

where $t$ is time. Taking the divergence of the simplified flux expression in Eq. (2) and assuming quasi-steady state, we find that the mass conservation is a balance between horizontal diffusion and vertical convection,

$$\frac{\partial |\omega|}{\partial t} = D \frac{\partial^2 |\omega|}{\partial z^2} + \frac{\partial |\omega|}{\partial x} \frac{\partial \psi}{\partial x} = 0.$$  \hspace{1cm} (4)

In order to arrive at the expression in Eq. (4), we have also assumed that density is constant $\rho = \rho_0$, and that for every component $i$, $\frac{\partial^2 |\omega_i|}{\partial z^2} = \frac{\partial^2 |\omega_i|}{\partial x^2}$. The latter follows from the small aspect ratio $L \ll h$. The net vertical mass transport $|j_z|$ is found by integrating the expression for total vertical mass flux in Eq. (2a) across the column. The second term is integrated twice by parts subject to the boundary conditions $\! \psi \! = 0$ and $|j_z| = 0$ at the impermeable vertical walls $x = \pm L/2$. With the help of Eq. (4) we arrive at

$$|j_z| = \rho_0 \left( H \left| D_T \right| \nabla T - K \left| D_f \right| \frac{\partial T}{\partial z} \right. \left. - L D \frac{\partial |\omega|}{\partial z} \right),$$  \hspace{1cm} (5)

where the two parameters $H$ and $K$ are related to the stream function $\psi$ by the integrals

$H = - \frac{\Delta T}{L} \int_{-L/2}^{L/2} \psi dx,$  \hspace{1cm} (6a)

$K = \int_{-L/2}^{L/2} \psi^2 dx.$  \hspace{1cm} (6b)

The first term in Eq. (5) is the thermogravitational effect and causes the components in the mixture to separate vertically. The last two terms express convective and diffusive mixing, respectively, and oppose separation. In a thermogravitational column, diffusive mixing is negligible compared to convective mixing. The final expression for net vertical mass transport in a TGC is, therefore,
\[ j_i = \rho_0 \left( \mathbf{H}^{-1} \mathbf{D}_T - K \mathbf{D}^{-1} \right) \frac{\partial \omega}{\partial z} \]. \tag{7}

The quantities to be measured are the component separations \( \Delta \omega_i \), i.e., the difference in concentration between the top and the bottom ends of the column. At steady state, there is no net vertical mass transport, and the steady-state separations \( \Delta \omega_{\infty} \) are found by setting Eq. (7) equal to zero,

\[ \Delta \omega_{\infty} = \frac{h H_{\infty}}{K_{\infty}} \mathbf{D}_T. \tag{8} \]

Here, \( \cdots_{\infty} \) denotes steady-state values.

### IV. COMPOSITION DEPENDENCE OF DENSITY

As mentioned in the derivation of Eq. (4), we use the Boussinesq approximation in our analysis. That is, we assume that the mixture density can be treated as a constant \( \rho = \rho_0 \) everywhere except in the buoyancy term. In the classical Boussinesq approximation, only the effect of temperature on buoyancy is accounted for, while in the Oberbeck-Boussinesq approximation, the effect of composition is also included. In the classical model when the temperature effect dominates, the parameters \( H \) and \( K \) will be constants. In an open thermogravitational column, where the flow is governed by the Navier-Stokes equation and the vertical walls act as impermeable, no-slip boundaries, these constants are given by

\[
H_0 = - \frac{\rho_0 g \beta \Delta T^2 L^3}{6! \mu}, \tag{9a}
\]

\[
K_0 = \frac{\rho_0^2 g^2 \Delta T^2 L^7}{9! \mu^2}. \tag{9b}
\]

Here, \( \rho_0 \) is average mixture density, \( g \) is acceleration of gravity, \( \beta \) is thermal expansion coefficient, and \( \mu \) is dynamic viscosity. Other symbols are defined in Fig. 1. In general, the composition dependence of density must be taken into account, and the parameters \( H \) and \( K \) depend on two parameters \( R \) and \( S \),

\[
H = (1 - S) h(R) H_0, \tag{10a}
\]

\[
K = (1 - S)^2 k(R) K_0, \tag{10b}
\]

where

\[
R = \frac{\rho_0 g \beta}{\mu} \left( \frac{L}{2} \right)^4 \gamma \mathbf{D}^{-1} \frac{\partial \omega}{\partial z}, \tag{11a}
\]

\[
S = \frac{1}{\beta} \gamma \mathbf{D}^{-1} \mathbf{D}_T. \tag{11b}
\]

Here, \( \gamma = - (1/\rho_0) \partial \rho / \partial \omega_0 \) is the compositional coefficient of component \( i \). The parameters \( R \) and \( S \) express the contribution that horizontal variations in composition make to the total buoyancy, \( S \) is a diffusive contribution and is always present, \( R \) is a convective contribution and arises as convection gradually changes the horizontal concentration variation. The importance of \( R \) increases as separation approaches steady state. Both \( R \) and \( S \) are expressed relative to the concentration distribution that thermal expansion makes to the total buoyancy.

The reason why \( R \) depends on the vertical concentration gradients despite being caused by horizontal concentration variations is the use of Eq. (4). Note that \( R \) depends on the concentration gradients and thus varies in time and space. Hence, when \( \gamma_1 \neq 0 \), \( H \) and \( K \) are no longer constants. The functions \( h(R) \) and \( k(R) \) are given by

\[
h(R) = \frac{6}{2 \pi^2} \frac{1}{\eta^4} \left( 1 - \frac{1}{\eta} \sin 2 \eta - \cos 2 \eta \right), \quad R = 4 \eta^4, \tag{12a}
\]

\[
k(R) = \frac{9}{2 \pi^2} \frac{1}{\eta^4} \left( 1 - \frac{5}{4 \eta} \sin 2 \eta + \frac{1}{4 \eta} \sin 2 \eta \right) \frac{\sinh 2 \eta + \sin 2 \eta}{\sinh 2 \eta + \sin 2 \eta}, \quad R = 4 \eta^4. \tag{12b}
\]

These expressions are consistent with the results from Refs. 6 and 8.

### V. TRANSIENT SEPARATION: CLASSICAL MODEL

In the classical model when buoyancy only varies with temperature, the parameters \( H \) and \( K \) are constants and the mass balance based on Eq. (7) yields

\[
\frac{\partial \omega}{\partial t} = \frac{K_0}{L} \mathbf{D}^{-1} \frac{\partial^2 \omega}{\partial z^2}. \tag{13}
\]

These governing equations form a set of coupled diffusion equations. The diffusion coefficient matrix \( \mathbf{D} \) can be diagonalized provided that all its eigenvectors are linearly independent,

\[
\lambda = V^{-1} \mathbf{D} V. \tag{14}
\]

Here, \( V \) and \( \lambda \) are the eigenvector and eigenvalue matrices of the molecular diffusion coefficient matrix \( \mathbf{D} \), respectively. As a consequence, the diffusion equations [Eq. (13)] can be decoupled by introducing the linear transformation \( \omega = V \Omega \), where \( \omega_0 \) is the average concentration of component \( i \) in the column and \( \Omega \) denotes the transformed concentrations,

\[
\frac{\partial \Omega}{\partial t} = \frac{K_0}{L} \mathbf{D}^{-1} \frac{\partial^2 \Omega}{\partial z^2}. \tag{15}
\]

Using the column height \( h \) as the characteristic length and

\[
\tau_i = \frac{L h^2 \lambda_i}{K_0}, \quad i = 1, \ldots, N - 1, \tag{16}
\]

as characteristic times makes all the diffusion equations in Eq. (15) collapse to the same dimensionless diffusion equation. The appropriate boundary conditions express no flux through the top and the bottom of the column. From Eq. (7) and the linear transformation \( \omega = V \Omega \), it follows that the transformed concentration gradients \( \partial \Omega / \partial z \) must be constant on the top and bottom boundaries. Whether or not a vector is an eigenvector does not depend on its magnitude, only on its direction. As a result, we are free to choose any constant we want. Choosing \( \partial \Omega / \partial z = 1/h \) yields identical di-
dimensionless boundary value problems for all $\Omega_i$,
\[
\frac{\partial \Omega_j}{\partial \bar{t}} = \frac{\partial^2 \Omega_j}{\partial \bar{z}^2}, \quad \frac{\partial \Omega_j}{\partial \bar{z}} = 1, \quad \text{at } \bar{z} = \pm \frac{1}{2}, \quad \bar{t} = 0, \quad i = 1, \ldots, N - 1,
\]
where the bar denotes dimensionless variables. Note that fixing the boundary conditions also fixes the magnitude of the eigenvectors in the eigenvector matrix $\mathbf{V}$. Once the eigenvector and eigenvalue matrices $\mathbf{V}$ and $\mathbf{\lambda}$ are obtained and the solution to Eq. (17) is known, the transient separations $|\Delta \omega|$ are readily obtained from the transformation
\[
|\Delta \omega| = |\mathbf{V}| |\Delta \Omega(t/\tau)|.
\]
To show how an arbitrary eigenvector matrix $\mathbf{U}$ relates to the desired eigenvector matrix $\mathbf{V}$, we set Eq. (7) equal to zero and solve for the steady-state separations $|\Delta \omega_s|$.
\[
|\Delta \omega_s| = \mathbf{U}|\Delta \Omega_s'\rangle = \mathbf{U}|\Delta \Omega_s'\rangle|1\rangle = \frac{hH_{0}}{K_0} |D_T\rangle.
\]
In the middle equality, we have used the diagonal matrix $\Delta \Omega_s'$ with elements $\Delta \Omega_s'$ to factor out $|1\rangle$, a column vector with all elements equal to unity. The reason is that the steady-state separations of all $\Omega_i$ defined by Eq. (17) are equal to one. The rightmost equality implies that the relationship between the arbitrary and desired eigenvector matrices $\mathbf{U}$ and $\mathbf{V}$ is given by $\mathbf{V} = \mathbf{U}\Delta \Omega_s'$, where $\Delta \Omega_s' = hH_{0}/K_0 |U^{-1}|D_T\rangle$.

VI. TRANSIENT SEPARATION: GENERAL MODEL

In general, buoyancy also depends on composition and the parameters $H$ and $K$ are not constants. Mass balance based on Eq. (7) leads to
\[
\frac{\partial \Omega_j}{\partial \bar{t}} = \frac{K_i}{L_{\bar{z}}} \frac{\partial}{\partial \bar{z}} \left( \frac{K_i}{K_{\bar{z}}} \frac{\partial \Omega_j}{\partial \bar{z}} \right) - \frac{H_i}{H_{\bar{z}}} \frac{\Delta \omega_s}{h}
\]
where we have used Eq. (8) to eliminate the thermal diffusion coefficients $|D_T\rangle$. Equation (20) is a set of coupled partial differential equations. They cannot be completely decoupled because $H$ and $K$ depend on the concentration gradients in a nontrivial way. Thus, all equations must be solved simultaneously and we do so numerically. To facilitate the regression analysis to be presented in the next section, we once again use the transformation $|\omega - \omega_0\rangle = |\Omega\rangle$ and obtain
\[
\frac{\partial \Omega_j}{\partial \bar{t}} = \frac{K_i}{L_{\bar{z}}} \frac{\partial}{\partial \bar{z}} \left( \frac{K_i}{K_{\bar{z}}} \frac{\partial \Omega_j}{\partial \bar{z}} \right) - \frac{H_i}{H_{\bar{z}}} \frac{\Delta \Omega_s}{h}
\]
The no-flux boundary condition at the column ends leads to Neumann boundary conditions on the transformed concentrations $|\Omega\rangle$. Numerically, it is more convenient to solve differential equations with Dirichlet boundary conditions, and we differentiate Eq. (21) once with respect to $\bar{z}$ and select the gradients $|\bar{\Omega}| = |\partial \Omega(\bar{z})/\partial \bar{z}|$ as the primary unknowns. Choosing the column height $h$ to be the characteristic length and its inverse $1/h$ to be the characteristic transformed concentration gradient, each dimensionless gradient $\bar{\Omega}_i$ must satisfy the differential equation
\[
\frac{\partial \bar{\Omega}_i}{\partial \bar{t}} = \frac{hH_{0}}{K_0} \frac{\partial^2 \bar{\Omega}_i}{\partial \bar{z}^2} - \frac{hH_{0}}{K_0} \frac{\partial \Omega_{s}}{h}
\]
subject to the initial condition $\bar{\Omega}_i(0) = 0$ and $\bar{t}=0$. Note that the time coordinate $\bar{t}$ in Eq. (22) is not nondimensionalized. The differential equations for the transformed concentration gradients $\bar{\Omega}_i$ are coupled through the parameters $H$ and $K$. Thus, their time dependences are not independent and we find it more convenient to keep the time coordinate in dimensional form. As in the classical model, we are free to choose any constant for the boundary conditions. Choosing $\bar{\Omega}_i(1) = 1$ guarantees that the transformed steady-state separations $\Delta \Omega_{s}$ are all equal to unity. Again fixing the boundary conditions fixes the magnitude of each eigenvector. Following the approach in the previous section, we can show that the relationship between an arbitrary eigenvector matrix $\mathbf{U}$ and the desired eigenvector matrix $\mathbf{V}$ is given by $\mathbf{V} = \mathbf{U}\Delta \Omega_{s}$, where $\Delta \Omega_{s} = hH_{0}/K_0 |U^{-1}|D_T\rangle$.

In order to solve Eq. (22), we need to calculate the parameters $H$ and $K$ at any given time step. Both of them are functions of the parameters $R$ and $S$. The former can be obtained from Eqs. (11a) and (14),
\[
R = \frac{\rho \bar{d}}{\mu} \left( \frac{L}{2} \right)^{\frac{3}{2}} |\mathbf{\gamma}| |\mathbf{V}\lambda^{-1}||\mathbf{\bar{G}}|
\]
and the latter is obtained from combining Eqs. (8)–(12),
\[
S = \frac{2R_{e}k(R_{e})}{2R_{e}k(R_{e}) - 63h(R_{e})}
\]
The steady-state value $R_{e}$ is obtained from Eq. (23) by setting $|\mathbf{\bar{G}}| = 1$.

The transient transformed separations in the column relate to the dimensionless gradients $\mathbf{\bar{G}}_i$ by the integral
\[
\Delta \Omega_i = \int_{-1/2}^{1/2} \mathbf{\bar{G}}_i d\bar{z}, \quad i = 1, \ldots, N - 1.
\]
When the eigenvector and eigenvalue matrices $\mathbf{V}$ and $\lambda$ are known and the transformed transient separation $\Delta \Omega_{i}$ is calculated, the physical transient separations $|\Delta \omega|$ can be determined by the transformation
\[
|\Delta \omega| = |\mathbf{V}| |\Delta \Omega_{i}|.
\]

VII. DETERMINATION OF DIFFUSION COEFFICIENTS

In the previous two sections, we showed how to predict the transient separation of a multicomponent liquid mixture in a thermogravitational column provided all mixture properties including the thermal and molecular diffusion coefficients are known. The purpose of this section is to show how one may calculate the molecular diffusion coefficient matrix $\mathbf{D}$ and the thermal diffusion coefficient vector $|D_T\rangle$ by fitting measured component separations to the classical and general models by nonlinear regression. For both models, the rela-
tionship between transformed and physical separations in the column is given by \(|\Delta \omega = V|\Delta \Omega|\). Assuming that we have made \(M\) measurements of the \(N\) separated separations in a \(N\)-component mixture, the sum of squared errors (SSE) is computed by

\[
\text{SSE} = \sum_{i=1}^{N-1} \sum_{j=1}^{M} \left( \sum_{k=1}^{N-1} V_{i,k} \Delta \Omega_{ij} - \Delta \omega_{ij}^m \right)^2,
\]

where \(\Delta \omega_{ij}^m\) is the \(j\)th measurement of the separation of the \(i\)th component and \(\Delta \Omega_{ij}\) is the predicted value of the \(i\)th transformed separation.

Minimization of the SSE must be done differently for the two models. The reason is that in the classical model, the transformed separations \(|\Delta \Omega|\) only depend on eigenvalues \(\lambda\), while in the general model, they also depend on eigenvectors \(V\).

**A. Classical model**

When \(|\Delta \Omega|\) only depends on \(\lambda\), minimizing Eq. (27) with respect to element \(V_{\alpha\beta}\) of the eigenvector matrix \(V\) yields

\[
\frac{\partial \text{SSE}}{\partial V_{\alpha\beta}} = 2 \sum_{j=1}^{N-1} \left( \sum_{k=1}^{N-1} V_{\alpha,k} \Delta \Omega_{ij} - \Delta \omega_{ij}^m \right) \Delta \Omega_{ij} = 0.
\]

We now introduce two \((N-1) \times M\) matrices \(\Delta \Omega\) and \(\Delta \omega^m\), where each column corresponds to a measurement and each row corresponds to the transformed and physical separation of a component respectively. Equation (28) can then be expressed in matrix form

\[
V \Delta \Omega \Delta \Omega^T - \Delta \omega^m \Delta \omega^T = 0,
\]

implying that the least-square value of the eigenvector matrix \(V\) is given by

\[
V = \Delta \omega^m \Delta \Omega^T \times (\Delta \Omega \Delta \Omega^T)^{-1}.
\]

Equation (30) shows how to obtain the eigenvalue matrix \(V\) when the time dependencies of the transformed separations \(\Delta \Omega\) are known. In order to find the correct time dependencies, we resort to numerical minimization of SSE.

**B. General model**

The proposed algorithm to minimize SSE when fitting the general model to measured separations is an iterative approach based on constrained successive substitution and a nested Newton method. It can be summarized in the following steps:

1. Obtain an initial estimate of \(V\) and \(\lambda\) by fitting the classical model to the measured separations. Starting from the analytical solution to Eq. (17), we stretch the time coordinate of each transformed separation \(\Delta \Omega\) until the least-square values of the characteristic times \(i\) are obtained. The eigenvalues \(\lambda_i\) are then obtained from Eq. (16) and the eigenvector matrix \(V\) is obtained from Eq. (30).

2. Obtain \(R_s\) from

\[
R_s = \frac{\rho_0 g \left( L \right)^4}{\mu} \left( \gamma |V\lambda^{-1}|^1 \right)
\]

and \(S\) from Eq. (24).

3. Solve Eq. (22) numerically and use Eq. (25) to find the transformed separations \(\Omega_i\). At each time step, calculate \(R\) from Eq. (23).

4. Update \(V\) and \(\lambda\) by assuming that \(|\Delta \Omega|\) does not depend on the eigenvectors. This means that we follow the same procedure as for the classical case. Starting from the transformed separations found in the previous step, we stretch the time coordinates of each \(\Delta \Omega\) until the least SSE is found. Assuming that each time coordinate is stretched by a factor \(\theta\), the eigenvalues \(\lambda_i\) are updated from

\[
\lambda_i = \theta \lambda_i',
\]

where \(\lambda_i'\) is the old eigenvalue. \(\theta>1\) implies an increased relaxation time for the corresponding \(\Delta \Omega\). The eigenvector matrix is obtained from Eq. (30). To reduce the error introduced by ignoring the fact that the transformed separations \(|\Delta \Omega|\) do depend on the eigenvectors \(V\), the amount of stretching is limited to \(\pm 10\%\) per iteration.

5. Repeat steps 2–4 until SSE no longer decreases or a maximum of ten iterations are reached. This portion of the algorithm is what we referred to as constrained successive substitution.

6. Perform a nested Newton method until convergence. The nested Newton method is an adaptation of the Newton method to avoid the ill-conditioned Hessian matrix generated by the Newton method. The problem arises because SSE is much more sensitive to variations in eigenvalues than eigenvectors. A detailed explanation of the nested Newton method is presented in Appendix A.

**VIII. ALGORITHM TESTING**

There are no reported transient separation measurements of multicomponent mixtures in open thermogravitational columns in the literature. Thus, in order to test our proposed algorithm to find \(D\) and \(|\Delta \omega|\), we use the properties of a ternary mixture to generate theoretical transient separations \(\Delta \omega_i\). To reduce noise, these separations are then interpreted as measurements in the regression analysis. The goal is to extract the diffusion coefficients from the measured separations.

The chosen test mixture is a 1:1:1 by mass mixture of normal octane (nC8), normal decane (nC10), and 1-methylnaphthalene used in a rectangular thermogravitational column by Leamy-Dios et al.\(^{13}\) The relevant mixture data are summarized in Table I. The column is \(h=53.0\) cm tall and has a width of \(L=1.59 \pm 0.02\) mm. The rate of separation in the column depends on \(L^6\) [see Eqs. (9b), (10b), and (20)]. It is, therefore, very important for the column to have a highly uniform width \(L\). The reported variations of \(\pm 0.02\) mm introduce an uncertainty in the estimation of the eigenvalues of about \(7\%–8\%\). The temperature difference
coefficients can be estimated more accurately than molecular than the diagonal terms. Also, note that thermal diffusion less accurate because in the test mixture, they are smaller ported in Table II. As expected, we observe that accuracy average values and standard deviations of ten runs are re-

Thus, only the general model was used in the final test. The classical model is completely unreliable for our mixture, even in the absence of noise.

random noise added was flat and with an amplitude of 1% of

points to be treated as measurements.

are plotted in Fig. 3 along with an example of a set of data

composition dependence of density has an appreciable effect on the transient separations

see Fig. 2

FIG. 2. A comparison of the separations of nC₈ (top graphs) and nC₁₀ (bottom graphs) predicted by the two models. The dashed lines are predictions from the classical model and the solid lines are predictions from the general model, where the composition dependence of density is accounted for.

TABLE I. Relevant data for a ternary mixture of nC₈ (component 1), nC₁₀ (component 2), and 1-methylnaphthalene (reference component). Data are from Leahy-Dios et al. (Ref. 13).

<table>
<thead>
<tr>
<th>T₀a (K)</th>
<th>ρ₀b (kg)</th>
<th>μ (mPa s)c</th>
<th>βd (10⁻³ K⁻¹)</th>
<th>γ₁e</th>
<th>γ₂e</th>
<th>α₁₁f</th>
<th>α₁₂f</th>
<th>α₁₁h</th>
</tr>
</thead>
<tbody>
<tr>
<td>295.65</td>
<td>795.67</td>
<td>0.9333</td>
<td>0.9817</td>
<td>0.3558</td>
<td>0.3168</td>
<td>0.3333</td>
<td>0.3333</td>
<td></td>
</tr>
</tbody>
</table>

Table II.

TABLE II. Molecular (Dij) and thermal (Dij) diffusion coefficients for the ternary test mixture of nC₈ (component 1), nC₁₀ (component 2), and 1-methylnaphthalene (reference component).

<table>
<thead>
<tr>
<th>Sample points</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₁₁ (10⁻⁹ m² s⁻¹)</td>
<td>+1.99a</td>
<td>+2.26b ±0.41c</td>
</tr>
<tr>
<td>D₁₂ (10⁻⁹ m² s⁻¹)</td>
<td>−0.93a</td>
<td>−1.31b ±0.60c</td>
</tr>
<tr>
<td>D₁₃ (10⁻⁹ m² s⁻¹)</td>
<td>−0.42a</td>
<td>−0.48b ±0.35c</td>
</tr>
<tr>
<td>D₂₂ (10⁻⁹ m² s⁻¹)</td>
<td>+2.40a</td>
<td>+2.48b ±0.51c</td>
</tr>
<tr>
<td>D₃₁ (10⁻¹² m² K⁻¹)</td>
<td>−1.19a</td>
<td>−1.18b ±0.009c</td>
</tr>
<tr>
<td>D₃₂ (10⁻¹² m² K⁻¹)</td>
<td>−0.98a</td>
<td>−0.98b ±0.008c</td>
</tr>
</tbody>
</table>

aFrom Ref. 13.
bAverage value from ten runs.
cStandard deviation from ten runs.

dThermal expansion coefficient.
eComposition coefficient of nC₈.
fComposition coefficient of nC₁₀.
gMass fraction of nC₈.
hMass fraction of nC₁₀.

accuracy for the smaller eigenvalue λ₂. As can be seen from the elements Vᵢⱼ of the eigenvector matrix, the corresponding transformed separation ΔΩ₂ contributes the most to the two physical separations Δωᵢ. Consequently, the regression analysis will have a bias toward obtaining accurate estimates of λ₂ and the associated elements of the eigenvector matrix V₂. A discussion of additional practical considerations is included in Appendix C.

As the compositional contribution to buoyancy increases the time it takes to reach steady state, trying to fit the classical model to the measured separations will underestimate the eigenvalues [see Eq. (16) and Fig. 5]. All other parameters being equal, this leads to an overestimation of the parameter S. Consequently, in the next iteration, there is a tendency for the opposite to happen: eigenvalues are overestimated and the parameter S is underestimated. Therefore, we expect an oscillatory approach toward convergence. Figures 4 and 5 show that the parameter S and the smaller eigenvalue (λ₂) indeed exhibit an oscillatory behavior. However, the larger eigenvalue (λ₁) does not oscillate about its converged value. This is not unexpected as the argument above is oversimplified by ignoring the effect of changing the eigenvector matrix. Moreover, the eigenvector matrix V

between the vertical walls is about ΔT=4.0 K. The measured molecular and thermal diffusion coefficients are listed in Table II.

From the mixture and column properties we find the parameter S to be −0.492. The composition dependence of density is too small to have a significant effect on the steady-state separations Δωᵢ. Nevertheless, the composition dependence of density has an appreciable effect on the transient separations (see Fig. 2). The separation process is faster (slower) than in the classical model for short (long) times. The net effect is that it takes longer to reach steady state. This is consistent with observations made by Ecenarro et al. for binary mixtures. The theoretical separations of nC₈ and nC₁₀, calculated from Eqs. (22) and (25), are plotted in Fig. 3 along with an example of a set of data points to be treated as measurements.

We performed the test described above twice, using 20 and 40 evenly distributed sample points. In both cases, the random noise added was flat and with an amplitude of 1% of the steady-state separations. Initial testing revealed that the classical model is completely unreliable for our mixture, even in the absence of noise (see Table III and Appendix B). Thus, only the general model was used in the final test. The average values and standard deviations of ten runs are reported in Table II. As expected, we observe that accuracy increases with the number of sample points. The off-diagonal elements in the molecular diffusion coefficient matrix D are less accurate because in the test mixture, they are smaller than the diagonal terms. Also, note that thermal diffusion coefficients can be estimated more accurately than molecular diffusion coefficients. Table IV reveals a significantly higher
indicates that the transformed separation $\Delta \Omega_1$ contributes significantly less to the physical separations than the transformed separation $\Delta \Omega_2$ does. As a result, the SSE is less sensitive to errors in $\lambda_1$ than errors in $\lambda_2$. Figure 6 shows the decrease in SSE with iteration number.

IX. CONCLUSIONS

As can be seen from Table II, the proposed algorithm can extract molecular and thermal diffusion coefficients from transient separation measurements of a ternary test mixture. The derivations are valid for any multicomponent mixture. However, the practical limit may be three- and four-component mixtures. Of course, the mass fractions $\omega_i$ are not measured directly but inferred from various mixture properties (density and refractive index). The number of calibration measurements grows exponentially with the number of components, and it is probably not feasible to apply the technique to mixtures of five components and more. Nevertheless, being able to obtain ternary diffusion coefficients is a significant improvement because it allows the study of cross-molecular diffusion. Any model for multicomponent diffusion will have to successfully predict ternary measurements.

ACKNOWLEDGMENTS

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APPENDIX A: NESTED NEWTON METHOD

A minimum in the SSE occurs when the first derivatives with respect to all independent variables are zero. In a $N$-component mixture, there are $N - 1$ thermal and $(N - 1) \times (N - 1)$ molecular diffusion coefficients to regress for. The regression analysis is performed in the eigenspace of the molecular diffusion coefficient matrix. Thus, the primary unknowns are the $N - 1$ eigenvalues and the $(N - 1) \times (N - 1)$ elements of the eigenvector matrix $V$. The standard Newton method suggests that the primary unknowns can be updated by the equation

$$\Delta = -H^{-1}\epsilon,$$

(A1)

where $|\Delta|$ contains the incremental change in the primary unknowns, $H$ is the Hessian matrix containing the second derivatives of SSE, and $|\epsilon|$ is a residual vector containing the first derivatives of SSE.

### Table II

<table>
<thead>
<tr>
<th>Sample points</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_1$ ($10^{-6}$ m$^2$ s$^{-1}$)</td>
<td>$+2.85^a$</td>
<td>$+3.15^a \pm 0.67^c$</td>
</tr>
<tr>
<td>$\lambda_2$ ($10^{-5}$ m$^2$ s$^{-1}$)</td>
<td>$+1.54^a$</td>
<td>$+1.59^a \pm 0.10^c$</td>
</tr>
<tr>
<td>$V_{11}$ ($10^{-3}$)</td>
<td>$-1.45^a$</td>
<td>$-2.59^a \pm 2.58^c$</td>
</tr>
<tr>
<td>$V_{12}$ ($10^{-3}$)</td>
<td>$+7.56^a$</td>
<td>$+8.67^a \pm 2.58^c$</td>
</tr>
<tr>
<td>$V_{21}$ ($10^{-3}$)</td>
<td>$+1.35^a$</td>
<td>$+1.02^a \pm 0.41^c$</td>
</tr>
<tr>
<td>$V_{22}$ ($10^{-3}$)</td>
<td>$+3.68^a$</td>
<td>$+4.01^a \pm 0.39^c$</td>
</tr>
</tbody>
</table>

$a$Based on Ref. 13.
bAverage value from ten runs.
cStandard deviation from ten runs.
The Hessian matrix can be divided into different blocks, according to the family of primary unknowns which SSE is differentiated with respect to

$$H = \begin{bmatrix} \frac{\partial^2 \text{SSE}}{\partial V_{ij} \partial V_{kl}} & \frac{\partial^2 \text{SSE}}{\partial V_{ij} \partial \kappa_l} \\ \frac{\partial^2 \text{SSE}}{\partial \kappa_i \partial V_{jk}} & \frac{\partial^2 \text{SSE}}{\partial \kappa_i \partial \kappa_j} \end{bmatrix}.$$  \hspace{1cm} (A2)

SSE is much more sensitive to changes in eigenvalues than changes in the elements of the eigenvector matrix. Thus, the elements of the diagonal blocks in Eq. (A2) are several orders of magnitude apart. As a consequence, the Hessian matrix in Eq. (A2) is ill-conditioned and Eq. (A1) cannot be solved numerically. The problem is circumvented by treating the eigenvalues as the only unknowns and $\frac{\partial \text{SSE}}{\partial V_{ij}} = 0$ as constraints. Thus, the standard Newton method is performed in an $(N-1)$-dimensional subspace of the original $N(N-1)$-dimensional search domain. In the new approach, the Hessian matrix and the residual vector are defined as

$$H = \begin{bmatrix} \frac{\partial^2 \text{SSE}}{\partial \kappa_i \partial \kappa_j} \big|_{\text{SSSE} = 0} \\ \frac{\partial^2 \text{SSE}}{\partial \kappa_i \partial \kappa_j} \big|_{\text{SSSE} = 0} \end{bmatrix}, \quad \{e\} = \begin{bmatrix} \frac{\partial \text{SSE}}{\partial \kappa_i} \big|_{\text{SSSE} = 0} \end{bmatrix},$$  \hspace{1cm} (A3)

respectively. All derivatives are calculated numerically and to ensure that the constraints $\frac{\partial \text{SSE}}{\partial V_{ij}} = 0$ are met, the standard Newton method is used to minimize SSE with respect to $V_{ij}$ each time an incremental change in the eigenvalues $\lambda_i$ is performed.

**APPENDIX B: FAILURE OF CLASSICAL MODEL**

As shown in Fig. 2, the separations predicted by the classical and general models are not very different. The deviation is about 8% at early times and quickly drops to less than 2%. Thus, it might be surprising that the diffusion coefficients predicted by the classical model are completely off target, even in the absence of noise (see Table III). It is important to remember that although the separations predicted by the classical model are close to the actual separations when the true diffusion coefficients are used, the predictions would be even closer if another set of diffusion coefficients is used instead. All the regression analysis does is to find the set of diffusion coefficients that corresponds to the smallest SSE. Using the classical model provides the wrong set of eigensolutions to work with because the effect of composition on buoyancy is not accounted for. Nevertheless, with four additional regression parameters, these eigensolutions can be combined to present the physical separations rather well.

**APPENDIX C: PRACTICAL CONSIDERATIONS**

To the best of our knowledge, the only attempt to determine molecular diffusion coefficients from transient measurements in a thermogravitational column was made for binary mixtures by Ecenarro et al.\textsuperscript{6,11} Each time a measurement is made by removing a sample for analysis of composition, the separation process is disturbed. Thus, Ecenarro et al. only made one measurement per experiment and the database for a given mixture was obtained from a series of independent experiments. In principle, such a procedure allows for an arbitrary number of measurements.

Ecenarro et al.\textsuperscript{11} used between 6 and 26 measurements in their work on binary mixtures. The 20-sample test lies within this range and our regression algorithm also works for smaller databases. However, as the number of sample points is reduced, there will be cases where the regression analysis fails to find two independent eigensolutions. Exactly when this happens depends on the level of noise. We will elaborate on this topic in our discussion on noise below.

The noise level of ±1% of steady-state values was chosen based on the measurements reported by Ecenarro et al.\textsuperscript{11} The separation data in Ref. 11 are presented in a transformed form. The actual separation data can be found in Ref. 8. The regression algorithm works for higher levels of noise as well. However, as noise increases, the algorithm will in some cases converge to a solution with two identical eigenvalues.
In other works, as far as molecular diffusion is concerned, the mixture is perceived as a binary. In order to understand why this happens, we take a close look at the eigenvector matrix presented in Table IV. The elements of the second column \( (V_{12}) \) are three to five times larger than the elements in the first column \( (V_{11}) \). This means that the first eigensolution contributes only 20%–30% to the physical separations. Consequently, if the noise level is, e.g., ±3% of the steady-state separations, the noise level perceived by the first eigensolution is ±9%–15% at steady-state and even larger during the transient period. As molecular diffusion is mainly important at early times, finding the eigenvalue corresponding to the first eigensolution under these conditions is difficult at best. Moreover, even if an eigenvalue is found, the accuracy will be very poor.

The small contribution from the first eigensolution indicates that the mixture can be described fairly well as a pseudobinary. The physical reason is that \( nC_8 \) and \( nC_{10} \) are very similar. Thus, the fact that the regression analysis sometimes finds two identical eigenvalues should not be perceived as a failure. It just means that the predicted off-diagonal elements will be zero. The diagonal elements are generally about \( 2 \times 10^{-9} \) m² s⁻¹. Thus, the diffusion coefficient matrix is still predicted fairly well. In these cases, the ternary nature of the mixture is only evident from two distinct thermal diffusion coefficients.