On the unsteady-state species separation of a binary liquid mixture in a rectangular thermogravitational column

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This paper investigates the unsteady-state species segregation of binary liquid mixtures in rectangular thermogravitational columns. The analysis leads to a procedure to obtain both molecular and thermal diffusion coefficients from transient separation measurements. Two models are presented: first, an ideal model where buoyancy only depends on temperature and second, a general model where buoyancy also varies with composition. Steady-state measurements are not required regardless of which model is chosen. As a result, the new procedure is faster than steady-state procedures. When either the molecular or thermal diffusion coefficient is known \textit{a priori}, the other can be obtained without knowledge of fluid properties such as density, viscosity, thermal expansion, and compositional coefficients. © 2006 American Institute of Physics. [DOI: 10.1063/1.2150431]

I. INTRODUCTION

The fact that a temperature gradient induces separation of a mixture was shown theoretically by Enskog\textsuperscript{1} in 1911 and Chapman\textsuperscript{2} in 1916. The first experimental verification of the phenomenon was made by Chapman and Dootson\textsuperscript{3} in 1917. They invented the so-called two-bulb method where two large containers were connected by a thin horizontal tube. Initially, the entire apparatus was filled with a homogeneous gas mixture. The two containers were maintained at different temperatures. As a result of thermal diffusion, a concentration difference between the gases in the two containers was developed. The two-bulb method has later been used to determine thermal diffusion coefficients of binary gas mixtures.

Thermal diffusion coefficients are perhaps the most complicated transport property to measure even in binary mixtures. Since the early work of Chapman and Dootson,\textsuperscript{3} a variety of methods have been developed to measure these coefficients. Among these are the optical methods with three different kinds in active use: (1) the optical beam deflection technique, (2) the holographic interference grating technique, and (3) the thermal lens technique.

In the optical beam deflection technique\textsuperscript{4–9} a Soret diffusion cell is filled with a given sample and a laser beam of low intensity is passed through the medium. When a vertical temperature gradient is imposed on the cell, thermal diffusion establishes a concentration gradient. The gradients in temperature and composition lead to a gradient in the refractive index. As a result, refraction of the laser beam changes. Thermal and molecular diffusion coefficients are calculated from the rate at which the refraction angle changes as well as its steady-state value.

The holographic interference grating technique\textsuperscript{10–12} uses two interfering laser beams to create local variations in the refractive index of the sample. The changes in refractive index are due to both temperature variations and the subsequent concentration variations caused by thermal diffusion. The result is a holographic grating which is used to scatter a third laser beam of a different wavelength. Thermal and molecular diffusion coefficients can then be calculated from the amplitude and time variation of the intensity of the resulting diffraction pattern.

In the thermal lens technique\textsuperscript{13–15} a laser beam is pointed at the sample. The beam creates a temperature gradient and as a response thermal diffusion causes a concentration gradient. Because refractive index varies with temperature and concentration, the net effect is to create a thermal/compositional lens in the sample. Molecular and thermal diffusion coefficients can be determined by allowing the intensity of the laser beam to vary with time and studying the intensity in the center of the beam exiting the sample.

The optical methods require small temperature gradients and provide both thermal and molecular diffusion coefficients. The use of both coefficients allows the determination of the Soret coefficient and the calculation of species’ mass fluxes from temperature and concentration gradients. The major drawback is that the techniques have not been extended to ternary or higher-order mixtures. The exception is ternary mixtures where molecular cross diffusion can be neglected and where the diagonal terms in the molecular diffusion matrix are of different orders.\textsuperscript{16} Such limitations do not exist in a thermogravitational column (TGC) where the coupling between convection and horizontal thermal diffusion leads to a vertical separation of the components in the column. For the most part, the TGC technique has been limited to binary mixtures, but recently the theory was extended to ternary\textsuperscript{17} and higher-order\textsuperscript{18} mixtures. Leahy-Dios \textit{et al.}\textsuperscript{19} have published the first paper with experimental results for the thermal diffusion coefficients in nonelectrolyte ternary mixtures.

Traditionally, a TGC has only been applied to obtain thermal diffusion coefficients from steady-state separation.
The molecular diffusion coefficients must then be determined using a different technique. To the best of our knowledge, there have been two attempts to obtain both thermal and molecular diffusion coefficients. Ecenarro et al.\textsuperscript{20} used the transient separation data to provide molecular diffusion coefficients after obtaining thermal diffusion coefficients from the steady-state separation. This method was later applied to various binary mixtures.\textsuperscript{21} Dutrieux et al.\textsuperscript{22} used the ratio between the initial and steady-state velocity fields in a TGC to find the Soret coefficient. Combined with the thermal diffusion coefficients calculated from the steady-state separation they could then determine the molecular diffusion coefficient. Both approaches rely on steady-state measurements. In general, the TGC technique is slower than the optical methods. In some columns it could take a couple of days to reach steady state, and it is therefore desirable to obtain both molecular and thermal diffusion coefficients from transient separation data only. Majumdar\textsuperscript{23} developed a procedure to find thermal diffusion ratios in binary gas mixtures from unsteady-state measurements and applied the method to oxygen in air. His procedure is indeed independent of the steady-state separation, but he assumed the molecular diffusion coefficient to be known.

In this work, we develop working equations and a procedure to obtain both molecular and thermal diffusion coefficients from transient separation data in binary liquid mixtures. Towards this end, we derive a solution to the unsteady-state separation in a TGC. Our work has major differences from the work of Ecenarro et al.\textsuperscript{20} and Majumdar.\textsuperscript{23} Ecenarro et al.\textsuperscript{20} assumed that the transient separation is to be measured at the very ends of the column where the vertical flux is zero. For practical reasons, the measurements are always made somewhat inside the column. Ecenarro et al.\textsuperscript{20} apparently replaced the actual column length with the distance between the measuring points. Such an approach may not describe the separation between the two measuring points properly even when the points are located fairly close to the ends of the column. Furthermore, since the column length rather than the distance between the measuring points is the characteristic length of the problem, using the latter in nondimensionalization of the governing equations will lead to an error in the estimation of the molecular and thermal diffusion coefficients. We will further comment on the work by Ecenarro et al.\textsuperscript{20} later. The work by Majumdar\textsuperscript{23} is based on the solution of the governing flow equations for low-pressure gases where density is small. He also made other restrictive assumptions.

This paper is organized along the following. We first briefly describe the experimental setup and conditions to be modeled in Sec. II. The expression for diffusion flux is then presented in Sec. III. In Sec. IV, we present the problem formulation and provide an analytical solution for the ideal case where the forgotten effect (that is, the effect of composition on buoyancy) is neglected. The analytical solution is the first to appear in the literature to the best of our knowledge. In Sec. V, we account for the forgotten effect. We conclude the work in Sec. VII with few remarks.

II. EXPERIMENTAL SETUP AND CONDITIONS

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 to be high, the gradient is a constant, $T_x=\Delta T/L$. The aspect ratio of the column is small $h/L\ll1$, 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 is considered Newtonian. As a consequence of incompressibility and zero horizontal bulk velocity, continuity implies that the vertical velocity component in the column only varies horizontally. This is also true for the corresponding stream function $\psi$.

III. DIFFUSIVE FLUX

Ignoring pressure diffusion, the diffusive flux $\vec{J}$ of each component in a binary mixture consists of two parts, i.e., molecular and thermal diffusions,

$$\vec{J} = -\rho_0(D \nabla \omega + D_T \nabla T),$$

where $\rho_0$ is the average density in the column, $\omega$ is the weight fraction of the component, $T$ is temperature, and $D$ and $D_T$ are the mass-based molecular and thermal diffusion coefficients. In the literature, the sign in front of the thermal diffusion coefficient is often chosen to be negative. However, such a choice is thermodynamically incorrect so we use a positive sign here (Firoozabadi et al.\textsuperscript{24}). This implies that a component with a positive thermal diffusion coefficient will go to the cold side and segregate to the bottom of the column. We treat the thermal diffusion coefficient as a constant. This is a valid approximation in an open TGC where the compositional variation is always small. In binary mixtures, it is common to treat the thermal diffusion factor $\alpha$ as a constant instead. The relationship between $\alpha$ as defined by

![FIG. 1. A sketch of the experimental setup used to measure molecular and thermal diffusion coefficients. The sides of a two-dimensional rectangular slab of width $L$ and height $h$ are maintained at temperatures $T_0-(\Delta T/2)$ and $T_0+(\Delta T/2)$, respectively. As a result, the binary fluid within the slab undergoes separation which can be related to its molecular and thermal diffusion coefficients.](http://jcp.aip.org/jcp/figure.jsp)
Ecenarro et al.\textsuperscript{20} and the thermal diffusion coefficient $D_T$ in Eq. (1) is given by

$$D_T = -\frac{\alpha \omega (1 - \omega)}{T_0},$$

where $T_0$ is the average temperature. The advantage of our approach of treating $D_T$ as a constant is that the procedure can be readily extended to multicomponent mixtures where there is no agreement between different authors on the definition of the thermal diffusion factors.

Because the temperature field is linear and independent of $z$, the no-flux boundary condition at the vertical walls is simply

$$\frac{\partial \omega}{\partial z} = -\frac{D_T \Delta T}{D L}, \quad x = \pm \frac{L}{2}.$$

**IV. IDEAL CASE**

We will first derive a model for the ideal case where the forgotten effect, i.e., the influence of composition on buoyancy, is neglected. In this case we are able to obtain an analytical solution to the problem in the form of an infinite sum of Green’s functions. The series converges very rapidly and can be truncated after a few terms. The analytical solution is an excellent tool to investigate the transient separation across the column when the forgotten effect can be neglected.

**A. Governing equation**

The expression for the net vertical flux $j_z$ across a given horizontal cross section of a TGC can be derived from Eqs. (1) and (3),

$$j_z = \rho_0 \left[ H \frac{D_T}{D} - \left( \frac{K}{D} + LD \right) \frac{\partial \bar{\omega}}{\partial z} \right],$$

where $\bar{\omega}$ is the horizontally averaged weight fraction, and the two constants $H$ and $K$ are related to the stream function $\psi$ by the integrals\textsuperscript{18}

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

The governing equation for the unsteady-state species separation is commonly derived by equating the temporal change in the horizontally averaged concentration $\bar{\omega}$ to the divergence of the flux expression given by Eq. (4),

$$\frac{\partial \bar{\omega}}{\partial t} = \left( \frac{K}{LD} + D \right) \frac{\partial^2 \bar{\omega}}{\partial z^2}.$$  

Note that Eq. (4) is derived for steady state and is in general not valid for unsteady state. In order to use the same flux expression we must assume the existence of species in the column to be quasi-steady, implying that the time derivative in the mass balance equation is negligible. Equation (4) is also based on the assumption of a constant concentration gradient. Figure 2 shows a sketch for the evolution of concentration field. As can be seen from this figure, the concentration gradient changes with time and position. In unsteady state Eq. (6) violates the assumption of constant composition gradient. However, the assumption of quasi-steady state, implies that the nondimensionalized time derivative is small. Hence, the nondimensional version of Eq. (6) implies that the second-order vertical concentration derivative is also small and can be safely neglected in the mass conservation equation. In the following, we will assume that the unsteady-state flux is adequately expressed by Eq. (4) and that Eq. (6) correctly describes the unsteady-state mass balance. There might be a short transient time where this is not a good assumption at the ends of the column.

**B. Analytical solution**

We now seek an analytical solution to the nondimensional form of Eq. (6). Introducing the dimensionless variables

$$\bar{\omega} = \Delta \omega \bar{\omega}, \quad \bar{z} = \bar{h} z, \quad \bar{t} = t \bar{t},$$

where $t_\epsilon$ is a characteristic time given by

$$t_\epsilon = h^2 \left( \frac{K}{LD} + D \right)^{-1},$$

and $\Delta \omega_{\infty}$ is the steady-state separation in the column found by setting the total flux from Eq. (4) equal to zero,

$$\Delta \omega_{\infty} = \frac{H h D_T}{K + LD^2},$$

we can transform Eq. (6) into its dimensionless form,

$$\frac{\partial \bar{\omega}}{\partial \bar{t}} = \frac{\partial^2 \bar{\omega}}{\partial \bar{z}^2}.$$  

The boundary conditions are zero net flux at both horizontal boundaries at all times, implying that at these boundaries the concentration gradient reaches its steady-state value at $\bar{t}=0^\circ$.

In dimensionless coordinates this translates into
\[
\frac{\partial \phi}{\partial \xi} = 1, \quad \bar{\varepsilon} = \pm \frac{1}{2}.
\] (11)

We have been able to obtain an analytical solution to this initial value problem by the method of images,

\[
\bar{\omega} - \omega_0 = \bar{\varepsilon} + \frac{1}{2} \sum_{n=-N}^{N} (-1)^{n} \bar{\varepsilon} - n \left( \text{erf} \left( \frac{2\bar{\varepsilon} - (2n+1)}{4\sqrt{\bar{\varepsilon}}} \right) - \text{erf} \left( \frac{2\bar{\varepsilon} - (2n-1)}{4\sqrt{\bar{\varepsilon}}} \right) \right)
+ \sqrt{\frac{\pi}{t_{c}}} \sum_{n=-N}^{N} (-1)^{n} \left( \exp \left( -\frac{(2\bar{\varepsilon} - (2n+1))^2}{16\bar{\varepsilon}} \right) \right) - \exp \left( -\frac{(2\bar{\varepsilon} - (2n-1))^2}{16\bar{\varepsilon}} \right) \right) \right).
\] (12)

In the Appendix, details of the solution steps are outlined. The separation between any two points \( z_1 \) and \( z_2 \) is readily found from Eq. (12),

\[
\Delta \omega(z_1, z_2, t) = \Delta \omega_n [\bar{\omega}(\bar{z}_1, \bar{t}, t_c) - \bar{\omega}(\bar{z}_2, \bar{t}, t_c)].
\] (13)

### C. Regression analysis

Our major goal is to determine both the molecular and thermal diffusion coefficients from unsteady-state separation measurements. In our approach, we can calculate the steady-state separation \( \Delta \omega_n \) and characteristic time \( t_c \) from fitting the data to Eq. (13). Determining \( t_c \) and \( \Delta \omega_n \) corresponds to stretching the time and concentration coordinates, respectively. Provided that the relevant mixture properties are known, we can then find the molecular diffusion coefficient from Eq. (8) and use this value to calculate the thermal diffusion coefficient from Eq. (9).

In the ideal case the two constants \( H \) and \( K \) are given by,

\[
H = H_0 = -\frac{\rho_0 g \beta (\Delta T)^2 L^3}{6! \mu}, \quad K = K_0 = \frac{\rho_0^2 g^2 \beta^2 (\Delta T)^2 L^7}{91 \mu^2},
\] (14)

where \( \beta \) is the thermal expansion coefficient and \( \mu \) is fluid viscosity. The two constants are related by

\[
H_0^2 = \frac{7}{10} \frac{(\Delta T)^2}{L} K_0.
\] (15)

We can now eliminate \( H \) and \( K \) from Eqs. (8) and (9),

\[
\frac{(\Delta \omega_n)}{t_c} = \frac{7}{10} \frac{D_T (\Delta T)^2}{L^2 D} \left( 1 - \frac{t_c}{t_d} \right), \quad t_d = \frac{h^2}{D}.
\] (16)

Equation (16) implies that once the characteristic time \( t_c \) and the steady-state separation \( \Delta \omega_n \) are estimated from fitting the separation data to Eq. (13), the relationship between the molecular and thermal diffusion coefficients is known without knowledge of additional physical properties of the mixture. Moreover, provided the molecular diffusion coefficient \( D \) is known a priori, the thermal diffusion coefficient \( D_T \) can be found from the regression analysis of the separation data, the width of the column, and the temperature difference between the vertical walls. Note that Eq. (16) does not provide the sign of \( D_T \). The correct sign must be inferred from whether the separation in the column is positive or negative.

### D. Model testing

The ideal model is tested with six sets of experimental data analyzed by Ecenarro et al.\(^{21}\) which have been recently made available to us in tabular form. These authors conducted their experiments in a cylindrical thermogravitational column of height \( h = 0.9 \) m and an annular gap of \( L = 0.95 \) mm. The distance between the sampling points is 0.791 mm. The temperature difference between the inner and outer walls was \( \Delta T = 4 \) K and the mean temperature was \( \bar{T} = 311 \) K. The first three data sets are from benzene-heptane mixtures while the last three are from benzene-hexane mixtures. The parameter related to compositional dependency (to be provided later) is small for all the six sets of data. Figure 3 shows the least-squares fit of our model to the experimental data. In all cases, the model seems to fit the data well. Tables I and II show the relevant physical properties for the six mixtures as well as three values for molecular diffusion coefficients and thermal diffusion factors estimated by the model. The leftmost value is the estimate from the model just described where the forgotten effect is neglected. The middle value is the estimate from the general model which we will describe later. The rightmost value is from Ecenarro et al.\(^{21}\) Also included is the forgotten effect parameter \( S \) (Haugen and Firoozabadi\(^{14}\)).

As Tables I and II show, there is a noticeable effect for small \( S \) values on the unsteady-state analysis. Despite some inaccuracy in the data of Ecenarro et al.\(^{21}\) which was discovered later by Bou-Ali et al.\(^{25}\) there is general agreement between our results and those from Ref. 21.
V. NONIDEAL CASE

We now derive the general model where the forgotten effect is taken into account. The estimates of thermal and molecular diffusion coefficients from the approach described in this paper are based on a least-squares fit of the separation data regardless of the location of the measuring points. Unlike Ecenarro et al.\textsuperscript{21} who assumed an approximate relationship between the forgotten effect parameters \( R \) and \( S \), we make no such approximation and our procedure is not limited to a given range of \( S \) values.

A. Governing equation

Assuming that the vertical mass transport is dominated by convection, (that is, neglecting Fickian diffusion in the vertical direction) the steady-state flux given by Eq. (4) reduces to

\[
j_z = \rho_0 \left( \frac{D_T}{D_H} H - \frac{K}{D_H} \frac{\partial \bar{\omega}}{\partial z} \right). \tag{17}\]

The constants \( H \) and \( K \) can be expressed as the product of their ideal values \( H_0 \) and \( K_0 \) given by Eq. (14) and the two forgotten effect parameters \( R \) and \( S \) (see Refs. 18 and 20), i.e.,

\[
H = (1 - S)H_0H(R), \quad K = (1 - S)^2K_0K(R), \tag{18}\]

where the functions \( H(R) \) and \( K(R) \) are defined as

\[
H(R) = \frac{6!}{2^9 \eta^4} \left( 1 - \frac{1}{\eta} \cosh 2 \eta - \cos 2 \eta \right), \quad R = 4\eta^4 \tag{19a}\]

\[
K(R) = \frac{9!}{2^{12} \eta^8} \left( 1 - \frac{5}{4\eta} \cosh 2 \eta - \cos 2 \eta \right. \\
\left. + \frac{\sinh 2 \eta \sin 2 \eta}{\sin 2 \eta + \sin 2 \eta^2} \right), \quad R = 4\eta^4. \tag{19b}\]

The forgotten effect parameters \( R \) and \( S \) are expressed by

\[
R = \frac{2\gamma \rho_0 \rho_0}{D_H} \left( \frac{L}{2} \right)^4 \frac{\partial \bar{\omega}}{\partial \zeta} \quad \text{and} \quad S = \frac{\gamma D_T}{\beta D_H}, \tag{20}\]

where \( \gamma \) is the compositional coefficient [see Eq. (16) of Ref. 18].

Mass balance requires the temporal change in mass to equal the negative divergence of Eq. (17), i.e.,

\[
\rho_0 \frac{\partial \bar{\omega}}{\partial t} = -\rho_0 \frac{D_T}{D_H} \frac{\partial H}{\partial \zeta} + \rho_0 \frac{\partial}{\partial \zeta} \left( K \frac{\partial \bar{\omega}}{\partial \zeta} \right). \tag{21}\]

Inserting the definitions from Eq. (18) and applying the chain rule leads to

\[
LD \frac{\partial \bar{\omega}}{\partial t} = -D_T(1-S)H_0 \frac{\partial H}{\partial R} \frac{\partial H}{\partial \zeta} + (1-S)^2K_0 \frac{\partial K}{\partial \zeta} \frac{\partial R}{\partial \zeta} \frac{\partial \bar{\omega}}{\partial \zeta} + (1-S)^2K_0 \frac{\partial^2 \bar{\omega}}{\partial \zeta^2}. \tag{22}\]

From Eq. (19) it follows that

\[
\frac{\partial H}{\partial \zeta} = -\frac{2^{16}}{9!} K(R). \tag{23}\]

Hence,

\[
K(R) = \frac{9!}{2^{12} \eta^8} \left( 1 - \frac{5}{4\eta} \cosh 2 \eta - \cos 2 \eta \right. \\
\left. + \frac{\sinh 2 \eta \sin 2 \eta}{\sin 2 \eta + \sin 2 \eta^2} \right), \quad R = 4\eta^4. \tag{19b}\]

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\[
R = \frac{2\gamma \rho_0 \rho_0}{D_H} \left( \frac{L}{2} \right)^4 \frac{\partial \bar{\omega}}{\partial \zeta} \quad \text{and} \quad S = \frac{\gamma D_T}{\beta D_H}, \tag{20}\]

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From Eq. (19) it follows that

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Hence,
no-flux boundary conditions are

It is more convenient to have fixed function values than fixed gradients as boundary conditions, we differentiate Eq. (25) with respect to \(z\) and introduce the function \(w\) defined by

\[
\frac{\partial \bar{w}}{\partial z} = \frac{\Delta \omega}{h}(1 - w).
\]

The governing equation in terms of \(w\) is, therefore,

\[
\frac{\partial w}{\partial t} = \frac{K_0}{LD} \frac{\partial}{\partial z} \left\{ \left( (1 - S)^2 \frac{\partial K}{\partial R} + (1 - S)(1 - 2S)K \right) \frac{\partial w}{\partial z} \right\}. 
\]

(B. Numerical solution)

Introducing the dimensionless variables \(\bar{w} = \Delta \omega / \omega_0, \bar{z} = h \bar{z}, \) and \(t = t_c \bar{t}\) with characteristic time defined as \(t_c = h^2 LD / K_0\), converts Eq. (27) into

\[
\frac{\partial w}{\partial t} = \frac{1}{(1 - S)^2} \frac{\partial K}{\partial R} (1 - S)(1 - 2S)K \frac{\partial w}{\partial z}.
\]

The initial condition of \(w\) is simply \(w = 1\) at \(t = 0\), and the no-flux boundary conditions are \(w = 0\) at \(\bar{z} = \pm 1 / 2\). The separation between any two points in the column is related to \(w\) by

\[
\Delta \bar{w}(\bar{z}_1, \bar{z}_2, t) = \Delta \omega_s[\bar{z}_2 - \bar{z}_1 - \Omega(\bar{z}_1, \bar{z}_2; \bar{t}, t_c)].
\]

where \(\Delta \omega_s\) is the steady-state separation between the ends of the column, and \(\Omega(\bar{z}_1, \bar{z}_2; \bar{t}, t_c)\) is defined by

\[
\Omega(\bar{z}_1, \bar{z}_2; \bar{t}, t_c) = \int_{\bar{z}_1}^{\bar{z}_2} w d\bar{z}.
\]

Figure 4 shows how the forgotten effect influences the unsteady-state separation in the column. The tendency is to first increase the rate of separation and then to decrease it. As can be seen from the figure, the forgotten effect hardly affects the steady-state separation for the range of investigated \(S\) values. Note that while \(t_c\) and \(\Delta \omega_s\) still stretch the coordinates, the forgotten effect changes the shape of the separation versus time curve. Our results indicating the pronounced influence of the forgotten effect on transient separation but not on steady-state separation are in line with those in Ref. 21.

(C. Regression analysis)

Once the characteristic time \(t_c\) and the steady-state separation \(\Delta \omega_s\) are found from fitting experimental data to Eq. (29), it is straightforward to calculate the molecular diffusion coefficient from the definition of \(t_c\). The thermal diffusion coefficient is found from the expression for the steady-state separation in the column from Eq. (17),

\[
\Delta \omega_s = \frac{D_{th} H_0 (R_{\gamma})}{1 - S K_0 K(R_{\gamma})},
\]

where \(R_{\gamma}\) is the steady-state value of \(R\). Before we can proceed, we need to know the values of \(S\) and \(R_{\gamma}\). In the convective regime we can find the relationship

\[
\frac{S}{1 - S} = \frac{2 R_{\gamma} K(R_{\gamma})}{63 H(R_{\gamma})}.
\]

Thus, it is enough to find an expression for one of the parameters \(S\) or \(R_{\gamma}\). Dividing Eq. (31) by \(t_c\) and using the definition of \(S\) given by Eq. (20) to eliminate the Soret coefficient \(D/D_T\) leads to

\[
\frac{\Delta \omega_s}{t_c} = \frac{S}{1 - S} \frac{H(R_{\gamma}) H_0 \beta}{K(R_{\gamma}) h L \gamma'}
\]

Combining Eqs. (32) and (33) and solving for \(R_{\gamma}\) yields

\[
R_{\gamma} = \frac{63 \gamma h L \Delta \omega_s}{2 \beta H_0 / t_c}.
\]

As in the ideal case, it is possible to eliminate \(H_0\) and \(K_0\) between the expression for the characteristic time and the steady-state separation [Eq. (31)] by using the relationship given by Eq. (15). The result is

\[
\frac{(\Delta \omega_s)^2}{t_c} = \frac{7 D_T^2}{10D} \left( \frac{1}{1 - S K(R_{\gamma})} \frac{H(R_{\gamma})}{L} \right)^2,
\]

Equations (35) and (36) reveal that provided the molecular diffusion coefficient of the mixture is known, the ratio between the compositional and the thermal expansion coefficients is the only additional data needed to find the thermal diffusion coefficient.
D. Model testing

The general model is tested with three sets of separation data provided in tabular form by the authors of Ref. 21. The data are all from carbon tetrachloride-hexane mixtures. For these mixtures the compositional effect on buoyancy is significant. Figure 5 shows the least-squares fit of our model to the experimental data. Once again, the model seems to fit the data well. Table III shows the relevant physical properties for these mixtures as well as values for molecular and thermal diffusion coefficients estimated by our model and those from Ecenarro et al.21 (columns 7 and 9). Note that our values are based on transient data and those of Ecenarro et al.21 are based on thermal diffusion calculations from steady-state separation and molecular diffusion calculations from unsteady-state separation.

VI. TRANSIENT DURATION

As mentioned above, the goal is to determine molecular and thermal diffusion coefficients of binary mixtures based on unsteady-state separation data. However, there is a limit to how short of a time period the experiment should be run for. Here we illustrate the effect of the duration of the experiment on model prediction by taking a closer look at the analytical solution [Eq. (12)] for the ideal case. For small times, the dimensionless separation between the ends of the column reduces to

\[ \Delta \delta(t) = 4 \sqrt{\frac{t}{\pi}}, \quad t \ll 1. \]  

(37)

As can be seen from Fig. 6 the approximation is good when \( t < 0.1 \). During this time, there is only one parameter to regress for, i.e., \( (\Delta \omega_c)^2/t_c \). Conclusively, if we end the measurements too early, we do not have enough data to determine the characteristic time \( t_c \) and the steady-state separation \( \Delta \omega_c \) independently.

The square-root approximation in Eq. (37) is only valid for the separation between the very ends of the column. Moving the measuring points inside the column will change the shape of the separation curve versus time in Fig. 6. In particular, it will take some time from the moment that temperature field is turned on to observe separation inside the column. In order to investigate how different locations of the measuring points can affect the accuracy of the estimates of the thermal and molecular diffusion coefficients, we performed the following analysis. Based on the ideal solution from Eq. (13), we generated sets of separation versus time data for different measuring point locations. Each location was specified by the distance between the measuring point

<table>
<thead>
<tr>
<th>( x )</th>
<th>( \rho_0 ) (kg/m³)</th>
<th>( \beta ) (10⁻³ K⁻¹)</th>
<th>( \gamma )</th>
<th>( \mu ) (10⁻⁵ Pa s)</th>
<th>( D ) (10⁻⁴ m² s⁻¹)</th>
<th>( \alpha )</th>
<th>( S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.28</td>
<td>847.2</td>
<td>1.263</td>
<td>-0.9565</td>
<td>0.3148</td>
<td>3.38 × 10⁻³</td>
<td>3.06 × 10⁻³</td>
<td>-1.81 × 10⁻²</td>
</tr>
<tr>
<td>0.51</td>
<td>1041.9</td>
<td>1.204</td>
<td>-0.9715</td>
<td>0.3866</td>
<td>3.07 × 10⁻³</td>
<td>2.69 × 10⁻³</td>
<td>-1.58 × 10⁻²</td>
</tr>
<tr>
<td>0.74</td>
<td>1266.7</td>
<td>1.138</td>
<td>-0.9854</td>
<td>0.5042</td>
<td>1.92 × 10⁻³</td>
<td>3.33 × 10⁻³</td>
<td>-1.24 × 10⁻²</td>
</tr>
</tbody>
</table>

1This work when compositional effect on buoyancy is included.
2Ecenarro et al. (Ref. 21). (Compositional effect on buoyancy is included.)
and the nearest end of the column. In all cases, the measuring points were placed symmetrically in the column. Each set of data contained ten data points evenly distributed between \( t = 0 \) and \( t = t_{\text{max}} \), where \( t_{\text{max}} \) represents the time when the last measurement was made. Subsequently, random noise with an amplitude of one percent of the steady-state separation between the ends of the column was added to each data point. We performed a regression analysis on each set of data to see how close the regression parameters would be to their ideal values. The results are depicted in Fig. 7. In the top plot, the last measurement is made at \( t = 0.05 \). In the bottom plot, the last measurement is made at \( t = 0.15 \). \( h \) represents the distance between the sample point and column end.

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**APPENDIX: ANALYTIC SOLUTION**

In this appendix we will show how to obtain an analytical expression for the transient concentration field in a TGC when the forgotten effect is negligible. All equations are expressed in terms of dimensionless variables. For simplicity, the “\( \sim \)” symbol used to separate dimensionless variables from their dimensional counterparts in the main text has been dropped.

We seek an analytical solution to the diffusion equation

\[
\frac{\partial \omega}{\partial t} = \frac{\partial^2 \omega}{\partial z^2},
\]

(A1)

subject to the following conditions:

\[
\omega = \omega_0, \quad t = 0, \quad -\frac{1}{2} \leq z \leq \frac{1}{2}, \quad \text{initial condition},
\]

\[
\frac{\partial \omega}{\partial z} = 1, \quad t \gg 0, \quad z \approx \pm \frac{1}{2}, \quad \text{no net flux boundaries},
\]

(A2)

\[
\omega = \omega_c = \omega_0 + z, \quad t \to \infty, \quad -\frac{1}{2} \leq z \leq \frac{1}{2},
\]

steady-state separation.

Here, \( \omega_c \) denotes the steady-state concentration field. Introducing the function

\[
\omega' = \omega - \omega_c,
\]

(A3)

does not alter the governing equation [Eq. (A1)], but the conditions by Eq. (A2) are recast into...
\[ \omega' = \omega'_0 = -z, \quad t = 0, \quad -\frac{1}{2} \leq z \leq \frac{1}{2}, \quad \text{initial condition,} \]

\[ \frac{\partial \omega'}{\partial z} = 0, \quad t \gg 0, \quad z = \pm \frac{1}{2}, \quad \text{no net flux boundaries,} \]

\[ \omega' = 0, \quad t \to \infty, \quad -\frac{1}{2} \leq z \leq \frac{1}{2}, \quad \text{steady-state separation.} \]

We can satisfy the no-flux boundary condition on \( \omega' \) by applying the method of images. Mirroring the initial condition on \( \omega' \) about both ends of the column yields

\[ \omega'_0 = -(-1)^n z + (-1)^n n, \quad n - \frac{1}{2} < z < n + \frac{1}{2}, \]

\[ n = 0, \pm 1, \pm 2, \ldots . \]  

Strictly speaking, the derivative of \( \omega'_0 \) is discontinuous and therefore not well defined at the boundaries, but from symmetry we conclude that \( \partial \omega'_0 / \partial z = 0 \) when \( z = \pm 1/2 \). We choose to work with \( \omega' \) instead of \( \omega \) since the former allows for a straightforward Green’s function solution. The initial condition on \( \omega' \) can be expressed as a Dirac delta integral,

\[ \omega'_0 = \int_{-\infty}^{\infty} \omega'_0(z_0) \delta(z-z_0) d\sigma_0. \quad \text{(A6)} \]

Since the diffusion equation Eq. (A1) is linear, we can solve for \( \omega'_0 = \delta(z-z_0) \) and then use Eq. (A6) to sum up the total solution. The procedure is as follows.

1. We find the Fourier transform of Eq. (A1) and the initial condition \( \omega'_0 = \delta(z-z_0) \),

\[ \tilde{\omega}' = -k^2 \omega' \quad \text{and} \quad \tilde{\omega}'_0 = e^{-ikz_0}, \quad t = 0. \quad \text{(A7)} \]

2. We solve the above initial value problem,

\[ \tilde{\omega}' = e^{-k^2 t - ikz_0}. \quad \text{(A8)} \]

3. We find the inverse Fourier transform of \( \tilde{\omega}' \),

\[ \omega' = \frac{1}{2 \sqrt{\pi t}} e^{-(z-z_0)^2/4t}. \quad \text{(A9)} \]

4. We apply Eq. (A6) to sum up the total solution,

\[ \omega' = \frac{1}{2 \sqrt{\pi t}} \int_{-\infty}^{\infty} \omega'_0(z_0) e^{-(z-z_0)^2/4t} d\sigma_0. \quad \text{(A10)} \]

So far we have not taken the steady-state condition \( \omega' \to 0 \), \( t \to \infty \) into account. However, as long as \( \omega'_0 \) is antisymmetric about \( z=0 \), this condition is automatically met. We now evaluate Eq. (A10) by substituting Eq. (A5) for \( \omega'_0 \),

\[ \omega' = -\frac{1}{2 \sqrt{\pi t}} \sum_{n=-N}^{N} (-1)^n \int_{-\infty}^{\infty} (z_0 - n) e^{-(z-z_0)^2/4t} d\sigma_0. \quad \text{(A12)} \]

The solution is exact in the limit \( N \to \infty \), but proves to converge rapidly. Thus, the series can be truncated for a finite \( N \). Rearranging the above summation leads to

\[ \omega' = -\frac{1}{2 \sqrt{\pi t}} \sum_{n=-N}^{N} (-1)^n \int_{-\infty}^{\infty} (z-n) e^{-(z-z_0)^2/4t} d\sigma_0 \]

\[ \quad + \frac{1}{2 \sqrt{\pi t}} \sum_{n=-N}^{N} (-1)^n \int_{-\infty}^{\infty} (z-z_0) e^{-(z-z_0)^2/4t} d\sigma_0. \quad \text{(A13)} \]

Making the substitution,

\[ \sigma = \frac{z-z_0}{2t}, \quad d\sigma = -\frac{d\sigma_0}{2t}, \quad \text{(A14)} \]

in the first integral, and the use of

\[ \tau = \frac{z-z_0}{2t}, \quad d\tau = -\frac{d\sigma_0}{2t}. \quad \text{(A15)} \]

in the second integral, we can rewrite Eq. (A13),

\[ \omega' = \frac{1}{2 \sqrt{\pi t}} \sum_{n=-N}^{N} (-1)^n \int_{z=n-1/2}^{z=n+1/2} (z-n) e^{-\sigma^2} d\sigma \]

\[ - \sqrt{\frac{t}{\pi}} \sum_{n=-N}^{N} (-1)^n \int_{z=n-1/2}^{z=n+1/2} e^{-\tau^2} d\tau. \quad \text{(A16)} \]

The two integrals are readily evaluated

\[ \omega' = \frac{1}{2 \sqrt{\pi t}} \sum_{n=-N}^{N} (-1)^n (z-n) \text{erf} \left( \frac{z-z_0}{2 \sqrt{\pi t}} \right) \]

\[ \quad + \sqrt{\frac{t}{\pi}} \sum_{n=-N}^{N} (-1)^n \exp \left( \frac{(z-z_0)^2}{4t} \right) \]  

\[ \quad \text{evaluated at } z=n \pm 1/2. \quad \text{(A17)} \]

Note that after integration, we have replaced the dummy variables \( \sigma \) and \( \tau \) by their definitions. Evaluating the above equation results in

\[ \omega' = \frac{1}{2 \sqrt{\pi t}} \sum_{n=-N}^{N} (-1)^n (z-n) \text{erf} \left( \frac{2z-(2n+1)}{4 \sqrt{4t}} \right) \]

\[ - \text{erf} \left( \frac{2z-(2n-1)}{4 \sqrt{4t}} \right) + \sqrt{\frac{t}{\pi}} \sum_{n=-N}^{N} (-1)^n \]

\[ \times \left( \exp \left( \frac{(2z-(2n+1))^2}{16t} \right) - \exp \left( -n(2z-(2n-1))^2 \right) \right). \quad \text{(A18)} \]

From the definition in Eq. (A3) we conclude that the concentration in the column varies in time and space as
\[ \omega - \omega_0 = z + \frac{1}{2} \sum_{n=-N}^N (-1)^n (z-n) \left( \frac{2z-(2n+1)}{4\sqrt{t}} \right) - \text{erf} \left( \frac{2z-(2n-1)}{4\sqrt{t}} \right) + \sqrt{\frac{t}{\pi}} \sum_{n=-N}^N (-1)^n \left( \exp \left( - \frac{(2z-(2n+1))^2}{16t} \right) - \exp \left( - \frac{(2z-(2n-1))^2}{16t} \right) \right) \frac{n}{2} \]

which is the same as Eq. (11) in the text.