

# On Measurement of Molecular and Thermal Diffusion Coefficients in Multicomponent Mixtures

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We have developed the theory for using the deflection of laser beams of various wavelengths to determine molecular and thermal diffusion coefficients in multicomponent mixtures. In the past, simultaneous determination of molecular and thermal diffusion coefficients have only been achieved for binaries. Our procedure is faster and more accurate than the current techniques to determine molecular diffusion coefficients. The analysis for an  $N$ -component mixture requires deflections from  $(N - 1)$  beams of different wavelengths. We show in an example that the molecular and thermal diffusion coefficients can be determined reliably in a ternary mixture.

## 1. Introduction

Because of cross diffusion coefficients, the molecular diffusion process in multicomponent mixtures is much more complicated than that in binaries. Current techniques (e.g., Loschmidt tube, open-ended capillary tube) are slow and require samples to be removed from the test mixture for analysis. Sampling disturbs the diffusion process and terminates the experiment. Thus, all measurements must come from independent experiments. In addition to introducing noise, such a procedure also puts a practical limit on the number of measurements one can make. The overall effect is that methods that require sampling are both time-consuming and of limited accuracy. Consequently, there are very few measurements of molecular diffusion coefficients for multicomponent mixtures in the literature, even for ternaries.

Since the discovery of thermal diffusion in the second half of the 19th century,<sup>1,2</sup> a variety of methods have been developed to measure thermal diffusion coefficients in binary mixtures. The oldest method in active use is the thermogravitational column technique.<sup>3</sup> The technique has recently been extended to multicomponent mixtures<sup>4,5</sup> and is the only technique to report measurements for nonelectrolyte ternary mixtures.<sup>6</sup> If transient measurements are made, the thermogravitational technique can also be used to obtain molecular diffusion coefficients.<sup>7,8</sup> However, sampling is required and the method faces the same challenges when it comes to speed and accuracy as explained above. Moreover, the working equations to obtain molecular diffusion coefficients have not yet been extended to multicomponent mixtures.

Accurate measurements of both molecular and thermal diffusion coefficients for binary mixtures are obtained from optical methods where the diffusion coefficients are measured through their influence on a laser beam passing through the test mixture. The high accuracy is a result of the fact that no sampling is required and that a large number of transient measurements can be made. The relaxation times for the optical

methods vary orders of magnitude, and depending on the design of the apparatus, thermal diffusion coefficients may be obtained faster in a thermogravitational column. However, when it comes to the measurement of molecular diffusion coefficients where transient measurements are required, the optical methods are faster than their alternatives. The oldest optical method is the beam deflection technique. In 1942, de Groot<sup>9</sup> developed working equations for dilute binary mixtures of negligible thermal expansion. Later, Bierlein<sup>10</sup> generalized de Groot's theory for binary mixtures. Several groups have employed the technique to determine both molecular and thermal diffusion coefficients of various binary mixtures.<sup>11–15</sup> To the best of our knowledge, there is no literature on the extension of the beam deflection technique or any other optical method to multicomponent mixtures. Kita et al.<sup>16</sup> studied a ternary mixture by an optical grating technique. However, their analysis is based on two very restrictive assumptions: (1) the off-diagonal diffusion coefficients are negligible, and (2) the diagonal diffusion coefficients are of different orders of magnitude. Conclusively, the work is essentially for a pseudobinary mixture.

The purpose of this paper is to extend the theory behind the beam deflection technique to multicomponent mixtures. Toward this end, we find an analytical solution to the unsteady-state behavior of multicomponent mixtures in a thermal diffusion cell and show how the analysis leads to a prediction of the transient deflection of laser beams passing through it.

## 2. Theory

The beam deflection technique relies on thermal diffusion, i.e., diffusive mass flux driven by a temperature gradient. In this section, we start the derivations with a brief discussion of diffusive mass flux in multicomponent mixtures.

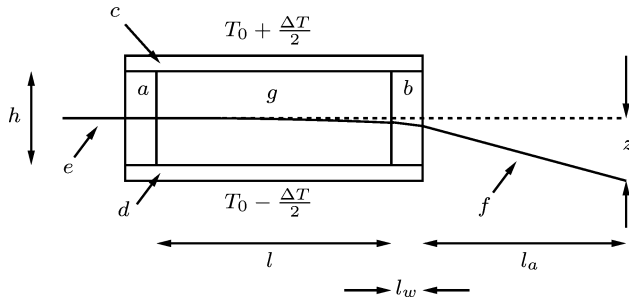
**2.1. Diffusive Flux.** The diffusive flux in an  $N$ -component mixture is driven by concentration gradients (molecular diffusion), temperature gradient (thermal diffusion), and pressure gradient (pressure diffusion). When pressure diffusion is ignored, diffusive flux can be expressed by

$$|\vec{J}\rangle = \mathbf{D}|\nabla\omega\rangle + \nabla T|D_T\rangle \quad (1)$$

where  $|\vec{J}\rangle$ ,  $|\nabla\omega\rangle$ , and  $|D_T\rangle$  are algebraic column vectors

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**Figure 1.** Principal sketch of the beam deflection technique. A diffusion cell consisting of an entrance window (a), an exit window (b), and two conducting plates (c and d) is filled with a multicomponent mixture (g) initially at temperature  $T_0$ . At time  $t = 0$ , the temperatures of the top (c) and bottom (d) plates are changed to introduce a temperature difference  $\Delta T$ . A laser beam (e) enters the diffusion cell through the entrance window, and the deflected beam (f) leaves through the exit window. The deflection is recorded as a vertical shift ( $z$ ) at a distance  $l_a$  from the exit window. Also shown are the height  $h$  and width  $l$  of the diffusion cell and the width  $l_w$  of the exit window.

containing the mass diffusive fluxes  $\bar{J}_i$ , mass fraction gradients  $\nabla \omega_i$ , and the thermal diffusion coefficients  $D_{Ti}$ , respectively.  $\mathbf{D}$  is the molecular diffusion coefficient matrix and  $T$  is temperature. There are only  $N - 1$  independent fluxes. Consequently, each column vector has  $N - 1$  elements and  $\mathbf{D}$  is an  $(N - 1) \times (N - 1)$  square matrix. The assumption of negligible pressure diffusion is valid as long as the mixture is far from the critical point and the vertical dimension of the experimental setup is sufficiently small. These two conditions are met for the thermal diffusion cell discussed below.

**2.2. Experimental Setup.** A diffusion cell consisting of an entrance window, an exit window, and two conducting plates (see Figure 1) is filled with a multicomponent mixture. Initially, the mixture is kept at a uniform temperature. At a given time, the temperatures of the top and bottom plates are changed to introduce a temperature difference  $\Delta T$ . As a result of thermal diffusion, the components of the mixture start to segregate. The temperature and concentration gradients in the mixture lead to a gradient of refractive index. Consequently, a laser beam passing through the diffusion cell is deflected.

**2.3. Composition.** The temperature difference  $\Delta T$  is chosen to avoid convection. Thus, component flux is given by eq 1. Thermal diffusivity is assumed to be much greater than molecular diffusivity. As a consequence, a constant linear temperature gradient is established before the composition of the mixture has time to change appreciably. Thus, mass balance yields the following governing equation for the components of the mixture

$$\left| \frac{\partial \omega}{\partial t} \right\rangle = \mathbf{D} \left| \frac{\partial^2 \omega}{\partial z^2} \right\rangle \quad (2)$$

Here,  $t$  is time and  $z$  is the vertical coordinate. The diffusion equations eq 2 are decoupled when  $\mathbf{D}$  is a diagonal matrix. However, this is not generally the case, and we are interested in determining both diagonal and off-diagonal elements.

A square matrix can be diagonalized provided its eigenvectors are all linearly independent. The diagonalizing matrix will be the eigenvector matrix  $\mathbf{V}$ , and the resulting diagonal matrix will be the eigenvalue matrix  $\lambda$

$$\mathbf{V}^{-1} \mathbf{D} \mathbf{V} = \lambda \quad (3)$$

Multiplying eq 2 by  $\mathbf{V}^{-1}$  and defining the linear transformation

$$|\omega\rangle = \mathbf{V} |\Omega\rangle \quad (4)$$

we find

$$\left| \frac{\partial \Omega}{\partial t} \right\rangle = \lambda \left| \frac{\partial^2 \Omega}{\partial z^2} \right\rangle \quad (5)$$

Because  $\lambda$  is a diagonal matrix, the transformed governing equations eq 5 are a set of decoupled diffusion equations. All have the same dimensionless solution. We have previously obtained an analytical expression for the dimensionless solution by a Green's function approach.<sup>8</sup>

The dimensional solution to each of the decoupled diffusion equations in eq 5 can be obtained from the dimensionless solution, the steady-state gradients  $\Delta \Omega_{i\infty}/h$  of the transformed concentrations  $\Omega_i$ , and the corresponding characteristic times  $\tau_i = h^2/\lambda_i$ . The physical concentrations  $\omega_i$  in the diffusion cell are then obtained from the transformation in eq 4. When all diffusion coefficients are known,  $\mathbf{V}$  and  $\lambda$  are found by diagonalizing the molecular diffusion coefficient matrix  $\mathbf{D}$ , while the transformed steady-state separations  $|\Delta \Omega_{\infty}\rangle$  are obtained from eq 1,

$$\mathbf{V} \lambda |\Delta \Omega_{\infty}\rangle = -|D_T\rangle \Delta T \quad (6)$$

**2.4. Beam Deflection.** The deflection  $z$  of a laser beam initially parallel to the conducting plates is proportional to the gradient in refractive index where the beam enters the diffusion cell<sup>14</sup>

$$z = l \left( \frac{l}{2n} + \frac{l_w}{n_w} + \frac{l_a}{n_a} \right) \frac{\partial n}{\partial z} \quad (7)$$

Here,  $n$  is the refractive index of the mixture, while  $n_w$  and  $n_a$  are the refractive indices of the exit window and air, respectively. The other symbols are defined by Figure 1. Equation 7 is only valid for small deflections.

The refractive index of the mixture is a function of temperature and composition. Thus, the gradient of refractive index can be expressed as

$$\frac{\partial n}{\partial z} = \frac{\partial n}{\partial T} \frac{\partial T}{\partial z} + \left( \frac{\partial n}{\partial \omega} \right) \frac{\partial \omega}{\partial z} \quad (8)$$

where  $\partial n/\partial T$  and  $\partial n/\partial \omega_i$  are the derivatives of the refractive index with respect to temperature and composition, respectively. Using eq 4, eq 8 is cast into

$$\frac{\partial n}{\partial z} = \frac{\partial n}{\partial T} \frac{\partial T}{\partial z} + \left( \frac{\partial n}{\partial \Omega} \right) \frac{\partial \Omega}{\partial z} \quad (9)$$

The derivatives of refractive index with respect to transformed concentrations  $\partial n/\partial \Omega_i$  relate to the derivatives of refractive index with respect to the physical concentrations  $\partial n/\partial \omega_i$  by

$$\left| \frac{\partial n}{\partial \Omega} \right\rangle = \mathbf{V}^T \left| \frac{\partial n}{\partial \omega} \right\rangle \quad (10)$$

where  $\mathbf{V}^T$  is the transpose of the eigenvector matrix.

To extend the beam deflection technique to an  $N$ -component mixture, we need to measure the deflection of  $N - 1$  beams of different wavelengths. Generalizing eq 7 shows that the deflections  $z_i$  can be expressed as

$$|z\rangle = \mathbf{A} \left| \frac{\partial n}{\partial z} \right\rangle \quad (11)$$

where  $\mathbf{A}$  is a diagonal matrix with elements

$$A_{ij} = \delta_{ij} l \left( \frac{l}{2n_i} + \frac{l_w}{n_{iw}} + \frac{l_a}{n_{ia}} \right) \quad (12)$$

and  $n_i$ ,  $n_{iw}$ , and  $n_{ia}$  are refractive indices for beam  $i$  in the mixture, exit window, and air, respectively. Combining eq 11 with a generalized version of eq 9 yields

$$|z\rangle = \mathbf{A} \left| \frac{\partial n}{\partial T} \right| \frac{\partial T}{\partial z} + \mathbf{A} \mathbf{N}_\Omega^T \left| \frac{\partial \Omega}{\partial z} \right\rangle \quad (13)$$

where each column in  $\mathbf{N}_\Omega$  corresponds to the derivatives of refractive index with respect to transformed concentrations for one of the beams. The relationship between  $\mathbf{N}_\Omega$  and its physical counterpart  $\mathbf{N}_\omega$  is given by

$$\mathbf{N}_\Omega = \mathbf{V}^T \mathbf{N}_\omega \quad (14)$$

**2.5. Working Equations.** In the eigenspace of the molecular diffusion coefficient matrix  $\mathbf{D}$ , all diffusion equations share the same dimensionless solution. Furthermore, the physical and transformed concentrations are linearly related. The regression analysis serves to stretch the time coordinate of each transformed dimensionless solution and simultaneously determine the linear combination of the transformed solutions which describes the observed beam deflections the best. Expressing eq 13 in terms of the nondimensional transformed concentrations leads to

$$|z\rangle = \mathbf{A} \left| \frac{\partial n}{\partial T} \right| \frac{\partial T}{\partial z} + \frac{1}{h} \mathbf{A} \mathbf{N}_\Omega^T \Delta \Omega_\infty \left| \frac{\partial \bar{\Omega}}{\partial \bar{z}} \right\rangle \quad (15)$$

where the bar denotes dimensionless variables and  $\Delta \Omega_\infty$  is a diagonal matrix with diagonal elements equal to the transformed steady-state separations  $\Delta \Omega_{i\infty}$ . Because the temperature gradient reaches steady state much more rapidly than the concentration gradients, we can treat the first term of eq 15 as a constant. Introducing the constant vector

$$|b\rangle = \mathbf{A} \left| \frac{\partial n}{\partial T} \right| \frac{\Delta T}{h} \quad (16)$$

and the regression coefficient matrix

$$\mathbf{C} = \frac{1}{h} \mathbf{A} \mathbf{N}_\Omega^T \Delta \Omega_\infty \quad (17)$$

we can express eq 15 as

$$|z\rangle = |b\rangle + \mathbf{C} \left| \frac{\partial \bar{\Omega}}{\partial \bar{z}} \right\rangle \quad (18)$$

In addition to the regression coefficient matrix  $\mathbf{C}$ , the regression analysis will also provide the eigenvalues  $\lambda_i$  of the diffusion coefficient matrix. These are calculated from the characteristic times  $\tau_i = h^2/\lambda_i$  found when stretching the time coordinate of the dimensionless solution. Thus, we can construct the eigenvalue matrix  $\boldsymbol{\lambda}$ .

To determine the molecular diffusion coefficient matrix  $\mathbf{D}$ , we also need the eigenvector matrix  $\mathbf{V}$ . Combining eqs 14 and 17, we find

$$\mathbf{U} = \mathbf{V} \Delta \Omega_\infty = h (\mathbf{N}_\omega^T)^{-1} \mathbf{A}^{-1} \mathbf{C} \quad (19)$$

Note that, because  $\Delta \Omega_\infty$  is a diagonal matrix,  $\mathbf{U} = \mathbf{V} \Delta \Omega_\infty$  will also be an eigenvector matrix of  $\mathbf{D}$ . The effect of multiplying  $\mathbf{V}$  by  $\Delta \Omega_\infty$  is only to change the magnitude of each eigenvector.

Conclusively, we can find  $\mathbf{D}$  by the transformation

$$\mathbf{D} = \mathbf{U} \boldsymbol{\lambda} \mathbf{U}^{-1} \quad (20)$$

The thermal diffusion coefficients  $|D_T\rangle$  can be found by replacing  $\mathbf{V}$  by  $\mathbf{U}$  in eq 6

$$|D_T\rangle = -\frac{1}{\Delta T} \mathbf{U} \boldsymbol{\lambda} |1\rangle \quad (21)$$

where  $|1\rangle$  is a column vector where all elements are equal to 1.

**2.6. Regression Analysis.** We choose the least-squares method as a means to find  $\mathbf{C}$  and  $\boldsymbol{\lambda}$ . From eq 18, the contribution from beam  $i$  to the sum of squared errors (SSE) is given by

$$\text{SSE}_i = \sum_{m=1}^M \left( b_i + \sum_{j=1}^{N-1} C_{ij} \frac{\partial \bar{\Omega}_{jm}}{\partial \bar{z}} - z_{0im} \right)^2 \quad (22)$$

where  $M$  is the total number of measurements,  $\partial \bar{\Omega}_{jm}/\partial \bar{z}$  is the value of the dimensionless gradient of the transformed concentration  $\Omega_j$  at the time of the  $m$ th measurement, and  $z_{0im}$  is the  $m$ th measured beam deflection of beam  $i$ . Note that the dimensionless gradients of the transformed concentrations each have one degree of freedom, i.e., the characteristic time  $\tau_i$ . The total SSE is found by summing the contributions eq 22 from all the beams. For a given set of characteristic times  $\tau_i$ , SSE is at its minimum when the derivatives with respect to all  $C_{ij}$ s are zero simultaneously. From differentiation eq 22

$$\sum_{m=1}^M \left( b_i + \sum_{j=1}^{N-1} C_{ij} \frac{\partial \bar{\Omega}_{jm}}{\partial \bar{z}} - z_{0im} \right) \frac{\partial \bar{\Omega}_{km}}{\partial \bar{z}} = 0 \quad (23)$$

where  $k = 1, \dots, N-1$ . To simplify further calculations, we introduce three  $(N-1) \times M$  element matrixes  $\mathbf{B}$ ,  $\nabla \bar{\Omega}$ , and  $\mathbf{Z}_0$ . These matrixes are the matrix counterparts of the vectors  $|b\rangle$ ,  $|\partial \bar{\Omega}/\partial \bar{z}\rangle$ , and  $|z_0\rangle$ . Each row corresponds to a beam and each column corresponds to a measurement. Because all  $b_i$  are time independent, all columns in  $\mathbf{B}$  are equal to  $|b\rangle$ . Expressing eq 23 in terms of the above-defined matrixes yields

$$(\mathbf{B} + \mathbf{C} \nabla \bar{\Omega} - \mathbf{Z}_0) \nabla \bar{\Omega}^T = 0 \quad (24)$$

Finally, we solve for  $\mathbf{C}$  to obtain

$$\mathbf{C} = (\mathbf{Z}_0 - \mathbf{B}) \nabla \bar{\Omega}^T \times (\nabla \bar{\Omega} \nabla \bar{\Omega}^T)^{-1} \quad (25)$$

Equation 25 shows how the regression coefficient matrix  $\mathbf{C}$  is fixed for a given set of characteristic times  $\tau_i$ . Each  $\tau_i$  is found through numerical minimization of SSE.

### 3. Results and Discussion

To test the reliability of the regression analysis to find the various diffusion coefficients of multicomponent mixtures, we used the model to predict the deflection of laser beams passing through a diffusion cell filled with a ternary mixture. Then, we added random noise to the predicted deflections and compared the diffusion coefficients calculated from the regression analysis to the values used in our beam deflection calculations.

There is very little data on the refractive index and its compositional dependencies for ternary mixtures. As an alternative, we chose to work with pure component refractive indices and calculated the refractive index of the mixture as the volume average of the refractive indices of the individual components

$$n = \left( \sum_{i=1}^N \frac{\omega_i n_i}{\rho_i} \right) \left( \sum_{i=1}^N \frac{\omega_i}{\rho_i} \right)^{-1} \quad (26)$$

where  $n_i$ ,  $\rho_i$ , and  $\omega_i$  are the refractive index, density, and weight fraction of component  $i$ , respectively. The compositional derivatives are given by

$$\frac{\partial n}{\partial \omega_i} = \left( \frac{n_i - n}{\rho_i} - \frac{n_N - n}{\rho_N} \right) \left( \sum_{i=1}^N \frac{\omega_i}{\rho_i} \right)^{-1} \quad (27)$$

where the subscript  $N$  refers to the reference component. We used dispersion relations for toluene, chloroform, and benzene from ref 17 to predict the dispersion relation for a 1:1:1 (by weight) mixture of these three components. Toluene was labeled component 1, chloroform was labeled component 2, and benzene was chosen as the reference component. On the basis of the calculated dispersion relations, we selected wavelengths of 600 and 1800 nm for the two beams to be used in the experiment. The values for the refractive index  $n$  of the mixture and its compositional derivatives  $\partial n / \partial \omega_i$  at these two wavelengths are summarized in Table 1.

To predict the compositional field in the diffusion cell, we need the molecular and thermal diffusion coefficients of the mixture. Their values were obtained from a method based on irreversible thermodynamics described in ref 18. The results are summarized in Table 2.

For the purpose of the test, the properties of the diffusion cell are chosen to match the experimental setup used by Zhang.<sup>14,19</sup> We used  $\Delta T = 1.591$  K,  $h = 3.39$  mm,  $l = 61.34$  mm,  $l_w = 4.00$  mm, and  $l_a = 444.8$  mm. (See Figure 1 for parameter definitions.) The values of the different refractive indices are given in Table 1. The temperature derivative of the refractive index of the mixture was assumed to be  $\partial n / \partial T = -5.500 \times 10^{-4}$  K<sup>-1</sup>; the value for an equimolar mixture of toluene and hexane at  $T = 25$  °C.<sup>19</sup> While this might not be a good approximation, we expect it to be of the right order of magnitude. The temperature derivative  $\partial n / \partial T$  will only affect the initial rapid deflection of the laser beams. The exact value is of little importance in testing the reliability of the model because all diffusion coefficients are calculated from the subsequent composition-induced changes to the beam deflections. We now use eq 13 to predict deflection vs time for both beams (see Figure 2). Zhang<sup>19</sup> reported the pointing stability of their laser to be about  $\pm 1.5$   $\mu$ m for a distance between the exit window and the beam collector of  $l_a = 1000$  mm. In our case,  $l_a$  is less than half this distance and we added flat random noise of a fixed amplitude of 1  $\mu$ m to the predicted deflections.

Two tests were performed on the ternary mixture. The first test was based on 100 sample points, while in the second test, 1000 sample points were used. In both cases, the sample points were evenly distributed. To get a feeling of the reliability of the diffusion coefficients predicted by the regression procedure, each test was performed 10 times. The average values and standard deviations are reported in Table 3. As expected, the accuracy of the predicted values increases with the number of sampling points. We also note that the diagonal elements of the molecular diffusion coefficient matrix  $\mathbf{D}$  are more accurate than the off-diagonal elements. This is because the off-diagonal elements have a smaller effect on the compositional field in the diffusion cell than the diagonal elements do. Thus, the beam deflections are less sensitive to errors in the off-diagonal elements. The error in the calculated off-diagonal molecular diffusion coefficients is small in comparison to those from

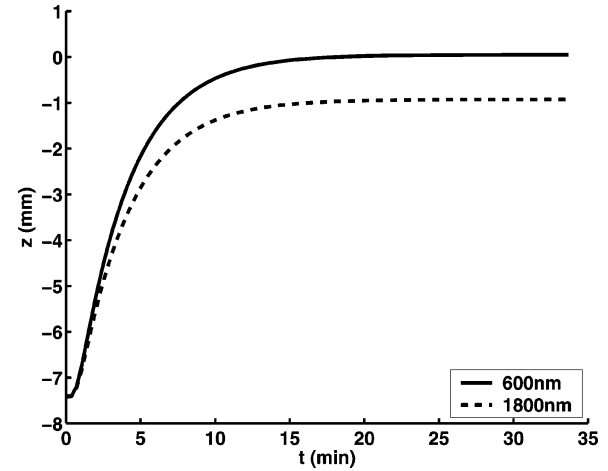
**TABLE 1: Refractive Indices and Derivatives**

wavelength	$n$	$\partial n / \partial \omega_1$	$\partial n / \partial \omega_2$	$n_w$	$n_a$
600 nm	1.4864	-0.0051	-0.0438	1.5000	1.0001
1800 nm	1.4679	-0.0020	-0.0363	1.4567	1.0000

**TABLE 2: Diffusion Coefficients Used in Composition Prediction**

$D_{11}^a$	$6.91 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
$D_{12}^a$	$0.97 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
$D_{21}^a$	$0.51 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
$D_{22}^a$	$6.02 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
$D_{T1}^b$	$-5.60 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1}$
$D_{T2}^b$	$7.80 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1}$

<sup>a</sup> Molecular diffusion coefficients. <sup>b</sup> Thermal diffusion coefficients.

**Figure 2.** A plot of the deflection of the two beams vs time for the ternary test mixture.**TABLE 3: Estimated Diffusion Coefficients**

sample points	100	1000
$D_{11}/10^{-9} \text{ m}^2 \text{ s}^{-1}$	$6.926^a \pm 0.3834^b$	$6.892^a \pm 0.1854^b$
$D_{12}/10^{-9} \text{ m}^2 \text{ s}^{-1}$	$0.984^a \pm 0.2820^b$	$0.957^a \pm 0.1354^b$
$D_{21}/10^{-9} \text{ m}^2 \text{ s}^{-1}$	$0.492^a \pm 0.0432^b$	$0.504^a \pm 0.0154^b$
$D_{22}/10^{-9} \text{ m}^2 \text{ s}^{-1}$	$6.007^a \pm 0.0317^b$	$6.027^a \pm 0.0073^b$
$D_{T1}/10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1}$	$-5.597^a \pm 0.0052^b$	$-5.600^a \pm 0.0017^b$
$D_{T2}/10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1}$	$7.800^a \pm 0.0004^b$	$7.800^a \pm 0.0001^b$

<sup>a</sup> Average values from 10 runs. <sup>b</sup> Standard deviations from 10 runs.

alternative techniques. A similar reasoning holds to explain why the predicted diffusion coefficients are more accurate for chloroform (component 2) than toluene (component 1). Table 1 shows that the refractive index of the mixture varies more with chloroform than toluene, so the beam deflections depend more strongly on the diffusion coefficients describing the flux of chloroform. Finally, we point out that the thermal diffusion coefficients are predicted more accurately than the molecular diffusion coefficients.

#### 4. Conclusions

We have shown that one can determine thermal and molecular diffusion coefficients of multicomponent mixtures from transient measurements of the deflections of laser beams of different wavelengths passing through a thermal diffusion cell. The derivations are based on the assumption that thermal diffusivity is much greater than molecular diffusivity. This is generally true for liquids but not for gases. Mathematically, the approach relies on the existence of an inverse for each of the two matrixes



$\mathbf{N}_\omega^T$  and  $\nabla \bar{\Omega} \nabla \bar{\Omega}^T$ . The former implies that the compositional dependencies of the refractive indices of the beams must be linearly independent. The latter requires that the eigenvalues of the molecular diffusion coefficient matrix  $\mathbf{D}$  are all different. These assumptions hold for mixtures where no two components are very similar. The practical limitations of the method (e.g., how different the compositional dependencies of the refractive indices of two beams must be or how close two eigenvalues can be) depends on the noise in the measurements and the sampling frequency.

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## Appendix

Subsection 2.6 shows how the eigenvalues and eigenvectors needed to calculate the molecular and thermal diffusion coefficients can be found through a least-squares method to fit the model to data. The vector notation makes the derivations very compact. In this appendix, we write the governing equation, eq 18, in summation form. The purpose is to make it easier to fit the model to data when the deflections of the various beams are recorded at different times or when the number of measurements of each beam is different.

The beam deflections can be written as

$$z_i = b_i + \sum_{j=1}^{N-1} C_{ij} G(t\lambda_j/h^2) \quad (\text{A1})$$

where  $b_i$  is a constant given by

$$b_i = l \left( \frac{l}{2n_i} + \frac{l_w}{n_{iw}} + \frac{l_a}{n_{ia}} \right) \frac{\partial n_i}{\partial T} \frac{\Delta T}{h} \quad (\text{A2})$$

and  $G(\bar{t}, \bar{z})$  is the dimensionless transformed concentration gradient and satisfies the boundary value problem

$$\frac{\partial G}{\partial \bar{t}} = \frac{\partial^2 G}{\partial \bar{z}^2}, \quad G(\bar{t}, \pm 1/2) = 1 \quad G(0, \bar{z}) = 0 \quad (\text{A3})$$

Once the eigenvalues  $\lambda_j$  and the regression parameters  $C_{ij}$  are determined by fitting eq A1 to the measured deflections, the thermal and molecular diffusion coefficients are obtained from eqs 19 through 21.

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