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Richard L. Rowley  
rowley@byu.edu

M. D. Hall

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# Heats of transport from the diffusion thermoeffect in binary liquid mixtures of toluene, chlorobenzene, and bromobenzene

R. L. Rowley and M. D. Hall<sup>(a,b)</sup>

Department of Chemical Engineering, Brigham Young University, Provo, Utah 84602

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Measurements of heats of transport in binary liquid mixtures of toluene, chlorobenzene, and bromobenzene utilizing the diffusion thermoeffect, or Dufour effect, are reported at 298 and 308 K. The corresponding heat-mass Onsager coefficients are also reported, from which thermal diffusion ratios have been calculated based on Onsager reciprocity. The resultant binary thermal diffusion ratios have been correlated as a function of composition in an attempt to study the relationship between values in binary and ternary mixtures. It was found that the single independent binary values can be used to estimate the two independent thermal diffusion ratios previously reported in toluene + chlorobenzene + bromobenzene ternary mixtures.

## I. INTRODUCTION

Not only will a temperature gradient give rise to a heat flux in fluid mixtures, but also so will composition gradients (more appropriately, isothermal chemical potential gradients). This latter effect, known as the diffusion thermoeffect or the Dufour effect, is characterized by a transport property called the heat of transport. The heat of transport of component  $i$ ,  $Q_i^*$ , relates the magnitude of the produced heat flux to the diffusional flux of component  $i$  under isothermal conditions. Generally the diffusion thermoeffect is considered to be small. Previous studies<sup>1,2</sup> have shown that while it is true that measured temperature gradients induced in initially isothermal liquid mixtures are small due to opposition by thermal conduction, the heat of transport itself is generally rather large, often on the order of several kJ/mol. As heats of transport contain significant information concerning the actual energy-diffusional relationship of molecular interactions, they are of interest in the development of molecular theory and generalized transport models.

Recently, Platt *et al.*<sup>2</sup> have reported heats of transport in ternary liquid mixtures for the system toluene + chlorobenzene + bromobenzene. In ternary mixtures, there are two independent heats of transport,<sup>3</sup> or equivalently, two independent Onsager coefficients. Platt *et al.*<sup>4</sup> reported Onsager coefficients obtained from their experimentally determined heats of transport, and then using Onsager reciprocity calculated the two independent thermal diffusion ratios  $K_T$  as a function of composition in the ternary mixture. However, in binary systems there is only one independent heat of transport or corresponding heat-mass Onsager coefficient. This leads to the natural questions: what is the compositional behavior of the two independent Onsager coefficients in the binary limit and what is the relationship, if any, of the ternary heats of transport to the binary? The natural extension of the second question is, of course, can ternary heats of transport be predicted from binary measurements. In this

work we report binary diffusion thermoeffect measurements made on binary mixtures consisting of toluene, chlorobenzene, and bromobenzene. From the results, binary heat-mass Onsager coefficients and, based on Onsager reciprocity, thermal diffusion ratios are computed. The composition dependence of the binary values are then used in an attempt to correlate the ternary values reported by Platt *et al.*<sup>2</sup>

## II. EXPERIMENTAL

The diffusion thermoeffect technique for measurement of heats of transport was utilized in this study. As before,<sup>2</sup>

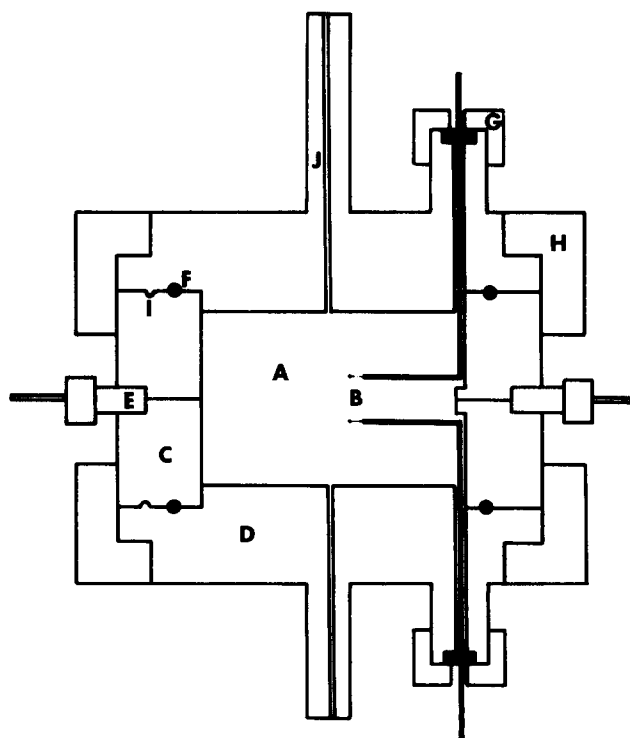


FIG. 1. Schematic diagram of boundary sharpening cell. A. Cell chamber. B. Thermocouples. C. Teflon body. D. Teflon end cap. E. Withdrawal ports. F. O-ring. G. Septum and cap for thermocouple lead seal to the tubes attached to micrometer heads. H. Brass securing ring. I. Alignment pin. J. Filling port.

<sup>a)</sup> Present address: Western Geophysical, Houston, TX.

<sup>b)</sup> Experimental and thesis work performed at Department of Chemical Engineering, Rice University, Houston, TX.

the cell was a modification of the boundary sharpening or Tiselius diffusion cell. The cell and experimental technique were the same as those used previously and are adequately described elsewhere.<sup>2</sup> For clarity of discussion just the concepts of the experiment are repeated here. To measure the heat of transport of a binary mixture of mean mass fraction  $\langle w_1 \rangle$ , an upper-phase mixture of composition  $w_1^u$ , and a lower-phase mixture of composition  $w_1^l$ , such that  $w_1^u + w_1^l = \langle w_1 \rangle$  and that the density of the upper solution is smaller than that of the lower, are prepared and thermostated in independent reservoirs within the same constant-temperature air bath as the cell itself. The cylindrical cell, 2.97 cm inside height and 3.0 cm i.d., is first completely filled from below with the lower solution. A schematic is shown in Fig. 1. An initial interface is formed between the upper and lower solutions in the bore of a large stopcock and the interface is lowered by withdrawal of fluid through equatorial ports of the cell. As withdrawal of the solution continues, fresh upper solution is introduced in the top of the cell as the rough interface between the upper and lower solutions is lowered in the cell. When the interface approaches the withdrawal plane, fluid from the lower-solution reservoir is allowed to enter at approximately half the total withdrawal rate. The net effect is infusion of fresh upper solution at the top of the cell, fresh lower solution at the bottom of the cell, and withdrawal at cell half-height of the fluid in which diffusion has occurred, thereby creating a sharp horizontal interface. Because the withdrawal rate is faster than diffusion, the interface is stable until the pumps are turned off at the start of the experiment.

There will obviously be temperature nonuniformities introduced into the initially isothermal mixtures by this boundary sharpening technique, but Platt *et al.*<sup>3</sup> have shown that temperature profiles measured in this type of cell, even when quite large initial temperature nonuniformities are present, can be accurately used to obtain heats of transport from the mathematical solution of the diffusion thermoeffect boundary-value problem with isothermal initial conditions by using values measured later than 800 s into the experiment. This is possible because of the establishment of a steady state between the much more rapid thermal conduction and the slower diffusion thermoeffect or molecular transport heat-transfer modes. Perturbations from this steady state due to initial temperature nonuniformities will always relax back to the appropriate temperature profiles governed by the slower molecular-transport rate.

Temperatures were monitored in the cell using two (one above and one below the initial interface) 40 gage copper-Constantan thermocouples of bead diameter less than 0.2 mm. The thermocouples were positioned equidistant from the plane of initial interface formation using micrometers located external to the cell and calibrated to zero for bead positions at the interface. For all the runs reported in this work, the cell location of the temperature probes was  $3.0 \pm 0.1$  mm from the interface, corresponding to reduced cell coordinates from bottom to top of  $z/a = 0.4$  and  $z/a = 0.6$  ( $z$  is vertical coordinate and  $a$  is cell height). The micrometer heads were attached to 25 gage stainless-steel sheaths which entered the cell through rubber-Teflon com-

posite septum seals, traveled along tiny grooves machined into the wall of the cell, and made right-angle bends to position the measurement beads in the radial center of the cell. The two thermocouples were referenced to each other to measure directly temperature differences. This was done in anticipation of the small values expected and in order to avoid junction errors and problems associated with an ice-point reference. Prior to each run, a thermocouple offset was monitored with the cell filled entirely with the lower-phase solution in order to eliminate spurious readings due to differences and inhomogeneities in the two beads. For 2 to 3 h, the temperature difference between the probes was monitored under isothermal conditions and found to be stable nearly to within the uncertainty of the temperature measurements, 2.6 mK. The value of this isothermal offset was subtracted from all readings during the run.

Thermocouple potential differences were monitored with a Hewlett-Packard, model 3456A, digital multimeter of high input impedance, of 100 nV resolution, and of  $\pm 0.008\%$  of the reading + two counts accuracy. The voltage to temperature conversion was done using a quadratic function originally obtained by fitting the data supplied by the thermocouple-wire manufacturer for the temperature-voltage response from 0 to 1 °C. Digital output in the form of temperature vs time was then output to a Commodore Super Pet computer where it was logged, saved on disk, and prepared for further analysis. In this manner, data could be logged continuously. The data set used for analysis, however, consisted of points spaced at 100 s intervals beginning 900 s into the run and ending after approximately 7200 s.

### III. ANALYSIS PROCEDURE

As was done by Rowley and Horne,<sup>1</sup> a numerical procedure was used to solve the partial differential equations describing the diffusion thermoeffect with isothermal initial and vanishing flux boundary conditions. The corresponding composition and temperature equations, simplified<sup>1</sup> for the cell geometry, types of fluids being studied, and experimental arrangement are

$$\rho \left( \frac{\partial w_1}{\partial t} \right) = \left\{ \frac{\partial [\rho D (\partial w_1 / \partial z)]}{\partial z} \right\}, \quad (1)$$

$$\begin{aligned} \rho C_p \left( \frac{\partial T}{\partial t} \right) &= \left\{ \frac{\partial [k (\partial T / \partial z)]}{\partial z} \right\} + \left\{ \frac{\partial [\rho D Q^* (\partial w_1 / \partial z)]}{\partial z} \right\} \\ &+ [\rho D M^3 / (M_1 M_2)^2] \left( \frac{\partial^2 H^E}{\partial x_1^2} \right) \left( \frac{\partial w_1}{\partial z} \right)^2, \quad (2) \end{aligned}$$

where  $\rho$  is density,  $C_p$  is specific heat,  $k$  is thermal conductivity,  $D$  is mutual diffusivity,  $M$  is mean molecular weight of the mixture,  $M_i$  is molecular weight of component  $i$ ,  $x_1$  is mole fraction of component 1, and  $H^E$  is the molar excess enthalpy. A Crank-Nicholson technique was used as before and the numerical solution was integrated into a nonlinear, weighted, least-squares fitting program which allowed determination of  $Q^*$  from the measured temperature differences at fixed and known thermocouple locations as a func-

TABLE I. Thermophysical properties for binary mixtures composed of toluene (1), chlorobenzene (2), and bromobenzene (3) at 1 atm.

(A) Density (Ref. 5) ( $10^{-3} \text{ kg m}^{-3}$ )								
$\rho = M/(x_i V_i^0 + x_j V_j^0 + V^E); V^E = x_i x_j \sum_{n=0}^3 A_n (1 - 2x_i)^n$								
Units = $10^{-3} \text{ m}^3 \text{ kg}^{-1}$								
<i>i</i>	<i>j</i>	<i>T/K</i>	$V_i^0$	$V_j^0$	$A_0$	$A_1$	$A_2$	$A_3$
1	2	298	107.26	102.05	-0.172	-0.01	0	0
1	2	308	108.26	103.15	-0.222	0	0	0
1	3	308	108.26	106.91	-1.052	0.28	-0.08	0.02
2	3	298	90.15	105.96	16.003	-0.35	-0.50	0.05
2	3	308	90.90	106.91	16.539	-0.35	-0.53	0.06
(B) Specific heat (Refs. 6 and 7) ( $\text{kJ kg}^{-1} \text{ K}^{-1}$ )								
$C_p = (x_i C_{p,i}^0 + x_j C_{p,j}^0 + C_p^E)/M; C_p^E = x_i x_j \sum_{n=0}^3 B_n (1 - 2x_i)^n$								
<i>i</i>	<i>j</i>	<i>T/K</i>	$C_{p,i}^0$	$C_{p,j}^0$	$B_0$	$B_1$	$B_2$	
1	2	298	152.39	125.12	10.987	-5.44	0.57	
1	2	308	155.13	125.13	10.987	-5.44	0.57	
1	3	308	155.13	152.94	7.907	6.51	12.12	
2	3	298	125.12	151.53	-8.186	6.71	5.90	
2	3	308	125.13	152.94	-8.186	6.71	5.90	
(C) Molar excess enthalpy (Ref. 7) ( $\text{J mol}^{-1}$ )								
$H^E = x_i x_j \sum_{n=0}^2 C_n (1 - 2x_i)^n$								
<i>i</i>	<i>j</i>	<i>T/K</i>	$C_0$	$C_1$	$C_2$			
1	2	298	-420.76	62.88	-104.51			
1	2	308	-310.94	8.50	110.23			
1	3	308	-255.90	-33.15	81.42			
2	3	298	81.21	-20.03	628.95			
2	3	308	-0.65	47.07	687.95			
(D) Mutual diffusivity (Ref. 8) ( $10^{-9} \text{ m}^2 \text{ s}^{-1}$ )								
$D = D_j w_i + D_i w_j$								
<i>i</i>	<i>j</i>	<i>T/K</i>	$D_i$	$D_j$				
1	2	298	1.678	2.206				
1	2	308	1.951	2.551				
1	3	308	1.533	2.454				
2	3	298	1.265	1.641				
2	3	308	1.478	1.908				
(E) Thermal conductivity (Refs. 9-11) ( $\text{mW m}^{-1} \text{ K}^{-1}$ )								
$k = w_i k_i^0 + w_j k_j^0 + k^E; k^E = w_i w_j [G_{ji}(k_{ij} - k_i^0)/(w_i + w_j G_{ji}) + G_{ij}(k_j^0 - k_j^0)/(w_j + w_i G_{ij})]$								
<i>i</i>	<i>j</i>	<i>T/K</i>	$k_i^0$	$k_j^0$	$k_{ij}$	$G_{ij}$	$G_{ji}$	
1	2	298	132.68	126.37	128.66	0.9638	1.0717	
1	2	308	129.92	124.10	126.22	0.9650	1.0693	
1	3	308	129.92	108.83	113.82	0.9910	1.0582	
2	3	298	126.37	110.81	115.74	0.9595	1.0292	
2	3	308	124.10	108.83	113.67	0.9608	1.0283	

tion of time. Temperatures calculated at the grid points corresponding to the locations of the centers of the thermocouple beads were subtracted from each other and these differences at the time rows corresponding to measured times were used in comparison to measured values to minimize the sum of the squares of the residuals, thereby obtaining best-fitted values of  $Q_1^*$ .

Also required in the analysis are the values of the thermophysical properties appearing in Eqs. (1) and (2). Table I contains the property correlations and constants that were used to compute the thermophysical properties at each grid-point composition in the numerical solution. Only the mean temperature of the run was used in the evaluation of the properties since the induced temperature profiles are small

TABLE II. Heats of transport measured in binary mixtures of toluene (1), chlorobenzene (2), and bromobenzene (3) at 1 atm.

<i>i</i>	<i>j</i>	$\langle w_i \rangle$	<i>T</i> /K	$-Q_i^*/(\text{kJ kg}^{-1})$	$1 + \Gamma_{ii}$	$-\Omega_{oi}/(10^{-7} \text{ kg m}^{-1} \text{ s}^{-1})$
1	2	0.3000	298	6.21	1.020	1.07
1	2	0.3996	298	12.08	1.020	2.29
1	2	0.5000	298	10.50	1.026	1.99
1	2	0.6025	298	14.98	1.025	2.63
1	2	0.3000	308	16.19	1.020	3.07
1	2	0.3000	308	15.38	1.020	2.92
1	2	0.4000	308	16.59	1.024	3.45
1	2	0.5500	308	20.81	1.026	4.22
1	2	0.6000	308	24.82	1.025	4.80
1	3	0.2010	308	23.35	1.019	3.90
1	3	0.7000	308	19.33	1.018	3.30
2	3	0.2000	298	14.20	1.0	2.34
2	3	0.3000	298	9.41	1.0	2.07
2	3	0.5000	298	8.55	1.0	2.14
2	3	0.6000	298	9.31	1.0	2.24
2	3	0.2000	308	23.71	1.0	4.20
2	3	0.3000	308	24.84	1.0	5.74
2	3	0.5000	308	12.30	1.0	3.37
2	3	0.6000	308	15.08	1.0	3.98
2	3	0.7000	308	16.57	1.0	3.84

(less than  $\pm 0.3$  K deviation from the initial value) and lead to insignificant effects in property values. This also serves to decouple Eq. (1) from Eq. (2), allowing solution of the composition equation at each time row independent of the temperature equation solution. Because the relaxation time of diffusion is slow compared to that of thermal conduction, the composition profile of the previous time step could be used in the temperature solution without loss of accuracy. Initially, very short time steps (2 s) were used when the composition gradient was steep. These were gradually expanded to 100 s steps as the composition gradient was diminished.

TABLE III. Thermal-diffusion coefficients and ratios obtained from Onsager reciprocity at 1 atm.

<i>i</i>	<i>j</i>	$\langle w_i \rangle$	<i>T</i> /K	$-D_{T,i}/(10^{-10} \text{ m}^2 \text{ s}^{-1})$	$-K_{T,i}$
1	2	0.3000	298	1.05	0.0565
1	2	0.3996	298	2.31	0.120
1	2	0.5000	298	2.06	0.104
1	2	0.6025	298	2.79	0.138
1	2	0.3000	308	3.05	0.141
1	2	0.3000	308	2.90	0.134
1	2	0.4000	308	3.52	0.158
1	2	0.5500	308	4.47	0.193
1	2	0.6000	308	5.14	0.220
1	3	0.2010	308	3.04	0.167
1	3	0.7000	308	3.38	0.149
2	3	0.2000	298	1.68	0.124
2	3	0.3000	298	1.48	0.109
2	3	0.5000	298	1.65	0.114
2	3	0.6000	298	1.74	0.120
2	3	0.2000	308	3.05	0.192
2	3	0.3000	308	4.29	0.263
2	3	0.5000	308	2.62	0.155
2	3	0.6000	308	3.12	0.185
2	3	0.7000	308	3.04	0.180

#### IV. RESULTS

The heats of transport obtained are shown in Table II. Also shown are the values of the heat-mass Onsager coefficient  $\Omega_{oi}$  obtained from the identity

$$\Omega_{oi} = \rho D Q_i^* M_i M_j w_i w_j / [MRT(1 + \Gamma_{ii})], \quad (3)$$

where the values of  $\Gamma_{ii}$  for the toluene + chlorobenzene and toluene + bromobenzene binaries were calculated from

$$\Gamma_{11} = x_1 x_2 (0.12265 - 0.0213x_2 - 0.0424x_2^2), \quad (4)$$

$$\Gamma_{11} = x_1 x_3 (0.5372 - 0.1285x_3 - 0.2204x_3^2), \quad (5)$$

respectively. Here, subscript *i* refers to the lowest component number in binaries of toluene (1), chlorobenzene (2), and bromobenzene (3) and *j* refers to the second component. Also,  $\Gamma_{ii} = (\partial \ln \gamma_i / \partial \ln x_i)_{T,P}$ , where  $\gamma_i$  is the activity coefficient of component *i* based on the pure-component standard state. Equations (4) and (5) were fitted using the free energy data of Khosla *et al.*<sup>12</sup> As these two binaries are nearly ideal in the thermodynamic sense ( $\Gamma_{ii} = 0$ ) and the chlorobenzene + bromobenzene binary is expected to be the most ideal of the three,  $\Gamma_{22}$  was assumed to be zero in chlorobenzene–bromobenzene mixtures for lack of data. It should be mentioned that the negative sign for all of the heats of transport and Onsager Coefficients is an artifact of the way we have numbered the components since it is easily shown that  $Q_2^* = -Q_1^*$  in a binary mixture of components 1 and 2. The negative sign in conjunction with the numbering system used here indicates that heat is transported down the composition gradient of the more-dense component or up the gradient of the less-dense component.

Based on Onsager reciprocity  $\Omega_{io} = \Omega_{oi}$ , which has been proven experimentally under similar circumstances,<sup>13</sup> one can calculate thermal diffusion coefficients  $D_T$  and thermal diffusion ratios  $K_T$  from diffusion thermoeffect measurements. The relationships between these latter coefficients and the Onsager coefficient are

$$D_{T,i} = \Omega_{i0}/\rho, \quad (6)$$

$$K_{T,i} = D_{T,i}/D = \Omega_{i0}/\rho D. \quad (7)$$

The values obtained are shown in Table III.

## V. DISCUSSION OF RESULTS

As Platt *et al.* have shown, there are two independent heats of transport in a ternary mixture. If the heat  $\mathbf{q}$  and mass (relative to the center of mass)  $\mathbf{j}$ , flux equations are written in terms of Onsager coefficients for an  $n$ -component system

$$-\mathbf{q} = \Omega_{00}\nabla \ln T + \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} \Omega_{0j} f_{jk} \mu_{kl} \nabla w_l, \quad (8)$$

$$-\mathbf{j}_i = \Omega_{i0} \nabla \ln T + \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} \Omega_{ij} f_{jk} \mu_{kl} \nabla w_l \quad (i = 1, 2, \dots, n-1), \quad (9)$$

where  $f_{jk}$  and  $\mu_{kl}$  are given by

$$f_{jk} = \delta_{jk} + w_k/w_n, \quad (10)$$

$$\mu_{kl} = \left( \frac{\partial \mu_k}{\partial w_l} \right)_{T,P}, \quad (11)$$

and  $\delta_{jk}$  is the Kronecker delta, then heats of transport can be written in terms of the Onsager coefficients as

$$Q_1^* = (\Omega_{01}\Omega_{22} - \Omega_{02}\Omega_{21})/(\Omega_{11}\Omega_{22} - \Omega_{12}\Omega_{21}), \quad (12)$$

$$Q_2^* = (\Omega_{02}\Omega_{11} - \Omega_{01}\Omega_{12})/(\Omega_{11}\Omega_{22} - \Omega_{12}\Omega_{21}). \quad (13)$$

These equations may be inverted and written as

$$\Omega_{01} = \Omega_{11}Q_1^* + \Omega_{21}Q_2^*, \quad (14)$$

$$\Omega_{02} = \Omega_{12}Q_1^* + \Omega_{22}Q_2^*. \quad (15)$$

On the other hand, the binary heat of transport is a simple ratio of two Onsager coefficients

$$Q_1^* = \Omega_{01}/\Omega_{11}. \quad (16)$$

The Onsager coefficients themselves are a function of composition, as can be seen from the results of Table II, so there is no *obvious* way to correlate Onsager coefficients in ternary mixtures with those in the constituent binaries. To make matters conceptually simpler, we attempt to correlate thermal diffusion ratios rather than Onsager coefficients, though the two are related for a binary as in Eq. (7) and for a ternary system by<sup>4</sup>

$$K_{T,i} = D_{T,i}/D_{ii} \quad (i = 1, 2). \quad (17)$$

The relationships used here between transport and Onsager coefficients are the same as those used by Platt *et al.*<sup>2</sup> so that the multicomponent flux equations, Eqs. (8) and (9), can be rewritten in terms of transport coefficients as

$$-\mathbf{q} = k\nabla T + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} \rho Q_k^* D_{kl} \nabla w_l, \quad (18)$$

$$-\mathbf{j}_i = \rho D_{T,i} \nabla \ln T + \sum_{l=1}^{n-1} \rho D_{il} \nabla w_l \quad (i = 1, 2, \dots, n-1), \quad (19)$$

where obviously

$$k = \Omega_{00}/T \quad (20)$$

and

$$\rho D_{il} = \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} \Omega_{ij} f_{jk} \mu_{kl}. \quad (21)$$

In a binary mixture one could speak of the thermal-diffusion ratio of either component in the mixture since  $\mathbf{j}_1 + \mathbf{j}_2 = 0$  requires that

$$K_{T,1} = -K_{T,2}. \quad (22)$$

In an attempt to correlate ternary thermal-diffusion ratios in terms of binary values, all the binary data were fitted to the form

$$K_{T,i} = w_j K_{T,i}^\infty + w_i K_{T,i}^0 + w_i w_j \alpha_{ij}, \quad (23)$$

where again  $i$  refers to the lowest component number in binaries of toluene (1), chlorobenzene (2), and bromobenzene (3) and  $j$  refers to the other component. In this manner,  $K_{T,i}^0$  can be thought of as the value in the pure-component- $i$  limit and  $K_{T,i}^\infty$  can be thought of as the infinitely dilute value, which according to Eq. (18) must be equal to  $-K_{T,j}^0$  in the  $i$ - $j$  binary. Thus, it is required that  $K_{T,i}^0$  be the same regardless of which of the two possible binaries containing component  $i$  it was determined from. Similarly, we require that  $K_{T,2}^0$  be the same in both possible binaries containing component 2. And,  $K_{T,3}^0$  is a pure-3 limit equal to  $-K_{T,2}^\infty$  in the 2-3 binary and  $-K_{T,1}^\infty$  in the 1-3 binary. Thus, we fit six parameters to describe all three binaries: three "pure component" thermal diffusion ratios and three mixture excess related constants,  $\alpha_{ij}$ , one for each binary.

While better fits of the binary data could certainly have been achieved by a nonsymmetric functionality for the excess portion, too many adjustable parameters would make fitting of physically reasonable pure-component values suspect. Even so, without additional information much closer to the pure component limits, we do not place much confidence in the physical significance of the  $K_{T,i}^0$  values and only use this procedure in an attempt to develop a rough estimation procedure for the ternary thermal diffusion ratios from the single independent values measured in binary experiments. The true behavior of these cross-transport coefficients in the pure component limit, however, is an interesting and yet unstudied problem that deserves further attention.

A simultaneous fit of Eq. (23) to the  $K_{T,i}$  values measured in the three binary mixtures toluene (1) + chlorobenzene (2), toluene (1) + bromobenzene (2), and chlorobenzene (2) + bromobenzene (3) yielded the values  $K_{T,1}^0 = 0.1596$ ,  $K_{T,2}^0 = 0.0523$ ,  $K_{T,3}^0 = -0.1905$ ,  $\alpha_{12} = 0.5659$ ,  $\alpha_{13} = -0.0995$ , and  $\alpha_{23} = 0.3152$ . These values were then used to estimate ternary values for  $K_{T,1}$  and  $K_{T,2}$  at the same compositions reported by Platt *et al.*<sup>2</sup> To estimate the values in the ternary mixtures, we used

$$K_{T,1} = w_1 K_{T,1}^0 - w_2 K_{T,2}^0 - w_3 K_{T,3}^0 + \alpha_{12} w_1 w_2 + \alpha_{13} w_1 w_3, \quad (24)$$

$$K_{T,2} = w_2 K_{T,2}^0 - w_1 K_{T,1}^0 - w_3 K_{T,3}^0 + \alpha_{23} w_2 w_3 - \alpha_{12} w_1 w_2, \quad (25)$$

where the minus signs arise from analogs of Eq. (22) for each binary. Thus, the three corners of a  $K_{T,1}$  vs ternary composition diagram are defined by  $K_{T,1}^0$  and  $K_{T,1}^\infty$  in the 1-2 binary (which is equal to  $-K_{T,2}^0$ ), and  $K_{T,1}^\infty$  in the 1-3

TABLE IV. Thermal-diffusion ratios correlated for binary mixtures and used to estimate values in ternary mixtures<sup>2</sup> of toluene (1), chlorobenzene (2), and bromobenzene (3) at 35 °C and 1 atm.

$\langle w_1 \rangle$	$\langle w_2 \rangle$	$-K_{T,1}$ (expt)	$-K_{T,1}$ (calc)	$-K_{T,2}$ (expt)	$-K_{T,2}$ (calc)
0.300	0.700	0.141	0.130	...	...
0.300	0.700	0.134	0.130	...	...
0.400	0.600	0.158	0.168	...	...
0.550	0.450	0.193	0.204	...	...
0.600	0.400	0.220	0.211	...	...
0.201	0.799	0.167	0.168	...	...
0.700	0.300	0.149	0.148	...	...
0	0.200	...	...	0.192	0.213
0	0.300	...	...	0.263	0.215
0	0.500	...	...	0.155	0.200
0	0.600	...	...	0.185	0.183
0	0.700	...	...	0.180	0.160
0.200	0.200	0.145	0.146	-0.040	0.108
0.200	0.400	0.095	0.125	0.048	0.070
0.200	0.600	0.074	0.103	0.049	0.075
0.325	0.175	0.128	0.154	0.024	0.048
0.326	0.274	0.141	0.151	0.055	0.022
0.400	0.100	0.194	0.157	0.029	0.030
0.400	0.300	0.156	0.161	0.091	-0.030
0.450	0.450	0.175	0.177	-0.055	-0.130
0.600	0.250	0.177	0.187	0.001	-0.127

binary (which is equal to  $-K_{T,3}^0$ ).

Table IV shows both the results of the correlation of the binary  $K_T$  values with Eq. (23) and the prediction of ternary values from Eqs. (24) and (25). The predicted values are compared to values determined from the measured heats of transport reported by Platt *et al.*<sup>2</sup> Agreement seems adequate for a rough estimation technique of this sort. It should also be pointed out that although we expect the accuracy of the binary measurements reported here to be 3%–4%, the accuracy of the ternary experiments are considerably less since  $Q_1^*$  and  $Q_2^*$  must be simultaneously fit. Furthermore, in the conversion from heats of transport to Onsager coefficients and then finally to thermal diffusion ratios, errors associated with the determination of  $\Gamma_{ii}$  and the errors in the diffusivity and density due to inadequacies of the correlations in Table I, introduce considerable more uncertainty. We, therefore, do not expect the binary  $K_T$  values to be any more accurate than about 10% and the ternary values than about 15%. The ternary estimation method of Eqs. (24) and (25) therefore appear adequate.

## VI. CONCLUSIONS

Measurements of the diffusion thermoeffect in binary liquid mixtures of toluene, chlorobenzene, and bromobenzene have been made at 298 and 308 K at 1 atm. Reduction of temperature response data vs time yields the heat of transport which was found to be typically on the order of 10–20 kJ/kg. While the diffusion-induced temperature response is small due to back thermal conduction, heats of transport are substantial in value and indicate considerable heat transfer by the molecular mode.

Onsager coefficients and thermal-diffusion coefficients and ratios have been calculated from the heats of transport. Study of these three binary mixtures allows for the first time investigation of the relationship between the single, independent thermal-diffusion ratio in binary mixtures and the two, independent, thermal diffusion ratios in ternary mixtures. The binary data can be correlated in terms of pure component limiting thermal-diffusion ratios, which can in turn be used to calculate ternary values. Comparison of ternary values estimated entirely from the binary data with those measured by Platt *et al.*<sup>2</sup> yields reasonable agreement.

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