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The diffusion thermoeffect in ternary nonelectrolyte liquid mixtures

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Expressions for that portion of the heat flux which is due to composition gradients in multicomponent nonelectrolyte liquid mixtures have been formulated in terms of heats of transport. The resultant thermal energy equation in combination with component mass balance equations constitute coupled partial differential equations descriptive of the diffusion thermoeffect in liquid mixtures. These equations were solved with a double perturbation technique subject to initial and boundary conditions consistent with experimental design conditions considered appropriate for successful measurement of multicomponent heats of transport. Based on the adiabatic type cell, the expected temperature response, dependent on cell variables, experimental conditions, and system thermophysical properties, has been modeled to provide design information for successful and optimum heats of transport measurements. In ternary systems, the two independent heats of transport can be experimentally determined from temperature response measurements only if two experiments are performed at the same mean composition but with different initial composition gradients. Experimental heats of transport in ternary systems are obtainable based upon the design principles of this work.

I. INTRODUCTION

Based on the principles of nonequilibrium thermodynamics, linear relations exist between the independent vector fluxes and forces which appear in the entropy production expression for a fluid, provided the system is not too far removed from equilibrium.¹ For isotropic n -component mixtures of nonelectrolytes in which there are no pressure gradients, the appropriate flux-force relations can be written as

$$-q = \Omega_{00} \nabla \ln T + \sum_{j=1}^{n-1} \Omega_{0j} \nabla_T (\mu_j - \mu_n), \quad (1.1)$$

$$-j_i = \Omega_{i0} \nabla \ln T + \sum_{j=1}^{n-1} \Omega_{ij} \nabla_T (\mu_j - \mu_n) \quad (i = 1, 2, \dots, n-1), \quad (1.2)$$

where q is the heat flux, j_i is the diffusion flux of component i relative to the barycentric velocity, T is temperature, Ω_{ij} are Onsager coefficients, μ_i is the specific chemical potential of component i , and ∇_T is the isothermal gradient operator defined by

$$\nabla_T = \nabla - (\partial/\partial T). \quad (1.3)$$

Ordinary diffusion, a diffusional flux induced by a chemical potential gradient, has been widely studied as has thermal conduction, a heat flux due to a temperature gradient. The heat-mass coupled phenomena, characterized by the Ω_{0j} and Ω_{i0} coefficients, have not been as extensively studied but should contain significant information concerning the molecular nature of transport phenomena.² These cross phenomena are very sensitive to the unlike potential parameters in pair potential models³; better estimates of potential parameters can be made if cross terms are used to obtain them.⁴ In a multicomponent system, a heat flux can be produced by a gradient of chemical potential in addition to a gradient of temperature. This is called the diffusion thermo-

effect, the magnitude of which is characterized by the Onsager coefficients Ω_{0j} . The diffusion thermoeffect has been studied in gases under a variety of conditions,^{5,6} but has only recently been accurately investigated in liquid mixtures because of the small magnitude of the temperature response to an isothermal chemical potential gradient. Following the implications for measurement optimization as mathematically derived by Ingle and Horne,⁷ Rowley and Horne were able to accurately measure heats of transport directly from the diffusion thermoeffect in binary mixtures containing carbon tetrachloride and cyclohexane at room temperature.⁸

The results of those experiments constituted the first experimental verification of the Onsager reciprocal relation for heat and mass transfer, namely, $\Omega_{01} = \Omega_{10}$.⁹ The diffusion thermoeffect has also been used to study the temperature behavior and critical exponent of Ω_{01} in the near critical region.¹⁰ However, a systematic study of the effects of composition, temperature, and chemical constituency has yet to be made. More importantly, studies in ternary systems have yet to be made to determine the nature of the phenomenon when characterized by two independent Onsager coefficients Ω_{01} and Ω_{02} rather than one. This paper addresses the latter problem including the nature of the diffusion thermoeffect in ternary mixtures, how to obtain the two independent heats of transport from temperature response data to the ternary diffusion thermoeffect experiment, and how to optimize those measurements. In the companion paper to this one,¹¹ heats of transport measured in toluene-chlorobenzene-bromobenzene mixtures are reported as a function of composition and temperature. Those measurements are based upon the findings of this work.

II. THEORETICAL

A. General

The Onsager coefficients Ω_{0j} relate an induced heat flux to the corresponding thermodynamic driving force,

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an isothermal gradient of chemical potential. An alternate description for Eqs. (1.1) and (1.2) can be made in terms of transport parameters. In particular, heats of transport Q_i^* are related to the Ω_{0j} and are defined by

$$Q_i^* = (q/j_i) (\nabla T = 0, j_{k \neq i} = 0). \quad (2.1)$$

The heat of transport of component i is therefore a measure of the local heat addition or withdrawal required to maintain isothermal conditions as molecular diffusion of component i occurs from a higher chemical potential environment to a lower one.¹² If the Gibbs–Duhem equation at constant temperature and pressure

$$\nabla_T \mu_n = - \sum_{k=1}^{n-1} (w_k/w_n) \nabla_T \mu_k, \quad (2.2)$$

the chain rule, and the definitions

$$f_{jk} = \delta_{jk} + w_k/w_n, \quad (2.3)$$

$$\mu_{kl} = (\partial \mu_k / \partial w_l)_{T,P} \quad (2.4)$$

are used, the fluxes of Eqs. (1.1) and (1.2) become

$$-q = \Omega_{00} \nabla \ln T + \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} \Omega_{0j} f_{jk} \mu_{kl} \nabla w_l \quad (2.5)$$

$$-j_i = \Omega_{i0} \nabla \ln T + \sum_{j=1}^{n-1} \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} \Omega_{ij} f_{jk} \mu_{kl} \nabla w_l \quad (i=1, 2, \dots, n-1), \quad (2.6)$$

where δ_{jk} is the Kronecker delta and w_l is mass fraction of component l . For simplicity, Eqs. (2.5) and (2.6) can be written as a single matrix equation

$$-J = \mathbf{A} \mathbf{B} \mathbf{X}, \quad (2.7)$$

where

$$\mathbf{J} = \begin{bmatrix} q \\ j_1 \\ j_2 \\ \vdots \\ j_{n-1} \end{bmatrix}; \quad \mathbf{A} = \begin{bmatrix} \Omega_{00} & \Omega_{01} & \Omega_{02} & \cdots & \Omega_{0,n-1} \\ \Omega_{10} & \Omega_{11} & \Omega_{12} & \cdots & \Omega_{1,n-1} \\ \Omega_{20} & \Omega_{21} & \Omega_{22} & \cdots & \Omega_{2,n-1} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \Omega_{n-1,0} & \Omega_{n-1,1} & \Omega_{n-1,2} & \cdots & \Omega_{n-1,n-1} \end{bmatrix},$$

$$\mathbf{B} = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ 0 & b_{11} & b_{12} & \cdots & b_{1,n-1} \\ 0 & b_{21} & b_{22} & \cdots & b_{2,n-1} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & b_{n-1,1} & b_{n-1,2} & \cdots & b_{n-1,n-1} \end{bmatrix}; \quad \mathbf{X} = \begin{bmatrix} \nabla \ln T \\ \nabla w_1 \\ \nabla w_2 \\ \vdots \\ \nabla w_{n-1} \end{bmatrix}, \quad (2.8)$$

and

$$b_{ij} = \sum_{k=1}^{n-1} f_{ik} \mu_{kj} \quad (i, j=1, 2, \dots, n-1). \quad (2.9)$$

Equation (2.7) expresses the flux matrix in terms of the product of an Onsager, a thermodynamic, and a force matrix.

The heat of transport for component i , as defined by Eq. (2.1), can be expressed in terms of Onsager coef-

ficients as

$$Q_i^* = \frac{|C_i|}{|A'|}, \quad (2.10)$$

where A' is the principal submatrix of A formed by elimination of the first row and column and C_i are matrices formed by replacing the i th row of A' with the elements Ω_{0j} ; $j=1, 2, \dots, n-1$. To complete the conversion of Eqs. (1.1) and (1.2) to flux-force relations involving transport properties, the Ω_{ij} must be identified. Consistent with Fick's law, the diffusion coefficient matrix is defined by

$$\rho \mathbf{D} = \mathbf{A}' \mathbf{B}', \quad (2.11)$$

where again B' is the principal submatrix of B obtained upon elimination of the first row and column. Fourier's law requires

$$k = \Omega_{00}/T. \quad (2.12)$$

Therefore, Eqs. (1.1) and (1.2) become

$$-q = k \nabla T + \sum_{k=1}^{n-1} \sum_{l=1}^{n-1} \rho Q_k^* D_{kl} \nabla w_l, \quad (2.13)$$

$$-j_i = \rho D_{Ti} \nabla \ln T + \sum_{l=1}^{n-1} \rho D_{il} \nabla w_l; \quad i=1, 2, \dots, n-1, \quad (2.14)$$

where

$$\rho D_{Ti} = \Omega_{i0}. \quad (2.15)$$

B. Ternary systems

Measurement of the diffusion thermoeffect in liquid systems can be optimized by a cell designed to restrict the effect to one direction with adiabatic boundaries at either end.⁷ For the case of three components, the conservation equations for mass and energy in one direction can be written in terms of time t and the single applicable spatial variable z ,

$$\rho (\partial w_i / \partial t) = -(\partial j_i / \partial z); \quad i=1, 2, \quad (2.16)$$

$$\rho \bar{C}_p (\partial T / \partial t) = -(\partial q / \partial z) - j_1 [\partial (\bar{H}_1 - \bar{H}_3) / \partial z] - j_2 [\partial (\bar{H}_2 - \bar{H}_3) / \partial z], \quad (2.17)$$

respectively.^{1,7} The above equations are valid for ternary systems containing no pressure gradients, negligible surface effects, and no gravitational or other external body forces. Additionally, the barycentric velocity is considered to be small. Rowley and Horne⁸ have shown this to be true even for an initially very sharp composition gradient. Under these same restrictions with the additional assumption that the thermal diffusion effect, characterized by the Ω_{i0} ($i \neq 0$) Onsager coefficients, constitutes an insignificant perturbation to the mass flux because of the small resultant diffusion thermoeffect temperature differences, the flux equations corresponding to Eqs. (2.13) and (2.14) are

$$-q = k(\partial T / \partial z) + \rho(Q_1^* D_{11} + Q_2^* D_{21})(\partial w_1 / \partial z) + \rho(Q_1^* D_{12} + Q_2^* D_{22})(\partial w_2 / \partial z), \quad (2.18)$$

$$-j_1 = \rho D_{11}(\partial w_1 / \partial z) + \rho D_{12}(\partial w_2 / \partial z), \quad (2.19)$$

$$-j_2 = \rho D_{21}(\partial w_1 / \partial z) + \rho D_{22}(\partial w_2 / \partial z). \quad (2.20)$$

Ingle and Horne have verified the insignificance of any

thermal diffusion contribution to the mass flux in diffusion thermoeffect experiments.⁷ As defined by Eq. (2.10), there are only two independent heats of transport in ternary mixtures. These are related to Onsager coefficients by

$$Q_1^* = (\Omega_{01}\Omega_{22} - \Omega_{02}\Omega_{21}) / (\Omega_{11}\Omega_{22} - \Omega_{12}\Omega_{21}), \quad (2.21)$$

$$Q_2^* = (\Omega_{02}\Omega_{11} - \Omega_{01}\Omega_{12}) / (\Omega_{11}\Omega_{22} - \Omega_{12}\Omega_{21}). \quad (2.22)$$

Substitution of Eqs. (2.19) and (2.20) into Eq. (2.16) yields partial differential equations which when solved subject to experimentally imposed boundary conditions will yield composition w_1 and w_2 as a function of time and location,

$$\rho(\partial w_i / \partial t) = \sum_{j=1}^2 \{ \partial [\rho D_{ij}(\partial w_j / \partial z)] / \partial z \}; \quad i=1, 2. \quad (2.23)$$

Similarly, substitution of Eq. (2.18) into Eq. (2.17) yields the partial differential energy equation; its solution subject to experimental boundary conditions will provide the temperature time-location surface dependent upon values of Q_1^* and Q_2^* . Thus,

$$\rho \bar{C}_p (\partial T / \partial t) = \left\{ \partial \left[k(\partial T / \partial z) + \rho \sum_{i=1}^2 \sum_{j=1}^2 Q_{ij}^* D_{ij}(\partial w_i / \partial z) \right] / \partial z \right\} + \rho \sum_{i=1}^2 \sum_{j=1}^2 \hat{H}_{ij}^E D_{ij}(\partial w_i / \partial z)(\partial w_j / \partial z), \quad (2.24)$$

where

$$\hat{H}_{ij}^E = (\partial^2 \hat{H}^E / \partial w_j^2)_{T,P}; \quad j=1, 2, \quad (2.25)$$

and \hat{H}^E is excess specific enthalpy. The identity

$$[\partial(\bar{H}_j - \bar{H}_3) / \partial z] = \hat{H}_{jj}^E(\partial w_j / \partial z); \quad j=1, 2 \quad (2.26)$$

has been used to obtain Eq. (2.24).

Equations (2.23) and (2.24) constitute the equations of change for composition and temperature, solution of which provides the temperature response to diffusion in systems with nonuniform compositions. For composition and temperature dependent properties, Eqs. (2.23) and (2.24) are obviously coupled, nonlinear, and nonhomogeneous.

III. ANALYTICAL SOLUTION

To obtain heats of transport from diffusion thermoeffect temperature measurements, Eqs. (2.23) and (2.24) must be solved subject to appropriate initial and boundary conditions. The solution of the temperature equation can then be fit to measured temperature profiles using Q_1^* and Q_2^* as adjustable parameters. To maximize the temperature response, a cell with impermeable, adiabatic walls should be used. The experiment would be initiated by an isothermal, step-function, composition gradient at the center of the cell. This corresponds to the following initial and boundary conditions for the composition $w_1(z, t)$, $w_2(z, t)$ and temperature $T(z, t)$ distributions:

$$\begin{aligned} w_1(z < a/2, 0) &= w_{1L}, & w_2(z < a/2, 0) &= w_{2L}, \\ w_1(z > a/2, 0) &= w_{1U}, & w_2(z > a/2, 0) &= w_{2U}, \\ T(z, 0) &= T_0, \end{aligned} \quad (3.1)$$

$$\begin{aligned} (\partial w_1 / \partial z)_{0,t=0} &= (\partial w_1 / \partial z)_{a,t}, \\ (\partial w_2 / \partial z)_{0,t=0} &= (\partial w_2 / \partial z)_{a,t}, \\ (\partial T / \partial z)_{0,t=0} &= (\partial T / \partial z)_{a,t}, \end{aligned} \quad (3.2)$$

where z is the spatial variable in the upward direction and a is total cell height.

The solutions of Eqs. (2.23) and (2.24) subject to initial conditions (3.1) and boundary conditions (3.2) can be obtained using a double perturbation technique and Taylor's series expansions for the composition dependence of the thermophysical properties. The temperature dependence of the properties need not be considered here since Rowley and Horne's measurements⁸ of binary liquid mixture heats of transport indicate that the temperature response to initial conditions of Eqs. (3.1) in a cell with boundary conditions of Eqs. (3.2) is quite small. The perturbation method of solution is analogous to that used by Ingle and Horne⁷ and is adequately described by them. The only difference between their expansion technique and ours is that we have treated the cross diffusion terms (D_{ij} , $i \neq j$) as small perturbations to the main diffusion terms (D_{ii}). Thus, instead of a single perturbation a double is used for the composition equation. The composition equation can then be written as

$$\begin{aligned} \rho(\partial w_i / \partial t) &= [\partial \rho D_{ii}(\partial w_i / \partial z) / \partial z] \\ &+ \delta [\partial \rho D_{ij}(\partial w_j / \partial z) / \partial z]; \quad i \neq j, \end{aligned} \quad (3.3)$$

where δ is a bookkeeping device that decouples Eq. (2.23) but is set equal to unity in the final solution. The δ has the effect of shifting cross diffusion terms to a higher order than the straight terms in the perturbation so that they become a nonhomogeneous contribution to noncoupled parabolic type partial differential equations. All properties are expanded with respect to composition in a Taylor's series expansion about the mean composition using a similar bookkeeping symbol ϵ for the composition perturbation order. Linearization of these equations via this technique yields solutions which are rapidly diverging in length and complexity. A numerical solution to the problem is preferred for those situations in which the composition dependence of the properties is large or of major importance. The real benefit of the solution technique described here is when the zeroth or low order terms are to be used to model the main effects or when heats of transport are to be obtained in ternary mixtures for which the compositional dependence of the properties is small. Additionally, the zeroth order solution yields the predominant behavior of the phenomenon and higher order corrections can be evaluated if required. Thus, truncation effects to the simple analytical solution can be examined. This is much preferred to the constant property solution of the above equations, although it would be equivalent to the zeroth order in ϵ solution, because (1) the error in assuming constant properties could be computed and (2) the composition at which the properties are to be evaluated is known to be the mean composition about which the Taylor's series expansion was made.

The zeroth order solutions in both ϵ and δ of the composition equations labeled w_i^{00} are

$$w_i^{00} = [2(\Delta w_i)/\pi] \sum_{n=1}^{\infty} [(-1)^n/(2n-1)] \exp[-(2n-1)^2 t/\theta_{ii}] \times \cos[(2n-1)\pi z/a], \quad (3.4)$$

where $\Delta w_i = w_{iU} - w_{iL}$, and

$$\theta_{ii} = \frac{a^2}{\pi^2 D_{ii}}. \quad (3.5)$$

The composition equation which is zero order in ϵ and first order in δ is

$$(\partial w_i^{01}/\partial t) = D_{ii}(\partial^2 w_i^{01}/\partial z^2) + D_{ij}(\partial^2 w_j^{00}/\partial z^2); \quad i \neq j \quad (3.6)$$

the solution of which is

$$w_i^{01} = 2D_{ij}(\Delta w_j)\pi[\theta_{ii}\theta_{jj}/a^2(\theta_{ii} - \theta_{jj})] \sum_{n=1}^{\infty} [(-1)^{n-1}/(2n-1)] \times \{\exp[-(2n-1)^2 t/\theta_{ii}] - \exp[-(2n-1)^2 t/\theta_{jj}]\} \times \cos[(2n-1)\pi z/a]. \quad (3.7)$$

Higher order terms in δ can be computed with the final composition profile for zeroth order in ϵ given by

$$w_i^0 = w_i^{00} + w_i^{01} + w_i^{02} + \dots \quad (3.8)$$

Similar solutions for higher orders in ϵ can be obtained with the total composition profile given by

$$w_i = w_{iA} + w_i^0 + w_i^1 + w_i^2 + \dots, \quad (3.9)$$

where

$$w_{iA} = (w_{iU} + w_{iL})/2.$$

The number of terms to be kept depends upon the magnitude of the cross diffusion terms D_{ij} . In general, we expect the D_{ij} to be relatively small such that the δ perturbation can be truncated after either the zeroth or first order.

The temperature equation, zeroth order in ϵ , can now be solved by substitution of Eq. (3.8) into Eq. (2.24) to yield

$$T^0 = T^{00} + T^{01} + T^{02} + \dots \quad (3.10)$$

The total temperature profile is then given by

$$T = T_0 + T^0 + T^1 + T^2 + \dots \quad (3.11)$$

Obviously, the solution becomes extremely complex when the thermophysical properties have a large composition dependence (more terms in the ϵ expansion required) or when the cross diffusion coefficients are large (more terms in the δ expansion required). This method of solution would be highly impractical in such cases and a numerical method, which can be shown to agree with the above equations for appropriate systems, could be used. However, for the sake of determining the measurability of heats of transport in ternary systems and to provide an indication of the nature of the temperature response to compositional gradients, the analytical equations truncated to first order in δ and zeroth order in ϵ will be used here.

The zeroth order temperature solution T^{00} is given by

$$T^{00} = (2/a^2 \bar{C}_p) \sum_{i=1}^2 (Q_1^* D_{1i} + Q_2^* D_{2i}) [(\Delta w_i)/(\theta_{ii}^{-1} - \tau^{-1})] \sum_{l=1}^{\infty} F_{il} \cos[(2l-1)\pi z/a] + \sum_{i=1}^2 D_{ii} \hat{H}_{ii}^E (\Delta w_i)^2 \theta_{ii} \times \sum_{k=1}^{\infty} \left(G_{ik} + \tau H_{ik} \cos[2(2l-1)\pi z/a] + 2\tau \sum_{k=l+1}^{\infty} \{ I_{ikk} \cos[2(k-l)\pi z/a] + J_{ikk} \cos[2(k+l-1)\pi z/a] \} \right), \quad (3.12)$$

where F_{il} , G_{il} , H_{il} , I_{ikk} , and J_{ikk} are functions of time given by

$$F_{il} = \pi(-1)^l \{ \exp[-(2l-1)^2 t/\theta_{ii}] - \exp[-(2l-1)^2 t/\tau] \} / (2l-1),$$

$$G_{il} = \{ 1 - \exp[-2(2l-1)^2 t/\theta_{ii}] \} / [2(2l-1)^2],$$

$$H_{il} = \tau \{ \exp[-4(2l-1)^2 t/\tau] - \exp[-2(2l-1)^2 t/\theta_{ii}] \} / [2(2l-1)^2(2\theta_{ii} - \tau)],$$

$$I_{ikk} = (-1)^{k+l} \{ \exp[-[(2k-1)^2 + (2l-1)^2] t/\theta_{ii}] - \exp[-(2k-2l)t/\tau] \} / \{ (2k-2l)^2 \theta_{ii} - [(2l-1)^2 + (2k-1)^2] \tau \},$$

$$J_{ikk} = (-1)^{k+l} \{ \exp[-(2k+2l-2)^2 t/\tau] - \exp[-[(2l-1)^2 + (2k-1)^2] t/\theta_{ii}] \} / \{ (2k+2l-2)^2 \theta_{ii} - [(2l-1)^2 + (2k-1)^2] \tau \}, \quad (3.13)$$

and

$$\tau = \rho \bar{C}_p a^2 / \pi^2 k. \quad (3.14)$$

A longer expression is obtained for T^{01} which is not reproduced here. Due to the usually small magnitude of cross diffusion coefficients, the T^{01} is often insignificant. Here, we wish to determine only the general form of the temperature response to the diffusion thermoeffect and how measurements of heats of transport can best be made. Therefore, we use only the T^{00} solution though the T^{01} solution can be added to obtain better data reduction from experiment for those systems which exhibit large cross diffusional effects.

Measurements of heats of transport in binary mixtures⁸ agree with predictions⁷ that the temperature re-

sponse measured as a temperature difference between points equidistant from the initial diffusional interface provides accurate heat of transport data independent of the heat of mixing. This is experimentally important because it allows the sometimes fairly substantial heat of mixing term to be nulled out, allowing temperature differences due entirely to the heat of transport to be more accurately measured. This experimental convenience is due to the quadratic form of the composition spatial derivative which appears in the heat of mixing portion of Eq. (2.24) as opposed to the second derivative nature which appears in conjunction with the heat of transport. This renders the heat of mixing portion of T^{00} symmetric about $z = a/2$ while the heat of transport term is antisymmetric as can be seen in Eqs. (3.12) and (3.13). To provide information directly related to

TABLE I. Typical thermophysical properties and run conditions used in simulation of the diffusion thermoeffect in ternary mixtures.

Property	Value
ρ	$1.15 \times 10^3 \text{ kg/m}^3$
C_p	1.26 kJ/kg K
k	105 mW/m K
D_{11}	$1.5 \times 10^{-9} \text{ m}^2/\text{s}$
D_{22}	$1.5 \times 10^{-9} \text{ m}^2/\text{s}$
D_{12}	$5.0 \times 10^{-11} \text{ m}^2/\text{s}$
D_{21}	$5.0 \times 10^{-11} \text{ m}^2/\text{s}$
Q_1^*	-20 kJ/kg
Q_2^*	-10 kJ/kg
Δw_1	$+0.8$
Δw_2	-0.2
z'	0.0035 m
a	0.030 m

expected experimental temperature profiles, it therefore becomes more important to compute $\Delta T(z')$ values, where

$$\Delta T(z') = T(a/2 + z') - T(a/2 - z') \quad (3.15)$$

and $z' = |a/2 - z|$. As all of the properties in Eq. (3.12) are evaluated at the mean composition about which the perturbation expansion was made, the entire spatial dependence resides in the trigonometric functions. All of the heat of mixing type terms are seen to be symmetric about $z = a/2$ and will therefore cancel in Eq. (3.15) when the difference between symmetric points is taken to yield

$$\Delta T(z') = (4/a^2 \bar{C}_p) \sum_{i=1}^2 (Q_1^* D_{1i} + Q_2^* D_{2i}) [(\Delta w_i) / (\theta_{ii}^{-1} - \tau^{-1})] \times \sum_{l=1}^{\infty} (-1)^l F_{il} \sin[(2l-1)\pi z'/a]. \quad (3.16)$$

IV. DISCUSSION

Experimental measurement of heats of transport in ternary mixtures should be based on Eq. (3.16), temperature difference data measured as a function of time and distances from cell center. Calculated ΔT values can then be fit to experimental data by treating Q_i^* and

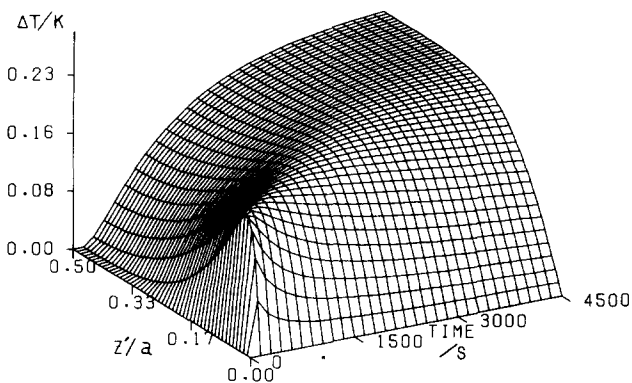


FIG. 1. Temperature difference ΔT response to the diffusion thermoeffect as a function of dimensionless distance of the thermocouples from the initial interface z'/a and time.

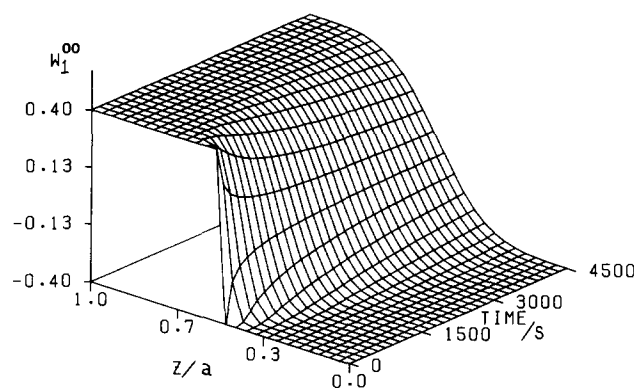


FIG. 2. Zeroth order solution in both ϵ and δ for the composition equation of component 1.

Q_2^* as adjustable parameters. It is instructive to plot the expected ΔT surface for the ternary diffusion thermo-effect experiment in order to examine the expected response behavior. This should aid experimental placement of thermocouples, optimization of data acquisition, proper loci and time conditions for probe placement and use, and the choice of experimental conditions for parameter estimation requirements. To do so requires representative estimates for the thermophysical properties which appear in Eq. (3.16). In the companion paper to this one, we report measurements of Q_1^* and Q_2^* in ternary mixtures of the toluene-chlorobenzene-bromobenzene system. Those measurements were based on the findings of this work and so the thermophysical properties of that system are used here in modeling Eq. (3.16). Values of the thermophysical properties characteristic of this system are shown in Table I. These are to be treated as data typical of nonelectrolyte liquid mixtures in order to model the magnitude and shape of the diffusion thermoeffect in ternary liquids. They also serve as a starting point from which individual properties can be varied one at a time in order to model the expected change in behavior of the diffusion thermoeffect due to the nature of the mixture's constituency. No composition dependence is required for the properties shown in Table I because all properties in the perturbation solution are evaluated at the mean composition about which the expansion was made. For the modeling done in this paper, Eqs. (3.8) and (3.10) were truncated after the first order in δ . Only zeroth order terms in ϵ were retained. Initial starting gradients were fixed at $\Delta w_1 = 0.8$ and $\Delta w_2 = -0.2$, respectively.

Figure 1 shows the three-dimensional $\Delta T(z', t)$ response typical of diffusion thermoeffect experiments performed in one-dimensional, adiabatic-boundary type cells with initial conditions given by Eq. (3.1). This plot was made from the evaluation of Eq. (3.16) using Table I values for the thermophysical properties. The corresponding composition plot for w_1^{00} is shown in Fig. 2. A similar result is obtained for w_2^{00} . Figure 2 is actually also a plot of the total deviation from w_{1A} since all terms of order $\delta > 0$ can be shown to be numerically negligible for this system. This is easily verified by plotting w_1^{01} as shown in Fig. 3. Note that w_1^{01} is nearly everywhere small with respect to w_1^{00} , the maximum contribution being on the order of only 0.2% right at the

center of the cell and at the initiation of the diffusional process.

From Figs. 1–3, it can be seen that the temperature response is initially quite large near the center of the cell ($z/a=0.5$). Conduction in both directions then tends to spread the temperature response toward the ends of the cell. Because the characteristic temperature relaxation time τ is so short relative to the diffusional relaxation times θ_{11} and θ_{22} , a balance (relative to compositional changes) between that portion of the heat flux due to heat transported by diffusing molecules and that due to conduction down the temperature gradient is soon set up. Thus, from Eq. (2.18), a balance of conducted and transported heat (at any one location) implies a “steady state” temperature profile as fixed by the local composition gradient

$$\begin{aligned} (\partial T/\partial z) = \rho[(Q_1^* D_{11} + Q_2^* D_{21})(\partial w_1/\partial z) \\ + (Q_1^* D_{12} + Q_2^* D_{22})(\partial w_2/\partial z)]/k. \end{aligned} \quad (4.1)$$

This steady state profile corresponds to the leveling off of ΔT following the occurrence of ΔT maxima in Fig. 1. It is not a steady state in every respect. It constitutes only a thermal steady state with respect to diffusional relaxation times because, as Figs. 2 and 3 show, $(\partial w_1/\partial z)$ and $(\partial w_2/\partial z)$ are slowly changing in time. Therefore, $(\partial T/\partial z)$ must also change in time in accord with Eq. (4.1). This corresponds to the slow ΔT decrease exhibited in Fig. 1 following the local maxima. Thus, on a thermal relaxation time scale, there exists a steady state, but on a diffusional time scale, the compositions are slowly changing, thereby giving a long time tail to the temperature decrease in accord with Eq. (4.1) and Eqs. (3.13) and (3.16). Since θ_{ii} is generally several times as large as τ , the difference in exponential terms shown in Eq. (3.13) reduces to simply the diffusional relaxation process (hence this thermal steady state is set up) and the long relaxation shown for ΔT in Fig. 1 results.

From Fig. 1 it appears that either the isochronal spatial or the isometric time dependent ΔT could be measured to obtain Q_1^* and Q_2^* . However, Eq. (3.16) clearly shows that the positional dependence of the measurements cannot be used entirely by itself to obtain both Q_1^* and Q_2^* . It does not, however, eliminate the possibility of determining both Q_1^* and Q_2^* from the time dependence.

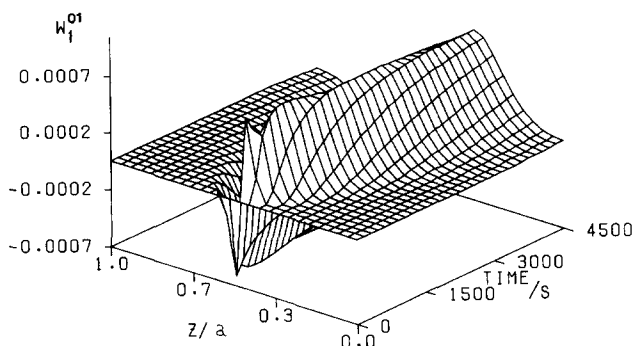


FIG. 3. First order in δ and zeroth order in ϵ solution for the composition equation of component 1.

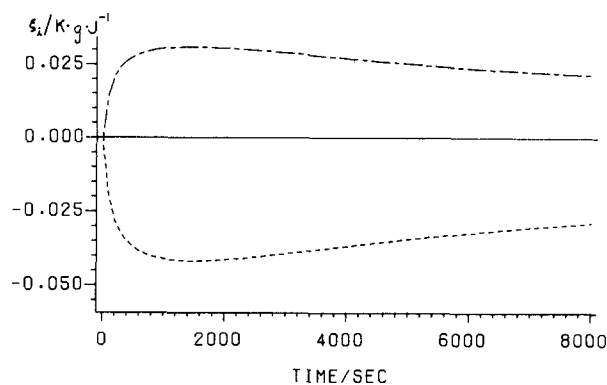


FIG. 4. Sensitivity coefficients $\xi_i = (\partial \Delta T / \partial Q_i^*) Q_i^*$ as a function of time for an initial composition difference of $\Delta w_1 = 0.8$ and $\Delta w_2 = -0.6$; ---, ξ_1 ; —, ξ_2 .

This is because the term dominated by $Q_1^* D_{11}$ contains the diffusional relaxation factor θ_{11} while the term dominated by $Q_2^* D_{22}$ contains θ_{22} . Unfortunately, when sensitivity coefficients are plotted, the two heats of transport appear to be quite hopelessly coupled and therefore unobtainable from the same experiment. This is illustrated in Fig. 4, where it can be seen that the sensitivity coefficient for Q_2^* is proportional to that for Q_1^* . Sensitivity analysis requires linear independence of sensitivity coefficients for simultaneous estimation of more than one parameter. Due to this coupling of Q_1^* and Q_2^* , two experiments at each mean composition must be performed in order to extract meaningful Q_1^* and Q_2^* data. Equation (3.16) indicates that two experiments performed at the same mean composition, but with different Δw_1 and Δw_2 values, effectively decouples Q_1^* and Q_2^* because the $Q_1^* D_{11} \Delta w_1$ term would then be distinct from the $Q_2^* D_{22} \Delta w_2$ term (D_{12} and D_{21} make the cross terms quite small). Both Q_1^* and Q_2^* could then be obtained from either t or z dependent data. The easiest measurement technique for the diffusion thermoeffect configuration is ΔT at a fixed z' as a function of t for two different starting compositional gradients.

In determining heats of transport from diffusion thermoeffect experiments, the experimentalist must try to maximize the measured ΔT response in order to maintain a large signal to noise level in the temperature measurements. The modeling shown here is based on reasonable estimates of Q_1^* and Q_2^* . It therefore appears that the magnitude of ΔT is large enough to realistically

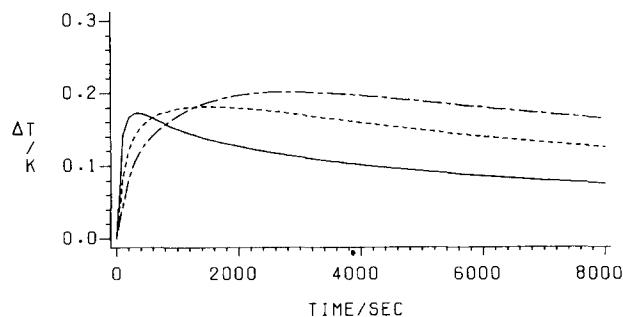


FIG. 5. Temperature difference ΔT time profiles for probes located at —, $z' = 0.07a$; ---, $z' = 0.12a$; - · -, $z' = 0.17a$.

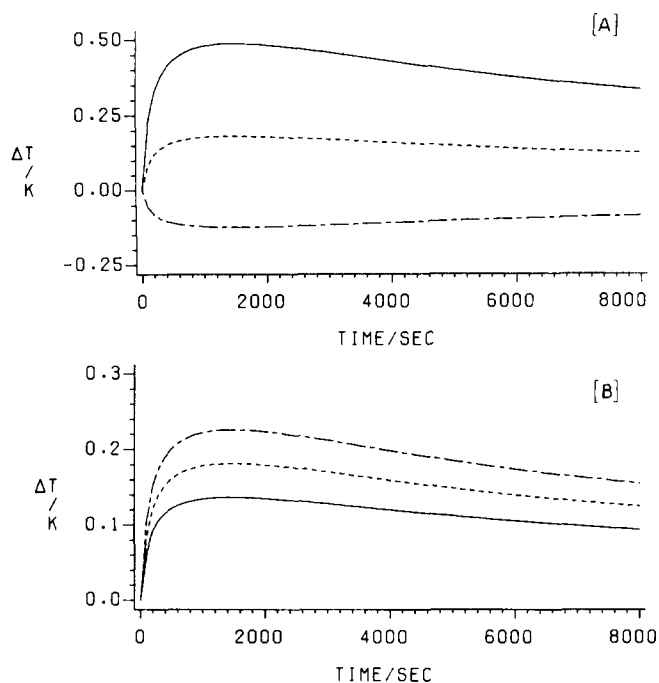


FIG. 6. Temperature difference ΔT time profiles for various values of Q_1^* : (A) —, $Q_1^* = -50$ J/g; ---, $Q_1^* = -20$ J/g; - - - , $Q_1^* = +10$ J/g; (B) —, $Q_2^* = -30$ J/g; ---, $Q_2^* = -10$ J/g; - - - , $Q_2^* = +10$ J/g.

obtain quite accurate heat of transport data provided $D_{11}Q_1^*$ and $D_{22}Q_2^*$ are not of equal magnitude and opposite sign. From the form of Eq. (3.16), experiments should be performed with as large of Δw_1 and Δw_2 as possible if Δw_1 , Δw_2 , Q_1^* , and Q_2^* all have the same sign. If Q_1^*

and Q_2^* have opposite signs while Δw_1 and Δw_2 have the same sign or if Q_1^* and Q_2^* have the same sign while Δw_1 and Δw_2 have opposite signs, then the magnitude of the measured ΔT , hence the accuracy of the heat of transport determinations, can be enhanced by starting with a large gradient for one component and a small gradient for the other.

The location at which experimental data should be taken can be seen from Fig. 5. Note that if the thermocouples are located too close to the interface, ΔT reaches a maximum fairly quickly in the experiment and then decays rapidly. If the thermocouples are placed too far from the interface there may not be sufficient ΔT vs t curvature to obtain reliable results for Q_1^* and Q_2^* . Location of thermocouples a distance of $0.06 < z'/a < 0.20$ should achieve optimum experimental results.

Figures 6 and 7 show the effect various thermo-physical properties have upon the measured temperature difference. These plots were obtained by fixing all properties at the values specified in Table I and varying the indicated property over a range expected to be consistent with actual liquid properties. Figure 6 shows that the value of Q_1^* and Q_2^* really affect only the magnitude of the measured temperature response; the shape remains the same. The sign and magnitude of the product $Q_i^*D_{ii}$ influences the direction of the transported heat flux.

The magnitude of the four independent diffusion coefficients affects both the magnitude and shape of the time-dependent ΔT profiles. Note that the cross diffusion terms do not greatly affect the profiles and that again the size of the effect depends not upon the relative sizes of the diffusion coefficients but upon $Q_i^*D_{ij}$. Like-

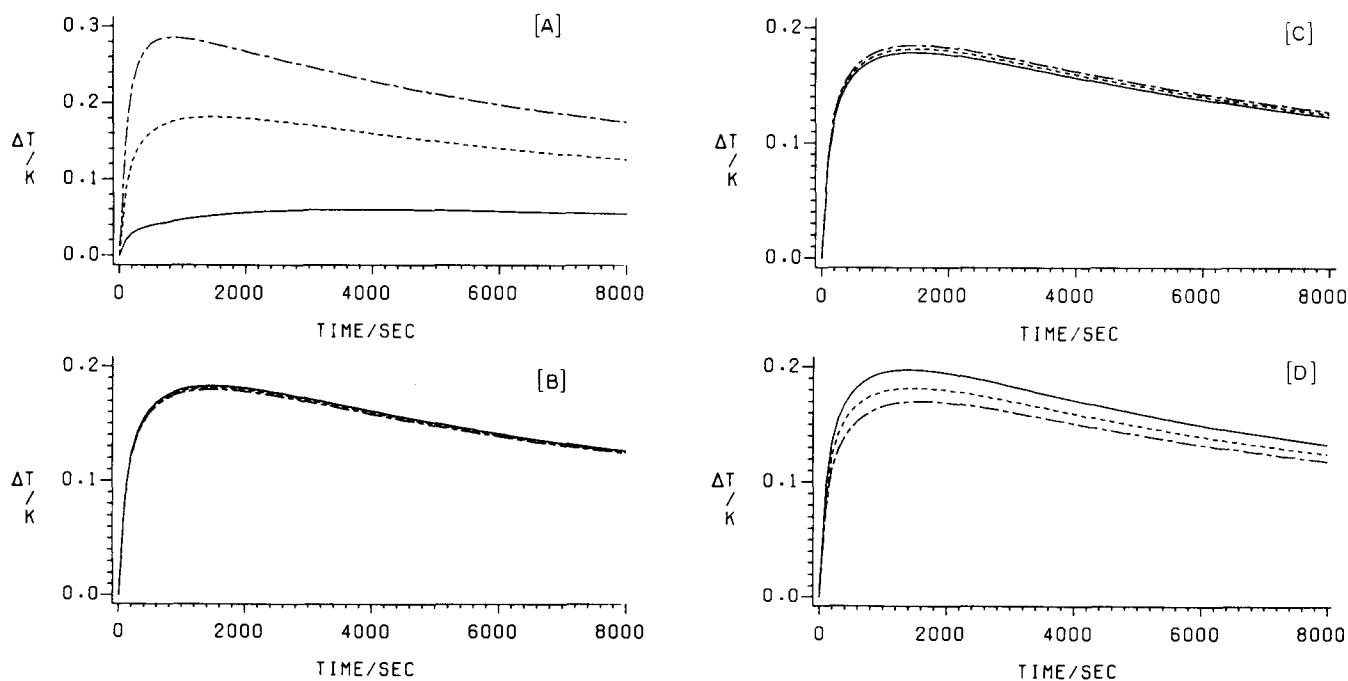


FIG. 7. Temperature difference ΔT time profiles for various values of the diffusion coefficients: (A) D_{11} : —, 5×10^{-10} m²/s; ---, 1.5×10^{-9} m²/s; - - - , 2.5×10^{-9} m²/s; (B) D_{12} : —, 5×10^{-12} m²/s; ---, 5×10^{-11} m²/s; - - - , 9.5×10^{-11} m²/s; (C) D_{21} : —, 5×10^{-12} m²/s; ---, 5×10^{-11} m²/s; - - - , 9.5×10^{-11} m²/s; (D) D_{22} : —, 5×10^{-10} m²/s; ---, 1.5×10^{-9} m²/s; - - - , 2.5×10^{-9} m²/s.

wise, the change in ΔT is more pronounced when D_{11} is doubled than when D_{22} is because of the respective magnitudes of Q_1^* and Q_2^* .

V. CONCLUSIONS

The composition and temperature equations for the multicomponent diffusion thermoeffect have been formulated. Heats of transport in multicomponent systems have been defined in terms of the flux-force Onsager coefficients. In particular, there are $n - 1$ independent heats of transport in an n component system. The composition and temperature equations have been solved for the three component case subject to boundary and initial conditions designed (1) to maximize the temperature response and (2) to be physically applicable to an appropriate experimental setup for measurement of heats of transport. Solution of the ternary equations were obtained using a double perturbation technique followed by a double transform (finite cosine and Laplace) technique. Though the terms in the expansion rapidly become complex, the predominate zero order terms (or first order in δ) can be used to obtain meaningful experimental design and optimization criteria in addition to a qualitative feel for the phenomenon itself.

The diffusion thermoeffect in ternary liquid mixtures should indeed be measurable if careful techniques guided by the simulations presented here are used. The temperature response from the diffusional process is not unmeasurably small as some have supposed.¹³ The effect can be used to obtain for the first time measurements of Q_1^* and Q_2^* in ternary mixtures. To do so, two experiments with different initial composition gradients must be performed at the same average composition in order to significantly decouple the two parameters. To maximize the effect, an adiabatic cell should be used with temperature probes placed symmetric about the initial interface to eliminate the symmetric background heat of mixing. In so doing, a temperature difference could then be monitored as a function of time, preferably at locations a distance of $0.06 < z'/a < 0.20$.

In the accompanying paper, we present the experimental investigation and results obtained for the diffusion thermoeffect in toluene-chlorobenzene-bromobenzene ternary mixtures. These measurements were based upon the findings and implications of this work.

ACKNOWLEDGMENT

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