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Prediction of Thermal Diffusion in Binary Mixtures of Nonelectrolyte Liquids by the Use of Nonequilibrium Thermodynamics[1]

A. G. Guy[2]

A derivation based on nonequilibrium thermodynamic leads to this expression for the thermal diffusion factor, $\alpha_T = M_2(h_2^{xs} - h_1^{xs})/RT\phi_2$, where M_2 is the molecular weight of the lighter of the two components, h_i^{xs} is the partial excess enthalpy of component i, J/g, R is 8.314 $J \cdot K^{-1} \cdot \mathrm{mol}^{-1}$, T is temperature in K, and ϕ_2 is the thermodynamic correction factor $(1 + d \ln \gamma_2 / d \ln X_2)$, where γ_2 is an activity coefficient and X_2 is the mole fraction. The correctness of this theoretical prediction is verified for the liquid system ethanol–water at 298 K.

KEY WORDS: binary mixture; diffusion; liquids; nonelectrolyte liquids; nonequilibrium thermodynamics; thermal diffusion; thermodynamics.

1. INTRODUCTION

For rate processes (such as diffusion), phenomenological thermodynamics is presently viewed [1] as serving mrely "... to lend credence to the kinetic results ..." and as furnishing far less information than do kinetic theoretical approaches. The present analysis of thermal diffusion demonstrates, on the contrary, that thermodynamics can produce a quantitative description of certain phenomena that have not been successfuly analyzed by mechanistic approaches.

Although thermal diffusion has been studied experimentally in solids, liquids, and gases, in the particular case of liquid mixtures, the theory [2] is often unable to predict even the *direction* of thermal diffusion. In con-

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[2] Department of Physics and Space Sciences, Florida Institute of Technology, Melbourne, Florida 32901, U.S.A.

trast, the thermodynamic analysis presented here gives quantitative agreement with experimental data for the interesting liquid system ethanol–water.

The present analysis for nonelectrolyte liquids has three essential features: (i) use of the procedures of nonequilibrium thermodynamics [3]; (ii) identification of the partial excess enthalpy, h_i^{xs}, of component i as the basic cause of thermal diffusion; and (iii) manipulation of diffusion fluxes relative to reference systems. Feature iii, which results in rather complex mathematical expressions, is discussed below.

The enthalpy enters into the formalism of nonequilibrium thermodynamics when the thermodynamic relation [4]

$$\frac{Td(\mu_i/T)}{dx}=\left(\frac{d\mu_i}{dx}\right)_T-\frac{h_i^{xs}}{T}\frac{dT}{dx} \tag{1}$$

is employed to permit the use of the usual, isothermal values of the specific chemical potential, μ_i, of component i. If, as in the present case, the process in question involves only mixing (or unmixing) of the components of a solution, enthalpy is the excess quantity h_i^{xs} [5]. The use of lowercase h for enthalpy indicates that the specific value (per gram) is employed rather than the more common value per gram-mole, H.

Adequate analysis of ordinary diffusion or thermal diffusion in a liquid requires two reference systems; the center-of-mass (barycentric) reference system for the theoretical analysis and the molecular reference system (or equivalent) for interpretation of the experimental data. These reference systems are described in the literature [6], and procedures are available for converting diffusional fluxes from one system to another. The reference system (such as the molecular system) chosen for analysis of experimental data is selected to permit accurate evaluation of the particular experiment in question. Generally the center-of-mass system is impractical for this purpose. On the other hand, as described more fully in Section 2, use of the molecular system would hamper the basic theoretical analysis. Consequently, although conversion between two reference systems complicates the present treatment, there is no practical alternative.

2. DERIVATION OF AN EXPRESSION FOR THE L_{iq} COEFFICIENTS

The basic derivations of nonequilibrium thermodynamics [7] involve balances of quantities such as mass, momentum, and energy. Therefore, the center-of-mass reference system is the logical choice, and its use avoids many complications that would be introduced if one of the more common reference systems (e.g., molecular) were employed. Consequently, this section develops equations for use with the center-of-mass system, and Section 3 then obtains useful connections with the molecular reference system.

The present analysis begins by using Eq. (1) to transform from $d\mu_i/dx$ to $(d\mu_i/dx)_T$ and identifying h_i^{xs} as the experimentally measured thermodynamic quantity. As is customary in treatments of diffusion, the molecule with the larger molecular weight is denoted component 1. With this notation a positive value of D_T corresponds (in most cases) to enrichment of component 2 in the high-temperature region. Because the particles of a nonelectrolyte liquid are uncharged, the electrochemical potential need not be used but can be replaced by the chemical potential. The basic phenomenological equations [8] can then be written in the form [omitting the subscript T on $(d\mu_i/dx)_T$ for simplicity],

$$J_1 = -\frac{L_{11}}{T}\frac{d\mu_1}{dx} - \frac{L_{12}}{T}\frac{d\mu_2}{dx} - \frac{L_{1q}}{T^2}\frac{dT}{dx} \tag{2}$$

$$J_2 = -\frac{L_{21}}{T}\frac{d\mu_1}{dx} - \frac{L_{22}}{T}\frac{d\mu_2}{dx} - \frac{L_{2q}}{T^2}\frac{dT}{dx} \tag{3}$$

$$J_q' = J_q - h_1^{\mathrm{xs}} J_1 - h_2^{\mathrm{xs}} J_2 = -\frac{L_{q1}}{T}\frac{d\mu_1}{dx} - \frac{L_{q2}}{T}\frac{d\mu_2}{dx} - \frac{L_{qq}}{T^2}\frac{dT}{dx} \tag{4}$$

Here L_{ij} are phenomenological coefficients, J_i is the flux of component i, and J_q is the flux of heat as usually defined and as measured experimentally. The quantity J_q' is often termed the "reduced heat flux." Physically it is the usual sum of lattice and electronic contributions minus the enthalpy carried by the particles that constitutes the net flux. The units of μ_i and h_i^{xs} are $\mathrm{J \cdot g^{-1}}$ and those of J_i are $\mathrm{g \cdot m^{-2} \cdot s^{-1}}$. In the center-of-mass system [9] $J_1 + J_2 = 0$, so the dependent flux can be eliminated by the use of the equation,

$$J_1 = -J_2 \tag{5}$$

This relation is valid for both ordinary diffusion and thermal diffusion.

Because the phenomenological coefficients L_{1q} and L_{2q} are cofficients of the "driving force" dT/dx, they play an important role in a process of thermal diffusion. A useful expression for these coefficients in terms of h_1^{xs} and h_2^{xs} is now obtained by the following analysis of a process of *isothermal* diffusion. Because both dT/dx and J_q are zero, and in view of Eq. (5) and the Gibbs–Duham equation [10],

$$\frac{d\mu_1}{dx} = -\frac{X_2 d\mu_2}{X_1\, dx} \tag{6}$$

Equations (2) and (3) can be written

$$J_2 = -\frac{1}{T}\left(L_{22} - \frac{X_2}{X_1}L_{21}\right)\frac{d\mu_2}{dx} \tag{7}$$

$$-(h_2^{\text{xs}} - h_1^{\text{xs}})J_2 = -\frac{1}{T}\left(L_{q2} - \frac{X_2}{X_1}L_{q1}\right)\frac{d\mu_2}{dx} \tag{8}$$

When the expression for J_2 from Eq. (7) is substituted in Eq. (8), the result is

$$L_{q2} - \frac{X_2}{X_1}L_{q1} = -(h_2^{\text{xs}} - h_1^{\text{xs}})\left(L_{22} - \frac{X_2}{X_1}L_{21}\right) \tag{9}$$

In view of the Onsager relations, $L_{1q} = L_{q1}$ and $L_{2q} = L_{q2}$, Eq. (9) is a step toward the desired evaluation of the L_{iq} coefficients in Eqs. (2) and (3).

Although Eq. (9) was derived for the condition $dT/dx = 0$, it can be employed in the presence of a temperature gradient, because in the usual formulation of nonequilibrium thermodynamics the phenomenological coefficients are not functions of the driving forces.

For the purpose of eliminating L_{q1} and L_{q2} from Eq. (9), one can form the sum $J_2 - (X_2/X_1)J_1$. When this sum is written using Eqs. (2) and (3), the result is

$$J_2 - \frac{X_2}{X_1}J_1 = -\frac{1}{T}\left(L_{21} - \frac{X_2}{X_1}L_{11}\right)\frac{d\mu_1}{dx} - \frac{1}{T}\left(L_{22} - \frac{X_2}{X_1}L_{12}\right)\frac{d\mu_2}{dx}$$
$$-\frac{1}{T^2}\left(L_{2q} - \frac{X_2}{X_1}L_{1q}\right)\frac{dT}{dx} \tag{10}$$

Equation (9) can now be substituted for the factor in parentheses in the last term. As before, J_1 can be eliminated by means of Eq. (5) and $d\mu_1/dx$ by Eq. (6). With these substitutions Eq. (10) becomes

$$J_2\left(1 + \frac{X_2}{X_1}\right) = -\frac{1}{T}\left[\left(L_{22} - \frac{X_2}{X_1}L_{12}\right) - \frac{X_2}{X_1}\left(L_{21} - \frac{X_2}{X_1}L_{11}\right)\right]\frac{d\mu_2}{dx}$$
$$+\frac{1}{T^2}(h_2^{\text{xs}} - h_1^{\text{xs}})\left(L_{22} - \frac{X_2}{X_1}L_{21}\right)\frac{dT}{dx} \tag{11}$$

Although J_2 is a flux relative to the experimentally inconvenient center-of-mass reference system, the following interesting conclusion can be drawn from Eq. (11). Thermal diffusion will not occur if the factor $(h_2^{\text{xs}} - h_1^{\text{xs}})$ is zero for either of two reasons. First, this condition could exist (theoretically) for an ideal solution, since both h_1^{xs} and h_2^{xs} would then be zero. Second, a technically important cause of zero thermal diffusion is equality of h_1^{xs} and h_2^{xs}. An example of this condition is discussed in Section 4, where the analogue of Eq. (11) is evaluated quantitatively for the ethanol–water liquid system and is shown to give agreement with experimental data.

3. INCORPORATION OF THE DIFFUSION COEFFICIENT INTO THE ANALYSIS

In this section the coefficients L_{ij} are evaluated in terms of the experimentally determined diffusion coefficient for the binary solution being considered. The coefficient, D, in question can be determined in a process of ordinary (isothermal) diffusion, by use of the molecular reference system [11] for which

$$_uJ_2 = -\frac{D}{\bar{V}}\frac{dX_2}{dx} \tag{12}$$

where $_uJ_2$ is the diffusion flux in $\mathrm{mol \cdot m^{-2} \cdot s^{-1}}$ referred to the molecular reference system and $\bar{V}$ is the molar volume. The symbol D_{12} is often used in place of D in the literature to emphasize the fact that this coefficient measures interdiffusion of both component 1 and component 2. The same coefficient describes the diffusion flux J_2 relative to the center-of-mass reference system, provided the following equation is employed [12]:

$$\frac{J_2}{M_2} = -\frac{M_1\rho D}{(M_1X_1 + M_2X_2)^2}\frac{dX_2}{dx} = -\frac{M_1 D}{\bar{V}(M_1X_1 + M_2X_2)}\frac{dX_2}{dx} \tag{13}$$

Here ρ is the density, $\mathrm{g \cdot m^{-3}}$, which can be expressed as $(M_1X_1 + M_2X_2)/\bar{V}$.

The definition of the molar chemical potential μ_i' is [13]

$$\mu_i' = {}^0\mu_i' + RT \ln \gamma_i X_i \tag{14}$$

where ${}^0\mu_i'$ is a convenient reference value, R is the gas constant, and γ_i is an experimentally determined activity coefficient. Consequently, the specific chemical potential of component 2 is

$$\mu_2 = \frac{\mu_2'}{M_2} = \frac{{}^0\mu_2'}{M_2} + \frac{RT}{M_2}\ln \gamma_2 X_2 \tag{15}$$

and therefore,

$$\frac{d\mu_2}{dx}=\frac{RT\Phi_2}{M_2X_2}\frac{dX_2}{dx} \tag{16}$$

where

$$\Phi_2=1+\frac{d\ln\gamma_2}{d\ln X_2} \tag{17}$$

When Eq. (16) is substituted in Eq. (7), the resulting expression can be equated to Eq. (13) to obtain the following equation for D:

$$D=R\bar{V}\phi_2\left(L_{22}-\frac{X_2}{X_1}L_{21}\right)\frac{(M_1X_1+M_2X_2)}{M_1M_2^2X_2} \tag{18}$$

The corresponding relation involving the other pair of coefficients, $L_{12}-(X_2/X_1)L_{11}$, can be obtained in the following manner. The analogue of Eq. (7) for component 1 is

$$J_1=-\frac{1}{T}\left(L_{12}-\frac{X_2}{X_1}L_{11}\right)\frac{d\mu_2}{dx} \tag{19}$$

When the expressions of Eqs. (7) and (19) are substituted in Eq. (5), the following useful result is obtained:

$$L_{12}-\frac{X_2}{X_1}L_{11}=-L \tag{20}$$

For convenience the symbol L is used to represent the quantity,

$$L=L_{22}-\frac{X_2}{X_1}L_{21}=\frac{M_1M_2^2X_2D}{R\bar{V}\Phi_2(M_1X_1+M_2X_2)} \tag{21}$$

where the final expression is obtained from Eq. (18).

Although Eq. (18) and the other relations given above have been derived for isothermal diffusion, they are also valid (as explained in Section 2) when a temperature gradient is present. When Eq. (11) is written in terms of L, the result is

$$J_2\left(1+\frac{X_2}{X_1}\right)=-\frac{L}{T}\left[\left(1+\frac{X_2}{X_1}\right)\frac{d\mu_2}{dx}-\frac{(h_2^{\mathrm{xs}}-h_1^{\mathrm{xs}})}{T}\frac{dT}{dx}\right] \tag{22}$$

Experimental studies of thermal diffusion usually employ a flux ${}_uJ_2$ relative to the molecular reference system. For the purpose of obtaining an expression for D_T, however, Eq. (22) can be employed since the analysis is for the steady-state condition for which $J_2 = 0 = {}_uJ_2$.

The equation employed to define D_T is [14]

$$ {}_uJ_2 = -\frac{1}{\bar{V}}\left[D\frac{dX_2}{dx} - \frac{D_T}{T}\frac{dT}{dx}\right] = -\frac{D}{T\bar{V}}\left[T\frac{dX_2}{dx} - \frac{D_T}{D}\frac{dT}{dx}\right] \tag{23} $$

The ratio $k_T = D_T/D$ is known as the thermal diffusion ratio, but a more widely employed experimental measure of thermal diffusion is the thermal difusion factor, α_T, defined as

$$ \alpha_T = \frac{D_T}{DX_1X_2} \tag{24} $$

The expression for α_T in terms of the h_i^{xs} will now be obtained by comparison of the expressions within the brackets in Eqs. (22) and (23) for the steady-state condition.

Equation (23) yields the expression

$$ \frac{D_T}{D} = \frac{T(dX_2/dx)}{dT/dx} \tag{25} $$

When Eq. (16) is substituted in Eq. (22), the result can be rearranged into the form

$$ \frac{M_2(h_2^{xs} - h_1^{xs})}{RT\phi_2(1/X_2 + 1/X_1)} = \frac{T(dX_2/dx)}{dT/dx} \tag{26} $$

Comparison of Eqs. (25) and (26) leads to the desired expression for α_T in terms of the h_i^{xs},

$$ \alpha_T = \frac{M_2(h_2^{xs} - h_1^{xs})}{RT\phi_2} \tag{27} $$

The excess enthalpies, h_i^{xs}, are the crucial quantities determining the thermal diffusion behavior of a given mixture. The experimental determination of h_i^{xs} is distinctly different for a liquid solution than for a mixture of two gases. Section 4 is an illustration of the use of Eq. (27) for a binary liquid solution. A corresponding treatment of a gaseous mixture will be the subject of a future paper.

4. APPLICATION TO BINARY-LIQUID SOLUTIONS

The system ethanol–water [15] shows interesting thermal-diffusion behavior at 298 K (Fig. 1), since α_T has a lowest value at $X_2 = 0.5$ and

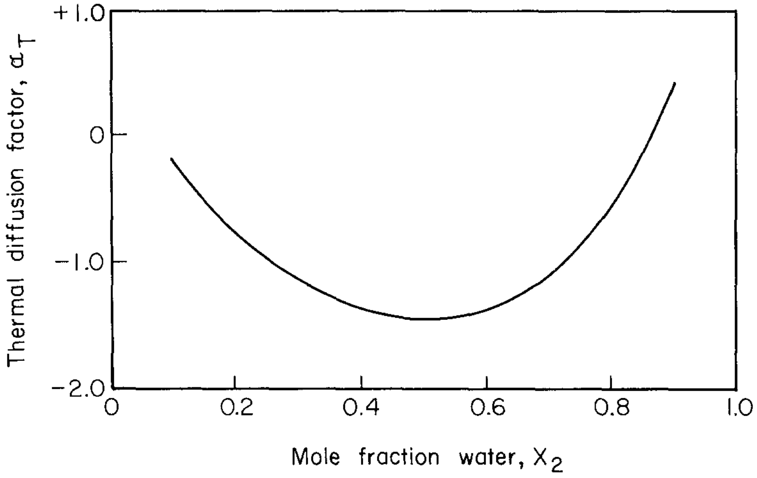

Fig. 1. Thermal diffusion factor α_T for the ethanol–water system at 298 K.

changes sign near $X_2 = 0.9$. Extensive data [16] exist on molar excess enthalpy as a function of composition (Fig. 2). Near the minimum on the curve in Fig. 2, a tangent can be drawn to satisfy the condition $h_2^{xs} = h_1^{xs}$ that yields $\alpha_T = 0$. The tangent shown leads to the values,

$$h_2^{xs} = \frac{H_2^{xs}}{M_2} = \frac{-625}{18.02} = -34.7\ \mathrm{J \cdot g^{-1}} \tag{28}$$

$$h_1^{xs} = \frac{H_1^{xs}}{M_1} = \frac{-1598}{46.07} = -34.7\ \mathrm{J \cdot g^{-1}} \tag{29}$$

The lowest value of α_T occurs at the point (near $X_2 = 0.5$) where the tangent has the steepest negative slope. The partial excess enthalpies in this case are

$$h_2^{xs} = \frac{-860}{18.02} = -47.7 \tag{30}$$

$$h_1^{xs} = \frac{+50}{46.07} = +1.1 \tag{31}$$

The thermodynamic factor for $X_2 = 0.5$ in this system [17] is about $\phi_2 = 0.25$; therefore Eq. (27) gives for α_T,

$$\alpha_T = \frac{18.02(-47.7 - 1.1)}{8.314 \times 298 \times 0.25} = -1.4 \tag{32}$$

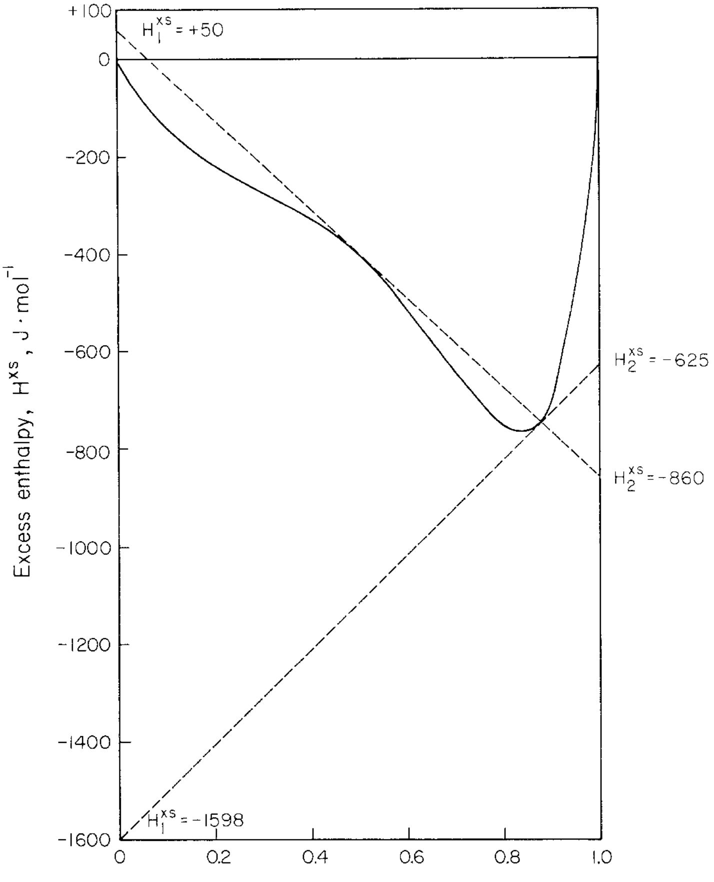

Fig. 2. Molar excess enthalpy for the ethanol–water system at 298 K. Tangents to the curve at $X_2 \simeq 0.5$ and $X_2 \simeq 0.9$ determine the partial molar excess enthalpies.

This excellent agreement of calculated and experimental values of α_T supports the view that the theoretical expression given by Eq. (27) applies for nonelectrolyte liquids.

5. DISCUSSION

The great potential of nonequilibrium thermoynamics, especially for treating steady-state processes, has been recognized for almost 50 years [3]. The essential feature of the present analysis that has resulted in a quantitative thermodynamic prediction of the process of thermal diffusion is the incorporation of Eq. (1) in the analysis. The model for the derivation of the L_{iq} coefficients in Section 2 is the analogous relation between L_{eq} and h_e in the case of conduction electrons (component e) undergoing thermal diffusion in a metal, a process that leads to the Seebeck effect [18]. The analogy is incomplete, however, because the electrochemical potential must be employed since the electrons carry a net charge.

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