Elementary transition state theory of the Soret and Dufour effects

(Onsager reciprocal relationship/ideal mixtures/temperature dependence of thermal diffusion factor)

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ABSTRACT   The elementary transition state approach has been used to obtain a simple model theory for the Soret effect (thermal diffusion) and the Dufour effect. The flow of heat in the Dufour effect is identified as the transport of the enthalpy change of activation as molecules diffuse. The theory as now formulated applies only to thermodynamically ideal mixtures of substances with molecules of nearly equal size. The results of the theory conform to the Onsager reciprocal relationship. When the results were fit to data on thermal diffusion for two liquid systems, a close fit was obtained and yielded reasonable values of between 2 and 3 kcal mol⁻¹ for enthalpy changes of activation and differences between the entropy changes of activation for the two components of between 0 and 1 cal K⁻¹ mol⁻¹.

The Soret effect (thermal diffusion) is the occurrence of a diffusion flux due to a temperature gradient. The Dufour effect is the reciprocal phenomenon, the occurrence of a heat flux due to a chemical potential gradient. Both effects have been extensively studied in gases, and the Soret effect has been studied both theoretically and experimentally in liquids. However, partly because of the smallness of the effect, accurate measurements of the Dufour effect in liquids have only recently been carried out (1). There does not seem to be a model theory of the liquid-state Dufour effect in the literature.

This paper presents a simple model theory for both effects in liquids, based on elementary transition state theory. The liquid is represented by a somewhat disordered quasi-lattice model in which a molecule can move from one equilibrium position to another, passing through a transition state of high potential energy. This beginning point has been used in previous theories of the Soret effect (2, 3).

The Soret effect

Consider a liquid two-component mixture that is uniform in the y and z directions but has a temperature and composition that depend on x and t, the time. Denote two adjacent equilibrium molecular positions by a and b, and assume that the two components are similar enough that these positions can be occupied by molecules of component 1 or component 2. Let x_a be the value of the x coordinate at site a and x_b (presumed larger than x_a) be the value of x at site b. Let the jump distance, λ, be given by

$$\lambda = x_b - x_a \qquad [1]$$

and assume that this distance is equal for all pairs of adjacent sites. The temperature at x_a is denoted by T_a, and the concentration of component 1 at x_a is denoted by c_{1a}, with similar definitions for T_b, c_{2a}, c_{1b}, and c_{2b}.

Assume that midway between site a and site b there is a position of high potential energy through which a molecule must pass in jumping from site a to site b or vice versa. The temperature at this position is denoted by T_m, and we can write

$$x_m - x_a = x_b - x_m = \lambda/2. \qquad [2]$$

In the elementary transition state theory of isothermal diffusion, the probability per unit time that a molecule of component i makes a transition from one equilibrium site to the next is given by

$$p_i = \mathcal{K} \frac{k_B T}{h} \exp(-\Delta G_i^\ddagger/RT) \quad (i = 1, 2) \qquad [3]$$

in which $\mathcal{K}$ is called the transmission coefficient, k_B is Boltzmann's constant, h is Planck's constant, R is the gas constant, and $\Delta G_i^\ddagger$ is the standard state molal Gibbs free energy change for the activation process, in which the molecule moves from the initial to the transition state of high potential energy between the initial and final states.

We must treat the nonisothermal case, so we assume that Eq. 3 is replaced for motion from site a to site b by

$$p_{ia} = \mathcal{K} \frac{k_B T_m}{h} \exp(-\Delta G_{ia}^\ddagger/RT_a) \qquad [4]$$

in which $\Delta G_{ia}^\ddagger$ is that value of the activation free energy change pertaining to temperature T_a. The motivation for this assumption is that the pre-exponential factor is derived from the partition function for motion through the transition state and should therefore contain T_m and not T_a, whereas the exponential factor is derived from the equilibrium constant for molecules moving from their initial state at temperature T_a.

We restrict our discussion to the case of small deviations from equilibrium (the linear case) and expand Eq. 4 in a Taylor series, truncating the expression at the linear term.

$$p_{ia} = p_{im} + (\partial p_{ia}/\partial T_a)_{T_a = T_m}(\partial T_a/\partial x_a)_{x_a = x_m}(x_a - x_m). \qquad [5]$$

We assume the pressure to be constant, and we apply a thermodynamic identity.

$$p_{ia} = p_{im} + p_{im}\left[-\frac{1}{R}\left(\frac{\partial(\Delta G_i^\ddagger/T)}{\partial T}\right)_P\left(\frac{\partial T}{\partial x}\right)\left(\frac{-\lambda}{2}\right)\right] \qquad [6a]$$

$$= p_{im}\left[1 - \frac{\lambda}{2}\frac{\Delta H_i^\ddagger}{RT^2}\left(\frac{\partial T}{\partial x}\right)\right] \quad (i = 1, 2). \qquad [6b]$$

The corresponding equation for motion from site b to site a is

$$p_{ib} = p_{im}\left[1 + \frac{\lambda}{2}\frac{\Delta H_i^\ddagger}{RT^2}\left(\frac{\partial T}{\partial x}\right)\right] \quad (i = 1, 2). \qquad [7]$$

The difference in sign between the two equations is due to the difference in sign between $x_a - x_m$ and $x_b - x_m$. In both equations, all quantities are to be evaluated at $x = x_m$.

The net diffusion flux of component i, in moles per unit area per unit time, in the coordinate frame, which is stationary with respect to the local quasi-lattice, is given by

$$J_{ix} = \lambda c_{ia} p_{ia} - \lambda c_{ib} p_{ib} \qquad [8]$$

in which the concentrations are measured in moles per unit volume. We expand c_{ib} in a Taylor series about x_a, truncating the series again at the linear term.

$$c_{ib} = c_{ia} + (\partial c_{ib}/\partial x_b)_{x_b = x_a}(x_b - x_a)$$

$$= c_{ia} + \lambda(\partial c_i/\partial x). \qquad [9]$$

Eqs. 6, 7, and 9 are substituted into Eq. 8, and only linear terms are kept. The result is

$$J_{ix} = -\lambda^2 p_i(\partial c_i/\partial x) - c_i p_i \lambda^2 \frac{\Delta H_i^\ddagger}{RT^2}(\partial T/\partial x). \qquad [10]$$

Note that subscripts specifying location are no longer necessary. The mean velocity of molecules of species i is in the x direction and is given by

$$\bar{v}_{ix} = J_{ix}/c_i = -\frac{\lambda^2 p_i}{c_i}\left(\frac{\partial c_i}{\partial x}\right) - \lambda^2 p_i \frac{\Delta H_i^\ddagger}{RT^2}\left(\frac{\partial T}{\partial x}\right). \qquad [11]$$

In order to determine the formulas which our model theory implies for the diffusion coefficient and the thermal diffusion coefficient, we compare our results with the macroscopic equation (4)

$$\bar{v}_1 - \bar{v}_2 = -\frac{c^2}{c_1 c_2}\mathcal{D}_{12}[\nabla X_1 + k_T \nabla(\ln T)]. \qquad [12]$$

In this equation, $\mathcal{D}_{12}$ is called the mutual diffusion coefficient and k_T is called the thermal diffusion ratio. The total concentration is denoted by c and given by

$$c = c_1 + c_2. \qquad [13]$$

The mole fraction of component 1 is denoted by X_1. Unfortunately there is a bewildering variety of equations and symbols used in the phenomenology of diffusion and thermal diffusion. We choose to compare with Eq. 12 because it is not restricted to a particular coordinate system.

We now assume that the partial molal volumes of our two components are nearly equal and that the thermal expansion of the liquid can be neglected. In this case,

$$(\partial c_1/\partial x) \approx c(\partial X_1/\partial x) = -c(\partial X_2/\partial x) \qquad [14]$$

and we can write from Eq. 11

$$\bar{v}_{1x} - \bar{v}_{2x} = -\lambda^2(p_1/X_1 + p_2/X_2)(\partial X_1/\partial x)$$

$$- \lambda^2\left(p_1 \frac{\Delta H_1^\ddagger}{RT} - p_2 \frac{\Delta H_2^\ddagger}{RT}\right)(\partial \ln T/\partial x). \qquad [15]$$

Comparison with Eq. 13 shows that

$$\mathcal{D}_{12} = \lambda^2(p_1 X_2 + p_2 X_1) \qquad [16]$$

and

$$\frac{c^2}{c_1 c_2}\mathcal{D}_{12}\, k_T = \lambda^2\left(p_1 \frac{\Delta H_1^\ddagger}{RT} - p_2 \frac{\Delta H_2^\ddagger}{RT}\right). \qquad [17]$$

Eq. 17 is the result for our elementary theory of the Soret effect. It resembles earlier results (5–7).

The Dufour effect

We proceed to write, for the heat flux, an expression analogous to Eq. 10 for the diffusion flux. We assume that the heat flux consists of a vibrational (phonon) contribution and a contribution due to particle motion (8, 9).

$$J_q' = J_q'(\text{phonon}) + J_q'(\text{particle}) \qquad [18]$$

To describe the Dufour effect, we seek a contribution to the heat flux that is proportional to a concentration gradient. Such a term will not occur in $J_q'(\text{phonon})$, so we focus our attention on $J_q'(\text{particle})$.

The crucial assumption which we now make is that, when a particle jumps from one equilibrium position to another, it carries with it not only the enthalpy that it had in its initial position but also the enthalpy of activation that it had to acquire to make the passage through the transition state. This idea was mentioned in earlier works on thermal diffusion but was not exploited to discuss the Dufour effect (3, 6, 7).

We first write the particle contribution to the enthalpy flux:

$$J_{qx}(\text{particle}) = \lambda \sum_{i=1}^{2}(c_{ia} p_{ia} H_{im} - c_{ib} p_{ib} H_{im}) \qquad [19]$$

in which H_{im} is the molal enthalpy of molecules of component i in the transition state, including the enthalpy of activation. We expand the p and c as before, stopping at the linear terms:

$$J_{qx}(\text{particle}) = \lambda \sum_{i=1}^{2}\left[c_{ia} p_{im}\left(1 - \frac{\lambda}{2}\frac{\Delta H_i^\ddagger}{RT^2}\frac{\partial T}{\partial x}\right)H_{im}\right.$$

$$\left. -\left(c_{ia} + \lambda\frac{\partial c_i}{\partial x}\right)p_{im}\left(1 + \frac{\lambda}{2}\frac{\Delta H_i^\ddagger}{RT^2}\frac{\partial T}{\partial x}\right)H_{im}\right] \qquad [20a]$$

$$J_{qx}(\text{particle}) = -\lambda^2 \sum_{i=1}^{2}\left[p_i H_{im}(\partial c_i/\partial x)\right.$$

$$\left. - p_i c_i \frac{\Delta H_i^\ddagger}{RT^2}H_{im}(\partial T/\partial x)\right]. \qquad [20b]$$

The heat flux is the enthalpy flux minus the enthalpy of the transported molecules. We write the particle contribution

$$J_q'(\text{particle}) = J_q(\text{particle}) - J_1 H_1 - J_2 H_2. \qquad [21]$$

Using the fact

$$\Delta H_i^\ddagger = H_{im} - H_i, \qquad [22]$$

we obtain

$$J_{qx}'(\text{particle}) = -\lambda^2 \sum_{i=1}^{2}\left[p_i \Delta H_i^\ddagger(\partial c_i/\partial x)\right.$$

$$\left. + p_i c_i \frac{(\Delta H_i^\ddagger)^2}{RT^2}(\partial T/\partial x)\right]. \qquad [23]$$

For each component, this expression contains one term corresponding to the Dufour effect (proportional to the concentration gradients) and one term corresponding to thermal conduction (proportional to the temperature gradient). We compare Eq. 23 with the macroscopic equation (10)

$$J_q' = -\lambda_t \nabla T - c_1 T D''(\partial \mu_1/\partial X_1)_{P,T}\nabla X_1 \qquad [24]$$

in which μ_1 is the chemical potential (partial molal Gibbs free energy) of component 1, λ_t is the thermal conductivity, and D'' is called the Dufour coefficient.

Comparison of Eqs. 23 and 24 shows that the particle contribution to the thermal conductivity is given by

$$\lambda_t(\text{particle}) = \frac{\lambda^2}{RT^2}[p_1 c_1(\Delta H_1^\ddagger)^2 + p_2 c_2(\Delta H_2^\ddagger)^2]. \qquad [25]$$

This differs from previous work (8, 9) but the particle contribution to the thermal conductivity is small compared with the phonon contribution, and it is probably not now possible to test Eq. 25 experimentally.

We now apply Eq. 14 to Eq. 23 and write, by comparison with Eq. 24,

$$c_1 T D''(\partial \mu_1/\partial X_1)_{P,T} = c\lambda^2(p_1 \Delta H_1^\ddagger - p_2 \Delta H_2^\ddagger). \qquad [26]$$

If the mixture is thermodynamically ideal,

$$(\partial\mu_1/\partial X_1)_{P,T} = RT/X_1, \qquad [27]$$

so that

$$D'' = \frac{\lambda^2}{RT^2}(p_1\Delta H_1^{\ddagger} - p_2\Delta H_2^{\ddagger}). \qquad [28]$$

This is the result for the Dufour coefficient in our model liquid system.

The Onsager reciprocal relationship

Because the Soret and Dufour effects are reciprocal effects, their phenomenological coefficients must be equal if the proper choice of forces and fluxes is used (11). In the center of mass coordinate frame, the proper diffusion fluxes are measured in mass per unit area per unit time, and the phenomenological relations are written (10)

$$\mathbf{j}_i = -L_{1q}\frac{\nabla T}{T^2} - L_{1l}\frac{(\nabla\mu_1')_T}{w_2 T} \qquad [29a]$$

$$\mathbf{J}_q = -L_{qq}\frac{\nabla T}{T^2} - L_{ql}\frac{(\nabla\mu_l')_T}{w_2 T} \qquad [29b]$$

in which w_2 is the mass fraction of component 2 and μ_1' is the chemical potential of component per unit mass (partial specific Gibbs free energy). The quantity $(\nabla\mu_1')_T$ is the equivalent isothermal chemical potential gradient, and is given by

$$(\nabla\mu_1')_T = \nabla\mu_1' + \bar{s}_1\nabla T \qquad [30]$$

in which $\bar{s}_1$ is the partial specific entropy of component 1.

The Onsager reciprocal relationship implies that

$$L_{1q} = L_{ql}. \qquad [31]$$

If we identify the coordinate frame of Eq. **24** with the center of mass coordinate frame, the coefficient D'' is related to L_{ql} by

$$D'' = \frac{L_{ql}}{\rho w_1 w_2 T^2} \qquad [32]$$

in which ρ is the density of the system in mass per unit volume. The thermal diffusion coefficient D' is related to L_{1q} by

$$D' = \frac{L_{1q}}{\rho w_1 w_2 T^2} \qquad [33]$$

so that the Onsager reciprocal relationship requires D' and D'' to be equal.

The thermal diffusion ratio, k_T is related to D' by

$$k_T = \frac{c_1 c_2 T D'}{c^2 \mathcal{D}_{12}}. \qquad [34]$$

Thermal diffusion results are also often expressed in terms of α, the thermal diffusion factor, given by

$$\alpha = \frac{TD'}{\mathcal{D}_{12}} = \frac{c^2}{c_1 c_2}k_T. \qquad [35]$$

This quantity is also apparently called the thermal diffusion ratio, as is k_T.

Using Eq. **34**, we obtain from Eq. **28**

$$D'' = \frac{\lambda^2}{RT^2}(p_1\Delta H_1^{\ddagger} - p_2\Delta H_2^{\ddagger}). \qquad [36]$$

Comparison with Eq. **28** shows that

$$D' = D'', \qquad [37]$$

so our theory conforms to the Onsager reciprocal relationship.

Discussion and comparison with experiment

Until recently (1), there has been no experimental verification of the Onsager reciprocal relationship for the Soret and Dufour effects in liquids, although Rastogi and his coworkers attempted measurements several years ago (9). One of us (R.G.M.) has also carried out preliminary measurements of the Dufour effect in liquid systems and obtained reasonable agreement between D' and D'' for the carbon tetrachloride/chloroform system and the carbon tetrachloride/benzene system at 25°C.

There are data in the literature on the thermal diffusion of binary mixtures of nearly special molecules, which should conform fairly nearly to the assumptions of our model theory, and these can be used to test the theory. Saxton *et al.* (12) used a diaphragm cell to measure α for several mixtures, including carbon tetrabromide/carbon tetrachloride and $C_2H_4Cl_2/C_2H_4Br_2$ (isomers unspecified), over a range of temperatures.

In order to compare our theory with their results, we write, from Eqs. **16** and **28**

$$\alpha = \frac{TD'}{\mathcal{D}_{12}} = \frac{p_1\Delta H_1^{\ddagger} - p_2\Delta H_2^{\ddagger}}{RT(X_2 p_1 + X_1 p_2)}. \qquad [38]$$

Using Eq. **3**, we obtain

$$\alpha = \frac{e^{-\Delta H_1^{\ddagger}/RT}\Delta H_1^{\ddagger} - e^{(\Delta S_2^{\ddagger}-\Delta S_1^{\ddagger})/R}e^{-\Delta H_2^{\ddagger}/RT}\Delta H_2^{\ddagger}}{RT[X_2 e^{-\Delta H_1^{\ddagger}/RT} + X_1 e^{(\Delta S_2^{\ddagger}-\Delta S_1^{\ddagger})/R}e^{-\Delta H_2^{\ddagger}/RT}]}. \qquad [39]$$

Notice that the transmission coefficient $\mathcal{H}$ has cancelled out, and that α depends only on the difference $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$ rather than on $\Delta S_1^{\ddagger}$ and $\Delta S_2^{\ddagger}$ separately. Therefore, the thermal diffusion factor α depends, as well as on the temperature, on three values: $\Delta H_1^{\ddagger}$, $\Delta H_2^{\ddagger}$, and $\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$.

The formula of Eq. **39** was fit to data of Saxton *et al.* (12) by using nonlinear regression. Unfortunately, the sum of the squares of the residuals appeared to be a complicated function of the parameters, possibly containing various saddle points and several relative extrema. Ordinary iterative numerical procedures failed to converge, so the minimum in this function was found by trial and error, using a computer program that repeatedly computed the sum of the squares for various values of the parameters.

Table 1 and Fig. 1 show the results for two different mixtures: CBr_4/CCl_4 (mole fraction of CBr_4, 0.09) and $C_2H_4Br_2/C_2H_4Cl_2$ (mole fraction of each component, 0.50). Table 1 gives the values of the parameters which correspond to the curves shown in Fig. 1. The values of the parameters found correspond to true relative minima in the sums of the squares of the residuals, and no smaller values of these functions were found, but there is no guarantee that a lower minimum does not exist. Also, the data show considerable scatter, and the expected errors in the parameters are presumably large, although no statistical procedure was found to estimate them.

However, the curves in Fig. 1 appear to fit the data reasonably well. The curves are nearly linear but, over a larger temperature range, there is a noticeable upward concavity.

Table 1.   Values of parameters in Eq. 38 to fit data for two-liquid mixtures

	CBr_4 (1)/ CCl_4 (2)	$C_2H_4Br_2$ (1)/ $C_2H_4Cl_2$ (2)
$\Delta H_1^{\ddagger}$, kcal mol^{-1} (kJ mol^{-1})	2.29 (9.58)	2.16 (9.04)
$\Delta H_2^{\ddagger}$, kcal mol^{-1} (kJ mol^{-1})	2.29 (9.58)	2.20 (9.21)
$\Delta S_2^{\ddagger} - \Delta S_1^{\ddagger}$, cal K^{-1} mol^{-1} (J K^{-1} mol^{-1})	−1.0 (−4.2)	−0.40 (−1.7)

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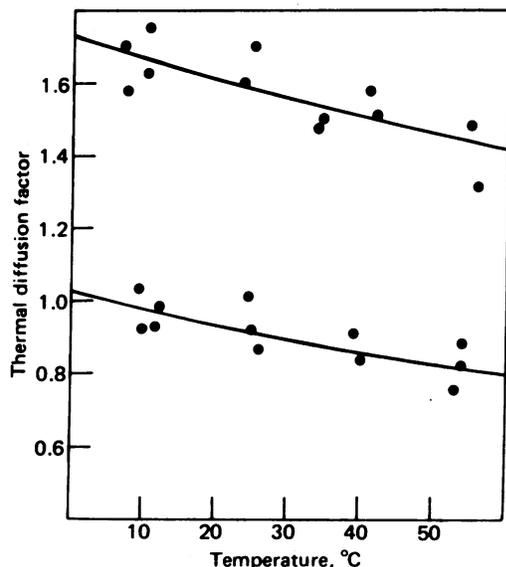

FIG. 1. Thermal diffusion factor, α, for two-liquid mixtures as a function of temperature. Upper curve, CBr_4/CCl_4; lower curve, $C_2H_4Br_2/C_2H_4Cl_2$. (Data from ref. 12.)

The positive sign of α corresponds to motion of component 1 toward the cold end of the cell in thermal diffusion and to a flow of heat away from the larger concentration of component 1 in the Dufour effect. In both of the systems analyzed, we have assigned the heavier molecular weight substance to be component 1, and in all six of the systems studied by Saxton *et al.* (12) the component with larger and heavier molecules moved toward the cold end of the cells. The same is true of the data of Jeener and Thomaes (13), who studied mixtures of CCl_4 and the other chlorinated methanes.

It is interesting that, for both mixtures analyzed, the values of the enthalpy changes of activation that fit the data are equal or nearly equal for both components in the mixture. It is also interesting that in both cases the entropy change of activation is more negative for component 2 (with smaller molecules) than for component 1. With enthalpy changes of activation nearly equal, this must always be true if component 1 is to move to the cold end of the cell.

The entropy change of activation is negative (probably ≈ 6 cal K^{-1} mol^{-1} for these substances), corresponding to an in-

crease in order at the transition state (compared to no molecule in the transition state). At first glance, it might seem that a larger molecule should lower the entropy more in moving to the transition state than would a smaller molecule, but it would also have more of an effect in disordering the liquid quasilattice in the equilibrium site than would a smaller molecule, and the effect in the equilibrium site seems to be more pronounced, according to our results.

The numerical values for the enthalpy changes of activation seem reasonable. For example, a self-diffusion data on CCl_4 (14) indicate an enthalpy change of activation of 2.8 kcal mol^{-1}; in the more disordered quasi-lattice of the CCl_4/CBr_4 mixture, our value of 2.3 kcal mol^{-1} is about what we might expect.

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