

# Thermodiffusion in binary liquids: The role of irreversibility

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We study thermal diffusion in binary mixtures in the framework of non-equilibrium thermodynamics. Our formal result displays the role of partial enthalpies  $h_i$  and Onsager's generalized mobilities  $A_i$ . The ratio  $A_1/A_2$  provides a measure for the irreversible character of thermal diffusion. Comparison with experimental data on benzene, cyclohexane, toluene, and  $n$ -alkanes shows that irreversibility is essential for thermal diffusion, and in particular for the isotope effect.

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*Introduction.* Thermal diffusion, or the Soret effect, describes the mass flow induced by a temperature gradient in complex fluids [1–3]. Together with the Dufour effect that accounts for heat flow in a concentration gradient, it constitutes a classical example of Onsager's reciprocal relations for non-equilibrium systems [4]. Thermal diffusion is one of the mechanisms governing the compositional grading in the Earth's petroleum reservoirs [5] and the isotope fractionation in silicate melts [6]. In recent years, thermal diffusion has proven a versatile means for confining colloidal suspensions [7, 8], manipulating DNA through nanopores [9], or self-propelling Janus particles [10, 11].

The Soret effect of macromolecules and colloidal particles is to a large extent determined by viscous effects and thus can be treated in the framework of macroscopic hydrodynamics [3]. Exploiting the reciprocal laws for heat and mass flows, Derjaguin related thermally driven transport to the solute-solvent interaction enthalpy [12]. Much recently much progress has been made for charged solute, confirming Derjaguin's picture of enthalpy flow as driving mechanism and pointing the out the role of the electrolyte Seebeck effect [13–15].

Much less is known, however, on thermal diffusion in molecular mixtures. In spite of the many experimental [16–23] and molecular dynamics data [24–26] on the composition, temperature, and mass dependencies, available models diverge on the driving mechanism [27–34]. Although the observed isotope effect [18] indicates irreversible behavior, there is at present no general agreement whether the Soret effect can be described by equilibrium thermodynamics, or on the contrary reflects the irreversible character of the underlying diffusion process.

The present Letter discusses these questions on the basis of formally exact expressions derived by de Groot & Mazur half a century ago, yet which so far have been given no attention. As a main purpose, we separate equilibrium and irreversible factors of the Soret coefficient. Comparison with recent experimental findings for binary mixtures, provides a simple physical picture for the driving mechanism and a clear signature of irreversibility.

Consider a two-component molecular liquid with volume fractions  $c_1$  and  $c_2 = 1 - c_1$ . Non-uniform composi-

tion and temperature induce a current

$$J_1 = -D\nabla c_1 - c_1 c_2 D_T \nabla T. \quad (1)$$

The first term or gradient diffusion tends to smoothen composition inhomogeneities, whereas the second one, or thermal diffusion, pushes one component to the cold and the other to the hot, and thus favors separation. The steady state  $J_1 = 0$  is characterized by a spatial composition gradient  $\nabla c_1 = -c_1 c_2 S_T \nabla T$ , where  $S_T = D_T/D$  is the Soret coefficient. Even for simple systems such as benzene-cyclohexane, both its sign and its dependence on composition and temperature lack a rationale so far.

*Non-equilibrium thermodynamics.* The coefficients  $D$  and  $D_T$  are related to the thermodynamic forces introduced by Onsager and worked out in detail by de Groot and Mazur. As a generalized state function, the Planck potential  $\mu_i/T$  of component  $i$  is given by the ratio of its chemical potential  $\mu_i$  (or partial Gibbs energy) and the absolute temperature  $T$ . Just like the gradient of gravitational or electric potentials give mechanical forces, that of the Planck potential defines thermodynamic forces acting on each molecular species. For an otherwise homogeneous system one has

$$\nabla \frac{\hat{\mu}_i}{T} = -\frac{\hat{h}_i}{T^2} \nabla T + \frac{\hat{\mu}_{ii}^c}{T} \nabla c_i, \quad (2)$$

where the first term arises from the Gibbs-Helmholtz relation  $d(\hat{\mu}_i/T)/dT = -\hat{h}_i/T^2$  and the second one from applying the Gibbs-Duhem relation to  $\hat{\mu}_{ij}^c = d\hat{\mu}_i/dc_j$ . For incompressible liquids, it is convenient to use volume specific quantities, e.g.,  $\hat{\mu}_i = \mu_i/v_i$  the volume per molecule  $v_i$ ; thus  $\hat{h}_i$  is the corresponding enthalpy density.

The thermodynamic force on species  $j$  induces a current  $a_{ij} \nabla(\hat{\mu}_j/T)$  of species  $i$ , where the mobility matrix  $a_{ij}$  is symmetric and positive definite. Eliminating the related heat flow and accounting for  $J_2 = -J_1$  results in [4]

$$J_1 = -(c_2 a_{11} - c_1 a_{12}) \nabla \frac{\hat{\mu}_1}{T} + (c_1 a_{22} - c_2 a_{21}) \nabla \frac{\hat{\mu}_2}{T}. \quad (3)$$

Inserting (2) and separating thermal and concentration gradients, one readily identifies  $D$  and  $D_T$  in (1),

$$D = \frac{c_1(c_1a_{22} - c_2a_{12}) + c_2(c_2a_{11} - c_1a_{12})}{c_1c_2T} c_1\hat{\mu}_{11}^c, \quad (4)$$

$$D_T = \frac{(c_1a_{22} - c_2a_{12})\hat{h}_2 - (c_2a_{11} - c_1a_{12})\hat{h}_1}{c_1c_2T^2}. \quad (5)$$

These relations for the diffusion and thermodiffusion coefficients have been obtained by de Groot and Mazur, albeit for mass instead of volume fractions [35]. They reveal several remarkable features. First, the coefficient  $D_T$  is proportional to the partial enthalpies of the components; this confirms the central role of enthalpy for thermo-osmosis pointed out by Derjaguin [12].

Second, the factors  $a_{ij}$  accounting for irreversibility, appear in both  $D$  and  $D_T$  in the form  $B_2 = c_1a_{22} - c_2a_{12}$  and  $B_1 = c_2a_{11} - c_1a_{12}$ . In view of a two-parameter model discussed below, we absorb the chemical potential derivative in these coefficients and separate the dynamic viscosity  $\eta$ . Thus we put  $A_i = B_i(\eta/c_1c_2T)c_1\hat{\mu}_{11}^c$  and have for the diffusion coefficient

$$D = \frac{c_1A_2 + c_2A_1}{\eta}. \quad (6)$$

Note that in general both  $a_{ij}$  and  $A_i$  are functions of composition and temperature. Inserting the  $A_i$  in the thermal diffusion coefficient we have

$$D_T = \frac{1}{c_1\hat{\mu}_{11}^c\eta T} \left( A_2 \frac{h_2}{v_2} - A_1 \frac{h_1}{v_1} \right). \quad (7)$$

The derivative of the chemical potential can be split in two factors,

$$c_1\hat{\mu}_{11}^c = \frac{k_B T}{c_1v_2 + c_2v_1} \Gamma, \quad (8)$$

where the first one arises from the mixing entropy; the remaining factor  $\Gamma$  is related to composition dependence of the ‘‘activity coefficient’’  $\gamma$  and thus accounts for non-ideal behavior [4].

The remainder of this paper deals with the Soret coefficient  $S_T = D_T/D$ . For its derivation it was advantageous to consider volume fractions  $c_i = n_i v_i$ , where  $n_i$  is the concentration. Since Soret data and thermodynamic excess quantities of binary mixtures are usually given in terms of mole fractions  $x_i = n_i/(n_1 + n_2)$ , we change variables and obtain

$$S_T = \frac{1}{\Gamma k_B T^2} \frac{h_2 A_2 / v_2 - h_1 A_1 / v_1}{x_1 A_2 / v_2 + x_2 A_1 / v_1}. \quad (9)$$

This formally exact expression reveals the intricate equilibrium and irreversibility aspects of  $S_T$ : The state function enthalpy is an equilibrium property, whereas the mobilities  $A_i$  account for the irreversible nature of thermal diffusion.

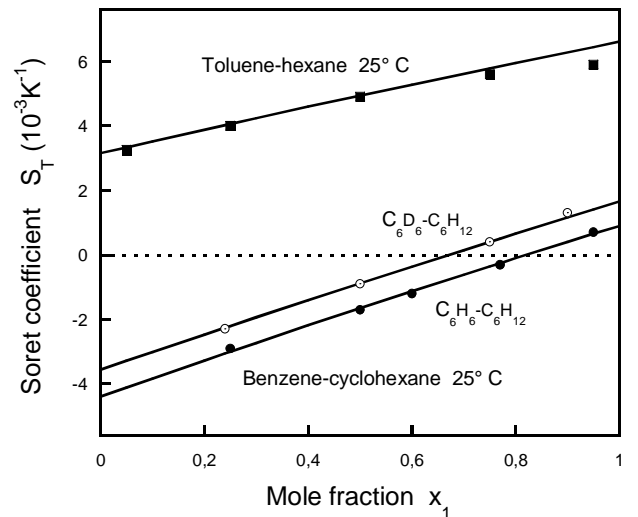


FIG. 1: Composition dependence of the Soret coefficient. The data for benzene-cyclohexane are from Debuschewitz and Köhler [18], those for toluene-hexane from Zhang et al. [17]. The solid lines are calculated from Eq. (12) with parameters from the tables. For protenated benzene we have used  $A_1/A_2 = 0.765$ , and for deuterated benzene  $A_1/A_2 = 0.785$ .

It turns out instructive to consider the case where the mobility coefficients are constant and identical to each other. Then the Soret coefficient takes the form

$$S_T = \frac{1}{\Gamma k_B T^2} \frac{h_2/v_2 - h_1/v_1}{x_1/v_2 + x_2/v_1} \quad (A_1 = A_2), \quad (10)$$

which is proportional to the difference in partial enthalpy per volume. In other words, the molecules with the more negative enthalpy density migrates to the cold, similar to gravity-driven sedimentation where the denser component accumulate at the bottom. Remarkably, the mobilities have dropped out, such that  $S_T$  depends on equilibrium properties only. This expression was first obtained by Haase for gas mixtures, with mole fractions weighted by molecular mass instead of volume [27]; later on it has been refined by several authors [28, 29].

Yet the equilibrium hypothesis is not generally valid, and in particular fails for molecular liquids. With the enthalpy and volume parameters given in the Tables, Haase’s expression (10) results in a strong positive Soret coefficient for benzene in cyclohexane, whereas the data [18] plotted in Fig. 1 rather show the opposite behavior. Even more strikingly, it misses the isotope effect: Since protonated and deuterated benzene,  $C_6H_6$  and  $C_6D_6$ , hardly differ in their enthalpies and molecular volumes, (10) gives the same Soret behavior, whereas the measured values are higher for the heavier isotope.

In the remainder of this paper, we discuss the parameters  $h_i$  and  $A_i$  in detail, and then compare Eq. (9) to measured Soret data. The partial enthalpies  $h_i$  in general depend on composition. In the follow-

TABLE I: Pure-component parameters at 25° C: vaporization enthalpy  $h_{\text{vap}}$ ; molar volume  $v$ ; viscosity  $\eta$ ; specific heat at normal pressure [38, 39]. Throughout this paper we identify  $h_{\text{vap}}$  with the interaction enthalpy  $h^0$ .

	$h_{\text{vap}} \equiv h^0$ (kJ/mol)	$v$ (cm <sup>3</sup> /mol)	$\eta$ (mPa.s)	$C_P$ (J/molK)
benzene	-33.9	89	0.61	135
cyclohexane	-33.3	108	0.88	156
toluene	-38	106	0.59	156
hexane	-30.7	132	0.31	198
heptane	-35.4	147	0.39	225

ing we consider “regular mixtures” where the mean molar value is a parabolic function of the mole fractions,  $h = x_1 h_1^0 + x_2 h_2^0 + x_1 x_2 h_E$ , with the pure-body enthalpies of molecular interactions  $h_i^0$  and the change upon mixing  $h_E$ . Then the partial enthalpies take the form

$$h_1 = h_1^0 + x_2 h_E, \quad h_2 = h_2^0 + x_1 h_E. \quad (11)$$

Most molecular liquids have positive excess enthalpy of the order of a few kJ/mole, with the noticeable exception of alcohols in water [38]. Equilibrium thermodynamics is mainly concerned with enthalpy differences with respect to some reference state. Eq. (9) on the contrary requires *absolute* values, which are neither easily measured nor easily calculated. In the following we identify  $h_i^0$  with the vaporization enthalpies given in Table I. Indeed, the enthalpy change upon removing one molecule from the liquid to the gas state is essentially determined by molecular interactions; typical values correspond to ten times the thermal energy and by far exceed conformational and volume expansion contributions.

The partial molar volumes  $v_i$  change upon mixing and have been discussed as one source for the composition dependence of  $S_T$  [34]. For the systems considered here, the excess volume  $v_E$  is rather small and thus has been neglected from the beginning. For example, for benzene-cyclohexane mixtures one has  $v_E = 0.65$  cm<sup>3</sup>/mol, which corresponds to less than one percent of the molar volumes [38], whereas the excess enthalpy  $h_E$  amounts to about 10 % of  $h_i^0$ .

The thermodynamic factor  $\Gamma$  defined in (8) describes the non-ideal behavior of the chemical potential. In analogy to the enthalpy, the excess chemical potential  $\mu_E$  is expected to be much smaller than the ideal values  $\mu_i^0$ . This implies that the activity coefficient  $\gamma$  and the quantity  $\Gamma$  vary only weakly with composition. Since the latter appears as an overall factor in  $S_T$ , its modulation is of little relevance and we may take  $\Gamma$  as a constant. On the contrary, the ideal enthalpies in the numerator of (9) largely cancel each other, thus enhancing the weight of the excess  $h_E$ .

The mobilities  $A_i$  account for the irreversible character of thermal diffusion. There is no thermodynamic theory for calculating these quantities; they have to be extracted

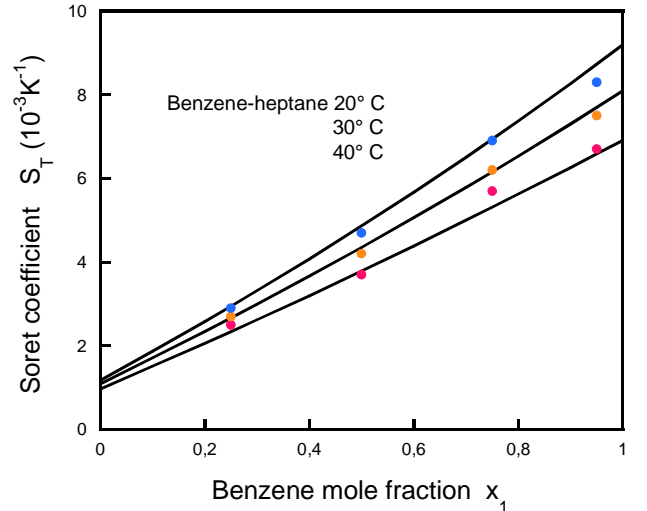


FIG. 2: Soret coefficient of benzene-heptane mixtures at three temperatures. Data are from Polyakov et al. [20]. The solid lines are calculated from (12) with parameters given in the Tables.

from molecular dynamics simulations or experiments, or to rely on model assumptions. Here we adopt the simplest two-parameter model that consists in taking  $A_1$  and  $A_2$  as constants. The experimental values of Table II are determined from data for the mutual diffusion coefficients at low dilution, e.g.,  $A_1 = (\eta_2/T)D_1$  for  $x_1 \rightarrow 0$ .

*Comparison with experiment.* Inserting the above partial enthalpies and defining  $\xi = A_1/A_2$ , we obtain

$$S_T = \frac{h_2^0/v_2 - \xi h_1^0/v_1 + h_E(x_1/v_2 - \xi x_2/v_1)}{\Gamma k_B T^2 (x_1/v_2 + \xi x_2/v_1)}. \quad (12)$$

In Fig. 1 we compare this expression with data for toluene-hexane [17] and benzene-cyclohexane [18], which show an almost linear variation with the mole fraction of the first component. The theoretical curves are calculated with the parameters given in the Tables; the fit values for the irreversibility parameter  $A_1/A_2$  and the excess enthalpy  $h_E$  agree rather well with diffusion and thermometry data. Both the numerator and the denominator of (12) contribute equally to the composition dependence.

Haase’s expression (10) would result in positive and much too large value of  $S_T$ . On the other hand, when including the irreversibility parameter Eq. (12) provides a good description for the data. The experimental and fit values of  $A_1/A_2$  agree rather well, yet one should be aware of the uncertainties of the diffusion coefficients  $D_i$ . As an important result, these fits show that the Onsager mobilities take a ratio which significantly differs from unity. This leads us to the conclusion that irreversibility is crucial for thermal diffusion.

This statement is confirmed by the isotope effect. Since the enthalpy density is insensitive to the molecular mass,

TABLE II: Parameters of protonated benzene (B), cyclohexane (CH), toluene (T), hexane (C<sub>6</sub>), and heptane (C<sub>7</sub>). The coefficient  $D_i$  describes tracer diffusion of component  $i$  [36]. The parameters  $A_i$  for tracer diffusion are calculated with the pure solvent viscosity, e.g.  $A_1 = \eta_2 D_1 / T$ . Since  $S_T$  depends on the ratio  $A_1/A_2$  only, we don't give absolute values. The viscosity of heptane at 40° C is 0.33 cP.

	$D_1$ (10 <sup>-9</sup> m <sup>2</sup> /s)	$D_2$	$A_1/A_2$ (exp)	$A_1/A_2$ (fit)	$h_E$ (kJ/mol) (exp)	$\Gamma$ (fit)	$\Gamma$
B-CH 25°	1.90 <sup>a</sup>	2.09 <sup>a</sup>	0.76	0.765	3.2 <sup>d</sup>	2.8	1.4
T-C <sub>6</sub> 25°	4.0 <sup>b</sup>	2.4 <sup>b</sup>	0.91	0.70		1.0	0.7 <sup>f</sup>
20°							
B-C <sub>7</sub> 30°	3.92 <sup>c</sup>	1.79 <sup>c</sup>	0.71 <sup>c</sup>	0.71	3.2 <sup>e</sup>	2.6	1
30°							
40°	4.74 <sup>c</sup>	2.28 <sup>c</sup>	0.73 <sup>c</sup>	0.695	2.5 <sup>e</sup>	2.3	1
40°				0.67		2.0	1

<sup>a</sup>[36]; <sup>b</sup>[16]; <sup>c</sup>Data at 25 and 40° C [37]; <sup>d</sup>[38]; <sup>e</sup>Data for B-C<sub>6</sub> at 25 and 40° C [38]; <sup>f</sup>[34].

the equilibrium expression (10) does not differentiate between protonated and deuterated benzene. On the other hand, the kinetics and thus the mobilities  $A_i$  depend on the molecular mass; possible mechanisms are the collision rate as discussed in a hard-sphere model [32] and the jump rate of activated diffusion [6]. From thermal diffusion in gases, it is well known that the isotope effect is not an equilibrium property. Finally we emphasize that the slight change from  $A_1/A_2 = 0.765$  for protonated benzene to 0.785 for the deuterated species results in a composition independent offset of  $S_T$ , in good agreement with the data.

Fig. 2 shows the temperature dependence of Soret data reported by Polyakov et al. for benzene-heptane [20]. An increase of 20 K reduces the Soret coefficient by one quarter, which corresponds to a relative change of about 1.2 % per K. Comparison with the thermal expansion coefficient

$d \ln v / dT \sim 10^{-3} \text{ K}^{-1}$ , suggests that the change of the molecular volume is of little relevance. The temperature derivative of the molar enthalpy  $h^0$  is determined by the heat capacities  $C_P$ ; with the numbers of Table I one finds that a relative change of about  $0.005 \text{ K}^{-1}$ , which accounts for almost half of the variation of the Soret coefficient. The fit curves in Fig. 2 are obtained by varying in addition both  $A_1/A_2$  and  $h_E$ , suggesting that the temperature dependence of  $S_T$  has not a single cause.

In the present work we have discarded viscous effects. This is appropriate for molecular components of similar size, where the two terms of the thermodynamic force (2) carry the same mobilities. On the contrary, the motion of large particles or polymers is accompanied by viscous flow; the Einstein coefficient  $D$  carries a size-dependent friction factor, whereas that the thermal diffusion coefficient  $D_T$  is constant [33]. Mixtures of normal alkanes would provide a model system for the emergence of viscous effects, because of their rather simple mixing properties and the available Soret data [23].

In summary, our comparison with experiments provides strong evidence for the irreversible character of thermal diffusion, even in systems where viscous effects are absent. The simple two-parameter model used here could be improved by considering three mobilities  $A_{ij} \sim a_{ij}/c_i c_j$ , and adjusting the diffusion and thermal diffusion coefficients independently. We conclude with a remark on the irregular alcohol-water mixtures. In accordance with (12), the measured Soret coefficient [19] roughly follows the excess enthalpy as a function of composition [38], and in particular reflects the cusp at  $x_{\text{eth}} = 0.15$ ; because of the strongly irregular behavior, a more rigorous comparison would require to go beyond the linear law (11) for the partial enthalpies.

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