

Definition of frame-invariant thermodiffusion and Soret coefficients for ternary mixtures^{*}

José M. Ortiz de Zárate^a

Facultad de Ciencias Físicas, Universidad Complutense, Plaza de las Ciencias 1, 28040 Madrid, Spain

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Abstract. The definitions of thermodiffusion and Soret coefficients for a binary mixture include a concentration prefactor $x(1-x)$, when mole fraction x is used, or $w(1-w)$, when mass fraction w is used. In this paper the physical reasons behind this choice are reviewed, emphasizing that the use of these prefactors makes the thermodiffusion and the Soret coefficients invariant upon changing in the concentration representation, using either mole fraction or mass fraction. Then, it is shown how this invariance property can be extended to ternary mixtures by using appropriate concentration prefactors in matrix form. The paper is completed with some considerations about alternative definitions of thermodiffusion coefficients, binary limits of the concentration triangle, selection of the dependent concentration in a ternary mixture, use of molar concentrations and, finally, extension to multi-component mixtures.

1 Introduction

Thermodiffusion, also referred to as thermal diffusion, Ludwig-Soret effect or simply Soret effect [1], is a transport phenomenon that generically exists in non-isothermal multi-component mixtures. The presence of a temperature gradient ∇T induces not only a heat flow, but also a matter flow. In the theoretical framework of linear non-equilibrium thermodynamics [2–5] thermodiffusion is a coupled transport phenomenon whose magnitude is, in a first approximation, proportional to ∇T .

For isotropic¹ binary mixtures, one single concentration variable is required to specify the composition. For the purpose of this paper it is important to clearly distinguish between the various possible ways of specifying the composition of a mixture, thus, x shall be used to denote mole fraction, w for mass fraction (both dimensionless) and c for molar concentration (units of mol m^{-3}). The last one will be considered in sect. 7. The relationship between mass w and mole x fractions is given by

$$w = \frac{xM_1}{xM_1 + (1-x)M_2}, \quad (1)$$

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^a e-mail: jmortizz@ucm.es

¹ The content of this paper only refer to isotropic fluids.

where M_1 and M_2 are the molecular weights of components 1 and 2 of the mixture, respectively (units of kg mol^{-1}).

In these isotropic binary systems, thermodiffusion is quantified by a single scalar thermodiffusion coefficient, D_T (units of $\text{m}^2 \text{s}^{-1} \text{K}^{-1}$). When using x as concentration variable, the total mole flux (including Fickian and thermodiffusion contributions) is given by [2–4]:

$$\mathbf{J}^{(x)} = -c_t [D \nabla x + x(1-x)D_T \nabla T], \quad (2)$$

where the scalar quantities $c_t = c_1 + c_2$, and D represent, respectively, the total molar concentration and the single Fick diffusion coefficient of a binary mixture. In eq. (2)

$$\mathbf{J}^{(x)} = c_t x \{ \mathbf{u}_1 - [x\mathbf{u}_1 + (1-x)\mathbf{u}_2] \} \quad (3)$$

represents the species-1 mole diffusion flux (units of $\text{mol m}^{-2} \text{s}^{-1}$) relative to the mole-average velocity. In eq. (3), the vector fields \mathbf{u}_1 and \mathbf{u}_2 are the velocities of species 1 and 2 in any inertial reference frame (laboratory). Notice Galilean invariance in the definition (3) of $\mathbf{J}^{(x)}$.

When a binary mixture is subjected to a steady temperature gradient, it follows from eq. (2) that, because of matter balance, thermodiffusion will cause composition separation. After some transient, a non-equilibrium steady state is reached where $\mathbf{J}^{(x)}$ vanishes and a constant (in time) concentration gradient is established. In isotropic fluids the applied temperature gradient and the induced

concentration one are always parallel (or antiparallel). Because of the pioneering research by Charles Soret (1879, see [6]), a so-called Soret coefficient S_T (units of K^{-1}) is typically introduced as proportional to the ratio of these steady concentration and temperature gradients, namely,

$$x(1-x)S_T \nabla T = -\nabla x. \quad (4)$$

On comparing eq. (2) with eq. (4) for parallel (or antiparallel) temperature and concentration gradients, one obtains

$$S_T = \frac{D_T}{D}. \quad (5)$$

The substitution of eq. (5) into eq. (2) allows to quantify thermodiffusion, even in the non-steady case, in terms of S_T , an option preferred by some authors. Others [7] introduce a thermal diffusion ratio, $k_T = S_T/T = D_T/(DT)$, instead of D_T or S_T .

Note, for binary mixtures, the presence of a concentration prefactor $x(1-x)$, both in the definition (2) of the thermodiffusion coefficient and in the definition (4) of the Soret coefficient. There are various reasons for introducing this prefactor.

First, the prefactor forces the thermodiffusion-induced flux (and corresponding concentration gradient in steady-state) to vanish in the two pure-component limits, *i.e.*, for $x \rightarrow 0$ and $x \rightarrow 1$. The prefactor is expected to carry most of the concentration dependence of thermodiffusion, so that D_T or S_T only depend weakly on x . Indeed, in many cases, a linear dependence on x is sufficient to represent S_T over the entire range of concentration, $x \in [0, 1]$.

Second and most fundamentally, the prefactor makes the values of D_T and S_T invariant under change in the representation of concentration (and associated diffusion frame of reference). Indeed, the differentiation of eq. (1) shows that

$$\frac{\nabla x}{x(1-x)} = \frac{\nabla w}{w(1-w)}, \quad (6)$$

so that the numerical value of S_T will be identically the same, independently of whether, for a steady state, it is computed like in eq. (4) with concentrations in mole fraction x , or by

$$w(1-w)S_T \nabla T = -\nabla w, \quad (7)$$

with concentrations in mass fraction w . Moreover, since for a binary mixture $\mathbf{J}^{(x)}$ is related to the mass diffusion flux in the center-of-mass (barycentric) frame of reference, by [8]:

$$\frac{\mathbf{J}^{(x)}}{c_t x(1-x)} = \frac{\mathbf{J}^{(w)}}{\rho_t w(1-w)}, \quad (8)$$

one concludes that the numerical values of D_T (and D) will be identically the same, independently of whether they are defined by eq. (2) in the mole-average frame of reference, or from

$$\mathbf{J}^{(w)} = -\rho_t [D \nabla w + w(1-w)D_T \nabla T] \quad (9)$$

in the barycentric frame of reference.

In eqs. (8) and (9), the species-1 mass diffusion flux (units of $\text{kg m}^{-2} \text{s}^{-1}$) relative to the center-of-mass velocity is

$$\mathbf{J}^{(w)} = \rho_t w \{ \mathbf{u}_1 - [w\mathbf{u}_1 + (1-w)\mathbf{u}_2] \}, \quad (10)$$

while $\rho_t = \rho_1 + \rho_2$ is the total mass density of the binary mixture. By solving eqs. (3) and (10) for the velocities \mathbf{u}_i , eq. (8) immediately follows.

The invariance of both S_T and D_T upon change in the reference frame is a quite convenient property, not only theoretically but also from a practical or experimental point of view. It makes life easier for scientists obtaining D_T or S_T values in binary mixtures, either experimentally or by computer simulations. They can continue to use their favorite concentration representation, in mole fraction [9–13] or in mass fraction [14–17], while comparison between values obtained by different teams is direct, not requiring any conversion or number manipulation.

Some authors [1] have stressed another interesting consequence of the use of concentration prefactors, *i.e.*, the interpretation of D_T as a thermophoretic mobility. Indeed, for a dilute mixture, when there are a few and well separated molecules of species-1, one can take $\nabla x \simeq 0$ in eq. (2). Then, comparison with eq. (3) gives for the drift velocity:

$$\mathbf{u}_1 - \mathbf{u}_2 = -D_T \nabla T. \quad (11)$$

The same result is obtained by comparing eqs. (9) and (10).

Historically, the concentration prefactor in its current form, $x(1-x)$ or $w(1-w)$, first appeared in the Enskog formula (1917) for the separation of isotopes by thermal diffusion. It was later adopted for arbitrary binary mixtures, in particular² through the 1942 work by Sybren de Groot [18]. Interestingly, as a reason for introducing $x(1-x)$, De Groot quotes yet another nice property, namely, invariance of S_T (or D_T) under permutation of components (it simply changes sign, see sect. 6). Other authors at that time were using proportionality to concentration, which breaks all invariance properties (see also sect. 7) and does not allow the direct interpretation of D_T as a mobility.

In more recent decades, and also partly due to the impulse given since 1994 by the *International Meeting on Thermodiffusion* (IMT) series of conferences [19], research in thermodiffusion has progressed significantly. Measuring Soret coefficients of binary mixtures now has become routine, and the various alternative experimental techniques used by different groups have progressed to a level where agreement is readily reached, and the experimental dataset of reliable D_T and/or S_T values for different binary mixtures has increased steadily [19, 20]. Maybe for these reasons the interest of the community has moved lately towards ternary mixtures, as a first step towards truly multi-component mixtures. Also, the establishment of large international collaborations associated with space

² I owe this information to a personal communication by Aliaksandr Mialdun.

science³, like DCMIX [21] or SCCO-SJ10 [22,23], has undoubtedly helped to switch the community focus towards ternaries and, in general, to complex mixtures like in NEUF-DIX [24].

2 Soret coefficients for ternary mixtures

In a ternary mixture there are two independent concentrations, x_1 and x_2 in mole fraction, while $x_3 = 1 - x_1 - x_2$ is a dependent concentration. Also, concentrations w_1 and w_2 in mass fraction are often used, related to mole fractions by

$$\begin{aligned} w_1 &= \frac{x_1 M_1}{x_1 M_1 + x_2 M_2 + (1 - x_1 - x_2) M_3}, \\ w_2 &= \frac{x_2 M_2}{x_1 M_1 + x_2 M_2 + (1 - x_1 - x_2) M_3}, \end{aligned} \quad (12)$$

with M_3 being the molecular weight of the third component of the mixture. Associated with the two independent concentrations there are also two independent diffusion fluxes. Hence, two independent Soret, $S_{T,1}$ and $S_{T,2}$, or thermodiffusion, $D_{T,1}$ and $D_{T,2}$, coefficients are needed to describe thermal diffusion in ternary systems.

Note that the step from binary to ternary systems is not trivial and, for diffusion, requires the introduction of a Fick diffusion matrix D instead of the single scalar Fick diffusion coefficient D needed for a binary mixture [8]. Associated with the matrix description of diffusion several complications appear, like the frame dependence of diffusion matrices, that are difficult to grasp experimentally. Indeed, very few experimental papers in ternary or multi-component mixtures contain any reference to the frame in which their diffusion matrices are measured.

There has been some confusion in the literature concerning the concentration prefactor in the definition of Soret and thermodiffusion coefficients [25]. For instance, Shevtsova *et al.* [26] adapted for ternaries a proposal by Kempers [27] and used a prefactor $x_1(1 - x_1)$ for the first Soret coefficient, and a prefactor $x_2(1 - x_2)$ for the second, a choice followed by some other authors [28]. On the other hand, Ghorayed and Firozabaadi [29] proposed to use prefactors $x_1 x_3$ for the first Soret and $x_2 x_3$ for the second. Because of these inconsistencies, in the first experimental benchmark on thermodiffusion in ternary systems [30] it was decided to introduce new Soret coefficients $S'_{T,i}$ simply defined as the ratio between concentration (in mass fraction) and temperature gradient, without any prefactors. A similar approach was adopted when reporting the results of the SCCO-SJ10 space mission [23]. Similarly, new

thermodiffusion coefficients, $D'_{T,i}$, defined without concentration prefactors, have been introduced [30]. Notice that none of the options mentioned above retain for ternaries the properties, enumerated in sect. 1, which make the definition eq. (4) of Soret coefficients, or the definition eq. (2) of thermodiffusion coefficients, so convenient for binary mixtures.

The main purpose of this paper is to show how to introduce a concentration prefactor in the definition of thermodiffusion and Soret coefficients for a ternary mixture that retains all the convenient properties that the D_T of eq. (2) or the S_T of eq. (4) have for binaries. The inconvenience is that such a prefactor has to be in the form of a matrix.

It is easier to start by considering Soret coefficients in a steady state. Then, if one defines for a ternary mixture⁴

$$\begin{bmatrix} x_1(1 - x_1) & -x_1 x_2 \\ -x_1 x_2 & x_2(1 - x_2) \end{bmatrix} \begin{bmatrix} S_{T,1} \\ S_{T,2} \end{bmatrix} \nabla T = - \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix}, \quad (13)$$

the resulting Soret coefficients, $S_{T,1}$ and $S_{T,2}$, are independent of whether concentrations are expressed in mole or mass fraction. Indeed, simple differentiation of eqs. (12) shows that (see exercise 1.5 in ref. [8]):

$$\begin{bmatrix} x_1(1 - x_1) & -x_1 x_2 \\ -x_1 x_2 & x_2(1 - x_2) \end{bmatrix}^{-1} \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix} = \begin{bmatrix} w_1(1 - w_1) & -w_1 w_2 \\ -w_1 w_2 & w_2(1 - w_2) \end{bmatrix}^{-1} \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \end{pmatrix}, \quad (14)$$

similar to eq. (6) for binary mixtures. Note that the definition of Soret coefficients given by eq. (13) is not only frame invariant⁵, but it also cancels the two concentration gradients at all pure-component limits which, for a ternary mixture are three: Pure component-1, $x_1 = 1$ and, thus, $x_2 = 0$. Pure component-2, $x_2 = 1$ and, thus, $x_1 = 0$. Pure component-3, $x_1 = 0$ and $x_2 = 0$.

While the question of the binary limits of the ternary concentration triangle will be addressed in detail later, in sect. 5, one direct consequence of eq. (13) is that, when $x_1 \rightarrow 0$ or $x_2 \rightarrow 0$, one of the Soret coefficients will approach the Soret coefficient for the corresponding binary mixture, with the correct concentration prefactor as given by eqs. (4) or (7). Thus, when one of the components is dilute, there is no need of conversion factors to compare Soret coefficients measured in a ternary mixture with binary tabulated values of S_T .

As already mentioned, one disadvantage of eq. (13) is the matrix character of the concentration prefactor, implying that Soret coefficient #1 will not only depend on the

³ DCMIX (Diffusion Coefficients Measurement in ternary mIXtures), SCCO-SJ10 (Soret Coefficients for Crude Oil at ShiJian-10) and NEUF-DIX (Non-Equilibrium Fluctuations during Diffusion in compleX liquids) are space missions sponsored by the European Space Agency (ESA) in collaboration with Roskosmos in the case of DCMIX, and with the Chinese Space Administration (CSA), in SCCO-SJ10 and NEUF-DIX.

⁴ Here, and in the rest of this paper, 2-vectors or 2×2 matrices (always printed with straight brackets) represent linear operators acting, either from \mathbb{R}^3 or from $\mathbb{R}^3 \times \mathbb{R}^3$, into $\mathbb{R}^3 \times \mathbb{R}^3$, *i.e.*, on single or pairs of 3D-vectors in the real space (∇T , ∇w_i , $\mathbf{J}_i^{(x)}$, etc.) to give pairs of 3D-vectors.

⁵ At least in the mole-average and barycentric frames of reference. Some considerations about the volume-average frame of reference follow in sect. 7.

ratio of $\nabla x_1/\nabla T$, but on a linear combination of $\nabla x_1/\nabla T$ and $\nabla x_2/\nabla T$. Hence, in general, no Soret coefficient can be unequivocally assigned to each one of the individual components of the mixture. Although in sect. 5, when discussing binary limits in more detail, the physical interpretation of $S_{T,i}$ will be revisited, the mix-up of components implied by eq. (13) is not fully alien to transport in ternary mixtures. For instance, it is becoming common to report experimental values for the eigenvalues of the diffusion matrix [30], which, as the Soret coefficients of eq. (13), cannot be unequivocally assigned to individual components of the mixture.

3 Thermodiffusion coefficients for ternary mixtures

The contents of sect. 2 refers to a steady state, in which the total mass fluxes (containing both purely diffusive and thermodiffusive contributions) vanish. However, as is the case for binary mixtures, the frame-invariant expression (13) of Soret coefficients for a ternary mixture can also be extended to transient situations, where mass fluxes are not zero, by introducing frame-independent thermodiffusion coefficients. To discuss thermodiffusion coefficients, as in sect. 1 for binary systems, one has to distinguish between mole and mass fluxes and associated frames of reference [8]. For instance, the two independent mole diffusion fluxes relative to the mole-average velocity are defined as

$$\begin{pmatrix} \mathbf{J}_1^{(x)} \\ \mathbf{J}_2^{(x)} \end{pmatrix} = c_t \begin{pmatrix} x_1 [\mathbf{u}_1 - (x_1 \mathbf{u}_1 + x_2 \mathbf{u}_2 + x_3 \mathbf{u}_3)] \\ x_2 [\mathbf{u}_2 - (x_1 \mathbf{u}_1 + x_2 \mathbf{u}_2 + x_3 \mathbf{u}_3)] \end{pmatrix}, \quad (15)$$

in terms of the velocities of the three species, \mathbf{u}_i , measured in an inertial reference frame. For introducing frame-independent thermodiffusion coefficients, it is convenient to first consider this mole-average frame of reference. For the general unsteady case, and inspired by eq. (13), one expresses the mole diffusion fluxes of eq. (15) as

$$\begin{pmatrix} \mathbf{J}_1^{(x)} \\ \mathbf{J}_2^{(x)} \end{pmatrix} = -c_t \left\{ \mathbf{D}^{(x)} \cdot \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \end{pmatrix} + \mathbf{X} \cdot \begin{bmatrix} D_{T,1} \\ D_{T,2} \end{bmatrix} \nabla T \right\}, \quad (16)$$

where \mathbf{X} represents a shorthand notation for the matrix

$$\mathbf{X} = \begin{bmatrix} x_1(1-x_1) & -x_1x_2 \\ -x_1x_2 & x_2(1-x_2) \end{bmatrix}, \quad (17)$$

$\mathbf{D}^{(x)}$ is the Fick diffusion matrix in the mole-average frame of reference, and $D_{T,1}$ and $D_{T,2}$ are the frame-independent thermodiffusion coefficients. The total molar density of the mixture is expressed in this case as $c_t = c_1 + c_2 + c_3$. Next, using eq. (14), one can rewrite eq. (16) as

$$\begin{pmatrix} \mathbf{J}_1^{(x)} \\ \mathbf{J}_2^{(x)} \end{pmatrix} = -c_t \left[\mathbf{D}^{(x)} \cdot \mathbf{X} \cdot \mathbf{W}^{-1} \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \end{pmatrix} + \mathbf{X} \cdot \begin{bmatrix} D_{T,1} \\ D_{T,2} \end{bmatrix} \nabla T \right],$$

where the matrix \mathbf{W} is similar to \mathbf{X} in eq. (17), but with the concentrations expressed in mass fractions. Next, recalling the relationship between the mole diffusion fluxes relative to the mole-average velocity, and mass diffusion fluxes relative to the center-of-mass velocity [8]:

$$\begin{pmatrix} \mathbf{J}_1^{(w)} \\ \mathbf{J}_2^{(w)} \end{pmatrix} = \frac{\rho_t}{c_t} \mathbf{W} \cdot \mathbf{X}^{-1} \cdot \begin{pmatrix} \mathbf{J}_1^{(x)} \\ \mathbf{J}_2^{(x)} \end{pmatrix}, \quad (18)$$

similar to eq. (8) for binary mixtures, it can be readily shown that

$$\begin{pmatrix} \mathbf{J}_1^{(w)} \\ \mathbf{J}_2^{(w)} \end{pmatrix} = -\rho_t \left\{ \mathbf{D}^{(w)} \cdot \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \end{pmatrix} + \mathbf{W} \cdot \begin{bmatrix} D_{T,1} \\ D_{T,2} \end{bmatrix} \nabla T \right\}, \quad (19)$$

where the total mass density is in this case $\rho_t = \rho_1 + \rho_2 + \rho_3$, and where

$$\mathbf{W}^{-1} \cdot \mathbf{D}^{(w)} \cdot \mathbf{W} = \mathbf{X}^{-1} \cdot \mathbf{D}^{(x)} \cdot \mathbf{X}. \quad (20)$$

Of course, eq. (20) is just the standard relationship between Fick diffusion matrices in the barycentric and in the mole-average frame of references and, taking into account the different notations, it exactly reproduces eq. (3.2.11) in the book by Taylor and Krishna [8].

On comparing eq. (16) with eq. (19) one sees that the use of concentration matrix prefactors, \mathbf{X} or \mathbf{W} , makes the thermodiffusion coefficients $D_{T,i}$ frame invariant⁶. As was the case for binaries, the numerical values for $D_{T,i}$ in eq. (16) and eq. (19) are exactly the same. Thus, the contribution of thermodiffusion to the total diffusive fluxes can be described in a frame-independent manner.

The relation between frame-invariant Soret and thermodiffusion coefficients can be readily obtained, either from eq. (16) or eq. (19), as

$$\begin{aligned} \begin{bmatrix} D_{T,1} \\ D_{T,2} \end{bmatrix} &= \mathbf{X}^{-1} \cdot \mathbf{D}^{(x)} \cdot \mathbf{X} \cdot \begin{bmatrix} S_{T,1} \\ S_{T,2} \end{bmatrix} \\ &= \mathbf{W}^{-1} \cdot \mathbf{D}^{(w)} \cdot \mathbf{W} \cdot \begin{bmatrix} S_{T,1} \\ S_{T,2} \end{bmatrix}, \end{aligned} \quad (21)$$

which, by virtue of eq. (20), are two perfectly consistent expressions. Substitution of (21) in either eq. (16) or eq. (19) allows, as in binary mixtures, the use of $S_{T,i}$ for characterizing thermodiffusion in transient states.

It is evident at this point that eq. (20) provides a route to define frame-invariant diffusion matrices for ternary systems, at the cost of re-writing Fick's law and introducing concentration prefactors in it. However, this line of research will not be further pursued here, leaving it for a more specific work. It is worth mentioning anyway that the use of eq. (20) to express the relation between Fick diffusion matrices in different reference frames represents a simplification when compared to the traditional way of

⁶ At least in the mole-average and barycentric frames of reference. Some considerations about the volume-average frame of reference follow in sect. 7.

expressing it [8]. First of all, current eq. (20) is more compact, as it requires fewer matrices. In addition, eq. (20) clearly shows that in binary systems, where all matrices reduce to scalars and the product is commutative, diffusion becomes frame-independent; while in the ternary case $D^{(x)} \neq D^{(w)}$. In the same line also notice that, for binary mixtures, all matrices in eq. (21) reduce to scalars, and eq. (5) is recovered.

The definition of frame-invariant Soret coefficients by eq. (13) and of frame-invariant thermodiffusion coefficients, by either eq. (14) or eq. (19), is the main purpose of the present work. In the remainder of this paper the contents of sects. 2 and 3 are complemented with additional, somewhat more technical, discussions of a comparison with other current definitions of thermodiffusion coefficients, binary limits, selection of dependent concentration, the usage of molar concentrations, and an extension to multi-component mixtures.

4 Alternative definitions of Soret and thermodiffusion coefficients

As mentioned at the beginning of sect. 2, there coexist currently in the literature alternative definitions of Soret and thermodiffusion coefficients for ternary mixtures, none of which has the frame-invariance properties of the ones presented here. Although it is a relatively simple exercise, for practical purposes it is convenient to explicitly display the relations among these various definitions, which is the purpose of this section. However, this exercise has to be incomplete, due to the (relatively) large number of competing definitions. Hence, to keep this discussion brief, only the Soret and thermodiffusion coefficients without any concentration prefactors, introduced by the ternary-mixtures benchmark [30], will be explicitly discussed here.

Soret and thermodiffusion coefficients defined without concentration prefactors [30] are frame dependent. To distinguish between the different families of coefficients, let us introduce the notation: $D_{T,i}^{(x)}$, $D_{T,i}^{(w)}$, $S_{T,i}^{(x)}$ and $S_{T,i}^{(w)}$. Then, the following set of relations can be established:

$$\begin{bmatrix} D_{T,1} \\ D_{T,2} \end{bmatrix} = \mathbf{X}^{-1} \cdot \begin{bmatrix} D_{T,1}^{(x)} \\ D_{T,2}^{(x)} \end{bmatrix} = \mathbf{W}^{-1} \cdot \begin{bmatrix} D_{T,1}^{(w)} \\ D_{T,2}^{(w)} \end{bmatrix}. \quad (22)$$

and

$$\begin{bmatrix} S_{T,1} \\ S_{T,2} \end{bmatrix} = \mathbf{X}^{-1} \cdot \begin{bmatrix} S_{T,1}^{(x)} \\ S_{T,2}^{(x)} \end{bmatrix} = \mathbf{W}^{-1} \cdot \begin{bmatrix} S_{T,1}^{(w)} \\ S_{T,2}^{(w)} \end{bmatrix}, \quad (23)$$

In a similar fashion, relationships between the frame-independent $D_{T,i}$ and $S_{T,i}$ with other families of Soret and thermodiffusion coefficients that various authors have introduced in ternary mixtures [25–29], can be readily established. For the sake of brevity, they will not be explicitly displayed here.

5 Binary limits

As often in ternary mixtures, it is interesting to discuss the frame-invariant thermodiffusion and Soret coefficients in the three binary sides of the ternary concentration triangle, *i.e.*, when one of the components is dilute. Initially, one has two degrees of freedom for the specification of the coefficients $S_{T,i}$ and $D_{T,i}$. However, consistency with Soret coefficients measured in the corresponding binary mixture, only leaves one degree of freedom over the three sides of the concentration triangle. In particular, the following connections with the binary coefficients hold:

$$\text{when } x_1 \rightarrow 0, \quad \begin{cases} S_{T,2} \rightarrow S_{T,2}^{(3,b)}, \\ D_{T,2} \rightarrow D_{T,2}^{(3,b)}, \end{cases} \quad (24a)$$

$$\text{when } x_2 \rightarrow 0, \quad \begin{cases} S_{T,1} \rightarrow S_{T,1}^{(3,b)}, \\ D_{T,1} \rightarrow D_{T,1}^{(3,b)}, \end{cases} \quad (24b)$$

$$\text{when } x_3 \rightarrow 0, \quad \begin{cases} S_{T,1} - S_{T,2} \rightarrow S_{T,1}^{(2,b)}, \\ D_{T,1} - D_{T,2} \rightarrow D_{T,1}^{(2,b)}, \end{cases} \quad (24c)$$

where $S_{T,i}^{(j,b)}$, $D_{T,i}^{(j,b)}$, denotes the corresponding Soret or thermodiffusion coefficient measured in the binary mixture of i and j , with j being the dependent concentration. As anticipated in sect. 2, the comparison with Soret and thermodiffusion coefficients measured in binary mixtures is direct and does not require the use of any conversion or data manipulation.

It was in the dilute limit where the binary thermodiffusion coefficient has been interpreted as a mobility [1]. The chain of arguments leading to eq. (11) for binaries can be, somehow, extended to ternaries. If we consider a dilute system of well-separated species-1 and species-2 molecules into a large majority species-3 solvent, one can take $\nabla x_1 \simeq 0$ and $\nabla x_2 \simeq 0$ in eq. (16). Then, comparing with eq. (15) one arrives at

$$\begin{aligned} \mathbf{u}_1 - \mathbf{u}_3 &= -D_{T,1} \nabla T, \\ \mathbf{u}_2 - \mathbf{u}_3 &= -D_{T,2} \nabla T. \end{aligned} \quad (25)$$

Hence, in the frame of reference where the solvent is at rest ($\mathbf{u}_3 = 0$) and for dilute $x_1, x_2 \simeq 0$, the coefficient $D_{T,1}$ represents the thermophoretic mobility associated with the drift velocity of species-1 molecules. Similarly, $D_{T,2}$ represents the thermophoretic mobility associated with the drift velocity of species-2 molecules. The same arguments can be applied to the other two vertexes of the concentration triangle.

To finalize this section it is worth mentioning that eqs. (24) also provide a clue for a possible physical interpretation of the Soret coefficients $S_{T,1}$ and $S_{T,2}$. Equation (13) would express thermodiffusion of 1 and 2 in the presence of 3 as a linear combination of (1, 3) thermodiffusion with (2, 3) thermodiffusion; with $S_{T,1}$ representing thermodiffusion of 1 in 3, congruent with eq. (24b); and $S_{T,2}$ representing thermodiffusion of 2 in 3, congruent with eq. (24a). The congruence of eq. (24c) within this picture will be analyzed next.

6 Choice of the dependent concentration

In a binary mixture one has two choices for the dependent concentration and, thus, two possible Soret coefficients to describe thermodiffusion. However, according to eq. (4), one of these Soret coefficients is minus the other, so that switching between them is quite straightforward.

In a ternary mixture the situation is more complicated since one has three choices for the dependent concentration, meaning three different possible pairs of Soret coefficients. However, only one of these pairs is independent. To establish the relationships between these different Soret pairs one uses $x_1 + x_2 + x_3 = 1$ to deduce from eq. (13):

$$\begin{bmatrix} x_1(1-x_1) & -x_1x_3 \\ -x_1x_3 & x_3(1-x_3) \end{bmatrix} \begin{bmatrix} S_{T,1} - S_{T,2} \\ -S_{T,2} \end{bmatrix} \nabla T = - \begin{pmatrix} \nabla x_1 \\ \nabla x_3 \end{pmatrix},$$

and

$$\begin{bmatrix} x_2(1-x_2) & -x_2x_3 \\ -x_2x_3 & x_3(1-x_3) \end{bmatrix} \begin{bmatrix} S_{T,2} - S_{T,1} \\ -S_{T,1} \end{bmatrix} \nabla T = - \begin{pmatrix} \nabla x_2 \\ \nabla x_3 \end{pmatrix}.$$

To summarize the expressions above, it is convenient to adopt the nomenclature $S_{T,i}^{(j)}$ with superscript j designating the component of the ternary mixture whose concentration is considered as the dependent variable; and subscript i , like in eq. (13), associates $S_{T,i}^{(j)}$ with the corresponding independent concentration at the right-hand side of eq. (13). Then, for instance, the two independent Soret coefficients used so far become $S_{T,1}^{(3)}$ (associated with component 1) and $S_{T,2}^{(3)}$ (associated with component 2). Adopting this nomenclature, the two precedent equations imply:

$$\begin{aligned} S_{T,1}^{(2)} &= S_{T,1}^{(3)} - S_{T,2}^{(3)}, & S_{T,3}^{(2)} &= -S_{T,2}^{(3)}, \\ S_{T,2}^{(1)} &= S_{T,2}^{(3)} - S_{T,1}^{(3)}, & S_{T,3}^{(1)} &= -S_{T,1}^{(3)}. \end{aligned} \quad (26)$$

The four eqs. (26) mean that, of the initially three different pairs of Soret coefficients, only one pair is independent. It is also interesting to note the consistency with eq. (24c) and with the situation in binaries, where exchange of independent concentration implies a sign change in the Soret coefficient.

Since there are more Soret coefficients, the relationships among them, eqs. (26), are a bit more complicated than in the case of binaries. However, simple ‘‘circular’’ relations like

$$\begin{aligned} S_{T,1}^{(3)} + S_{T,3}^{(2)} + S_{T,2}^{(1)} &= 0, \\ S_{T,2}^{(3)} + S_{T,3}^{(1)} + S_{T,1}^{(2)} &= 0, \end{aligned} \quad (27)$$

hold, which would be certainly very useful when interchanging the order of components in a ternary mixture. Alternative proposals to describe the Soret effect in ternary mixtures using the $D'_{T,i}$ of sect. 4 or thermal diffusion ratios [31] cite as an advantage the existence of ‘‘circular’’ relationships equivalent to the current eqs. (27).

Similarly to what was done explicitly here for Soret coefficients, it is also possible to discuss relations between the various thermodiffusion coefficients obtained by swapping the components of the mixture. They are quite similar to eqs. (26), (27), and are not going to be explicitly displayed here.

7 Molar concentrations

It is also quite common to express the concentrations of components in a mixture as mole per unit volume, $c_i = c_t x_i$. However, because typically c_t depends on temperature, this choice introduces complications when temperature gradients are present, and has not been the most popular for the description of thermodiffusion. As an illustration of these complications consider that, for a non-isothermal binary mixture, one has that in general $\nabla(c_1 + c_2) \neq 0$, in contrast with concentrations in mole or mass fraction where $\nabla(x_1 + x_2) = \nabla(w_1 + w_2) = 0$ always.

In spite of these difficulties, some books or reviews present the theory of thermodiffusion in binaries in terms of molar concentrations [5,32], as well as some experimentalists report on binary Soret coefficients using these concentration units [33,34]. However, a detailed examination shows that in these works [5,32–34] it is implicitly assumed: i) That the dependence of c_t on temperature can be neglected. ii) That the concentration x of the ‘‘solute’’ is very low, so that $1 - x \simeq 1$. In that case, multiplying eq. (4) for a binary mixture by c_t , one obtains [5,32]:

$$cS_T \nabla T = -\nabla c. \quad (28)$$

Equation (28) shows that, with the restrictions mentioned above, Soret coefficients can be defined in a binary mixture in terms of molar concentrations, and that they are equal to the more general definitions of eq. (4) or eq. (7), in terms of mole fraction or mass fraction, respectively. Regarding transient states, within the same approximations above, thermodiffusion coefficients in terms of molar concentration have also been defined [5]. In this case, the relevant diffusion flux is in the volume-average frame of reference [8].

Solving eq. (28) leads to the so-called exponential depletion law [35], which is the starting point of many experimental works reporting Soret coefficients, in particular of macromolecules, biomolecules or colloidal particles [33–36]. In these cases the assumptions mentioned in the previous paragraph typically hold. Notice that the term thermophoresis is often used to refer to thermodiffusion in these colloidal or macromolecular systems with low ‘‘solvent’’ concentration.

Regarding ternary mixtures it is not the intention of this paper to go into the details, but one can convince oneself readily that, within the same approximations mentioned above for binary mixtures, Soret or thermodiffusion coefficients can be defined on the basis of molar concentrations that will be numerically the same as those of eq. (13).

8 Extension to multi-component mixtures

So far this work has been restricted to a explicit discussion of ternary mixtures, mainly because of the recent experimental interest on thermodiffusion in these systems [21–23]. However, the ideas presented here can be readily generalized to multi-component mixtures. Indeed, for a n -component mixture one can define $(n-1) \times (n-1)$ matrices \mathbf{X} and \mathbf{W} as

$$X_{ij} = x_i \delta_{ij} - x_i x_j, \quad W_{ij} = w_i \delta_{ij} - w_i w_j, \quad (29)$$

with $i, j \in \{1, n-1\}$ being the independent components, while x_n or w_n are the dependent concentrations, and δ_{ij} the Kronecker deltas. Then, a little bit of algebra shows that eq. (14) holds in general, namely:

$$\mathbf{X}^{-1} \cdot \begin{pmatrix} \nabla x_1 \\ \nabla x_2 \\ \vdots \\ \nabla x_{n-1} \end{pmatrix} = \mathbf{W}^{-1} \cdot \begin{pmatrix} \nabla w_1 \\ \nabla w_2 \\ \vdots \\ \nabla w_{n-1} \end{pmatrix}; \quad (30)$$

as well as eq. (18)

$$\begin{pmatrix} \mathbf{J}_1^{(w)} \\ \mathbf{J}_2^{(w)} \\ \vdots \\ \mathbf{J}_{n-1}^{(w)} \end{pmatrix} = \frac{\rho_t}{c_t} \mathbf{W} \cdot \mathbf{X}^{-1} \cdot \begin{pmatrix} \mathbf{J}_1^{(x)} \\ \mathbf{J}_2^{(x)} \\ \vdots \\ \mathbf{J}_{n-1}^{(x)} \end{pmatrix}. \quad (31)$$

Hence, matrices \mathbf{X} and \mathbf{W} can be used to define frame-independent Soret and thermodiffusion coefficients for multi-component systems in an exactly similar fashion as explicitly elucidated in this paper for ternary mixtures. In particular, eqs. (16), (19) and (20) hold in general, for an arbitrary number of components, which opens the way to a description of thermodiffusion in a frame-independent way for the most general case.

9 Summary and conclusions

It was shown how, by introducing appropriate concentration prefactors in matrix form, \mathbf{X} or \mathbf{W} as given by eq. (29), it is possible to define frame-independent thermodiffusion and Soret coefficients for ternary and multi-component mixtures. Invariance is exact when switching between barycentric and mole-average frames of reference while, for the volume frame of reference (molar concentrations), invariance only holds in the dilute limit and neglecting thermal expansion. Also in the dilute limit, frame-invariant thermodiffusion coefficients can be interpreted as thermophoretic mobilities, and related to the drift velocity under a temperature gradient of each type of molecules.

As a corollary of the present developments, nice and compact expressions have been presented for switching between different representations of concentration gradients,

eq. (14); diffusion fluxes, eq. (18); and diffusion matrices, eq. (20). These expressions involve the same matrices, \mathbf{X} or \mathbf{W} , introduced in eq. (29) and in the definition of the frame-invariant coefficients. It has also been suggested how, eventually, frame-independent diffusion matrices might be defined.

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