

**Fick's law: A derivation based on continuum mechanics**

**La ley de Fick: Una deducción basada en la mecánica del continuo**

F.J. Valdés-Parada<sup>1</sup>, B.D. Wood<sup>2\*</sup>, S. Whitaker<sup>3†</sup>

<sup>1</sup>*División de Ciencias Básicas e Ingeniería. Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco 186, col. Vicentina, CDMX, 09340, Mexico.*

<sup>2</sup>*School of Chemical, Biological and Environmental Engineering, Oregon State University. Corvallis 97331 OR, United States.*

<sup>3</sup>*Department of Chemical Engineering, University of California at Davis. Davis 95616 CA, United States.*

Received: July 25, 2023; Accepted: September 19, 2023

**Abstract**

In this study we derive Fick's law on the basis of the principles of chemical species mass and momentum conservation. The goal is to provide a simple derivation of this equation using a continuum mechanics approach. In addition, the associated assumptions and constraints that may limit its application are clearly identified. Our result is an analysis that derives Fick's law in liquid systems, and it is presented so that only a basic knowledge of continuum mechanics is needed to follow the derivation.

*Keywords:* Fick's law, dilute solution, diffusion velocity, continuum mechanics, multicomponent mixtures.

**Resumen**

En este estudio deducimos la ley de Fick con base en los principios de conservación de masa y de cantidad de movimiento de especies químicas. El propósito es proporcionar una deducción sencilla de esta ecuación usando la mecánica del medio continuo. Además, las suposiciones y restricciones asociadas que pueden limitar su aplicación son claramente identificadas. Nuestro resultado es un análisis que deduce a la ley de Fick en sistemas líquidos y está presentada de tal forma que sólo se requiera un conocimiento básico de la mecánica del continuo para seguir la deducción.

*Palabras clave:* ley de Fick, solución diluida, velocidad de difusión, mecánica del continuo, mezclas multicomponentes.

\* Corresponding author. E-mail: [brian.wood@oregonstate.edu](mailto:brian.wood@oregonstate.edu);

<https://doi.org/10.24275/rmiq/Fen23102>

ISSN:1665-2738, issn-e: 2395-8472

† Professor Stephen Whitaker passed away 9 May 2023.

## 1 Introduction

Most chemical transport processes involving diffusive transport of chemical species are represented by Fick's law under the assumption that the solution is appropriately dilute. From a theoretical perspective, Fick's law is a special case of the more general governing equations for the diffusion velocity,  $\mathbf{u}_A$ , in binary and multicomponent systems. A short, but useful, review of the theoretical results is presented by Bird and Klingenberg (2013). While the governing equation for  $\mathbf{u}_A$  is not well known, Fick's law (which ultimately depends on the diffusion velocity) is widely used in the literature (see for example Bird *et al.*, 2006; Slattery, 1999; Deen, 2012; Cussler, 2009; Bailey and Ollis, 1986; Levenspiel, 1998; Hirschfelder *et al.*, 1964; Rosner, 2000; Borja-Málaga *et al.*, 2022; Jaramillo-Gutiérrez *et al.*, 2022, among many others). The original source of Fick's work has been identified by many researchers; however, the original text is in German, indicating that it has been actually read by only a fraction of those citing it. A detailed description and analysis of Fick's work has been provided by Patzek (2014a,b). The author of these works was fortunate to have a German speaking neighbor who helped translate the relevant sections of the text for his analysis. Patzek (2014a,b) noted that the original text was reported in 1855

Fick, A. (1855). Ueber Diffusion. *Annalen der Physik und Chemie von J.C. Pogendorff*, 94, 59-86.

and highlighted the fact that Fick did not *derive* what is known today as Fick's law, although it is often stated in the literature that Fick provided a derivation. Instead, Fick *suggested* what he thought was a reasonable mathematical proposition for the diffusive flux in a binary system by making an analogy with Fourier's and Ohm's laws. In a vectorial form, Fick's description can be expressed as

$$\mathbf{J}_A = -D\nabla c_A. \quad (1)$$

Since the time of Fick's experiments, there have been many efforts to derive Fick's law from more fundamental principles [e.g., from the tenants of Rational Mechanics, as presented by Truesdell (1984)]. Moreover, both Pekař and Samohyl (2014) and Liu and Müller (1984) present examples of the development of Fick's law arising from an analysis via Rational Mechanics for linear fluids.

The objective of this work is to provide a simple, yet still rigorous, derivation of Fick's law in the form given in Eq. (1) from the framework of continuum mechanics, and to analyze the *assumptions* and *restrictions* behind it. The distinction of this

work with previous reports in the literature relies on the systematic use of simplification of the species equations of motion to yield the Maxwell-Stefan equations and subsequently to Fick's law. This provides a simple derivation that has pedagogical value. In particular, our focus has been to develop a presentation that can be understood by students in engineering and science, requiring primarily familiarity with the balances arising in continuum mechanics.

The work is organized as follows: In section 2, a brief historical background is provided regarding the various derivations of Fick's law. Then, in section 3, the main axioms related to species mass and momentum transport are presented and discussed. Section 4 is dedicated to the derivation and simplification of the governing equation for the species mass diffusion velocity. In section 5, we discuss the assumptions that lead to *ideal* linear behavior for liquid solutions, which are applied to the simplified species momentum balance equation. The discussion is then focused on  $N$ -component (section 6) and subsequently simplified to consider binary (section 7) systems. In the latter, the classical expression of Fick's law is derived. Finally, the main conclusions of this work are provided in section 8.

## 2 Historical background

A pertinent starting point in the study of diffusion is the work of Graham (1829), who performed experiments on gases (in particular hydrogen and oxygen) and found that hydrogen escaped through a plate four times faster than oxygen. This was probably the first report of diffusion (or *spontaneous intermixture* in Graham's words). He noted [and later confirmed with better experiments (Graham, 1863)] that this phenomenon was increased by heat and established that flow velocities were inversely proportional to the square root of the gases densities. He also conducted experiments in liquid mixtures (Graham, 1850) and found that, in this case, diffusion takes place at a much slower rate than in gases (and this process only got slower over time), although it was also favored by temperature. The differences between liquid and gas diffusion became more evident when he used concentrated solutions.

Motivated by Graham's experiments in liquids, and by the success of Fourier's law to study heat transfer, Fick (1855) proposed a one-dimensional version of equation (1) and was able to reproduce Graham's experimental results and he even performed experiments on his own (see analysis by Patzek (2014a,b)). In fact, he noticed that the diffusion coefficient  $D$  increases (in a nonlinear manner) with the temperature.

Graham's experiments motivated another scientist, Joseph Loschmidt (1870), to carry out experiments of gas diffusion using a device similar to Graham's, and to quantify the corresponding diffusion coefficient of ten pairs of gases. Soon after Loschmidt's experiments, Maxwell (1873) developed an early version of the kinetic theory of gases that allowed him to predict the diffusion coefficient for binary mixtures of gases. Maxwell was subsequently able to validate his kinetic theory using Loschmidt's results. Furthermore, the theories of Maxwell and Stefan (1871) constitute the cornerstone for the study of diffusion in multicomponent systems. The Maxwell-Stefan equations are an alternative to Fick's law and will be presented later on in the text.

The extension to colloids (and large molecules) in liquids was investigated by Einstein (1905). He derived the following expression for the diffusion coefficient in liquids

$$D = \frac{\Delta^2}{2t}. \quad (2)$$

Here,  $\Delta$  is the mean square displacement of the molecules in a given direction at a certain time  $t$ . The relevance of the above equation is that it relates a quantity at the continuum-scale level, the diffusion coefficient, with a quantity defined at the molecular scale. Certainly,  $\Delta^2$  can be expressed in terms of the temperature,  $T$  as follows (see, for example, Chap. 4 in Perrin, 1913)

$$\Delta^2 = \frac{2RTt}{N_A C}, \quad (3)$$

where  $N_A$  is the Avogadro number and, following Stokes (1851),  $C = 6\pi\mu r$ , with  $\mu$  and  $r$  being the fluid viscosity and the radius of the solute particle, respectively. Substituting the above relations into Eq. (2) leads to the well-known Stokes-Einstein equation

$$D = \frac{RT}{6\pi\mu r N_A}. \quad (4)$$

The above is just one among many expressions available for the prediction of the diffusion coefficient that have been developed using various theoretical approaches (see, for instance Chap. 17 in Bird et al., 2006).

During the first half of the twentieth century, Fick's law gained much interest, however, in its original conception it was limited to binary mixtures. Onsager (1945), suggested generalizing Fick's law to an  $N$ -component system as follows

$$\mathbf{J}_A = - \sum_{k=1}^{N-1} D_{Ak} \nabla c_k. \quad (5)$$

Here,  $D_{Ak}$  represent multicomponent diffusion coefficients. This expression shows that the diffusive

mass flux of a chemical species is influenced by the concentration gradients of  $N - 1$  chemical species. The above equation can be derived on the basis of nonequilibrium thermodynamics as shown by Curtiss and Bird (1999). Using this same approach, it is also possible to derive the generalized Maxwell-Stefan equations (see, for example, Krishna and Wesselingh, 1997).

Truesdell (1962) identified four approaches to model diffusive mass transfer of a chemical species in a mixture. These are:

1. The kinematic approach, which he viewed as being unsupported by fundamental principles, and leads to Fick's law.
2. The hydrodynamical approach, which is focused on the arguments originally presented by Stefan (1871) that suggest using a species momentum equation absent of viscous stress and chemical reactions contributions.
3. The kinetic theory approach where diffusion is a sum of binary phenomena as a first-order approximation of the Boltzmann equation (*i.e.*, the Chapman-Enskog process in Maxwell kinetic theory).
4. The thermodynamic approach that leads to the Eckart-Meixner equations for diffusion.

He then proposed a mechanical theory of diffusion, which starts with a species momentum balance expression that incorporates viscous effects. Truesdell (1962) suggested a linear relationship between the species momentum supply and the relative species diffusive velocities. He then illustrated how his theory was related to the four approaches listed above. However, in the conclusion of this work, the particular conditions that lead to Fick's law were not clearly detailed.

Shortly after, Adkins (1963) reported an analysis similar to the one by Truesdell (1962) and proposed a theory for diffusion under a mechanical basis in the absence of chemical reactions. In his analysis, Adkins assumed that the body force in the species momentum equation could be decomposed into an external body force and a diffusive force, the latter was assumed to depend only on the mixture composition and the relative motions of the chemical species. In addition, he proposed the following assumptions to be applied to binary mixtures in order to retrieve Fick's law: 1) the chemical species are perfect fluids so that the contribution from viscous stress can be ignored, 2) the inertial contributions are discarded, 3) the total density of the mixture can be approximated as constant, and 4) there are no significant external body forces. This theory was applied to several study cases including diffusion under non-Newtonian flow conditions through elastic solids (Green and Adkins,

1964; Adkins, 1964), diffusion in a compressible and incompressible mixture of ideal fluids (Mills, 1966). These assumptions are consistent with those adopted in this work (see inequalities (34) and (36) in the material following).

Many derivations of Fick's law from other perspectives have been reported over the past fifty years. As further examples, Atkin and Craine (1976) used both irreversible thermodynamics and gas kinetics theory to derive a version of Fick's law. Later on, Lowney and Larrabee (1980) regarded diffusion as a Markov process and derived Fick's law for the case in which the diffusion coefficient depends on the solute concentration. More recently, Kerkhof and Geboers (2005) proposed an approximate solution of the Boltzmann equation for dilute monoatomic gases that yielded a momentum balance equation for chemical species, which eventually lead to Fick's law.

Finally, there has been some work dedicated to the derivation of Fick's law from a continuum mechanics approach, *i.e.*, that rely on simplifying the species equations of motion. This is the approach adopted in the developments below; we have attempted to identify similarities and differences with previous developments. We note that the derivations provided in the following start with balances developed by Whitaker (1986) and continued in part by the works of Whitaker (2009a,b) and del Río and Whitaker (2016). However, the derivations presented here represent the first completed presentation of the results from a purely mechanical perspective.

### 3 Fundamental axioms for species mass and momentum transport

Our derivation of Eq. (1) begins with the fundamental axiom for the mass conservation of chemical species that can be expressed, on a mass basis, in the form [Whitaker, 2012; Truesdell and Toupin, 1960, Truesdell (1984, Eq. 5.11 ff.)]

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}_A) = r_A, \quad A = 1, 2, \dots, N. \quad (6)$$

A comment regarding notation is useful here. We assume that there are  $N$  chemical species forming a liquid solution. Each chemical species is uniquely identified by consecutive integer numbers, so that the species are labeled  $1, 2, \dots, N$ . The  $N^{\text{th}}$  species will always be considered the *redundant* species, and this will be defined in detail later. We will use the letters  $A$  and  $B$  as dummy indexes, so that  $A$  and  $B$  represent some integer in the sequence  $(1, 2, \dots, N)$ . Thus, for example, we may write the sum of the mole fractions of the  $N$  species by any of the equivalent expressions

following

$$1 = x_1 + x_2 + \dots + x_N = \sum_{A=1}^{A=N} x_A = \sum_{B=1}^{B=N} x_B. \quad (7)$$

With this notation in place, we proceed by providing the supplemental axiom that the sum of the net mass rates of production and consumption of all chemical species is zero. This is expressed in the following form

$$\sum_{A=1}^{A=N} r_A = 0. \quad (8)$$

Equation (6) is often referred to as the *species continuity equation* and it can be used to derive the *total continuity equation*. This is obtained by summing Eq. (6) over all species, taking into account Eq. (8), in order to obtain

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (9)$$

Here, the total density,  $\rho$ , the mass average velocity,  $\mathbf{v}$ , and the species mass fraction,  $\omega_A$ , are defined by

$$\rho = \sum_{A=1}^{A=N} \rho_A, \quad \mathbf{v} = \sum_{A=1}^{A=N} \omega_A \mathbf{v}_A, \quad \omega_A = \frac{\rho_A}{\rho}. \quad (10)$$

The species velocity,  $\mathbf{v}_A$ , can be decomposed into the mass average velocity,  $\mathbf{v}$ , and the mass diffusion velocity,  $\mathbf{u}_A$ , according to (see Appendix A)

$$\mathbf{v}_A = \mathbf{v} + \mathbf{u}_A, \quad A = 1, 2, \dots, N. \quad (11)$$

Clearly, in order to retrieve the definition of the mass average velocity, it is necessary that the sum of the diffusive fluxes is zero; this is

$$\sum_{A=1}^{A=N} \rho_A \mathbf{u}_A = \mathbf{0}. \quad (12)$$

Use of the decomposition given in Eq. (11) into Eq. (6) leads to

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}) = -\nabla \cdot (\rho_A \mathbf{u}_A) + r_A, \quad A = 1, 2, \dots, N. \quad (13)$$

The molar form of the above result is obtained by the use of the definitions

$$\rho_A = c_A M_A, \quad r_A = R_A M_A, \quad A = 1, 2, \dots, N, \quad (14)$$

with  $M_A$  being the molecular weight of species  $A$ . This leads to the following versions of Eqs. (13) and (8)

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = -\nabla \cdot \mathbf{J}_A + R_A, \quad A = 1, 2, \dots, N, \quad (15a)$$

$$\sum_{A=1}^{A=N} R_A M_A = 0. \quad (15b)$$

In Eq. (15a), we have adopted a form for the diffusive flux that mixes the molar concentration with the mass-averaged velocity. While this form is not common

[see Eq. 16.1-8 and discussion in §16.2 in Bird *et al.* (1960)], this mixed term creates no conceptual or mathematical difficulties at this juncture in the development. The diffusive flux of species  $A$  is defined as

$$\mathbf{J}_A = c_A \mathbf{u}_A, \quad A = 1, 2, \dots, N. \quad (16)$$

In order to determine the *diffusion velocity*,  $\mathbf{u}_A$ , we need the governing differential equation for  $\mathbf{u}_A$ , which is developed in the following section. Here, it should be kept in mind that the objective of this work is to obtain a representation for the diffusive flux,  $\mathbf{J}_A$ , that leads to Fick's law.

The two *fundamental axioms* for the laws of continuum mechanics (the axioms for conservation of linear and angular momentum) can be expressed by [see, for instance Whitaker, (2009b); Truesdell and Toupin (1960, Sect. 215 and 295), Truesdell (1984, Eq. 5.11 ff.)]

$$\frac{\partial \rho_A \mathbf{v}_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}_A \otimes \mathbf{v}_A) = \rho_A \mathbf{b}_A + \nabla \cdot \mathbf{T}_A + \sum_{B=1}^{B=N} \mathbf{P}_{AB} + r_A \mathbf{v}_A^*, \quad A = 1, 2, \dots, N, \quad (17)$$

$$\mathbf{T}_A = \mathbf{T}_A^T, \quad A = 1, 2, \dots, N. \quad (18)$$

Here,  $\mathbf{V} = \mathbf{v} \otimes \mathbf{v}$  is the dyadic  $V_{ij} = v_i v_j$ . Note that Eq. (18) arises directly from the conservation of species angular momentum (also known as *moment of momentum*), and thus replaces it in this set of equations [cf. Slattery (1999, Eq. 8.3.3-2)].

The equations above resemble to Cauchy's equations of motion with the notable difference that (1) they are referred to chemical species (rather than a single phase), (2) the last two terms in Eq. (17) contain contributions due to the diffusive force exerted by the thermomechanical interaction of the other species on species  $A$  ( $\mathbf{P}_{AB}$ ) (Bowen, 1967), and (3) they reflect the possible increase (or decrease) of momentum due to chemical reactions. Note that, by definition,  $\mathbf{P}_{AA} = \mathbf{0}$ . In the reaction term, the velocity associated with the net production rate of species  $A$  momentum due to chemical reactions is represented by  $\mathbf{v}_A^*$ , which is not, in general, equal to the species velocity  $\mathbf{v}_A$ , although some authors have adopted such assumption (Datta and Vilekar, 2010). Note that the terms dealing with volume forces and chemical reactions (first and last terms on the right-hand side in Eq. (17), respectively) could also have been written as sums of all the external forces and all the production reactions associated to species  $A$  (see, for example, Eq. (2) in Datta and Vilekar, 2010). Nevertheless, these terms are kept in their current form in the rest of the analysis for the sake of simplicity.

Two supplemental axioms were given by Whitaker (2009b) and Truesdell and Toupin (1960) in the form

$$\sum_{A=1}^{A=N} \sum_{B=1}^{B=N} \mathbf{P}_{AB} = \mathbf{0}, \quad (19a)$$

$$\sum_{A=1}^{A=N} r_A \mathbf{v}_A^* = \mathbf{0}. \quad (19b)$$

Similar axioms are given for binary mixtures by Truesdell and Toupin (1960, p. 568, 707). The axiom given by Eq. (19a) is also specified by Hirschfelder *et al.* (1964, Eq. 7.3-30); they do not consider reaction, thus there is no axiom corresponding to Eq. (19b). The above axioms show that  $\sum_{B=1}^{B=N} \mathbf{P}_{AB}$  and  $r_A \mathbf{v}_A^*$  only have an internal effect (*i.e.*, they only influence the species momentum transport), that end up having no effect in the entire mixture as anticipated by Atkin and Craine (1976).

The total linear momentum equation is obtained by summing Eq. (17) over all species and imposing the two *supplemental axioms* given by Eqs. (19). This leads to a consistency relationship for the entire phase (where the phase is equal to the sum of all species)

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) = \rho \mathbf{b} + \nabla \cdot \mathbf{T}. \quad (20)$$

Here, the following definitions have been employed

$$\rho \mathbf{v} = \sum_{A=1}^{A=N} \rho_A \mathbf{v}_A, \quad \rho \mathbf{b} = \sum_{A=1}^{A=N} \rho_A \mathbf{b}_A, \quad (21)$$

and

$$\mathbf{T} = \sum_{A=1}^{A=N} (\mathbf{T}_A - \rho_A \mathbf{u}_A \otimes \mathbf{u}_A). \quad (22)$$

This expression can be compared with cf. Truesdell (1984, Eq. 5.14), where Truesdell writes  $\mathbf{T}_I = \sum_{A=1}^{A=N} \mathbf{T}_A$ . Our objective at this point is to use Eqs. (17) and (20) to obtain the governing equation for the species diffusion velocity,  $\mathbf{u}_A$ . We begin with the following proposal for the species  $A$  stress tensor

$$\mathbf{T}_A = -p_A \mathbf{I} + \boldsymbol{\tau}_A, \quad A = 1, 2, \dots, N, \quad (23)$$

in which  $p_A$  is the partial pressure of species  $A$  and  $\boldsymbol{\tau}_A$  its corresponding viscous stress. The total stress tensor takes the following form after substitution of Eq. (23) into Eq. (22)

$$\mathbf{T} = \sum_{A=1}^{A=N} (-p_A \mathbf{I} + \boldsymbol{\tau}_A - \rho_A \mathbf{u}_A \otimes \mathbf{u}_A), \quad (24)$$

or, equivalently

$$\mathbf{T} = -p \mathbf{I} + \boldsymbol{\tau} - \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \otimes \mathbf{u}_A, \quad (25)$$

in which the following definitions have been used

$$\rho = \sum_{A=1}^{A=N} \rho_A, \quad \boldsymbol{\tau} = \sum_{A=1}^{A=N} \boldsymbol{\tau}_A. \quad (26)$$

Note that in Eq. (25), the term  $\sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \otimes \mathbf{u}_A$  is identically zero when there is global equilibrium of diffusive fluxes for species  $A$  [*i.e.*, there are no spatial gradients of the density, specific internal energy, or temperature of species  $A$  in the solution; cf. Truesdell (1984), Eq. 5.31]. There may be instances (e.g., in dilute solutions) where this term can be assumed to be small compared to other terms in the stress tensor. While we do not pursue such restrictions at this juncture, it is worth keeping in mind that the sum of the species deviation velocities  $\sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \otimes \mathbf{u}_A$  is unlikely to play a significant role in many practical cases of interest.

It is important to recognize that the application of Eqs. (23) and (25) requires an assumption of *local thermodynamic equilibrium* [Batchelor (1967, §1.2), DeGroot and Mazur (1967, p. 23)], and this should be satisfactory for many, but not all, mass transfer processes under a wide range of conventional engineering conditions.

## 4 Extraction of the diffusion term from the momentum conservation equation

The next step in the derivation of Eq. (1) requires the development of the governing equation for the species mass diffusion velocity,  $\mathbf{u}_A$ . We begin by multiplying Eq. (6) by the species velocity,  $\mathbf{v}_A$ , to obtain

$$\mathbf{v}_A \left[ \frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}_A) \right] = r_A \mathbf{v}_A, \quad A = 1, 2, \dots, N, \quad (27)$$

and then subtract this equation from Eq. (17) to rewrite it in the following form

$$\rho_A \left( \frac{\partial \mathbf{v}_A}{\partial t} + \mathbf{v}_A \cdot (\nabla \otimes \mathbf{v}_A) \right) = \rho_A \mathbf{b}_A + \nabla \cdot \boldsymbol{\tau}_A + \sum_{B=1}^{B=N} \mathbf{P}_{AB} + r_A (\mathbf{v}_A^* - \mathbf{v}_A), \quad A = 1, 2, \dots, N. \quad (28)$$

Note that the above equation is equivalent to Eq. (2.20) in the work of Atkin and Craine (1976). Here, we have defined the gradient of the vector field by the dyadic expression  $(\nabla \otimes \mathbf{v}_A) = \frac{\partial v_{Aj}}{\partial x_i}$  which is appropriate this dyadic in *postfactor* position (Gibbs, 1906b, Art. 109).

Following an analogous approach, multiplication of Eq. (9) by the mass average velocity yields

$$\mathbf{v} \left[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right] = \mathbf{0}, \quad (29)$$

and then subtract this equation from Eq. (20) to obtain

$$\rho \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot (\nabla \otimes \mathbf{v}) \right) = \rho \mathbf{b} + \nabla \cdot \boldsymbol{\tau}. \quad (30)$$

Multiplication of this result by the mass fraction,  $\omega_A$ , and the use of Eq. (22) leads to

$$\rho_A \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot (\nabla \otimes \mathbf{v}) \right) = \rho_A \mathbf{b} + \omega_A \nabla \cdot \left[ \sum_{B=1}^{B=N} (\boldsymbol{\tau}_B - \rho_B \mathbf{u}_B \otimes \mathbf{u}_B) \right]. \quad (31)$$

We now subtract this result from Eq. (28) to obtain the desired *governing differential equation* for  $\mathbf{u}_A$  given by

$$\begin{aligned} \rho_A \left( \frac{\partial \mathbf{u}_A}{\partial t} + \mathbf{v}_A \cdot (\nabla \otimes \mathbf{u}_A) + \mathbf{u}_A \cdot (\nabla \otimes \mathbf{v}) \right) &= \rho_A (\mathbf{b}_A - \mathbf{b}) \\ &+ \nabla \cdot \boldsymbol{\tau}_A - \omega_A \nabla \cdot \left[ \sum_{B=1}^{B=N} (\boldsymbol{\tau}_B - \rho_B \mathbf{u}_B \otimes \mathbf{u}_B) \right] \\ &+ \sum_{B=1}^{B=N} \mathbf{P}_{AB} + r_A (\mathbf{v}_A^* - \mathbf{v}_A), \quad A = 1, 2, \dots, N-1. \end{aligned} \quad (32)$$

Here, we note that there are only  $N-1$  independent equations represented by this result because we have used the sum of all equations to obtain it. The selection of which species to exclude from the the system is arbitrary, but, as noted previously, this species is *redundant*, and will always be indexed by the integer  $N$ . The conservation of the  $N^{\text{th}}$  species can be determined by summing the results for the first  $N-1$  species in  $A$ , and subtracting this balance from Eq. (20).

At this point, we make use of the proposal given by Eq. (23) along with the definitions given by Eqs. (26) to obtain the following form of the governing equation for the diffusion velocity

$$\begin{aligned} \rho_A \left( \frac{\partial \mathbf{u}_A}{\partial t} + \mathbf{v}_A \cdot (\nabla \otimes \mathbf{u}_A) + \mathbf{u}_A \cdot (\nabla \otimes \mathbf{v}) \right) \\ - \omega_A \nabla \cdot \left[ \sum_{B=1}^{B=N} \rho_B \mathbf{u}_B \otimes \mathbf{u}_B \right] &= -(\omega_A \nabla \cdot \boldsymbol{\tau} - \nabla \cdot \boldsymbol{\tau}_A) \\ - \nabla p_A + \omega_A \nabla p + \rho_A (\mathbf{b}_A - \mathbf{b}) &+ \sum_{B=1}^{B=N} \mathbf{P}_{AB} \\ + r_A (\mathbf{v}_A^* - \mathbf{v}_A), \quad A = 1, 2, \dots, N-1. \end{aligned} \quad (33)$$

Simplification of this result has been explored by Whitaker (2009b) using order of magnitude estimates. Such estimates *suggest but do not confirm* the conditions necessary for the simplification of Eq. (33), and more detailed studies would be welcome. A plausible set of restrictions (Whitaker, 2009b) arise from regarding the species partial pressure gradient as the leading term, so that

$$R1. \quad \rho_A \frac{\partial \mathbf{u}_A}{\partial t} \ll \nabla p_A, \quad (34a)$$

$$R2. \quad \rho_A (\mathbf{v}_A \cdot (\nabla \otimes \mathbf{u}_A) + \mathbf{u}_A \cdot (\nabla \otimes \mathbf{v})) \ll \nabla p_A, \quad (34b)$$

$$R3. \quad \omega_A \nabla \cdot \sum_{B=1}^{B=N} \rho_B \mathbf{u}_B \otimes \mathbf{u}_B \ll \nabla p_A, \quad (34c)$$

$$R4. \quad (\omega_A \nabla \cdot \boldsymbol{\tau} - \nabla \cdot \boldsymbol{\tau}_A) \ll \nabla p_A, \quad (34d)$$

$$R5. \quad r_A (\mathbf{v}_A^* - \mathbf{v}_A) \ll \nabla p_A. \quad (34e)$$

Here  $R1$ ,  $R2$ , etc. refer to *restrictions* (Whitaker, 1988) and the corresponding *constraints* are given in Appendix B. When these five restrictions are imposed on Eq. (33), and we accept the plausible assumption that small causes give rise to small effects (Birkhoff, 1960) for linear equations, we obtain

$$\begin{aligned} & \nabla p_A - \omega_A \nabla p - \rho_A (\mathbf{b}_A - \mathbf{b}) \\ & = \sum_{B=1}^{B=N} \mathbf{P}_{AB}, \quad A = 1, 2, \dots, N-1. \end{aligned} \quad (35)$$

Truesdell (1962) represents the left-hand side of this result by  $p\mathbf{d}_A$  and cites Hirschfelder *et al.* (1964) as the source. Curtiss and Bird (1999) represent the left-hand side of Eq. (35) by  $cRT\mathbf{d}_A$  and refer to it as the *generalized driving force for diffusion*. The term  $\mathbf{P}_{AB}$  is frequently presented without a particular name, but here we might follow Truesdell (1962) and give these quantities the moniker *diffusive drags*.

As an additional assumption, we impose the restriction that all body forces (e.g., electrical and gravitational fields) can be neglected with respect to diffusion. While this approximation may not be valid for solutions with significant density differences, we impose it with this note of warning. The more general case where external forces are maintained is covered by del Río and Whitaker (2016). The associated restriction for neglecting body forces is

$$R6. \quad \rho_A (\mathbf{b}_A - \mathbf{b}) \ll \nabla p_A, \quad (36a)$$

and we assume that  $\omega_A \nabla p$  can be neglected on the basis of

$$R7. \quad \omega_A \nabla p \ll \nabla p_A. \quad (36b)$$

The constraints related to the above two restrictions are given in Appendix B. Imposing these two restrictions on Eq. (35) leads to

$$\nabla p_A = \sum_{B=1}^{B=N} \mathbf{P}_{AB}, \quad A = 1, 2, \dots, N-1. \quad (37)$$

Clearly, the restrictions proposed above could have also been proposed in terms of  $\sum_{B=1}^{B=N} \mathbf{P}_{AB}$  as this term is equally important as  $\nabla p_A$ .

## 5 Ideal solutions

The concept of *ideal solutions* (or, sometimes *ideal mixtures*) has been adopted as an essential thermodynamic model for many years [e.g., Gibbs (1906a, p. 164), Guggenheim (1933, Chp. VI)]. Perhaps the most succinct definition of an ideal mixture comes from Hildebrand (1936, p. 53) who stated, correctly and boldly, “An ideal solution obeys Raoult’s law at all temperatures and pressures”. There are a number of necessary conditions that arise from this statement, and there are also a number of equivalent statements defining the ideal solution. For example, Prigogine (1967, p. 22) states that an ideal solution has a chemical potential for component  $A$  defined by

$$\mu_A = \mu_A^\bullet(p, T) + RT \ln x_A, \quad (38)$$

where  $\mu_A^\bullet(p, T)$  is independent of composition. Pitzer (1995, Chp.11) offers an identical definition, with additional commentary. While Eq. (38) does allow one to express the constitutive theory of Fick’s law in terms of the *chemical potential* rather than the concentration, for ideal solutions Eq. (38) allows this interchange to be made quite easily *a posteriori*. Thus, we will adopt the use of the mole fraction over the chemical potential for the remainder of the manuscript.

The goal of this work is to illustrate how one might derive Fick’s law in a reasonably straightforward manner directly from the laws of continuum mechanics. To do the conventional assumption of a linear (or linearized, if under the appropriate restrictions) constitutive equation for the partial pressure of the solute in the liquid mixture is required. Such relationships are obtained by primarily two methods: (1) they are based on *experimental data*, and, because of the complexity and/or nonlinearity of the problem, are fit with empirical relationships (this is typical in engineering sciences); or (2) an appropriate theory based on a *constitutive theory*, of which there are many possibilities [e.g., equilibrium or non-equilibrium thermodynamics, equilibrium or non-equilibrium statistical mechanics, kinetic theory and extensions (the Onsager reciprocal relations), molecular dynamics computations, etc.]. While the framework developed to this point is relatively general, the analysis is limited to only *linear* dependencies of the partial pressure on the mole fraction. Thus, the analysis is limited to either (1) systems that behave as ideal solutions [e.g., as illustrated in Fig. 1 (top)], or (2) systems where the solute of interest is either sufficiently dilute or sufficiently near unimolar that the approximation of linearity is valid, such as the system illustrated near  $x = 0$  and  $x = 1$  in Fig. 1 (bottom).

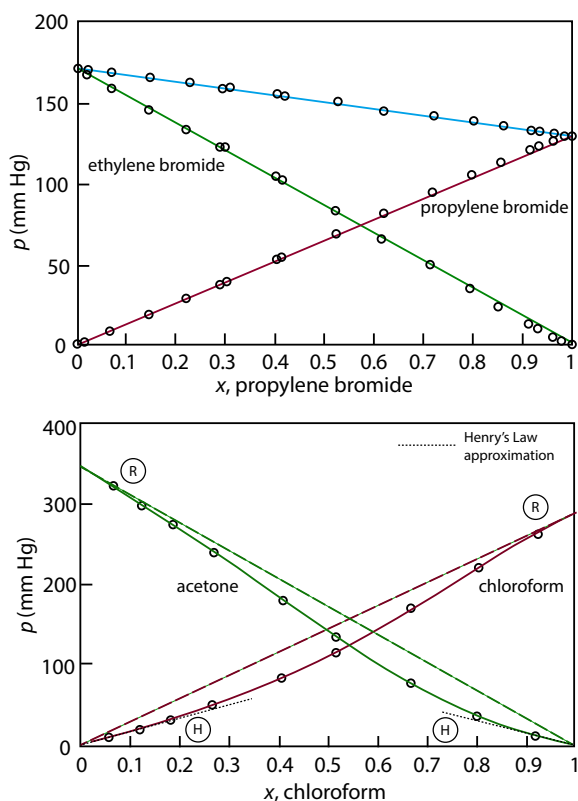


Figure 1. (Top) An example of an ideal binary solution that obeys Raoult's law [after Guggenheim (1949, p. 198)]. (Bottom) An example of a binary solution that deviates from Raoult's law [after Hildebrand (1936, p. 38)]. Note that at high mole fraction, each of the two solutes behaves nearly as an ideal solution.

### 5.1 Raoult's law and Henry's law

While *ideal solutions* that obey Raoult's law over the entire range of compositions are the exception rather than the rule, such solutions can nonetheless be realized in the lab [cf. Fig. 1 (top)]. More importantly, a species in even a non-ideal solution will frequently exhibit nearly ideal behavior when its mole fraction is near unity. This leads to the following observation by Hildebrand (1936, p. 20):

It may be noted, further, that when the solution is sufficiently dilute for the *solute* to obey Henry's law to a given degree of approximation, the *solvent* must obey Raoult's law with a corresponding degree of approximation and *vice versa*... These conditions, accordingly, are the criteria of ideality, through a limited range, as Raoult's law for both components is the criterion for ideality throughout the entire range of composition [emphasis added].

For the remainder of this work, we assume that

ideality exists in this sense; hence, for the solutions we consider we assume either (1) the solution exhibits ideal behavior over the entire range of compositions, or (2) the analysis is applied only to a solvent with  $N-1$  dilute solutes, such that Raoult's law is applicable to the solvent, and Henry's law is applicable to the solutes.

A note is required at this juncture regarding the treatment of the roles of Raoult's law, Henry's law in the development to follow. First, we note that these are both *linear* laws in terms of the mole fractions. Each of them states that the partial pressure,  $p_A$  of chemical species  $A$  (where  $A$  can represent either a solute or a solvent) is given by the form

$$\frac{p_A}{p_A^\circ} = \alpha_A x_A, \quad (39)$$

where  $p_A^\circ$  is the reference pressure, taken as the vapor pressure associated with a pure state for species  $A$  (Hildebrand, 1936, p. 19; p. 26) and  $x_A$  is the mole fraction of species  $A$ . For Raoult's law, one has  $\alpha_A = 1$  identically. Raoult's law generally applies when the mole fraction of species  $A$ , is near unity. Thus, even non-ideal solutions exhibit a range of mole fractions where Raoult's law is valid. As an example, the non-ideal solution illustrated in Fig. 1 (bottom) clearly behaves as an ideal solution as  $x_A$  approaches unity (for both acetone and chloroform); these regions are indicated by the letter "R" on the figure.

For Henry's law, the constant  $\alpha_A$  is generally different from unity; in Fig. 1 (bottom), dotted lines indicate the Henry's law approximation for the two species illustrated when they are respectively at concentrations  $x_A \ll 1$ ; this is indicated by the letter "H" on the figure. Note that when solutions behave in an ideal manner over the range of compositions, then the Henry's law and Raoult's law coefficients coincide, with  $\alpha_A = 1$ . For completeness, we note that we have imposed an additional restriction in our analysis.

R8. The solution involved behaves either ideally (via Raoult's law) over the entire range of compositions, or the analysis is applied only to mass fractions in which Raoult's law and Henry's law are valid approximations.

### 5.2 The momentum balance for ideal solutions

For ideal solutions (also known as *ideal liquid mixtures*), the partial pressure and mole fraction are related by Eq. (39), or, by the following gradient relationship

$$\nabla p_A = (\alpha_A p_A^\circ) \nabla x_A. \quad (40)$$



With this result, we can express the momentum balance from Eq. (37) in the form

$$\nabla x_A = \sum_{B=1}^{B=N} (\alpha_A p_A^\circ)^{-1} \mathbf{P}_{AB}, \quad A = 1, 2, \dots, N-1. \quad (41)$$

At this juncture, it is helpful to point out that one could *in principle* generate a theory for non-ideal solutions over the entire range of concentrations by extending Eq. (39). For example, if one were interested in accounting for the *activity* of the solutes (for ideal mixtures the activities are identically unity), then the coefficient  $\alpha_A$  would become a function of the mole fraction of all species in the system [e.g.,  $\alpha_A = \alpha_A(x_1, x_2, \dots, x_N)$ ]. Accounting for temperature gradients could be handled in a similar way. Because our focus is on a simple, linear theory, we do not pursue these considerations further in this work.

The task now is to express the diffusive drags,  $\mathbf{P}_{AB}$ , by a constitutive equation. From dilute gas kinetic theory, we know that  $\mathbf{P}_{AB|gas}$ , is given by

$$\text{Ideal gas mixture: } \mathbf{P}_{AB|gas} = p_{gas} \frac{x_A x_B}{\mathcal{D}_{AB}} (\mathbf{u}_B - \mathbf{u}_A), \quad A = 1, 2, \dots, N-1, \quad (42)$$

where  $p_{gas}$  is the gas mixture pressure. This result can be obtained by comparing Eq. (35) of this work with Eqs. 7.3-27 and 7.4-48 of Hirschfelder *et al.* (1964) and neglecting the effect of thermal diffusion. Note that there are approximations in this result even for gases; for example, the drags are assumed to be pairwise additive, which neglects interactions among three or more species simultaneously.

For the case of liquids, we need an analogous representation for  $\mathbf{P}_{AB|liq}$ . One possibility is to posit the use of Eq. (42) as a *model*. This leads to

*Ideal liquid mixture:*

$$\mathbf{P}_{AB|liq} = p_{liq} \frac{x_A x_B}{D_{AB}^\circ} (\mathbf{u}_B - \mathbf{u}_A), \quad A = 1, 2, \dots, N-1. \quad (43)$$

Here,  $p_{liq}$  represents the *thermodynamic* pressure associated with the liquid phase as stated in the first of Eqs. (26)

$$p_{liq} = \sum_{B=1}^{B=N} p_B. \quad (44)$$

It is important to recall that there is no *body force* component in this expression as these have been neglected based on the analysis above. While this representation is an *empirical expression* for the diffusive force,  $\mathbf{P}_{AB|liq}$ , it is one that is based on an analogous process in gases. As such,  $D_{AB}^\circ$  represents an *empirical coefficient* to be determined by experiment.

## 6 N-Component liquid systems

Our system of the momentum balance equations for an  $N$ -component system consist of the total momentum balance given by Eq. (20) and the  $N-1$  species momentum balance equations (with index set  $A$ ) based on the combination of Eqs. (41) and (43). We can use these two results, to obtain the following expression analogous to the Maxwell–Stefan equation

$$\mathbf{0} = -\nabla x_A + \sum_{B=1}^{B=N} \frac{1}{\alpha_A p_A^\circ / p_{liq}} \frac{x_A x_B}{D_{AB}^\circ} (\mathbf{u}_B - \mathbf{u}_A), \quad A = 1, 2, \dots, N-1. \quad (45)$$

Some interpretation is helpful here. It is best to think of this momentum balance as applying to some *fixed* species,  $A$ . Then, the result suggests that the balance of species  $A$  is dependent upon the pairwise drags with all other species. Note that when the value of the index  $B$  coincides with that of  $A$  we have  $(\mathbf{u}_A - \mathbf{u}_A) = \mathbf{0}$ , thus there is no self-interaction among the species. In the interest of clarity, note that the two balances for a binary system composed of species  $A$  and species  $B$  are given by

$$\mathbf{0} = -\nabla x_A + \frac{1}{\alpha_A p_A^\circ / p_{liq}} \frac{x_A x_B}{D_{AB}^\circ} (\mathbf{u}_B - \mathbf{u}_A), \quad (46a)$$

$$\mathbf{0} = -\nabla x_B + \frac{1}{\alpha_B p_B^\circ / p_{liq}} \frac{x_A x_B}{D_{BA}^\circ} (\mathbf{u}_A - \mathbf{u}_B). \quad (46b)$$

While we might proceed using this formulation, the analysis would be complicated by the presence of  $p_{liq}$ , which is generally not a constant. However, when we have a dilute solution of  $N-1$  solutes in a single solvent, then  $p_{liq}$  is nearly identical to the thermodynamic pressure of the solvent. To be clear, suppose we set the solvent to index  $A=1$ . Then we require

$$\sum_{B=2}^{B=N-1} x_B \ll x_1. \quad (47)$$

Under these conditions,  $p_{liq}$  can be assumed to be a constant that depends only upon the solvent properties. Similarly,  $\alpha_A$  is a constant that is specific to each solvent-solute pair. Thus, we propose the following definition

$$D_{AB} \equiv D_{AB}^\circ \frac{\alpha_A p_A^\circ}{p_{liq}}, \quad A = 1, 2, \dots, N-1, B = 1, 2, \dots, N. \quad (48)$$

With this definition, the momentum balance takes the form

$$\mathbf{0} = -\nabla x_A + \sum_{B=1}^{B=N} \frac{x_A x_B}{D_{AB}} (\mathbf{u}_B - \mathbf{u}_A), \quad A = 1, 2, \dots, N-1. \quad (49)$$

This result offers a closure to the problem, but one resulting behavior of this choice is that, in general, we have  $D_{AB} \neq D_{BA}$ . As pointed out by Truesdell (1962), this is the result that should be obtained unless additional constraints are imposed.

While Fick's law is frequently expressed in terms of gradients of the mole fraction, here our goal is to put it in the conventional form as the gradient of a molar concentration. To this end, we note that Fick's law applies for the *special case* in which the total density of the solution,  $\rho$ , is constant; we pursue the impact of this assumption in the remainder of this section.

The total molar concentration is given by  $c = c_1 + c_2 + \dots + c_N$ ; similarly, the total density is given by  $\rho = \rho_1 + \rho_2 + \dots + \rho_N$ . The density can be rewritten in the form

$$\rho = c_1 M_1 + c_2 M_2 + \dots + c_N M_N. \quad (50)$$

Note that, by definition, we have  $x_A = c_A/c$ . Thus, we can make use of the relation

$$c_A M_A = c x_A M_A, \quad (51)$$

in order to express Eq. (50) in the form

$$\rho = c \sum_{A=1}^{A=N} x_A M_A, \quad \sum_{A=1}^{A=N} x_A = 1. \quad (52)$$

The total molar concentration can now be written as

$$c = \sum_{A=1}^{A=N} \frac{\rho_A}{M_A}. \quad (53)$$

Defining the mass fraction of species  $A$  by  $\omega_A = \rho_A/\rho$  (with  $\sum_{A=1}^{A=N} \omega_A = 1$ ) we can develop the relation

$$\frac{\rho_A}{M_A} = \rho \frac{\omega_A}{M_A}, \quad (54)$$

in order to express Eq. (53) in the form

$$c = \rho \sum_{A=1}^{A=N} \frac{\omega_A}{M_A}. \quad (55)$$

At this point, we can make use of Eqs. (52) and (55) to obtain the useful relations given by

$$\bar{M} = \frac{\rho}{c} = \frac{\sum_{A=1}^{A=N} x_A M_A}{\sum_{A=1}^{A=N} \omega_A / M_A}. \quad (56)$$

This result can be used to express the mole fraction of species  $A$  as

$$x_A = \frac{c_A}{c} = \frac{\rho_A / M_A}{c} = \left( \frac{\rho}{c} \right) \frac{\omega_A}{M_A} = \bar{M} \left( \frac{\omega_A}{M_A} \right), \quad (57)$$

and from this we see that the gradient of  $x_A$  is given by

$$\nabla x_A = \left( \frac{\nabla \bar{M}}{\bar{M}} \right) \omega_A + \left( \frac{\bar{M}}{M_A} \right) \nabla \omega_A, \quad A = 1, 2, \dots, N. \quad (58)$$

At this point, we note that we want the right-hand side of this result to be expressed entirely in terms of  $\nabla \omega_A$ . We begin to accomplish this by using Eq. (56) in the form

$$\bar{M} = \frac{1}{\sum_{B=1}^{B=N} \omega_B / M_B}, \quad (59)$$

so that  $\nabla \bar{M}$  can be expressed as

$$\nabla \bar{M} = -\bar{M}^2 \sum_{B=1}^{B=N} \frac{\nabla \omega_B}{M_B}. \quad (60)$$

Use of this expression for  $\nabla \bar{M}$  in Eq. (58) allows writing the gradient of the mole fraction as

$$\nabla x_A = \frac{\bar{M}^2}{M_A} \left[ \frac{1}{\bar{M}} \nabla \omega_A - \omega_A \sum_{B=1}^{B=N} \frac{\nabla \omega_B}{M_B} \right]. \quad (61)$$

From this point in the analysis, one may follow the developments reported in Section 7 of the work by Whitaker (2009b) or in Section 2 of Krishna (2019) in order to develop a generalized Fick's law for *multicomponent systems*. However, our goal is to retrieve Fick's law in the form given in Eq. (1). For this reason, at this point we simplify the analysis by restricting it to *binary systems*.

## 7 Binary liquid systems

Binary systems are often used to introduce the phenomenon of diffusion, and we will follow that approach here. For binary systems, one expects that  $D_{AB} = D_{BA}$ , and one can find by adding Eqs. (46) that this relationship does indeed result.

The binary version of Eq. (61) is given by

$$\nabla x_A = \frac{\bar{M}^2}{M_A} \left[ \frac{1}{\bar{M}} \nabla \omega_A - \omega_A \sum_{B=1}^{B=2} \frac{\nabla \omega_B}{M_B} \right] = \frac{\bar{M}^2}{M_A} \left[ \frac{1}{\bar{M}} \nabla \omega_A - \omega_A \left( \frac{\nabla \omega_A}{M_A} + \frac{\nabla \omega_B}{M_B} \right) \right]. \quad (62)$$

Here we note that

$$\begin{aligned} \frac{\nabla \omega_A}{M_A} + \frac{\nabla \omega_B}{M_B} &= \frac{\nabla \omega_A}{M_A} - \frac{\nabla \omega_A}{M_B} = \nabla \omega_A \left( \frac{1}{M_A} - \frac{1}{M_B} \right) \\ &= \nabla \omega_A \left( \frac{M_B - M_A}{M_A M_B} \right), \end{aligned} \quad (63)$$

and this allows expressing Eq. (62) as

$$\nabla x_A = \frac{\bar{M}^2}{M_A} \nabla \omega_A \left[ \left( \frac{\omega_A}{M_A} + \frac{\omega_B}{M_B} \right) - \omega_A \left( \frac{M_B - M_A}{M_A M_B} \right) \right], \quad (64)$$

and this can be simplified to the convenient form given by

$$\nabla x_A = \frac{\overline{M}^2}{M_A M_B} \nabla \omega_A. \quad (65)$$

At this point, we return to the two mass continuity equations given by Eqs. (13)

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}) = -\nabla \cdot (\rho_A \mathbf{u}_A) + r_A, \quad (66a)$$

$$\frac{\partial \rho_B}{\partial t} + \nabla \cdot (\rho_B \mathbf{v}) = -\nabla \cdot (\rho_B \mathbf{u}_B) + r_B, \quad (66b)$$

and note that representations for  $\mathbf{u}_A$  and  $\mathbf{u}_B$  are needed to complete our analysis of these two equations. Given the binary form of Eqs. (49)

$$\mathbf{0} = -\nabla x_A + \frac{x_A x_B}{D_{AB}} (\mathbf{u}_B - \mathbf{u}_A), \quad (67)$$

we make use of Eq. (12) to obtain the following relation between  $\mathbf{u}_A$  and  $\mathbf{u}_B$

$$\omega_A \mathbf{u}_A + \omega_B \mathbf{u}_B = \mathbf{0}, \quad (68)$$

that allows expressing Eq. (67) in the form

$$\mathbf{0} = -\nabla x_A - \frac{x_A x_B}{D_{AB} \omega_A \omega_B} (\omega_A \mathbf{u}_A). \quad (69)$$

Multiplying and dividing the last term of this result by the mixture density leads to

$$\mathbf{0} = -\nabla x_A - \frac{x_A x_B}{\rho D_{AB} \omega_A \omega_B} (\rho_A \mathbf{u}_A). \quad (70)$$

Here we have a mixed-mode representation in which the *mass diffusive flux*,  $\rho_A \mathbf{u}_A$ , is expressed in terms of the gradient of the *mole fraction*,  $\nabla x_A$ , along with the mixed-mode term,  $x_A x_B / \omega_A \omega_B$ . At this point, we can use Eq. (65) to write Eq. (70) as

$$\frac{\overline{M}^2}{M_A M_B} \nabla \omega_A = -\frac{x_A x_B}{\rho D_{AB} \omega_A \omega_B} (\rho_A \mathbf{u}_A). \quad (71)$$

Next, we make use of the following relations between the mole and mass fractions

$$x_A = \frac{c_A}{c} = \frac{c_A \overline{M}}{\rho} = \frac{(\rho_A / M_A) \overline{M}}{\rho} = \frac{\overline{M}}{M_A} \omega_A, \quad (72a)$$

$$x_B = \frac{c_B}{c} = \frac{c_B \overline{M}}{\rho} = \frac{(\rho_B / M_B) \overline{M}}{\rho} = \frac{\overline{M}}{M_B} \omega_B, \quad (72b)$$

which lead to

$$\frac{x_A x_B}{\omega_A \omega_B} = \frac{(\overline{M} / M_A) \omega_A (\overline{M} / M_B) \omega_B}{\omega_A \omega_B} = \frac{\overline{M}^2}{M_A M_B}. \quad (73)$$

Substitution of this result into Eq. (71) provides

$$\rho_A \mathbf{u}_A = -\rho D_{AB} \nabla \omega_A, \quad (74)$$

that can be expressed as

$$\rho_A \mathbf{u}_A = (c_A \mathbf{u}_A) M_A = -\rho D_{AB} \nabla \omega_A. \quad (75)$$

If we assume that the density is constant

$$A1. \quad \rho = \text{constant}, \quad (76)$$

Eq. (75) can be used to obtain the following result

$$(c_A \mathbf{u}_A) = -D_{AB} \nabla (\rho \omega_A / M_A) = -D_{AB} \nabla c_A. \quad (77)$$

We now make use of Eq. (16) to obtain the classic form of Fick's law given by

$$\text{Fick's law: } \boxed{\mathbf{J}_A = -D_{AB} \nabla c_A}. \quad (78)$$

Use of this result in Eq. (15a) leads to

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = \nabla \cdot (D_{AB} \nabla c_A) + R_A, \quad \left\{ \begin{array}{l} \rho = \text{constant} \\ \text{binary system} \end{array} \right. \quad (79a)$$

while the analysis for species *B* leads to the analogous result given by

$$\frac{\partial c_B}{\partial t} + \nabla \cdot (c_B \mathbf{v}) = \nabla \cdot (D_{AB} \nabla c_B) + R_B, \quad \left\{ \begin{array}{l} \rho = \text{constant} \\ \text{binary system} \end{array} \right. \quad (79b)$$

Rather than accepting this result on the basis of the *assumption* given by Eq. (76), it would be better to impose the *restriction* given by

$$R9. \quad \omega_A \nabla \rho \ll \rho \nabla \omega_A. \quad (80)$$

This restriction is an indication that there is a related *constraint* (Whitaker, 1988) associated with Eqs. (79) that dictates when this restriction is a valid one; this constraint has yet to be developed.

## 8 Conclusions

The use of Fick's law is usually advised to be applicable under dilute solution conditions. However, by performing a careful analysis of its derivation departing from the simplification of the species momentum transport equation in an *N*-component mixture, it was found that more assumptions are required to retrieve it. In particular, the gradient of species *A* partial pressure was regarded as the leading term in the species momentum transport equation. This implies assuming that, under diffusive conditions, species *A* experiences spatial variations at larger distances (*L*) than the total mixture (*ℓ*). In this way, for conditions in which  $Re^2 \ell^2 \ll t_{ref} v_{ref} L$ ,  $Re \ell / L \ll 1 \ll Fr$  [with *Re* and *Fr* being the Reynolds and Froude numbers defined in equation

(B.7)], and assuming ideal mixture conditions, the species momentum transport equation reduces to the Maxwell-Stefan equations. From this result a version of Fick's law for multicomponent systems is certainly possible to be obtained and the classical version of Fick's law was retrieved for binary systems. The simplifications provided in this work motivate further theoretical and experimental verification and suggest that caution must be taken when using Fick's law. In addition, this work motivates the derivation of more sophisticated closure relationships that may be used in situations where Fick's law is not applicable.

## Nomenclature

$\mathbf{b}_A$	body force per unit mass exerted on species A, N/kg
$\mathbf{b}$	body force per unit mass exerted on the mixture, N/kg
$c_A$	molar concentration of species A, moles/m <sup>3</sup>
$c$	total molar concentration, moles/m <sup>3</sup>
$D_{AB}$	liquid-phase binary diffusion coefficient for species A and B, m <sup>2</sup> /s
$\mathbf{g}$	gravitational body force per unit mass, N/kg
$\mathbf{J}_A$	$c_A \mathbf{u}_A$ , diffusive flux of species A, moles/m <sup>2</sup> s
$M_A$	molecular mass of species A, g/mole
$\bar{M}$	$x_A M_A + x_B M_B$ , mean molecular mass of a binary mixture, g/mole
$N$	number of chemical species
$\mathbf{P}_{AB}$	force per unit volume exerted by species B on species A, N/m <sup>3</sup>
$p$	$\sum_{A=1}^N p_A$ , total pressure, N/m <sup>2</sup>
$p_A$	partial pressure of species A, N/m <sup>2</sup>
$r_A$	net mass rate of production of species A owing to homogeneous reactions, kg/m <sup>3</sup> s
$R$	universal gas constant J/mol K
$R_A$	net molar rate of production of species A owing to homogeneous reactions, moles/m <sup>3</sup> s
$t$	time, s
$T$	phase temperature, K,
$\mathbf{T}_A$	stress tensor for species A, N/m <sup>2</sup>
$\mathbf{T}$	total stress tensor for the mixture, N/m <sup>2</sup>
$\mathbf{u}_A$	$\mathbf{v}_A - \mathbf{v}$ , species A mass diffusion velocity, m/s
$\mathbf{v}_A$	velocity of species A, m/s
$\mathbf{v}$	$\sum_{A=1}^N \omega_A \mathbf{v}_A$ , mass average velocity, m/s
$\mathbf{v}_A^*$	velocity associated with the net rate of production of species A momentum owing to chemical reaction, m/s
$x_A$	$c_A/c$ , mole fraction of species A

## Greek letters

$\alpha_A$	coefficient of the linear constitutive equation for the pressure-mole fraction relationship for species A
$\rho_A$	mass density of species A, kg/m <sup>3</sup>
$\rho$	total mass density, kg/m <sup>3</sup>
$\mu$	viscosity, N/m <sup>2</sup> s,
$\mu_A$	chemical potential of species A, J/mol,
$\boldsymbol{\tau}$	viscous stress tensor, N/m <sup>2</sup>
$\boldsymbol{\tau}_A$	viscous stress tensor for species A, N/m <sup>2</sup>
$\omega_A$	$\rho_A/\rho$ , mass fraction of species A

## References

- Adkins, J. (1963). Non-Linear Diffusion - Non-linear diffusion I. Diffusion and flow of mixtures of fluids. *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences* 255(1064), 607-633. <https://doi.org/10.1098/rsta.1963.0013>
- Adkins, J. E. (1964). Diffusion of fluids through aeolotropic highly elastic solids. *Archive for Rational Mechanics and Analysis*, 15(3), 222-234. <https://doi.org/10.1007/BF00275632>
- Atkin, R. J. and Craine, R. E. (1976). Continuum theories of mixtures: Basic theory and historical development. *The Quarterly Journal of Mechanics and Applied Mathematics* 29(2), 209-244. <https://doi.org/10.1093/qjmam/29.2.209>
- Bailey, J. E. and Ollis, D. F. (1986). *Biochemical Engineering Fundamentals*. McGraw Hill, second edition, 928 pp.
- Batchelor, G. K. (1967). *An Introduction to Fluid Dynamics*. Cambridge University Press, Cambridge, UK, 615 pp.
- Bird, R. B. and Klingenberg, D. J. (2013). Multicomponent diffusion-a brief review. *Advances in Water Resources* 62, 238-242.
- Bird, R. B., Stewart, W. E., and Lightfoot, E. N. (1960). *Transport Phenomena*, first edition. John Wiley & Sons, Inc., 808 pp.
- Bird, R. B., Stewart, W. E., and Lightfoot, E. N. (2006). *Transport Phenomena*, Revised 2nd Edition. John Wiley & Sons, Inc., 905 pp.
- Birkhoff, G. (1960). *Hydrodynamics: A Study in Logic, Fact and Similitude*. Princeton University Press, 202 pp.

- Borja-Málaga, M., Jiménez-Ochoa, A., de Miranda, E. M., and Escobedo-Vargas, F. A. (2022). Effect of drying on the extraction yield of luma chequen (molina) a. gray essential oil. *Revista Mexicana de Ingeniería Química* 21(2), Proc2623. <https://doi.org/10.24275/rmiq/Proc2623>
- Bowen, R. (1967). Toward a thermodynamics and mechanics of mixtures. *Archive for Rational Mechanics and Analysis* 24, 370-403. <https://doi.org/10.1007/BF00253154>
- Curtiss, C. F. and Bird, R. B. (1999). Multicomponent diffusion. *Industrial & Engineering Chemistry Research* 38(7), 2515-2522. <https://doi.org/10.1021/ie9901123>
- Cussler, E. L. (2009). *Diffusion*. third edition. Cambridge University Press, 655 pp.
- Datta, R. and Vilekar, S. A. (2010). The continuum mechanical theory of multicomponent diffusion in fluid mixtures. *Chemical Engineering Science* 65(22), 5976-5989. <https://doi.org/10.1016/j.ces.2010.08.022>
- Deen, W. M. (2012). *Analysis of Transport Phenomena. Topics in Chemical Engineering*. Oxford University Press, New York, 2nd edition, 688 pp.
- DeGroot, S. R. and Mazur, P. (1967). *Non-Equilibrium Thermodynamics*. North-Holland, Amsterdam, 510 pp.
- del Río, J. A. and Whitaker, S. (2016). Diffusion of charged species in liquids. *Scientific Reports* 6(1), 35211. <https://doi.org/10.1038/srep35211>
- Einstein, A. (1905). Über die von der molekularinetischen theorie der wärme geforderte bewegung von in ruhenden flüssigkeiten suspendierten teilchen. *Annalen der Physik* 322, 549-560. <https://doi.org/10.1002/andp.19053220806>
- Fick, A. (1855). Ueber diffusion. *Annalen der Physik und Chemie* 170(1), 59-86. <https://doi.org/10.1002/andp.18551700105>
- Gibbs, J. W. (1906a). *Scientific Papers of J. Willard Gibbs, in Two Volumes*, Vol. I, Longmans, Green & Co., New York, 434 pp.
- Gibbs, J.W. (1906b). Elements of vector analysis, arranged for the use of students in physics. Chapter III in *Scientific Papers of J. Willard Gibbs, in Two Volumes*, Vol. II, Longmans, Green & Co., New York, 284 pp.
- Graham, T. (1829). A short account of experimental researches on the diffusion of gases rough each other, and their separation by mechanical means. *Quarterly Journal of Science, Literature, and Art* 2, 74-83.
- Graham, T. (1850). I. The Bakerian lecture.-on the diffusion of liquids. *Philosophical Transactions of the Royal Society of London* 140,1-46. <https://doi.org/10.1098/rstl.1850.0001>
- Graham, T. (1863). On the molecular mobility of gases. *Philosophical Transactions of the Royal Society of London* 153, 385-405. <https://doi.org/10.1098/rstl.1863.0017>
- Green, A. E. and Adkins, J. E. (1964). A contribution to the theory of non-linear diffusion. *Archive for Rational Mechanics and Analysis* 15(3), 235-246. <https://doi.org/10.1007/BF00275633>
- Guggenheim, E. A. (1933). *Modern Thermodynamics by the Methods of Willard Gibbs*, Methuen & Co. Ltd., London, 206 pp.
- Guggenheim, E. A. (1949). *Thermodynamics. An advanced treatment for Chemists and Physicists*. Monographs on Theoretical and Applied Physics, Vol. II, H.B.G. Casimir and H. Brinkman, eds. North-Holland Publishing Co., Amsterdam, 395 pp.
- Hildebrand, J. H. (1936). *Solubility of Non-electrolytes*. Reinhold Pub., New York, 203 pp.
- Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B. (1964). *The Molecular Theory of Gases and Liquids*. Wiley-Interscience, 1280 pp.
- Jaramillo-Gutiérrez, M., Pedraza-Avella, J., González, I., Rivero, E., and Cruz-Díaz, M. (2022). Design equations based on micro/macromixing theoretical analysis of rtd curves for a tubular concentric electrochemical reactor with expanded meshes as electrodes. *Revista Mexicana de Ingeniería Química* 21(1), Cat2434. <https://dx.doi.org/10.24275/rmiq/Cat2434>
- Kerkhof, P. and Geboers, M. (2005). Toward a unified theory of isotropic molecular transport phenomena. *AIChE Journal* 51(1), 79-121. <https://doi.org/10.1002/aic.10309>
- Krishna, R. (2019). Diffusing uphill with James Clerk Maxwell and Josef Stefan. *Chemical Engineering Science* 195, 851-880. <https://doi.org/10.1016/j.ces.2018.10.032>

- Krishna, R. and Wesselingh, J. (1997). The Maxwell-Stefan approach to mass transfer. *Chemical Engineering Science* 52(6), 861-911. [https://doi.org/10.1016/S0009-2509\(96\)00458-7](https://doi.org/10.1016/S0009-2509(96)00458-7)
- Levenspiel, O. (1998). *Chemical Reaction Engineering*, third edition. John Wiley & Sons, 688 pp.
- Liu, I.-S. and Müller, I. (1984). Appendix 5b. thermodynamics of mixtures of fluids. In Truesdell, C., editor, *Rational Thermodynamics*, Second Edition, pages 264-285. Springer-Verlag, New York. [https://doi.org/10.1007/978-1-4612-5206-1\\_14](https://doi.org/10.1007/978-1-4612-5206-1_14)
- Loschmidt, J. (1870). Sitzungsber. *Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Mathematisch- Naturwissenschaftliche Classe* 62, 468.
- Lowney, J. and Larrabee, R. (1980). The use of Fick's law in modeling diffusion processes. *IEEE Transactions on Electron Devices* 27, 1795-1798. <https://doi.org/10.1109/T-ED.1980.20105>
- Maxwell, J. (1873). On Loschmidt's experiments on diffusion in relation to the kinetic theory of gases. *Nature* 8, 298-300. <https://doi.org/10.1038/008298a0>
- Mills, N. (1966). Incompressible mixtures of Newtonian fluids. *International Journal of Engineering Science* 4, 97-112. [https://doi.org/10.1016/0020-7225\(66\)90018-8](https://doi.org/10.1016/0020-7225(66)90018-8)
- Onsager, L. (1945). Theories and problems of liquid diffusion. *Annals of the New York Academy of Sciences*, 46(5 The Diffusion), 241-265. <https://doi.org/10.1111/j.1749-6632.1945.tb36170.x>
- Patzek, T. W. (2014a). Fick's diffusion experiments revisited-part I. *Advances in Historical Studies* 03(04), 194-206. <http://dx.doi.org/10.4236/ahs.2014.34017>
- Patzek, T. W. (2014b). Fick's diffusion experiments revisited-part II (English Translation of Fick's original thinking). *Advances in Historical Studies* 03(04), 207-220. <http://dx.doi.org/10.4236/ahs.2014.34018>
- Pekař, M. and Samohyl, I. (2014). *The Thermodynamics of Linear Fluids and Fluid Mixtures*. Springer, Cham, Switzerland, 308 pp.
- Perrin, J. (1913). *Les Atoms*. Paris: Félix Alcan, 240 pp.
- Pitzer, K. S. (1995). *Thermodynamics*. McGraw-Hill, Inc., New York, 626 pp.
- Prigogine, I. (1967). *Thermodynamics of Irreversible Processes*. Interscience Publishers (Wiley), New York, third edition, 147 pp.
- Rosner, D. E. (2000). *Transport Processes in Chemically Reacting Flow Systems*. Dover Publications, 1043 pp.
- Slattery, J. C. (1999). *Advanced Transport Phenomena* (Cambridge Series in Chemical Engineering). Cambridge University Press, 734 pp.
- Stefan, J. (1871). Über das gleichgewicht und die bewegung, insbesondere die diffusion von gasgemengen. *Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften Wien, 2te Abteilung* 63, 63-124.
- Stokes, G. G. (1851). On the effect of the internal friction of fluids on the motion of pendulums. *Transactions of the Cambridge Philosophical Society* 9, 8-106.
- Truesdell, C. (1962). Mechanical basis of diffusion. *The Journal of Chemical Physics* 37(10), 2336-2344. <https://doi.org/10.1063/1.1733007>
- Truesdell, C. (1984). *Rational Thermodynamics*, second Edition. Springer-Verlag, New York, 578 pp. <https://doi.org/10.1007/978-1-4612-5206-1>
- Truesdell, C. and Toupin, R. (1960). The classical field theories. In *Principles of Classical Mechanics and Field Theory / Prinzipien Der Klassischen Mechanik Und Feldtheorie*, pages 226-858. Springer Berlin Heidelberg. [https://doi.org/10.1007/978-3-642-45943-6\\_2](https://doi.org/10.1007/978-3-642-45943-6_2)
- Whitaker, S. (1986). Transport processes with heterogeneous reaction. In Whitaker, S. and Cassano, A., editors, *Concepts and Design of Chemical Reactors*, chapter 1, pages 1-94. Gordon and Breach.
- Whitaker, S. (1988). Levels of simplification: The use of assumptions, restrictions and constraints in engineering analysis. *Chemical Engineering Education* 22, 104-108.
- Whitaker, S. (2009a). Chemical engineering education: Making connections at interfaces. *Revista Mexicana de Ingeniería Química* 8(1), 1-33. [http://rmiq.org/iqfvp/Pdfs/Vol%208%20no%201/RMIQ\\_Vol\\_8\\_No\\_1\\_1.pdf](http://rmiq.org/iqfvp/Pdfs/Vol%208%20no%201/RMIQ_Vol_8_No_1_1.pdf)

Whitaker, S. (2009b). Derivation and application of the Stefan-Maxwell equations. *Revista Mexicana de Ingeniería Química* 18(3), 213-243. <http://rmiq.org/iqfvp/Pdfs/Vol%208%20no%203/2009paper.pdf>

Whitaker, S. (2012). Mechanics and thermodynamics of diffusion. *Chemical Engineering Science* 68(1), 362-375. <https://doi.org/10.1016/j.ces.2011.09.050>.

## APPENDIX A. Mass diffusion velocity

The objective of this section is to provide a derivation for the decomposition of the species velocity given in Eq. (11). To this end, let us commence with the mass average velocity definition, which can be written as

$$\mathbf{v} = \omega_A \mathbf{v}_A + \sum_{B=1}^{B=N-1} \omega_B \mathbf{v}_B. \quad (\text{A.1})$$

Note that the mass fraction of species A can be expressed in terms of those of the other components of the mixture as follows

$$\omega_A = 1 - \sum_{B=1}^{B=N-1} \omega_B. \quad (\text{A.2})$$

Substituting this expression into Eq. (A.1) leads to the following expression for the species velocity

$$\mathbf{v}_A = \mathbf{v} + \sum_{B=1}^{B=N-1} \omega_B (\mathbf{v}_A - \mathbf{v}_B). \quad (\text{A.3})$$

The last term on the right-hand side of the above equation represents the weighted average of the species A velocity relative to those of the other species. This term thus defines the *species diffusive velocity*, i.e.,

$$\mathbf{u}_A = \sum_{B=1}^{B=N-1} \omega_B (\mathbf{v}_A - \mathbf{v}_B). \quad (\text{A.4})$$

Substitution of this result into Eq. (A.3) leads to the decomposition given in Eq. (11).

## APPENDIX B. Simplification of the governing equation for the diffusion velocity

The purpose of this appendix is to derive a set of constraints that allow simplifying Eq. (33) to the form

given in Eq. (37). One way to achieve this goal is to reformulate Eq. (33) in a dimensionless form, to later ponder about the weights of different terms. Therefore, let us commence by introducing the dimensionless time and gradient operator as

$$\hat{t} = \frac{t}{t_{ref}}; \hat{\nabla} = \ell \nabla. \quad (\text{B.1})$$

Here,  $t_{ref}$  and  $\ell$  denote a reference length and a characteristic length of the transport process. Next, let us introduce the following dimensionless definitions for the flow variables

$$\hat{\mathbf{v}} = \frac{\mathbf{v}}{v_{ref}}; \hat{p} = \frac{p}{p_{ref}}; \hat{\tau} = \frac{\tau \ell}{\mu_{ref} v_{ref}}. \quad (\text{B.2})$$

In the above, the reference pressure can be defined in terms of the reference velocity as follows  $p_{ref} = \mu_{ref} v_{ref} / \ell$ . At this point, it is convenient to introduce a reference value for the species A mass fraction, which is denoted as  $\omega_{Aref} < 1$ . On the basis of this definition, the species A mass fraction can be rescaled as

$$\hat{\omega}_A = \frac{\omega_A}{\omega_{Aref}}, \quad A = 1, 2, \dots, N. \quad (\text{B.3})$$

Finally, let us introduce the following definitions that are applicable to all chemical species

$$\begin{aligned} \hat{\rho}_A &= \frac{\rho_A}{\rho_{ref}}; \hat{\mathbf{u}}_A = \frac{\mathbf{u}_A}{\omega_{Aref} v_{ref}}; \hat{\mathbf{v}}_A = \frac{\mathbf{v}_A}{v_{ref}}; \hat{\mathbf{v}}_A^* = \frac{\mathbf{v}_A^*}{v_{ref}}; \\ \hat{\tau}_A &= \frac{\tau_A \ell}{\omega_{Aref} \mu_{ref} v_{ref}}; \hat{p}_A = \frac{p_A}{p_{Aref}}; \hat{\mathbf{P}}_{AB} = \frac{\mathbf{P}_{AB} \ell}{p_{Aref}}; \\ \hat{\mathbf{b}}_A &= \frac{\mathbf{b}_A - \mathbf{b}}{\omega_{Aref} b_{ref}}; \hat{r}_A = \frac{r_A t_{ref}}{\omega_{Aref} p_{ref}}, \quad A = 1, 2, \dots, N. \end{aligned} \quad (\text{B.4})$$

Note that  $\hat{r}_A$  can be conceived as a Damköhler number. In the following, it is assumed that  $p_A$  experiences changes over a distance  $L$ , which is assumed to be much larger than  $\ell$ . Such separation of length scales has been previously suggested by Whitaker (1986) and it is supported by the hypothesis that, under diffusive conditions, species A experience changes in its concentration at larger distances than the total mixture concentration. This means that  $p_{Aref}$  can be related to  $p_{ref}$  according to

$$p_{Aref} = \frac{L}{\ell} \omega_{Aref} p_{ref} = \frac{L^2}{\ell^2} \frac{\omega_{Aref} \mu_{ref} v_{ref}}{L}. \quad (\text{B.5})$$

Substituting the above definitions into Eq. (33), leads

to

$$\begin{aligned} & \frac{\rho_{ref}\ell^2}{t_{ref}\mu_{ref}}\hat{\rho}_A\frac{\partial\hat{\mathbf{u}}_A}{\partial\hat{t}} + Re\hat{\rho}_A(\hat{\mathbf{v}}_A\cdot\hat{\nabla}\hat{\mathbf{u}}_A + \hat{\mathbf{u}}_A\cdot\hat{\nabla}\hat{\mathbf{v}}) \\ & - \omega_{Aref}^2 Re\hat{\omega}_A\hat{\nabla}\cdot\left[\sum_{B=1}^{B=N}\hat{\rho}_B\hat{\mathbf{u}}_B\otimes\hat{\mathbf{u}}_B\right] = -(\hat{\omega}_A\hat{\nabla}\cdot\hat{\boldsymbol{\tau}} - \hat{\nabla}\cdot\hat{\boldsymbol{\tau}}_A) \\ & - \frac{L}{\ell}\hat{\nabla}\hat{\rho}_A + \hat{\omega}_A\hat{\nabla}\hat{\rho} + \frac{Re}{Fr}\hat{\rho}_A\hat{\mathbf{b}}_A + \frac{L}{\ell}\sum_{B=1}^{B=N}\hat{\mathbf{P}}_{AB} \\ & + \frac{\rho_{ref}\ell^2}{t_{ref}\mu_{ref}}\hat{\tau}_A(\hat{\mathbf{v}}_A^* - \hat{\mathbf{v}}_A), \quad A = 1, 2, \dots, N-1. \end{aligned} \quad (\text{B.6})$$

In the above equation, the Reynolds and Froude numbers were defined as follows

$$Re = \frac{\rho_{ref}v_{ref}\ell}{\mu_{ref}}; \quad Fr = \frac{v_{ref}^2}{b_{ref}\ell}. \quad (\text{B.7})$$

From Eq. (B.6), it follows that, for situations in which the reference time is such that

$$\frac{\rho_{ref}\ell^3}{L\mu_{ref}} = \frac{Re\ell^2}{v_{ref}L} \ll t_{ref}, \quad (\text{B.8})$$

it is reasonable to adopt restrictions R1 and R5 given in (34a) and (34e) in the main text. Note that restriction R5 also requires assuming that  $\hat{\tau}_A \leq \mathbf{O}(1)$ . At this point it is pertinent to point out that the inequality given in (B.8) is equivalent to (1-47) in Whitaker (1986) as long

as the reference density is taken to be  $\rho_{ref} = p_{ref}/C^2$ , with  $C$  being the speed of sound in the  $N$ -component mixture. Moreover, this choice for  $\rho_{ref}$  leads to  $Re = Ma^2$ , with  $Ma = v_{ref}/C$  being the Mach number.

Directing the attention to the inertial-like terms, restricting the Reynolds number (or, equivalently  $Ma^2$ ) to meet the following length-scale constraint

$$Re \ll \frac{L}{\ell}, \quad (\text{B.9})$$

it is reasonable to adopt restrictions R2 and R3. Note that the latter is easier to satisfy than the former since  $\omega_{Aref} < 1$ . The above constraint is equivalent to inequality (1-51) in Whitaker (1986).

Focusing on the viscous terms, the length-scale constraint  $\ell \ll L$ , allows justifying restrictions R4 (34d) and R7 (36b). Finally, on the basis of (B.9), the following constraint is proposed for the Froude number

$$Re\frac{\ell}{L} \ll 1 \ll Fr, \quad (\text{B.10})$$

which allows imposing restriction R6 (36a). Under these conditions, Eq. (33) can be reduced to the form given in Eq. (37) in the main text. The constraints derived here are consistent with those originally proposed by Whitaker (1986) as well as those more recently reported by Whitaker (2009a) and applied to the Stefan diffusion tube.