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Diffusion of Charged Species in Liquids

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In this study the laws of mechanics for multi-component systems are used to develop a theory for the diffusion of ions in the presence of an electrostatic field. The analysis begins with the governing equation for the species velocity and it leads to the governing equation for the species diffusion velocity. Simplification of this latter result provides a momentum equation containing three dominant forces: (a) the gradient of the partial pressure, (b) the electrostatic force, and (c) the diffusive drag force that is a central feature of the Maxwell-Stefan equations. For ideal gas mixtures we derive the classic Nernst-Planck equation. For liquid-phase diffusion we encounter a situation in which the Nernst-Planck contribution to diffusion differs by several orders of magnitude from that obtained for ideal gases.

The study of ion transport in fluids is an important topic with a wide range of applications. Some classic examples are batteries, fuel cells, electroplating, and protection of metal structures against corrosion. In addition to the traditional battery, the flow battery or rechargeable fuel cell represents an important new technology involving the transport of ions. Ion exchange membranes have a wide range of applications, and the underlying theory has been a matter of concern for several decades. Other examples of complex electro-chemical systems are the transport of charged particles in ion channels, in protein channels, and during the primordial conversion of light to metabolic energy. Often upscaling is necessary for a complete analysis of the transport of electrolytes in charged pores.

Much of ion transport occurs at the nano-scale, and most of the studies use the Nernst-Planck equation to describe this type of phenomena. However, there are molecular dynamic simulations indicating that the Nernst-Planck equation does not always provide a complete description, and there are experimental studies that lead to the same conclusion. The need to analyze the limits of the Nernst-Planck contribution to diffusion has been emphasized in an exploration of the transport of divalent ions in ionic channels.

The authors of this paper have not found a derivation of the Nernst-Planck equation that does not make use of the ideal gas assumption. To be precise we note that ideal gas behavior for mixtures is based on Dalton’s laws (see page 114 in ref. 20) that we list as

\[ \frac{p_A V}{n_A RT} = 1, \, 2, \ldots, \, N \]

\[ p = \sum_{A=1}^{A=N} p_A \]

\[ p_A = x_A \rho, \quad A = 1, \, 2, \ldots, \, N \]

Some care must be taken with the interpretation of Eq. 2 since it applies to all Stokesian fluids and is therefore not limited to ideal gas mixtures (see Appendix B in ref. 21). Caution must also be used with the interpretation of Eq. 3 which is applicable to all ideal fluid mixtures. For example, Eq. 3 should provide reliable results for a liquid mixture of hexane and heptane, but it should not be used for a mixture of ethanol and water.

Here it is important to emphasize that Eq. 1 can only describe a fluid composed of non-interacting particles. To provide a reliable framework in which a fluid is considered to be composed of interacting particles — as in the case of a liquid — it is necessary to understand the process of Nernst-Planck diffusion in a fluid different from an ideal gas. This is the problem under consideration in this paper.

In this work we analyze the ion transport process from a fundamental point of view using an axiomatic mechanical perspective. Our analysis is for ideal fluid mixtures, and from the analysis we find that the classic
Nernst-Planck relation is only valid for ideal gas mixtures. For ideal liquid mixtures we find an alternative expression in which the form is similar to that for ideal gas mixtures, but significant other terms appear in the final result.

In the following section we present a detailed analysis based on axiomatic statements for the mechanics of multi-component systems. Our objective is a search for clarity and rigor in terms of a diffusion equation that is applicable to both gas and liquid mixtures, i.e., applicable to fluid mixtures. We first derive a general equation for the species velocity, and from this we extract a general equation for the species diffusion velocity. This equation is the origin of Fick’s law of diffusion; however, the derivation of Fick’s law from the governing equation for the species diffusion velocity is complex. We begin our study of the general equation for the species diffusion velocity with a series of plausible restrictions that lead to a special form of the governing equation for the diffusion velocity. This provides a transport equation for the diffusion of charged molecules in fluids, and this general form can be used to clearly establish that the classic Nernst-Planck equation is only valid for ideal gas mixtures.

Analysis
The analysis in this study is presented in terms of axiomatic statements concerning the species A body illustrated in Fig. 1. There we have used $V_A(t)$ to identify the volume occupied by the species A body, and we have illustrated

Figure 1. Species A Body.
only the presence of one other species, species B; however, one should image the presence of many other species.

We begin with a review of the axioms for mass and mechanics of multi-component systems, and then move on to explore the dominant terms in the species momentum equation. If one accepts the simplification that the electric field represents a specified force, the motion of both charged and uncharged species can be treated in terms of the axioms for mass and momentum that are given in the following paragraphs. It is crucial to understand that the following development is applicable to both gases and liquids.

**Mass.** We begin our study with the two axioms for mass given by

\[
\frac{d}{dt} \int_{V_A(t)} \rho_A \, dV = \int_{V_A(t)} r_A \, dV, \quad A = 1, 2, \ldots, N
\]

(time rate of change of mass of species A)

**Axiom IA:**

The net rate of production of mass of species A owing to chemical reactions

\[
\sum_{A=1}^{A=N} r_A = 0
\]

(net rate of production of mass owing to chemical reactions)

**Axiom IIA:**

The volume of the species A body is represented by \( V_A(t) \) and the speed of displacement of the surface of this volume is \( v_A \). Axiom I A can be used to derive the species A continuity equation by using the transport theorem and the divergence theorem (see Sec. 1.3.2 in ref. 22). This leads to

\[
\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A v_A) = r_A, \quad A = 1, 2, \ldots, N
\]

(6)

The total continuity equation is obtained by summing Eq. 6 over all \( N \) species and imposing Eq. 5 in order to obtain (see page 83 in ref. 23)

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0
\]

(7)

Here the total density, \( \rho \), and the total mass flux, \( \rho \mathbf{v} \), are defined by

\[
\rho = \sum_{A=1}^{A=N} \rho_A, \quad \rho \mathbf{v} = \sum_{A=1}^{A=N} \rho_A \mathbf{v}_A
\]

(8)

The mass fraction of species A is defined according to

\[
\omega_A = \frac{\rho_A}{\rho}
\]

(9)

and use of this definition with Eq. 8 provides a constraint for the mass fractions and a representation for the mass average velocity. These two results take the form

\[
1 = \sum_{A=1}^{A=N} \omega_A, \quad \mathbf{v} = \sum_{A=1}^{A=N} \omega_A \mathbf{v}_A
\]

(10)

The objective of this study is the development of an expression for the diffusive flux of species A. This requires that we decompose the species velocity according to

\[
\mathbf{v}_A = \mathbf{v} + \mathbf{u}_A, \quad A = 1, 2, \ldots, N
\]

(11)

in which \( \mathbf{u}_A \) is the mass diffusion velocity. This decomposition allows us to express Eq. 6 in terms of convective and diffusive fluxes according to (see Eq. 19.1–7 in ref. 23)

\[
\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}) = -\nabla \cdot \mathbf{j}_A + r_A, \quad A = 1, 2, \ldots, N
\]

(12)

Here we note that the mass diffusive flux is defined by

\[
\mathbf{j}_A = \rho_A \mathbf{u}_A, \quad A = 1, 2, \ldots, N
\]

(13)

and this flux is constrained by

\[
\sum_{A=1}^{A=N} \mathbf{j}_A = \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A = 0
\]

(14)

Given these forms of the species continuity equation and the total continuity equation, we are ready to move on to the analysis of the mechanics of multi-component fluids.
Mechanics. The first of the four axioms associated with the species A body is the linear momentum principle given by (see page 85 in ref. 24)

\[
\frac{d}{dt} \int_{V_A(t)} p_A v_A dV = \int_{V_A(t)} \frac{\partial}{\partial t} p_A v_A dV + \int_{A_A} t_A(n) dA + \int_{A_B} \frac{\partial}{\partial t} \rho_A b_A dV + \int_{A_B} \frac{\partial}{\partial t} \rho_A b_A dV
\]

\[
\text{Axiom IB:} \quad + \int_{V_A(t)} \sum_{B=1}^{B=N} p_{AB} dV + \int_{V_A(t)} r_A v'_A dV, \quad A = 1, 2, \ldots, N
\]

Here the species stress vector, \( t_{A}(n) \), represents the force that the surroundings (into which \( n \) is directed) exert on species \( A \) within the species \( A \) body. We have used \( P_{AB} \) to represent the diffusive force exerted by species \( B \) on species \( A \) and it is understood that

\[
P_{AA} = 0, \quad A = 1, 2, \ldots, N
\]

In the last term in Eq. 15 we have indicated the possibility that species \( A \) entering or leaving the species \( A \) body owing to chemical reaction may have a velocity \( v'_A \) different than the continuum velocity \( v_A \).

The second axiom is the angular momentum principle that takes the form

\[
\frac{d}{dt} \int_{V_A(t)} \mathbf{r} \times \rho_A v_A dV = \int_{V_A(t)} \mathbf{r} \times \rho_A b_A dV + \int_{A_A} \mathbf{r} \times t_A(n) dA + \int_{A_B} \sum_{B=1}^{B=N} \mathbf{r} \times \rho_{AB} dV + \int_{A_B} \sum_{B=1}^{B=N} \mathbf{r} \times \rho_{AB} dV
\]

\[
\text{Axiom IIB:} \quad + \int_{V_A(t)} \sum_{B=1}^{B=N} \mathbf{r} \times \mathbf{v}'_A dV, \quad A = 1, 2, \ldots, N
\]

Here \( \mathbf{r} \) represents the position vector relative to a fixed point in an inertial frame. Truesdell (see page 85 in ref. 24) presents a more general version of Axiom II B in which a growth of rotational momentum is included, and Aris (see Sec. 5.13 in ref. 25) considers an analogous effect for polar fluids.

The third axiom requires that there be no net diffusive force in the total momentum equation (see page 133 in ref. 26) and we express this idea as

\[
\sum_{A=1}^{A=N} \sum_{B=1}^{B=N} P_{AB} = 0
\]

\[
\text{Axiom IIIIB:}
\]

In terms of chemical reactions, Hirschfelder et al. (see page 497 in ref. 27) point out that “even in a collision which produces a chemical reaction, mass, momentum and energy are conserved”. The continuum version of this idea for linear momentum gives rise to the fourth axiom that we express as

\[
\sum_{A=1}^{A=N} r_A v'_A = 0
\]

\[
\text{Axiom IVB:}
\]

Returning to Eq. 15 we note that Axiom I B can be used to develop Cauchy’s lemma given by (see Section 203 in ref. 28)

\[
t_A(n) = -t_A(-n)
\]

in which \( t_{A(-n)} \) represents the force that species \( A \) exerts on the surroundings. Cauchy’s fundamental theorem for the species stress vector is given by (see Lecture 5 in ref. 24).

\[
t_A(n) = n \cdot T_A
\]

and one can use this result in Eq. 15 to obtain the following Species A Momentum Equation:
At this point we can use the continuity equation given by Eq. 6 to obtain
\[
\frac{\partial}{\partial t} \rho + \nabla \cdot (\rho \mathbf{v}_A) = \rho_A \mathbf{b}_A + \nabla \cdot \mathbf{T}_A + \sum_{B=1}^{B=N} \mathbf{P}_{AB} + r_A \mathbf{v}_A
\]
\(A = 1, 2, \ldots, N\)
\(\text{(22)}\)

and this allows us to express Eq. 22 in the form
\[
\rho \frac{\partial \mathbf{v}_A}{\partial t} + \rho_A \mathbf{v}_A \cdot \nabla \mathbf{v}_A = \rho_A \mathbf{b}_A + \nabla \cdot \mathbf{T}_A + \sum_{B=1}^{B=N} \mathbf{P}_{AB} + r_A (\mathbf{v}_A - \mathbf{v}_A)
\]
\(A = 1, 2, \ldots, N\)
\(\text{(24)}\)

Both Eq. 22 and Eq. 24 can be found in the literature; however, locating them requires some effort because of the lack of a uniform nomenclature (see Sec. 1.2 in ref. 21). Chapman and Cowling (see page 135 in ref. 29) obtained Eq. 24 for dilute gases with \(r_A = 0\) by means of a generalized equation of change. In addition, this result was presented by Truesdell and Toupin (see Eq. 215.2 in ref. 28) and by Truesdell (see Eq. 22 in ref. 30). Bearman and Kirkwood (see Eq. 4.20 in ref. 31) presented Eq. 22 for the case of \(r_A = 0\) as did Curtiss and Bird (see Eq. A2 in ref. 32). Datta and Vilekar (see Eq. 2 in ref. 33) have derived Eq. 22 beginning with Eq. 15, and Jou et al. (see Eq. 1.21 in ref. 34) present Eq. 22 with the last two terms identified as “…contributions due to the interaction forces and the exchange of momentum between various components…” Most recently the developments leading to Eqs 22 and 24 have been summarized by Whitaker (see ref. 35).

The analysis of Axiom II B is rather long; however, after some algebra one finds that Eq. 17 leads to the symmetry of the species stress tensor indicated by (see Lecture 5 in ref. 24)
\[
\mathbf{T}_A = \mathbf{T}_A^T, \quad A = 1, 2, \ldots, N
\]
\(\text{(25)}\)

This is identical in form to Cauchy’s second law of motion (see page 187 in ref. 36). At this point it seems clear that there is general agreement concerning the form of the species linear momentum equation that represents the governing equation for the species velocity, \(\mathbf{v}_A\). In the study of diffusion processes, it is the diffusion velocity, \(\mathbf{u}_A\), that is important, and in the following paragraphs we develop the governing equation for this velocity.

**Diffusion Velocity**

The total linear momentum equation is obtained by summing Eq. 22 over all species and imposing the axioms given by Eqs 18 and 19. This leads to
\[
\frac{\partial}{\partial t} \rho \mathbf{v} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \rho \mathbf{b} + \nabla \cdot \mathbf{T} - \nabla \cdot \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \mathbf{u}_A
\]
\(\text{(26)}\)
in which the total stress tensor and the total body force are defined by
\[
\mathbf{T} = \sum_{A=1}^{A=N} \mathbf{T}_A, \quad \mathbf{b} = \sum_{A=1}^{A=N} \omega_A \mathbf{b}_A
\]
\(\text{(27)}\)

At this point we recall that a Stokesian fluid (see Sec. 59 of ref. 37, see Sec. 5.21 of ref. 25, see Secs. 3.3 and 3.4 of ref. 38, see Sec. 2.3.2 of ref. 22) can be described by

Stokesian fluid:
\[
\mathbf{T} = -p \mathbf{I} + \mathbf{\tau}
\]
\(\text{(28)}\)

Here \(\mathbf{\tau}\) is the viscous stress tensor, and \(p\) is the local thermodynamic pressure given by
\[
p = \rho \left( \frac{\partial e}{\partial \rho} \right)_{T, \varphi, \varphi', \varphi''} - \rho \mathbf{\varphi}_s\mathbf{\varphi}_c
\]
\(\text{(29)}\)
in which \(e\) is the internal energy per unit mass. To relate this expression for the pressure to that given by Slattery (see page 444 of ref. 22) and to that given by Callen (see Eq. 2.4 of ref. 39), one makes use of the following
\[
e = \dot{U}\text{Slattery} = \frac{U}{m}\text{Callen}, \quad \rho = \frac{1}{\dot{V}}\text{Slattery} = \frac{m}{\dot{V}}\text{Callen}
\]
\(\text{(30)}\)

Here \(m\) represents the mass of the closed system preferred by Callen. Use of Eq. 28 with Eq. 26 allows us to express the total momentum equation in the form
\[
\frac{\partial}{\partial t} (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \rho \mathbf{b} - \nabla p + \nabla \cdot \mathbf{\tau} - \nabla \cdot \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \mathbf{u}_A
\]
\(\text{(31)}\)

Returning to the species momentum equation given by Eq. 22, we propose that the species stress tensor can be represented by
Stokesian fluid mixture:

\[ T_A = -p_A I + \tau_A, \quad A = 1, 2, \ldots, N \]  

(32)

Here \( p_A \) is the partial pressure defined by (see Chapter 10 of ref. 40)

\[ p_A = \rho_A^2 \left( \frac{\partial e_A}{\partial p_A} \right)_{e_A, \rho_A, \ldots, \rho_N} \]  

(33)

in which \( e_A \) is the internal energy of species \( A \) per unit mass of species \( A \). The classic relation between the partial pressures and the total pressure is given by

\[ p = \sum_{A=1}^{A=N} p_A \]  

(34)

and this requires that

\[ \rho^2 \left( \frac{\partial e}{\partial p} \right)_{e, \rho, \ldots, \rho_N} = \sum_{A=1}^{A=N} P \rho_A^2 \left( \frac{\partial e_A}{\partial p_A} \right)_{e_A, \rho_A, \ldots, \rho_N} \]  

(35)

The proof of this result is rather long and is given by Whitaker (see Appendix B of ref. 21). We can use Eq. 27 through Eq. 34 to conclude that

\[ \tau = \sum_{A=1}^{A=N} \tau_A \]  

(36)

It is important to recognize that the application of Eqs 29 and 33 requires an assumption of local thermodynamic equilibrium (see Sec. 3.4 of ref. 38), and this should be satisfactory for many, but not all, mass transfer processes. The use of Eq. 32 in Eq. 22 leads to the following form of the species \( A \) momentum equation

\[ \frac{\partial}{\partial t} (\rho_A \mathbf{v}_A) + \nabla \cdot (\rho_A \mathbf{v}_A \mathbf{v}_A) = \rho_A b_A - \nabla p_A + \nabla \cdot \tau_A + \sum_{B=1}^{B=N} \rho_{AB} B_A + r_A \mathbf{v}_A - v_A, \quad A = 1, 2, \ldots, N \]  

(37)

Here one should note that the diffusive force is constrained by Eq. 16.

At this point it will be convenient to use Eq. 7 with Eq. 26 to obtain the following form of the total momentum equation

\[ \rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = \rho \mathbf{b} + \nabla \cdot T - \nabla \cdot \left[ \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \right] \]  

(38)

The analogous form of the species momentum equation is given by Eq. 24 and repeated here as

\[ \rho \frac{\partial \mathbf{v}_A}{\partial t} + \rho \mathbf{v}_A \cdot \nabla \mathbf{v}_A = \rho \mathbf{b}_A + \nabla \cdot \tau_A + \sum_{B=1}^{B=N} \rho_{AB} B_A + r_A \mathbf{v}_A - v_A \]  

(39)

At this point we wish to use Eqs 38 and 39 to derive the governing equation for the mass diffusion velocity, \( \mathbf{u}_A \). We begin by multiplying Eq. 38 by the mass fraction \( \omega_A \) leading to

\[ \rho \frac{\partial \mathbf{u}_A}{\partial t} + \rho \mathbf{u}_A \cdot \nabla \mathbf{u}_A + \rho \omega_A \mathbf{v}_A = \rho \mathbf{b}_A + \nabla \cdot T - \nabla \cdot \left[ \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \right] \]  

(40)

and we subtract this result from Eq. 39 to obtain the desired governing differential equation for the mass diffusion velocity, \( \mathbf{u}_A \), given by

\[ \rho \frac{\partial \mathbf{u}_A}{\partial t} + \rho \mathbf{u}_A \cdot \nabla \mathbf{u}_A + \rho \omega_A \mathbf{v}_A = \rho \mathbf{b}_A - \mathbf{b} + \nabla \cdot \mathbf{T}_A \]

\[ - \omega_A \nabla \cdot \mathbf{T} + \omega_A \nabla \cdot \left[ \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \right] + \sum_{B=1}^{B=N} \rho_{AB} B_A + r_A \mathbf{v}_A - v_A, \quad A = 1, 2, \ldots, N - 1 \]  

(41)

This governing equation for \( \mathbf{u}_A \) is the origin of Fick’s law (see Eq. 1 of ref. 41; see page 45 of ref. 42); however, some simplifications are required in order to achieve that classic result. To be clear about this point, we note that Fick’s law for a binary system is given by (see Table 17.8-2 of ref. 23)

\[ \mathbf{p}_A \mathbf{u}_A = j_A = -\mathbf{D}_{AB} \nabla \omega_A \]  

(42)
and the path between Eq. 41 and Eq. 42 is rather long (see Eq. 110 of ref. 21).

We now make use of Eqs 28 and 32 with Eq. 41 to obtain the following form of the governing equation for the species A mass diffusion velocity

$$
\rho_A \frac{\partial \mathbf{u}_A}{\partial t} + \rho_A \mathbf{v} \cdot \nabla \mathbf{u}_A = -\nabla p_A + \omega_A \nabla p + \rho_A (\mathbf{b}_A - \mathbf{b}) + \sum_{B=1}^{B=N} \mathbf{P}_{AB} \\
- \rho_A \mathbf{u}_A \cdot \nabla \mathbf{v} - (\omega_A \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{v}_A) + \omega_A \nabla \cdot \left[ \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \mathbf{u}_A \right] + r_A (\mathbf{v}_A - \mathbf{v}_A)
$$

(43)

Plausible restrictions associated with this governing equation for $u_A$ are given by (see Sec. 1.2 in ref. 21) and are listed here as

$$
\rho \frac{\partial u_A}{\partial t} \ll \nabla p_A \tag{44}
$$

$$
\rho_A u_A \cdot \nabla u_A \ll \nabla p_A \tag{45}
$$

$$
\rho_A \mathbf{u}_A \cdot \nabla \mathbf{v} \ll \nabla p_A \tag{46}
$$

$$
(\omega_A \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{v}_A) \ll \nabla p_A \tag{47}
$$

$$
\omega_A \nabla \cdot \sum_{A=1}^{A=N} \rho_A \mathbf{u}_A \mathbf{u}_A \ll \nabla p_A \tag{48}
$$

$$
r_A (\mathbf{v}_A - \mathbf{v}_A) \ll \nabla p_A \tag{49}
$$

An effort to justify these restrictions is given by Whitaker (see Secs. 2.6 and 2.7 in ref. 43); however, a rigorous analysis leading to constraints is still unavailable. Equation 44 indicates that the governing equation for $u_A$ is quasi-steady; Eq. 45 indicates that diffusive inertial effects are negligible, Eq. 46 indicates that the influence of mass average rotational flow is negligible, Eq. 47 indicates that viscous effects are negligible, Eq. 48 indicates that diffusive stresses are negligible, and Eq. 49 indicates that the effects of homogeneous chemical reactions are negligible.

When the restrictions given by Eqs 44 through 49 are imposed, the governing equation for the mass diffusion velocity takes the form

$$
\nabla p_A - \omega_A \nabla p - \rho_A (\mathbf{b}_A - \mathbf{b}) = \sum_{B=1}^{B=N} \mathbf{P}_{AB}, \quad A = 1, 2, \ldots, N - 1
$$

(50)

Curtiss & Bird (see Eq. 7.6 in ref. 44) represent the left hand side of Eq. 50 by $cRT_d$ and refer to it as the generalized driving force for diffusion. Truesdell (see Eq. 7 in ref. 30) represents the left hand side of Eq. 50 by $pd_1$ and cites as the source. To illustrate the connection with, we need Eq. 3 repeated here as

$$
\text{Ideal fluid mixture:} \quad p_A = x_A P, \quad A = 1, 2, \ldots, N \tag{51}
$$

Use of this representation for the partial pressure indicates that our analysis is restricted to ideal fluid mixtures and it allows us to express Eq. 50 in the form

$$
\nabla (x_A) + p^{-1} (x_A - \omega_A) \nabla p - p^{-1} \rho_A (\mathbf{b}_A - \mathbf{b}) = \sum_{B=1}^{B=N} p^{-1} \mathbf{P}_{AB}, \quad A = 1, 2, \ldots, N - 1
$$

(52)

The left hand side of this result is identical to Enskog’s perturbation solution (see Eq. 7.3–27 in ref. 27). This indicates that the simplifications represented by Eqs 44 through 49 are consistent with the perturbation analysis. It is important to keep in mind that Eq. 50 represents a special form of the governing equation for the diffusion velocity, $u_A$, subject to the restrictions indicated by Eqs 44 through 49. In addition, this equation for the diffusion velocity is restricted by the thermodynamic results indicated by Eqs 29 and 33. Finally, we remind the reader that Eq. 50 is a continuum result that is not restricted to either gases or liquids but is restricted to Stokesian fluid mixtures.

We begin our analysis of Eq. 52 by neglecting the pressure diffusion term. This represents a satisfactory simplification for many diffusion processes; however, it is not acceptable for centrifugation processes (see page 776 in ref. 23; see page 452 in ref. 42). Given this simplification, Eq. 52 takes the form
and we are ready to analyze the term on the right hand side.

**Diffusive Force**

From dilute gas kinetic theory we know that \( P_{AB,\text{gas}} \) is given by

\[
P_{AB,\text{gas}} = \frac{x_B x_A}{D_{AB}} (v_B - v_A), \quad A = 1, 2, \ldots, N - 1
\]

(54)

This result can be obtained by comparing Eq. 52 of this work with Eqs 7.3–27 and 7.4–48 of ref. 27 and neglecting the effect of thermal diffusion. At this point we need a representation for \( P_{AB,\text{liq}} \), and one possibility is to use Eq. 54 as a model. This leads to

Ideal liquid mixture:

\[
P_{AB,\text{liq}} = P_{\text{liq}} \frac{x_B x_A}{D_{AB}} (v_B - v_A), \quad A = 1, 2, \ldots, N - 1
\]

(55)

where it is understood that all the terms on the right side are associated with a liquid mixture. It should be clear that Eq. 55 represents an empirical expression for the diffusive force, \( P_{AB,\text{liq}} \), and that \( D_{AB} \) represents an empirical coefficient to be determined by experiment. We can generalize Eqs 54 and 55 to the single form

\[
P_{AB} = P \frac{x_B x_A}{D_{AB}} (v_B - v_A), \quad A = 1, 2, \ldots, N - 1
\]

(56)

in which the diffusivity \( D_{AB} \) is given by

\[
D_{AB,\text{gas}} = D_{AB}, \quad \text{ideal gas mixtures}
\]

(57)

\[
D_{AB,\text{liq}} = D_{AB}, \quad \text{ideal liquid mixtures}
\]

(58)

Use of Eq. 56 in Eq. 53 leads to

\[
\nabla (x_A) - \frac{p^{-1} \rho_A (b_A - b)}{D_{AB}} = \sum_{B=1}^{B=N} \frac{x_B x_A}{D_{AB}} (v_B - v_A), \quad A = 1, 2, \ldots, N - 1
\]

(59)

In Appendix A we show that for dilute solutions we obtain the result given by (see page 776 in ref. 23)

\[
\sum_{B=1}^{B=N} x_A x_B (v_B - v_A) = -J_A / c D_{AB}, \quad x_A \ll 1
\]

(60)

Here \( J_A \) represents the mixed-mode diffusive flux (see page 537, Eq. H in ref. 23, see Sec. 4, Eq. 90 in ref. 21) defined according to

\[
J_A = c_A u_A
\]

(61)

and \( D_{AB} \) is a mixture diffusion coefficient given by

\[
\frac{1}{D_A} = \sum_{B=1}^{B=N} \frac{x_B}{D_{AB}}
\]

(62)

We refer to \( J_A \) as the mixed-mode diffusive flux since it is made up of the molar concentration, \( c_A \), and the mass diffusion velocity, \( u_A \).

Use of Eq. 60 in Eq. 59 allows us to express the mixed-mode diffusive flux according to

\[
J_A = -c D_{AB} \nabla x_A + (c D_{AB} / p \rho_A) (b_A - b)
\]

(63)

At this point we make use of the analysis given in Appendix B where we demonstrate the well-known result given by (see page 776 in ref. 23)

\[
\rho_A (b_A - b) = -z_A c_A F \nabla \Psi
\]

(64)

Here \( z_A F \) represents the charge per mole of species A in which \( z_A \) is the valence (i.e., \(-2 \) for \( \text{SO}_4^2- \) and \(+1 \) for \( \text{H}_3\text{O}^+ \)) and \( F \) is the conversion factor known as Faraday’s constant. It is important to note that Eq. 64 is subject to the approximation of electro-neutrality (see page 454 in ref. 42; see ref. 46) and this simplification will not be valid near charged surfaces. Use of Eq. 64 in Eq. 63 leads to the following result...
At this point we impose the dilute solution condition given by
\[ x_A \nabla c \ll c \nabla x_A \] (66)
so that Eq. 65 takes the form
\[ J_A = -D_{AA} \nabla c_A + (c \nabla p_A) z_A c_A F \nabla \Psi \] (67)

In order to represent the second term on the right hand side of Eq. 67 in terms of what is usually called Nernst-Planck diffusion, we introduce the product \( RT \) and arrange that term to obtain the following result
\[ J_A = -D_{AA} \nabla c_A + (c RT / p_A) D_{AA} z_A c_A (F / RT) \nabla \Psi \] (68)

For ideal gas mixtures we have \( cRT / p = 1 \) and the diffusivity takes the form \( D_{AA} = D_A \) as indicated by Eq. 57, Eq. A10 and Eq. A13. Under these circumstances Eq. 68 simplifies to the classic Nernst-Planck equation (see page 149 in ref. 47, see Eq. 3 in ref. 11, see Eq. 11.7–6 in ref. 42, see page 1844 in ref. 48) given by
\[ J_A = -D_{AA} \nabla (c_A)_{gas} - \nabla z_A (c_A)_{gas} (F / RT) \nabla \Psi \] (69)

For liquid mixtures we have \( cRT / p = c_{liq}RT / p_{liq} \) and the diffusivity takes the form \( D_{AA} = D_A \) as indicated by Eq. 58, Eq. A10, and Eq. A16. Under these circumstances Eq. 68 takes the form
\[ J_A|_{liq} = -D_{AA} \nabla (c_A)_{liq} - (c_{liq}RT / p_{liq}) D_{AA} z_A (c_A)_{liq} (F / RT) \nabla \Psi \] (70)

At this point it is important to realize that \( c_{liq}RT / p_{liq} \approx 1200 \) and there is no simplification of Eq. 68 to the form given by Eq. 69 for liquid phase diffusion. The development based on Eqs 54 and 55 is not the only route to Eqs 69 and 70, and another approach making use of the relation \( p_{liq} = c_{liq}RT \) is given in Appendix C.

The analysis presented here indicates that the classic result for dilute solution diffusion of ions in an electric field is only valid for ideal gas mixtures. When confronting this situation one must keep in mind that the results given in Appendix A for the third term in Eq. 53 would appear to be universally accepted (see page 47 in ref. 49, see page 448 in ref. 42). In addition, the result given in Appendix B for the second term in Eq. 53 would also appear to be universally accepted (see page 279 in ref. 49, see page 19 in ref. 47, see page 448 in ref. 42).

Conclusions

In this paper we have derived an ion transport equation for ideal fluid mixtures, and we have shown that the classic Nernst-Planck equation applies only to ideal gas mixtures. For ideal liquid mixtures, the laws of mechanics, the laws of electrostatics, and the thermodynamic representation for the partial pressure all lead to a new result. Non-ideal gases and liquids can be analyzed using the approach presented in this paper; however, that subject has not been explored in this work.}

Nomenclature

- \( J_A \): body force per unit mass exerted on species \( A \), N/kg
- \( b_{AA} \): body force per unit mass exerted on the mixture, N/kg
- \( c_A \): molar concentration of species \( A \), mol/m³
- \( p_A \): partial pressure of species \( A \), N/m²
- \( p_{liq} \): total pressure, N/m²
- \( r_A \): net mass rate of production of species \( A \) owing to homogeneous reactions, kg/m³s
- \( R \): gas constant, cal/mol K
- \( T_A \): stress tensor for species \( A \), N/m²
- \( \gamma_{AB} \): dilute solution liquid-phase binary diffusion coefficient for species \( A \) and \( B \), m²/s
- \( \gamma_{AA} \): dilute solution liquid-phase binary diffusion coefficient for species \( A \), m²/s
- \( \Delta G_{AB} \): ide engaged binary diffusion coefficient for species \( A \) and \( B \), m²/s
Greek Letters

$\rho_A$ = mass density of species $A$, kg/m$^3$

$\beta$ = total mass density, kg/m$^3$

$\tau$ = viscous stress tensor, N/m$^2$

$\tau_A$ = viscous stress tensor for species $A$, N/m$^2$

$\omega_A$ = $\rho_A/\rho$, mass fraction of species $A$

$\Psi$ = electric potential function, V

References


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**Author Contributions**

J.A.d.R. discussed and participated in writing the manuscript. S.W. proposed the problem, discussed and participated in writing the manuscript.

**Additional Information**

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