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DERIVATION AND APPLICATION OF THE STEFAN-MAXWELL EQUATIONS

DESARROLLO Y APLICACIÓN DE LAS ECUACIONES DE STEFAN-MAXWELL

Stephen Whitaker*

Department of Chemical Engineering & Materials Science
University of California at Davis

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Abstract

The Stefan-Maxwell equations represent a special form of the species momentum equations that are used to determine species velocities. These species velocities appear in the species continuity equations that are used to predict species concentrations. These concentrations are required, in conjunction with concepts from thermodynamics and chemical kinetics, to calculate rates of adsorption/desorption, rates of interfacial mass transfer, and rates of chemical reaction. These processes are central issues in the discipline of chemical engineering.

In this paper we first outline a derivation of the species momentum equations and indicate how they simplify to the Stefan-Maxwell equations. We then examine three important forms of the species continuity equation in terms of three different diffusive fluxes that are obtained from the Stefan-Maxwell equations. Next we examine the structure of the species continuity equations for binary systems and then we examine some special forms associated with *N*-component systems. Finally the general *N*-component system is analyzed using the mixed-mode diffusive flux and matrix methods.

Keywords: continuum mechanics, kinetic theory, multicomponent diffusion.

Resumen

Las ecuaciones de Stefan-Maxwell representan una forma especial de las ecuaciones de cantidad de movimiento de especies que son usadas para determinar las velocidades de especies. Estas velocidades de especies aparecen en las ecuaciones de continuidad de especies que son usadas para predecir las concentraciones de especies. Estas concentraciones son requeridas, en conjunción con los conceptos de termodinámica y cinética química, para calcular las velocidades de adsorción/desorción, las velocidades de transferencia de masa interfacial, y las velocidades de reacción química. Estos procesos son elementos centrales en la disciplina de la ingeniería química.

En este artículo presentamos primeramente un desarrollo de las ecuaciones de cantidad de movimiento de especies e indicamos como se simplifican a las ecuaciones de Stefan-Maxwell. Posteriormente examinamos tres formas importantes de la ecuación de continuidad de especies en términos de tres diferentes fluxes difusivos que se obtienen de las ecuaciones de Stefan-Maxwell. Más adelante examinamos la estructura de las ecuaciones de continuidad de especies para sistema binarios y examinamos algunas formas especiales asociados con sistemas de *N*-componentes. Finalmente se analiza el sistema general de *N*-componentes usando métodos matriciales y de flux difusivo de modo mixto.

Palabras clave: mecánica del continuo, teoría cinética, difusión multicomponente.

* *Corresponding author. E-mail: whitaker@mcn.org*

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Contents

1. Introduction

Our derivation of multi-component transport equations is based on the concept of a *species body*. In Part I of Fig. 1 we have illustrated a system containing both species *A* and species *B* and these are illustrated as discrete particles. We have also illustrated a region from which we have *cut out* both a species *A* body and a species *B* body. In Part II of Fig. 1 we have indicated that the species *A* body will be treated as a *continuum* while the discrete character of species *B* is retained for contrast. As time evolves the two species bodies separate because their velocities are different. This separation is illustrated in Part III of Fig. 1 where we have also indicated that the species *B* body will be treated as a *continuum*. The continuum velocities of species *A* and species *B* are designated as $\mathbf{v}_A$ and $\mathbf{v}_B$. In general, the continuum hypothesis should be satisfactory when the distance between molecules is very small compared to a characteristic length for the system.

1.1 Conservation of mass

In terms of the species *A* body illustrated in Fig. 1, we state the two axioms for the mass of multi-component systems as

Axiom I:

$$\frac{d}{dt}\int_{\mathscr{V}_A(t)} \rho_A \, dV = \int_{\mathscr{V}_A(t)} r_A \, dV \,, \quad A = 1, 2, ..., N \tag{1}$$

Axiom II:

$$\sum_{A=1}^{A=N} r_A = 0 \tag{2}$$

Here ρ_A represents the mass density of species *A* and r_A represents the net mass rate of production per unit volume of species *A* owing to chemical reaction. In Eqs. (1) and (2) we have used a mixed-mode nomenclature making use of both letters and numbers to identify individual species. For example, Axiom II could be expressed in terms of alphabetic subscripts as

$$\text{Axiom II: } r_A + r_B + r_C + r_D + ... + r_N = 0 \tag{3}$$

or we could use numerical subscripts to represent this axiom as

$$\text{Axiom II: } r_1 + r_2 + r_3 + r_4 + ... + r_N = 0 \tag{4}$$

This latter result can obviously be compacted to produce Eq. 2; however, the use of alphabetic subscripts to represent molecular species is prevalent in the chemical engineering literature. Because of this we will use alphabetic subscripts to identify distinct molecular species, and we will use the nomenclature contained in Eq. 2 to represent the various sums that appear in this paper.

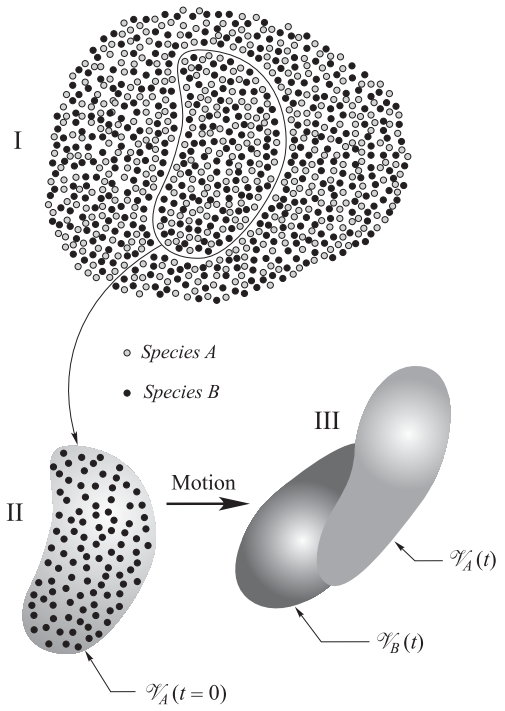

Fig.1. Motion of species *A* and species *B* bodies

In order to extract a governing differential equation from Eq. 1, we make use of the *general transport equation* (Whitaker, 1981, Sec. 3.4, with $\mathbf{w} = \mathbf{v}_A$)

$$\frac{d}{dt}\int_{\mathscr{V}_A(t)} \rho_A \, dV = \int_{\mathscr{V}_A(t)} \frac{\partial \rho_A}{\partial t} dV + \int_{\mathscr{A}_A(t)} \rho_A \mathbf{v}_A \cdot \mathbf{n} \, dA \,, \quad A = 1, 2, ..., N \tag{5}$$

and the *divergence theorem* (Stein and Barcellos, 1992, Sec. 17.2)

$$\int_{\mathscr{A}_A(t)} \rho_A \mathbf{v}_A \cdot \mathbf{n} \, dA = \int_{\mathscr{V}_A(t)} \nabla \cdot (\rho_A \mathbf{v}_A) \, dV \,, \quad A = 1, 2, ..., N \tag{6}$$

in order to express Eq. 1 in the form

$$\int_{\mathscr{V}_A(t)} \left[\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}_A) - r_A \right] dV = 0 \,, \quad A = 1, 2, ..., N \tag{7}$$

Since $\mathscr{V}_A(t)$ illustrated in Fig. 1 is arbitrary, and since it is plausible to assume that the integrand in Eq. (7) is continuous, the integrand in Eq. (7) must be zero and the governing differential equation associated with Eq. 1 is given by

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}_A) = r_A \,, \quad A = 1, 2, ..., N \tag{8}$$

If we sum Eq. (8) over all species and impose the Axiom II we obtain

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

in which the total density and the total mass flux are determined by

$$\rho = \sum_{A=1}^{A=N} \rho_A \,, \qquad \rho \mathbf{v} = \sum_{A=1}^{A=N} \rho_A \mathbf{v}_A \qquad (10)$$

The mass average velocity, $\mathbf{v}$, can be expressed in terms of the mass fraction, ω_A, and the species velocity, $\mathbf{v}_A$, according to

$$\mathbf{v} = \sum_{A=1}^{A=N} \omega_A \mathbf{v}_A \,, \quad \omega_A = \rho_A / \rho \,, \quad A = 1, 2, ..., N \qquad (11)$$

The typical treatment of Eq. (8) involves the solution of $N-1$ species continuity equations along with a solution of Eq. (9). This suggests a decomposition of the species velocity into the mass average velocity, $\mathbf{v}$, and the mass diffusion velocity, $\mathbf{u}_A$

$$\mathbf{v}_A = \mathbf{v} + \mathbf{u}_A \,, \quad A = 1, 2, ..., N \qquad (12)$$

so that the species continuity equations take the form

$$\underbrace{\frac{\partial \rho_A}{\partial t}}_{\text{accumulation}} + \underbrace{\nabla \cdot (\rho_A \mathbf{v})}_{\text{convective transport}} = \underbrace{-\nabla \cdot (\rho_A \mathbf{u}_A)}_{\text{diffusive transport}} + \underbrace{r_A}_{\text{chemical reaction}} \,, \quad A = 1, 2, ..., N-1 \qquad (13)$$

Here we note that only $N-1$ of the diffusive transport terms are independent since Eqs. (10) and (12) require the constraint

$$\sum_{A=1}^{A=N} \rho_A \mathbf{u}_A = 0 \qquad (14)$$

In order to solve Eqs. (9) and (13) we need governing differential equations for the mass diffusion velocity, $\mathbf{u}_A$, and the mass average velocity, $\mathbf{v}$. These are determined by the axioms for the mechanics of multi-component systems.

1.2 Laws of mechanics

Our approach to the laws of mechanics for multi-component systems follows the work of Euler and Cauchy (Truesdell, 1968), the seminal works of Chapman & Cowling (1939) and Hirschfelder, Curtiss & Bird (1954), along with the recent work of Curtiss & Bird (1996, 1999). In terms of the species body illustrated in Fig. 1 the linear momentum principle for species A is given by

$$\frac{d}{dt} \int_{\mathscr{V}_A(t)} \rho_A \mathbf{v}_A \, dV = \int_{\mathscr{V}_A(t)} \rho_A \mathbf{b}_A \, dV$$

$$\text{Axiom I:} \quad + \int_{\mathscr{A}_A(t)} \mathbf{t}_{A(\mathbf{n})} \, dA + \int_{\mathscr{V}_A(t)} \sum_{B=1}^{B=N} \mathbf{P}_{AB} \, dV + \int_{\mathscr{V}_A(t)} r_A \mathbf{v}_A^* \, dV \,, \quad A = 1, 2, ..., N \qquad (15)$$

With an appropriate interpretation of the nomenclature, one finds that this result is identical to the second of Eqs. 5.10 of Truesdell (1969, page 85) provided that one interprets Truesdell's *growth of linear momentum* as the last two terms in Eq. (15). In terms of the forces *acting on* species A, we note that $\rho_A \mathbf{b}_A$ represents the *body force*, $\mathbf{t}_{A(\mathbf{n})}$ represents the *surface force*, and $\mathbf{P}_{AB}$ represents the *diffusive force* exerted by species B on species A. This diffusive force is constrained by

$$\mathbf{P}_{AA} = 0 \,, \qquad A = 1, 2, 3, ..., N \qquad (16)$$

The last term in Eq. (15) represents the increase or decrease of species A momentum resulting from the increase or decrease of species A caused by chemical reaction, and this term is discussed in Appendix A.

The angular momentum principle for the species A body is given by

$$\frac{d}{dt} \int_{\mathscr{V}_A(t)} \mathbf{r} \times \rho_A \mathbf{v}_A dV = \int_{\mathscr{V}_A(t)} \mathbf{r} \times \rho_A \mathbf{b}_A dV$$

$$\text{Axiom II:} + \int_{\mathscr{A}_A(t)} \mathbf{r} \times \mathbf{t}_{A(\mathbf{n})} \, dA + \int_{\mathscr{V}_A(t)} \sum_{B=1}^{B=N} \mathbf{r} \times \mathbf{P}_{AB} \, dV + \int_{\mathscr{V}_A(t)} \mathbf{r} \times r_A \mathbf{v}_A^* \, dV \,, \quad A = 1, 2, ..., N \qquad (17)$$

in which $\mathbf{r}$ represents the position vector relative to a fixed point in an inertial frame. Truesdell (1969, page 84) presents a more general version of Axiom II in which a *growth of rotational momentum* is included, and Aris (1962, Sec. 5.13) considers an analogous effect for polar fluids. The analysis of Eq. (17) is rather long; however, the final result is simply the symmetry of the species stress tensor as indicated by

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

The constraint on $\mathbf{P}_{AB}$ is given by Truesdell (1962, Eq. 22) as

$$\text{Axiom III:} \qquad \sum_{A=1}^{A=N} \sum_{B=1}^{B=N} \mathbf{P}_{AB} = 0 \qquad (19)$$

and a little thought will indicate that this is satisfied by

$$\mathbf{P}_{AB} = -\mathbf{P}_{BA} \qquad (20)$$

One can think of this as the *continuum version* of Newton's third law of *action and reaction* (Whitaker, 2009a).

Hirschfelder *et al*. (1954, page 497) point out that "even in a collision which produces a chemical reaction, mass, momentum and energy are conserved" and the continuum version of this idea for linear momentum gives rise to the constraint:

$$\text{Axiom IV:} \qquad \sum_{A=1}^{A=N} r_A \mathbf{v}_A^* = 0 \tag{21}$$

This result, along with Eq. (19), is contained in the second of Eqs. 5.12 of Truesdell (1969).

Returning to the linear momentum principle, we note that the analysis associated with Cauchy's fundamental theorem (Truesdell, 1968) can be applied to Eq. (15) in order to express the species stress vector in terms of the species stress tensor according to

$$\mathbf{t}_{A(\mathbf{n})} = \mathbf{n} \cdot \mathbf{T}_A \tag{22}$$

This representation can be used in Eq. (15), along with the *divergence theorem* and the *general transport theorem*, to extract the governing differential equation for the linear momentum of species *A* given by

$$\underbrace{\frac{\partial}{\partial t}\left(\rho_A \mathbf{v}_A\right)}_{\substack{\text{local}\\ \text{acceleration}}} + \underbrace{\nabla \cdot \left(\rho_A \mathbf{v}_A \mathbf{v}_A\right)}_{\substack{\text{convective}\\ \text{acceleration}}} = \underbrace{\rho_A \mathbf{b}_A}_{\substack{\text{body}\\ \text{force}}} + \underbrace{\nabla \cdot \mathbf{T}_A}_{\substack{\text{surface}\\ \text{force}}} + \underbrace{\sum_{B=1}^{B=N} \mathbf{P}_{AB}}_{\substack{\text{diffusive}\\ \text{force}}} + \underbrace{r_A \mathbf{v}_A^*}_{\substack{\text{source of momentum}\\ \text{owing to reaction}}}, \quad A = 1, 2, ..., N \tag{23}$$

Equation (23) is identical to Eq. A2 of Curtiss and Bird (1996) for the case in which $r_A = 0$ provided that one takes into account the different nomenclature indicated by

Curtiss & Bird:

$$\rho_A \mathbf{b}_A = \mathbf{G}_A, \quad \nabla \cdot \mathbf{T}_A = -\nabla \cdot \boldsymbol{\sigma}_A, \quad \sum_{B=1}^{B=N} \mathbf{P}_{AB} = \mathbf{F}_A \tag{24}$$

One can make use of the identity

$$\rho_A \mathbf{v}_A \mathbf{v}_A = \rho_A \left(\mathbf{v}_A \mathbf{v} + \mathbf{v} \mathbf{v}_A - \mathbf{v} \mathbf{v}\right) + \rho_A \mathbf{u}_A \mathbf{u}_A \tag{25}$$

in order to express Eq. (23) in the from

$$\frac{\partial}{\partial t}\left(\rho_A \mathbf{v}_A\right) + \nabla \cdot \left[\rho_A \left(\mathbf{v}_A \mathbf{v} + \mathbf{v} \mathbf{v}_A - \mathbf{v} \mathbf{v}\right)\right] = \rho_A \mathbf{b}_A + \nabla \cdot \left(\mathbf{T}_A - \rho_A \mathbf{u}_A \mathbf{u}_A\right) + \sum_{B=1}^{B=N} \mathbf{P}_{AB} + r_A \mathbf{v}_A^*, \quad A = 1, 2, ..., N \tag{26}$$

This result is identical to Eq. 4.20 of Bearman and Kirkwood (1958) for the case in which $r_A = 0$ provided that one takes into account the different nomenclature indicated by (with the subscript $\alpha = A$)

Bearman and Kirkwood:

$$\rho_A \mathbf{b}_A = c_A \mathbf{X}_A, \quad \nabla \cdot \left(\mathbf{T}_A - \rho_A \mathbf{u}_A \mathbf{u}_A\right) = -\nabla \cdot \boldsymbol{\sigma}_A, \quad \sum_{B=1}^{B=N} \mathbf{P}_{AB} = c_A \overline{\mathbf{F}}_A^{(1)*} \tag{27}$$

Bearman and Kirkwood refer to $\boldsymbol{\sigma}_A$ as the *partial stress tensor* and note that it consists of a "molecular force contribution" represented by $-\mathbf{T}_A$ and a "kinetic contribution" represented by $\rho_A \mathbf{u}_A \mathbf{u}_A$.

Equation (23) can be represented in more compact form using the species continuity equation. We begin by multiplying Eq. (8) by the species velocity to obtain

$$\mathbf{v}_A \left[\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}_A)\right] = r_A \mathbf{v}_A, \quad A = 1, 2, ..., N \tag{28}$$

Subtraction of this equation from Eq. (23) leads to

$$\rho_A \left(\frac{\partial \mathbf{v}_A}{\partial t} + \mathbf{v}_A \cdot \nabla \mathbf{v}_A\right) = \rho_A \mathbf{b}_A + \nabla \cdot \mathbf{T}_A + \sum_{B=1}^{B=N} \mathbf{P}_{AB} + r_A \left(\mathbf{v}_A^* - \mathbf{v}_A\right), \quad A = 1, 2, ..., N \tag{29}$$

Bird (1995) has pointed out that Chapman and Cowling (1939) first obtained this result[1] for dilute gases by means of kinetic theory provided that $r_A = 0$. From the continuum point of view, Eq. (29) is given by Truesdell and Toupin (1960, Eq. 215.2), Truesdell (1962, Eq. 22), and Curtiss and Bird (1996, Eqs. 7b and A7) all with $r_A = 0$. The correspondence with Truesdell (1962) is based on the nomenclature

Truesdell:

$$\rho_A \mathbf{b}_A = \rho_A \mathbf{f}_A, \quad \nabla \cdot \mathbf{T}_A = \operatorname{div} \mathbf{t}_A, \quad \sum_{B=1}^{B=N} \mathbf{P}_{AB} = \rho \hat{\mathbf{p}}_A \tag{30}$$

In its present form, Eq. (29) represents a governing equation for the species velocity, $\mathbf{v}_A$, and we want to use this result to derive a governing equation for the mass diffusion velocity, $\mathbf{u}_A$. To carry out this derivation, we need the total momentum equation that is developed in the following paragraphs.

[1] See species momentum equation following Eq. 6 on page 135.

1.2.1 Total momentum equation

The traditional analysis of momentum transport in multi-component systems makes use of the sum of Eqs. (23) over all *N* species to obtain the *total momentum equation* that is used to determine the mass average velocity, $\mathbf{v}$. The remaining $N-1$ independent *species momentum equations* can then used to determine the individual species velocities, $\mathbf{v}_A$, $\mathbf{v}_B$, $\ldots \mathbf{v}_{N-1}$. We begin by taking into account Axioms III and IV so that the sum of Eq. (23) leads to

$$\frac{\partial}{\partial t}\sum_{A=1}^{A=N}\rho_A\mathbf{v}_A + \nabla\cdot\sum_{A=1}^{A=N}\rho_A\mathbf{v}_A\mathbf{v}_A = \sum_{A=1}^{A=N}\rho_A\mathbf{b}_A + \nabla\cdot\sum_{A=1}^{A=N}\mathbf{T}_A \tag{31}$$

The first and third terms in this result can be simplified by the definitions

$$\sum_{A=1}^{A=N}\rho_A\mathbf{v}_A = \rho\mathbf{v}\,, \qquad \sum_{A=1}^{A=N}\rho_A\mathbf{b}_A = \rho\mathbf{b} \tag{32}$$

and Eqs. (10) and (12) can be used to obtain

$$\sum_{A=1}^{A=N}\rho_A\mathbf{v}_A\mathbf{v}_A = \rho\mathbf{v}\mathbf{v} + \sum_{A=1}^{A=N}\rho_A\mathbf{v}_A\mathbf{u}_A \tag{33}$$

Application of Eq. (14) allows us to simplify the convective momentum transport to the form

$$\sum_{A=1}^{A=N}\rho_A\mathbf{v}_A\mathbf{v}_A = \rho\mathbf{v}\mathbf{v} + \sum_{A=1}^{A=N}\rho_A\mathbf{u}_A\mathbf{u}_A \tag{34}$$

and substitution of Eqs. (32) and (34) in Eq. (31) provides

$$\frac{\partial}{\partial t}(\rho\mathbf{v}) + \nabla\cdot(\rho\mathbf{v}\mathbf{v}) = \rho\mathbf{b} + \nabla\cdot\left[\sum_{A=1}^{A=N}\left(\mathbf{T}_A - \rho_A\mathbf{u}_A\mathbf{u}_A\right)\right] \tag{35}$$

Concerning the last term in this result, we note that Truesdell and Toupin (1960, Sec. 215) refer to $\rho_A\mathbf{u}_A\mathbf{u}_A$ as the "apparent stresses arising from diffusion" and we note that this term also appears in the analysis of Curtiss and Bird (1996, Eq. A7). In that case one needs to make use of the second of Eqs. (24) along with

$$\boldsymbol{\pi} = \sum_{A=1}^{A=N}\boldsymbol{\pi}_A = -\sum_{A=1}^{A=N}\left(\mathbf{T}_A - \rho_A\mathbf{u}_A\mathbf{u}_A\right) \tag{36}$$

to complete the correspondence. At this point we can use Eq. (9) to obtain

$$\mathbf{v}\left[\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\mathbf{v})\right] = 0 \tag{37}$$

and this allows us to express Eq. (35) in the form

$$\rho\left(\frac{\partial\mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = \rho\mathbf{b} + \nabla\cdot\left[\sum_{A=1}^{A=N}\left(\mathbf{T}_A - \rho_A\mathbf{u}_A\mathbf{u}_A\right)\right] \tag{38}$$

In order to use this result to predict the mass average velocity, we need a constitutive equation for the sum of the species stress tensors. This problem is considered in the following paragraphs.

1.2.2 Governing equation for the mass diffusion velocity

Our objective here is to develop the governing differential equation for the mass diffusion velocity, $\mathbf{u}_A$. We begin by multiplying Eq. (38) by the mass fraction ω_A

$$\rho_A\left(\frac{\partial\mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = \rho_A\mathbf{b} + \omega_A\nabla\cdot\left[\sum_{A=1}^{A=N}\left(\mathbf{T}_A - \rho_A\mathbf{u}_A\mathbf{u}_A\right)\right] \tag{39}$$

and subtracting this result from Eq. (29) to obtain the desired governing differential equation given by

$$\rho_A\left(\frac{\partial\mathbf{u}_A}{\partial t} + \mathbf{v}_A\cdot\nabla\mathbf{u}_A + \mathbf{u}_A\cdot\nabla\mathbf{v}\right) = \rho_A(\mathbf{b}_A - \mathbf{b}) + \nabla\cdot\mathbf{T}_A - \omega_A\nabla\cdot\left[\sum_{A=1}^{A=N}\left(\mathbf{T}_A - \rho_A\mathbf{u}_A\mathbf{u}_A\right)\right] + \sum_{B=1}^{B=N}\mathbf{P}_{AB} + r_A\left(\mathbf{v}_A^* - \mathbf{v}_A\right), A = 1, 2, \ldots, N-1 \tag{40}$$

Here it is important to note that this result is based *only* on the two axioms for mass given by Eqs. 1 and 2, and the four axioms for the mechanics of multi-component systems given by Eqs. (15), (17), (19) and (21). In addition, we have made use of classical continuum mechanics to obtain the result given by Eq. (22).

At this point we need to be specific about the species stress tensor, $\mathbf{T}_A$, and to guide our thinking and *constrain* the subsequent development, we propose that:

> *The analysis is restricted to mixtures that behave as Newtonian fluids*
> (Serrin, 1959, Sec. 59; Aris, 1962, Sec. 5.21).

Given this restriction for the mixture, we follow Slattery (1999, Sec. 5.3) and write

$$\mathbf{T} = \sum_{A=1}^{A=N}\mathbf{T}_A = -p\mathbf{I} + \boldsymbol{\tau} \tag{41a}$$

in which p is the thermodynamic pressure and $\boldsymbol{\tau}$ is the extra stress tensor given by (Serrin, 1959, Eq. 61.1; Slattery, 1999, Eq. 5.3.4-3; Bird *et al*., 2002, page 843)

$$\boldsymbol{\tau} = \mu\left(\nabla\mathbf{v} + \nabla\mathbf{v}^T\right) + \lambda(\nabla\cdot\mathbf{v})\mathbf{I} \qquad (41b)$$

Given these results, Eq. (38) provides the Navier-Stokes equations containing an additional term associated with the sum of the diffusive stresses.

Here we need to point out that Eqs. (41) can be obtained by following a classic continuum mechanics analysis; or this result can be obtained from kinetic theory (Hirschfelder, Curtiss & Bird, 1954, Eqs. 7.2-45 and 7.6-29). The advantage of this latter approach is that a method of calculating the coefficients μ and λ is created within the framework of the theory. The disadvantage is that the calculations associated with the determination of μ for a dense gas or a liquid may be much more difficult than the associated experiment.

Given that the behavior of the mixtures under consideration is described by Eqs. (41), we propose that the species stress tensor can be represented by

$$\text{Proposal:} \quad \mathbf{T}_A = -p_A\mathbf{I} + \boldsymbol{\tau}_A, \quad A = 1,2,...,N \qquad (42)$$

in which p_A is the partial pressure defined by (Truesdell, 1969, page 97)

$$p_A = \rho_A^2\left(\partial\psi_A/\partial\rho_A\right)_{T,\rho_B,\rho_C,.....} \qquad (43)$$

Here ψ_A is the Helmholtz free energy of species *A* per unit mass of species *A*. In general it is more convenient to work with the internal energy and define the partial pressure by (Whitaker, 1989, Chapter 10)

$$p_A = \rho_A^2\left(\partial e_A/\partial\rho_A\right)_{s,\rho_B,\rho_C,.....} \qquad (44)$$

in which e_A is the internal energy of species *A* per unit mass of species *A*. A detailed discussion of the partial pressure and the total pressure is given in Appendix B. At this point we define the total pressure and the total viscous stress tensor by

$$p = \sum_{A=1}^{A=N} p_A, \quad \boldsymbol{\tau} = \sum_{A=1}^{A=N}\boldsymbol{\tau}_A \qquad (45)$$

and we use these definitions along with Eq. (42) in order to express Eq. (40) as

$$\begin{aligned}&\rho_A\left(\frac{\partial\mathbf{u}_A}{\partial t} + \mathbf{v}_A\cdot\nabla\mathbf{u}_A + \mathbf{u}_A\cdot\nabla\mathbf{v}\right)\\ &-\omega_A\nabla\cdot\left[\sum_{A=1}^{A=N}\rho_A\mathbf{u}_A\mathbf{u}_A\right] = -\left(\omega_A\nabla\cdot\boldsymbol{\tau} - \nabla\cdot\boldsymbol{\tau}_A\right)\\ &-\nabla p_A + \omega_A\nabla p + \rho_A(\mathbf{b}_A - \mathbf{b})\\ &+\sum_{B=1}^{B=N}\mathbf{P}_{AB} + r_A\left(\mathbf{v}_A^* - \mathbf{v}_A\right)\end{aligned} \qquad (46)$$

In Appendix A we show that difference between $\mathbf{v}_A^*$ and $\mathbf{v}_A$ should be on the order of the diffusion velocity

$$\left(\mathbf{v}_A^* - \mathbf{v}_A\right) = \mathbf{O}(\mathbf{u}_A) \qquad (47)$$

Arguments are given elsewhere (Whitaker, 1986, 2009b) indicating that several of the terms in Eq. (46) are generally negligible. This leads to the *simplifications* given by

$$\rho_A\frac{\partial\mathbf{u}_A}{\partial t} << \nabla p_A \qquad (48a)$$

$$\rho_A\left(\mathbf{v}_A\cdot\nabla\mathbf{u}_A + \mathbf{u}_A\cdot\nabla\mathbf{v}\right) << \nabla p_A \qquad (48b)$$

$$\omega_A\nabla\cdot\sum_{A=1}^{A=N}\rho_A\mathbf{u}_A\mathbf{u}_A << \nabla p_A \qquad (48c)$$

$$\left(\omega_A\nabla\cdot\boldsymbol{\tau} - \nabla\cdot\boldsymbol{\tau}_A\right) << \nabla p_A \qquad (48d)$$

$$r_A\left(\mathbf{v}_A^* - \mathbf{v}_A\right) << \nabla p_A \qquad (48e)$$

The first of these indicates that the governing equation for $\mathbf{u}_A$ is *quasi-steady*; the second indicates that *diffusive inertial effects* are negligible, the third indicates that the *diffusive stresses* are negligible, the fourth indicates that *viscous effects* are negligible, and the final inequality indicates that the effects of homogeneous chemical reactions are negligible.

When the restrictions given by Eqs. (48) are imposed, the governing equation for the mass diffusion velocity takes the form

$$\begin{aligned}&\nabla p_A - \omega_A\nabla p - \rho_A(\mathbf{b}_A - \mathbf{b})\\ &\qquad = \sum_{B=1}^{B=N}\mathbf{P}_{AB}, \quad A = 1,2,...,N-1\end{aligned} \qquad (49)$$

Truesdell (1962, Eq. 7) represents the left hand side of this result by $p\mathbf{d}_A$ and cites Hirschfelder, Curtiss & Bird (1954) as the source. Curtiss & Bird (1999, Eq. 7.6) represent the left hand side of Eq. (49) by $cRT\mathbf{d}_A$ and refer to it as the *generalized driving force for diffusion*. At this point we make use of the *identity*

$$\nabla\left(p_A/p\right) = \frac{1}{p}\nabla p_A - \frac{p_A}{p^2}\nabla p \qquad (50)$$

in order to express Eq. (49) in the form

$$\begin{aligned}&\nabla\left(p_A/p\right) + p^{-1}\left[\left(p_A/p\right) - \omega_A\right]\nabla p\\ &-p^{-1}\rho_A(\mathbf{b}_A - \mathbf{b}) = p^{-1}\sum_{B=1}^{B=N}\mathbf{P}_{AB}, \quad A = 1,2,...,N-1\end{aligned} \qquad (51)$$

In order to see how this result is related to the work of Hirschfelder, Curtiss & Bird (1954), we make use of their Eqs. 7.4-48 and 7.3-27 (in terms of the nomenclature used in this work) to obtain

Hirschfelder *et al*.

$$\nabla x_A + p^{-1}\left[x_A - \omega_A\right]\nabla p - p^{-1}\rho_A(\mathbf{b}_A - \mathbf{b}) = \sum_{B=1}^{B=N}\frac{x_A\, x_B}{\mathscr{D}_{AB}}\left(\mathbf{v}_B - \mathbf{v}_A\right) + \sum_{B=1}^{B=N}\frac{x_A\, x_B}{\mathscr{D}_{AB}}\left(\frac{D_B^T}{\rho_B} - \frac{D_A^T}{\rho_A}\right)\nabla \ln T,\ \ A = 1, 2, ..., N-1 \tag{52}$$

The right hand side of this result is approximate in that (1) it is based on dilute gas kinetic theory, and (2) the binary diffusivities, $\mathscr{D}_{AB}$, have been used in place of the coefficient of diffusion, D_{AB} (see Hirschfelder, Curtiss & Bird, 1954, page 485). The left hand side of Eq. (52) is identical to the left hand side of Eq. (51) *provided* that p_A is replaced by x_A, p, and this is consistent with the idea that Eq. (52) was developed for ideal gases. In terms of the work of Chapman and Cowling (1970), we note that their Eqs. 18.2,6 and 18.3,13 lead to Eq. (52) with the last term in Eq. (52) expressed as

$$k_{TA}\nabla \ln T = \sum_{B=1}^{B=N}\frac{x_A\, x_B}{\mathscr{D}_{AB}}\left(\frac{D_B^T}{\rho_B} - \frac{D_A^T}{\rho_A}\right)\nabla \ln T \tag{53}$$

When dealing with ideal gases, one can proceed with Eq. (52); however, for more general cases that are consistent with Eq. (42), one should make use of Eq. (51) and this means dealing with the force, $\mathbf{P}_{AB}$.

1.2.3 Non-ideal mixtures

The simplest approach for non-ideal mixtures is to use the *form* associated with dilute gas kinetic theory in order to represent the right hand side of Eq. (51) as

Proposal:

$$p^{-1}\mathbf{P}_{AB} = \frac{x_A\, x_B}{\mathscr{D}_{AB}}\left(\mathbf{v}_B - \mathbf{v}_A\right) + \frac{x_A\, x_B}{\mathscr{D}_{AB}}\left(\frac{D_B^T}{\rho_B} - \frac{D_A^T}{\rho_A}\right)\nabla \ln T \tag{54}$$

Here the diffusion coefficients are to be determined experimentally with the idea that this *form* for $\mathbf{P}_{AB}$ is an acceptable approximation, and that Eq. (20) would be utilized as a solution to Axiom III. Truesdell (1962, Sec. 6) refers to this approximation as the special case of *binary drags*. However, multicomponent diffusion in liquids is more complex than suggested by Eq. (54), and Rutten (1992), among many others, has documented these complexities for ternary systems. Putting aside the seminal problem associated with $\mathbf{P}_{AB}$, we make use of Eq. (54) in Eq. (51) to obtain

$$\nabla\left(p_A/p\right) + \underbrace{p^{-1}\left[\left(p_A/p\right) - \omega_A\right]\nabla p}_{\text{pressure diffusion}} - \underbrace{p^{-1}\rho_A(\mathbf{b}_A - \mathbf{b})}_{\text{forced diffusion}} = \sum_{B=1}^{B=N}\frac{x_A\, x_B}{\mathscr{D}_{AB}}\left(\mathbf{v}_B - \mathbf{v}_A\right) + \underbrace{\sum_{B=1}^{B=N}\frac{x_A\, x_B}{\mathscr{D}_{AB}}\left(\frac{D_B^T}{\rho_B} - \frac{D_A^T}{\rho_A}\right)\nabla \ln T}_{\text{thermal diffusion}},\ A = 1, 2, ..., N-1 \tag{55}$$

Here we have explicitly identified the terms associated with pressure diffusion, forced diffusion, and thermal diffusion. This form of the species momentum equation is restricted by the following:

I. The basic assumptions associated with continuum mechanics.

II. The constitutive equation given by Eq. (42)

III. The simplifications indicated by Eqs. (48).

IV. The form of the terms that appear on the right hand side of Eq. (55).

One should remember that Eq. (55) is the governing equation for the diffusion velocity, and this becomes more apparent if we replace $\mathbf{v}_B - \mathbf{v}_A$ with $\mathbf{u}_B - \mathbf{u}_A$.

In general, thermal diffusion creates very small fluxes that are difficult to measure (Whitaker and Pigford, 1958) and in this study we will neglect this term to obtain

$$\nabla\left(p_A/p\right) + \underbrace{p^{-1}\left[\left(p_A/p\right) - \omega_A\right]\nabla p}_{\text{pressure diffusion}} - \underbrace{p^{-1}\rho_A(\mathbf{b}_A - \mathbf{b})}_{\text{forced diffusion}} = \sum_{B=1}^{B=N}\frac{x_A\, x_B}{\mathscr{D}_{AB}}\left(\mathbf{v}_B - \mathbf{v}_A\right),\qquad A = 1, 2, ..., N-1 \tag{56}$$

Chapman & Cowling (1970, page 257) discuss the impact of pressure diffusion on the distribution of chemical species in the atmosphere, and both Deen (1998, page 452) and Bird *et al*. (2002, page 772) provide an example of this effect in terms of a separation process using an ultracentrifuge. The process of forced diffusion of electrically charged particles is analyzed by Chapman & Cowling (1970, Chap. 19) among others.

Estimates (Whitaker, 2009b, Sec. 5.6) of the terms on the left hand side of Eq. (56) indicate that these terms are generally quite small leading to the relatively simple relation given by

$$0 = -\nabla\left(p_A/p\right) + \sum_{B=1}^{B=N}\frac{x_A\, x_B}{\mathscr{D}_{AB}}\left(\mathbf{v}_B - \mathbf{v}_A\right),\qquad A = 1, 2, ..., N-1 \tag{57}$$

Here one should remember that the first term in this result is based on the use of Eq. (42) and that the

second term represents a less than robust model for non-ideal mixtures in which the binary diffusivities, $\mathscr{D}_{AB}$, must be determined experimentally.

1.2.4 Ideal mixtures

At this point we are ready to make the final simplification given by

$$p_A = x_A\, p\,, \qquad \textit{ideal mixture} \tag{58}$$

in order to obtain the classic Stefan-Maxwell equations that will be examined in the remainder of this paper

Species Momentum:

$$0 = -\nabla x_A + \sum_{B=1}^{B=N} \frac{x_A x_B(\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}}\,, A = 1, 2, ..., N-1 \tag{59}$$

To complete our formulation of the mechanical problem, we recall Eq. (38) in the form of the Navier-Stokes equations

Total Momentum:

$$\rho\left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = \rho\mathbf{b} - \nabla p + \mu\nabla^2\mathbf{v} \tag{60}$$

in which the diffusive stresses have obviously been neglected. The determination of $\mathbf{v}_A$, $\mathbf{v}_B$, …, $\mathbf{v}_N$ using Eqs. (59) and (60) is a very complex problem and the chemical engineering literature contains many simplified treatments of this problem. However, the domain of validity of these simplified treatments is not always clear, and in the following sections we attempt to clarify the basis for some of the special forms of the Stefan-Maxwell equations.

2. Mass continuity equation

We begin this study with the total mass continuity equation [see Eq. (9)]

Total Mass: $$\frac{\partial \rho}{\partial t} + \nabla\cdot(\rho\mathbf{v}) = 0 \tag{61}$$

along with $N-1$ species mass continuity equations [see Eqs. (13)]

Species Mass:

$$\frac{\partial \rho_A}{\partial t} + \nabla\cdot(\rho_A\mathbf{v}) = -\nabla\cdot(\rho_A\mathbf{u}_A) + r_A\,, \qquad A = 1, 2, ..., N-1 \tag{62}$$

These equations can (in principle) be used to determine all the species mass densities, ρ_A, ρ_B,…, ρ_N in the same way that the momentum equations represented by Eqs. (59) and (60) can be used to determine all the species velocities, $\mathbf{v}_A$, $\mathbf{v}_B$, …, $\mathbf{v}_N$.

The mass diffusive flux, $\rho_A\mathbf{u}_A$, is often represented as (Bird *et al*, 2002, page 537)

$$\mathbf{j}_A = \rho_A\mathbf{u}_A \tag{63}$$

so that Eq. (62) takes the form

Species Mass:

$$\frac{\partial \rho_A}{\partial t} + \nabla\cdot(\rho_A\mathbf{v}) = -\nabla\cdot\mathbf{j}_A + r_A\,, \quad A = 1, 2, ..., N-1 \tag{64}$$

Here we note that the mass diffusive fluxes are constrained by

$$\sum_{A=1}^{A=N} \mathbf{j}_A = 0 \tag{65}$$

and we need to determine $N-1$ of these diffusive fluxes in order to develop a solution for Eq. (64).

In many liquid-phase diffusion processes, the governing equation for the total density given by Eq. (61) is replaced by the assumption

Assumption: $$\rho = \text{constant} \tag{66}$$

and we need only solve the $N-1$ species continuity equations given by Eqs. (64).

3. Molar continuity equation

Chemical engineers are primarily interested in chemical reactions, interfacial mass transfer, and adsorption/desorption phenomena, thus molar concentrations and mole fractions are more useful than mass densities and mass fractions. Because of this, the molar form of the species continuity equation is often preferred. This form is obtained from Eqs. (8) by the use of the relations

$$\rho_A = c_A M_A\,, \quad r_A = R_A M_A\,, \quad A = 1, 2, ..., N \tag{67}$$

This leads to the species molar continuity equation given by

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\mathbf{v}_A) = R_A\,, \quad A = 1, 2, ..., N \tag{68}$$

while the constraint on the mass rate of reaction given by Eq. 2 provides

$$\sum_{A=1}^{A=N} R_A M_A = 0 \tag{69}$$

The total molar continuity equation is analogous to Eq. (61) and it is developed by constructing the sum of Eqs. (68) over all species to obtain

Total Molar: $$\frac{\partial c}{\partial t} + \nabla\cdot(c\,\mathbf{v}^*) = \sum_{B=1}^{B=N} R_B \tag{70}$$

Here the total molar concentration and the molar average velocity are defined by

$$c = \sum_{A=1}^{A=N} c_A \,, \qquad c\,\mathbf{v}^* = \sum_{A=1}^{A=N} c_A\,\mathbf{v}_A \tag{71}$$

The development in Sec. 2 indicates that Eq. (70) should be solved along with the $N-1$ species continuity equations given by

Species Molar:

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\,\mathbf{v}_A) = R_A \,, \quad A = 1, 2, ..., N-1 \tag{72}$$

This allows for the determination of all the species molar concentrations, c_A, c_B,…, c_N.

The form of Eqs. (70) through (72) suggests (but does not require) a decomposition of the species velocity given by

$$\mathbf{v}_A = \mathbf{v}^* + \mathbf{u}_A^* \,, \quad A = 1, 2, ..., N \tag{73}$$

in which $\mathbf{u}_A^*$ is the *molar diffusion velocity*. A little thought will indicate that the molar diffusion velocities are constrained by

$$\sum_{A=1}^{A=N} c_A\,\mathbf{u}_A^* = 0 \tag{74}$$

When Eq. (73) is used in Eq. (72) the transport of species *A* can be represented in terms of a *convective part*, $c_A\mathbf{v}^*$, and a *diffusive part*, $c_A\mathbf{u}_A^*$, leading to

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\mathbf{v}^*) = -\nabla\cdot(c_A\mathbf{u}_A^*) + R_A \,, \quad A = 1, 2, ..., N-1 \tag{75}$$

The molar diffusive flux, $c_A\mathbf{u}_A^*$, is often identified as (Bird *et al*, 2002, page 537)

$$\mathbf{J}_A^* = c_A\mathbf{u}_A^* \tag{76}$$

so that Eq. (75) takes the form

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\mathbf{v}^*) = -\nabla\cdot\mathbf{J}_A^* + R_A \,, \quad A = 1, 2, ..., N-1 \tag{77}$$

This result is similar in form to Eq. (64) for the species mass density; however, there is no *governing equation* for the molar average velocity, $\mathbf{v}^*$, whereas the mass average velocity in Eq. (64) can be determined by the application of Eq. (60). In order to eliminate the molar average velocity from Eq. (77) we return to Eq. (73), multiply by ω_A, and sum over all species to obtain

$$\sum_{B=1}^{B=N} \omega_B\mathbf{v}_B = \sum_{B=1}^{B=N} \omega_B\mathbf{v}^* + \sum_{B=1}^{B=N} \omega_B\,\mathbf{u}_B^* \tag{78}$$

On the basis of the second of Eqs. (10) this takes the form

$$\mathbf{v} = \mathbf{v}^* + \sum_{B=1}^{B=N} \omega_B\,\mathbf{u}_B^* \tag{79}$$

and we are now confronted with the *mixed-mode* term $\omega_B\,\mathbf{u}_B^*$ that involves a *mass* fraction and a *molar* diffusion velocity. We would like to express $\omega_B\mathbf{u}_B^*$ in terms of molar diffusive fluxes, and to do so we manipulate this term as follows

$$\begin{aligned}\omega_B\mathbf{u}_B^* &= \frac{\rho_B\mathbf{u}_B^*}{\rho_A + \rho_B + \rho_C + ... + \rho_N} \\ &= \frac{M_B\,c_B\mathbf{u}_B^*}{M_A\,c_A + M_B\,c_B + ... + M_N\,c_N} \\ &= \frac{M_B\,\mathbf{J}_B^*}{c\left(x_AM_A + x_BM_B + ...x_NM_N\right)}\end{aligned} \tag{80}$$

If we define the mean molecular mass as

$$\bar{M} = x_AM_A + x_BM_B + ... + x_NM_N \tag{81}$$

we can express Eq. (80) in compact form according to

$$\omega_B\,\mathbf{u}_B^* = \frac{M_B\,\mathbf{J}_B^*}{c\,\bar{M}} \tag{82}$$

At this point we return to Eq. (79) to develop the following relation between the molar average velocity and the mass average velocity:

$$\mathbf{v}^* = \mathbf{v} - \frac{1}{c}\sum_{B=1}^{B=N}\frac{M_B}{\bar{M}}\mathbf{J}_B^* \tag{83}$$

Substitution of this expression for the molar average velocity into Eq. (77) allows us to express that form of the species continuity equation as

Species Molar:

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\mathbf{v}) = -\nabla\cdot\left(\mathbf{J}_A^* - x_A\sum_{B=1}^{B=N}\frac{M_B}{\bar{M}}\mathbf{J}_B^*\right) + R_A \,, \quad A = 1, 2, ..., N-1 \tag{84}$$

in which the molar diffusive fluxes are constrained by

$$\sum_{A=1}^{A=N} \mathbf{J}_A^* = 0 \tag{85}$$

Here we can see that this convection-diffusion problem is *inherently nonlinear* in terms of the diffusive flux; however, if the mole fraction of

species *A* is sufficiently small it is possible that the term involving the sum of the diffusive fluxes in Eq. (84) can be neglected. By "sufficiently small" we mean that the following inequality

$$x_A \sum_{B=1}^{B=N} \frac{M_B}{\overline{M}} \mathbf{J}_B^* << \mathbf{J}_A^* \tag{86}$$

is satisfied and Eq. (84) becomes linear in the molar diffusive flux, $\mathbf{J}_A^*$.

To complete our formulation of the molar forms of the species continuity equation, we make use of Eq. (83) in Eq. (70) to obtain

Total Molar:

$$\frac{\partial c}{\partial t} + \nabla \cdot (c\,\mathbf{v}) = \nabla \cdot \sum_{B=1}^{B=N} \frac{M_B}{\overline{M}} \mathbf{J}_B^* + \sum_{B=1}^{B=N} R_B \tag{87}$$

This total molar transport equation should be compared with Eq. (61) in order to appreciate the complexity associated with the molar form of the species transport equations. In many gas phase mass transfer processes, Eq. (87) can be replaced by the assumption

Assumption: c = constant (88)

and we need only solve the $N-1$ species continuity equations given by Eqs. (84).

4. Mixed-mode continuity equation

The motivation for a mixed-mode or *hybrid* species continuity equation is based on the applications that are dominant in the area of chemical engineering, and on the mechanical problem under consideration. To be explicit, we note two facts:

(1) Chemical reactions and interfacial mass transfer are usually represented in terms of the molar concentration, c_A, or the mole fraction, x_A, thus we are motivated to use the molar form of the continuity equation given by Eq. (68) as opposed to the mass form given by Eq. (62).

(2) The species continuity equation involves velocities that must be determined by the laws of mechanics, thus we are motivated to use the mass decomposition of the species velocity given by Eq. (12) as opposed to the molar decomposition given by Eq. (73).

In order to obtain a mixed-mode or hybrid continuity equation, we begin with the species mass continuity equation given by Eq. (62) and divide by the molecular mass of species *A* to obtain

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = -\nabla \cdot (c_A \mathbf{u}_A) + R_A\,, \qquad A = 1, 2, ..., N-1 \tag{89}$$

Here the diffusive flux is represented in terms of a *molar* concentration and a *mass* diffusion velocity. This mixed-mode diffusive flux is often referred to as a hybrid flux and identified as (Bird *et al*, 2002, page 537)

$$\mathbf{J}_A = c_A \mathbf{u}_A \tag{90}$$

Use of this representation in Eq. (89) leads to

Species Molar:

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = -\nabla \cdot \mathbf{J}_A + R_A\,, \qquad A = 1, 2, ..., N-1 \tag{91}$$

The constraint on this diffusive flux is more complex than that for either the mass diffusive flux or the molar diffusive flux and is given by

$$\sum_{A=1}^{A=N} M_A \mathbf{J}_A = 0 \tag{92}$$

This hybrid diffusive flux, $\mathbf{J}_A$, lacks popularity; however, the transport equation given by Eq. (91) has the advantage that it is linear in the diffusive flux. In terms of the mixed-mode diffusive flux, the total molar continuity equation takes the form

Total Molar:

$$\frac{\partial c}{\partial t} + \nabla \cdot (c\mathbf{v}) = -\nabla \cdot \sum_{B=1}^{B=N} \mathbf{J}_B + \sum_{B=1}^{B=N} R_B \tag{93}$$

and we are still confronted with a complex form of the total molar transport equation. This complexity often serves to generate the assumption that the total molar concentration is constant as indicated by

Assumption: c = constant (94)

Often gas phase diffusion problems lead to the use of a molar form of the species continuity equation because Eq. (94) provides a reasonable simplification. On the other hand, liquid phase diffusion problems suggest the use of the mass form of the species continuity equation because Eq. (66) provides a reasonable simplification. The author is unaware of any solution to a diffusion problem that does not make use of either Eq. (66) or Eq. (94), and removing these assumptions remains as a significant challenge.

5. Binary systems

Binary systems are often used to introduce the phenomena of diffusion, and we will follow that approach in order to explore the nature of the mass,

molar, and mixed-mode forms of the species continuity equation.

5.1 Mass diffusive flux

For a binary system, Eq. (59) reduces to

$$0 = -\nabla x_A + \frac{x_A x_B(\mathbf{v}_B - \mathbf{v}_A)}{\mathscr{D}_{AB}} \tag{95}$$

and we think of this as the governing differential equation for $\mathbf{v}_A$. The value of $\mathbf{v}_B$ is available from a solution for $\mathbf{v}$ and $\mathbf{v}_A$ which can be used in the second of Eqs. (10) to obtain

$$\mathbf{v}_B = \frac{1}{\omega_B}\left(\mathbf{v} - \omega_A \mathbf{v}_A\right) \tag{96}$$

For a binary system, the two mass continuity equations are given by

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}) = -\nabla \cdot (\rho_A \mathbf{u}_A) + r_A \tag{97}$$

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \tag{98}$$

and we need to determine $\mathbf{u}_A$ and $\mathbf{v}$ in order to solve these equations. Given the form of Eq. (97) it will be convenient to express Eq. (95) in terms of *mass diffusion velocities*, and the use of Eq. (12) leads to

$$0 = -\nabla x_A + \frac{x_A x_B(\mathbf{u}_B - \mathbf{u}_A)}{\mathscr{D}_{AB}} \tag{99}$$

For a binary system, Eq. (14) provides

$$\omega_A \mathbf{u}_A + \omega_B \mathbf{u}_B = 0 \tag{100}$$

and this can be used in Eq. (99) to obtain

$$0 = -\nabla x_A - \frac{1}{\mathscr{D}_{AB}} \frac{x_A x_B}{\omega_A \omega_B}(\omega_A \mathbf{u}_A) \tag{101}$$

Multiplying and dividing the second term by the total density allows us to express this result as

$$0 = -\nabla x_A - \frac{1}{\rho \mathscr{D}_{AB}} \frac{x_A x_B}{\omega_A \omega_B}(\rho_A \mathbf{u}_A) \tag{102}$$

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*, ∇x_A, along with the mixed-mode term, $x_A x_B / \omega_A \omega_B$.

Before attacking the binary result given by Eq. (102) it is convenient to list some results for *N*-component systems. We begin with the definitions for the mass fraction, ω_A, the mole fraction, x_A, and the mean molecular mass, $\bar{M}$. These are given by

$$\begin{aligned} \omega_A &= \rho_A / \rho, \qquad x_A = c_A / c, \\ \bar{M} &= x_A M_A + x_B M_B + ... + x_N M_N \end{aligned} \tag{103}$$

in which M_A represents the molecular mass of species *A*. In addition to these results, we make use of

$$c_A = \rho_A / M_A, \quad c = \rho / \bar{M}, \quad A = 1, 2, ...N \tag{104}$$

to obtain the following relations between the mole fractions and the mass fractions

$$x_A = \frac{c_A}{c} = \frac{c_A \bar{M}}{\rho} = \frac{(\rho_A / M_A)\bar{M}}{\rho} = \frac{\bar{M}}{M_A}\omega_A, \qquad A = 1, 2, ...N \tag{105}$$

At this point we direct our attention to *binary systems* and make use of the following relations

$$\begin{aligned} \nabla x_A &= -\nabla x_B, \quad \omega_B = 1 - \omega_A, \\ \frac{1}{\bar{M}} &= \frac{\omega_A}{M_A} + \frac{\omega_B}{M_B} \end{aligned} \tag{106}$$

along with several algebraic steps (see Appendix C) to arrive at

$$\nabla x_A = \frac{\bar{M}^2}{M_A M_B} \nabla \omega_A \tag{107}$$

Substitution of this expression for the gradient of the mole fraction of species *A* into Eq. (102) leads to

$$0 = -\frac{\bar{M}^2}{M_A M_B} \nabla \omega_A - \frac{1}{\rho \mathscr{D}_{AB}} \frac{x_A x_B}{\omega_A \omega_B}(\rho_A \mathbf{u}_A) \tag{108}$$

From Eqs. (105) we see that

$$\frac{x_A x_B}{\omega_A \omega_B} = \frac{\bar{M}^2}{M_A M_B} \tag{109}$$

and Eq. (108) simplifies to the classic form of Fick's Law given by

$$\text{Fick's Law:} \qquad \mathbf{j}_A = \rho_A \mathbf{u}_A = -\rho \mathscr{D}_{AB} \nabla \omega_A \tag{110}$$

Returning to Eq. (97), we make use of this form of Fick's Law to obtain the following governing equation for the species density, ρ_A

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}) = \nabla \cdot \left[\rho \mathscr{D}_{AB} \nabla \left(\rho_A / \rho\right)\right] + r_A \tag{111}$$

For liquid systems this result can often be simplified on the basis of the assumption

$$\text{Assumption:} \qquad \rho = \text{constant} \tag{112}$$

which leads to

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}) = \nabla \cdot \left(\mathscr{D}_{AB} \nabla \rho_A \right) + r_A \,, \quad \begin{cases} \rho = \text{constant} \\ \text{binary system} \end{cases} \tag{113}$$

Here we have an attractive, linear transport equation for the species density, ρ_A.

When confronted with chemical reactions and interfacial transport, we generally prefer to work with the molar form of the species continuity equation. This form can be extracted from Eq. (113) by the use of

$$\rho_A = c_A M_A \,, \quad r_A = R_A M_A \tag{114}$$

which leads to

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = \nabla \cdot \left(\mathscr{D}_{AB} \nabla c_A \right) + R_A \,, \begin{cases} \rho = \text{constant} \\ \text{binary system} \end{cases} \tag{115}$$

This is an attractive form to use with liquids where the assumption of a constant density is likely to be a valid approximation. When the total density is *not constant*, one must solve Eq. (111) simultaneously with Eq. (98).

5.2 Molar diffusive flux

Because of the prevalence of molar concentrations and mole fractions in chemical engineering analysis, the *species molar continuity equation* is generally preferred. This form can be extracted from Eq. (84) according to

Species Molar:

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = -\nabla \cdot \left(\mathbf{J}_A^* - x_A \sum_{B=1}^{B=2} \frac{M_B}{\bar{M}} \mathbf{J}_B^* \right) + R_A \tag{116}$$

while the *total molar continuity equation* given earlier by Eq. (87) takes the form

Total Molar:

$$\frac{\partial c}{\partial t} + \nabla \cdot (c \mathbf{v}) = \nabla \cdot \sum_{B=1}^{B=2} \frac{M_B}{\bar{M}} \mathbf{J}_B^* + \left(R_A + R_B \right) \tag{117}$$

Ignoring for the moment the difficulties associated with the total molar continuity equation, we direct our attention to the molar diffusive flux represented by $\mathbf{J}_A^*$. We begin by using Eq. (73) to express the single Stefan-Maxwell equation as

$$0 = -\nabla x_A + \frac{x_A x_B (\mathbf{u}_B^* - \mathbf{u}_A^*)}{\mathscr{D}_{AB}} \tag{118}$$

and employ the form of Eq. (76) for both species to obtain

$$0 = -\nabla x_A + \frac{x_A \mathbf{J}_B^* - x_B \mathbf{J}_A^*}{c \mathscr{D}_{AB}} \tag{119}$$

Application of the binary version of Eq. (85)

$$\mathbf{J}_A^* + \mathbf{J}_B^* = 0 \tag{120}$$

allows us to express Eq. (119) in the classic form of Fick's Law given by

$$\text{Fick's Law:} \quad \mathbf{J}_A^* = c_A \mathbf{u}_A^* = -c \mathscr{D}_{AB} \nabla x_A \tag{121}$$

This is the molar analogy of Eq. (110), and substitution of this result into Eq. (116) leads to the molar analogy of Eq. (111).

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = \nabla \cdot \left[\left(M_B / \bar{M} \right) c \mathscr{D}_{AB} \nabla \left(c_A / c \right) \right] + R_A \tag{122}$$

If we ignore variations in the total molar concentration on the basis of the *assumption*

$$\text{Assumption:} \quad c = \text{constant} \tag{123}$$

we see that Eq. (122) takes the form

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = \nabla \cdot \left[\left(M_B / \bar{M} \right) \mathscr{D}_{AB} \nabla c_A \right] + R_A \,, \quad \begin{cases} c = \text{constant} \\ \text{binary system} \end{cases} \tag{124}$$

in which the presence of $\bar{M}$ leads to the non-linearity associated with

$$M_B / \bar{M} = \left[x_A \left(M_A / M_B - 1 \right) + 1 \right]^{-1} \tag{125}$$

In order to obtain the so-called *dilute solution* form of Eq. (124), we impose

$$\text{Restriction:} \quad x_A \left(M_A / M_B - 1 \right) << 1 \tag{126}$$

and Eq. (124) simplifies to the classic convective-diffusion equation given by

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = \nabla \cdot \left(\mathscr{D}_{AB} \nabla c_A \right) + R_A \,, \quad \begin{cases} c = \text{constant} \\ x_A \left(M_A / M_B - 1 \right) << 1 \\ \text{binary system} \end{cases} \tag{127}$$

Here it is very important to note that this result is *identical* to Eq. (115). However, Eq. (127) is *not based on* the constraint that the density is constant. Instead, Eq. (127) is based on the assumption of "constant total molar concentration" indicated by Eq. (123), and the assumption of a "dilute solution"

indicated by Eq. (126). For binary systems we have (see Eqs. (103) and (104))

$$\rho = c\left(x_A M_A \; + \; x_B M_B\right) \tag{128}$$

which can be arranged in the form

$$\rho = c\left\{x_A\left[\left(M_A/M_B\right)-1\right]+1\right\}M_B \tag{129}$$

When the two restrictions associated with Eq. (127) are imposed, the total density is essentially constant and Eq. (127) is consistent with Eq. (115).

Returning to Eq. (127), we note that the maximum value of the mole fraction for species *A* will usually be known *a priori*, and this allows us to express the constraint associated with Eq. (127) as

$$\text{Constraint:} \quad (x_A)_{\max}\left(M_A/M_B \; - \; 1\right) << 1 \tag{130}$$

One should remember that there is a *restriction* associated with every *assumption* and when one imposes the restriction one always assumes that *small causes give rise to small effects* (Birkhoff, 1960). In addition, one should remember that behind every *restriction* there is a *constraint* (see Appendix D); however, constraints can often be very difficult to develop.

5.3 Mixed-mode diffusive flux

In this case we return to the mixed-mode species continuity equation [see Eq. (89)]

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\,\mathbf{v}) = -\nabla\cdot(c_A\,\mathbf{u}_A) + R_A \tag{131}$$

and direct our attention to the single Stefan-Maxwell equation given by Eq. (101) and repeated here as

$$0 = -\nabla x_A - \frac{1}{\mathscr{D}_{AB}}\frac{x_A x_B}{\omega_A \omega_B}(\omega_A\mathbf{u}_A) \tag{132}$$

It is convenient to rearrange this result in the form

$$0 = -\nabla x_A - \frac{1}{c\,\mathscr{D}_{AB}}\frac{x_B}{\omega_B}(c_A\mathbf{u}_A) \tag{133}$$

in order to obtain the mixed-mode diffusive flux given by

$$c_A\,\mathbf{u}_A = -\frac{\omega_B}{x_B}c\,\mathscr{D}_{AB}\nabla x_A \tag{134}$$

At this point we can use Eq. (105) to obtain the mixed-mode form of Fick's Law given by

Fick's Law:

$$\mathbf{J}_A = c_A\,\mathbf{u}_A = -\left(M_B/\bar{M}\right)c\,\mathscr{D}_{AB}\nabla x_A \tag{135}$$

Substitution of this result into Eq. (131) provides the following governing equation for the species *A* molar concentration

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\mathbf{v}) = \nabla\cdot\left[\left(M_B/\bar{M}\right)c\,\mathscr{D}_{AB}\nabla\left(c_A/c\right)\right] + R_A \tag{136}$$

This result is *identical* to Eq. (122) indicating that both the molar representation given by Eq. (116) and the mixed-mode representation given by Eq. (131) lead to the *same result* for a binary system.

It is of some interest to note that the mixed-mode diffusive flux can be expressed as

$$c_A\,\mathbf{u}_A = \frac{1}{M_A}\rho_A\,\mathbf{u}_A \tag{137}$$

and on the basis of Eq. (110) this takes the form

$$c_A\,\mathbf{u}_A = -\frac{1}{M_A}\rho\mathscr{D}_{AB}\nabla\omega_A \tag{138}$$

Use of this result in Eq. (131) yields what appears to be an unattractive form given by

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\,\mathbf{v}) = \nabla\cdot\left[\frac{1}{M_A}\rho\mathscr{D}_{AB}\nabla\omega_A\right] + R_A \tag{139}$$

However, if we impose the condition

$$\text{Assumption:} \qquad \rho = \text{constant} \tag{140}$$

and make use of the first of Eqs. (114) we find

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\,\mathbf{v}) = \nabla\cdot\left(\mathscr{D}_{AB}\nabla c_A\right) + R_A\,, \begin{cases} \rho \;=\; \text{constant} \\ \text{binary system} \end{cases} \tag{141}$$

which was given earlier by Eq. (115).

6. Special forms for *N*-component systems

Given the complexity of the binary forms described in the previous sections, we should expect additional complexities for *N*-component systems. This naturally leads to the search for simplifications, and we will examine some of these simplifications in this section.

6.1 Dilute solution diffusion

There are mass transfer processes in which all the molar fluxes are the same order of magnitude and the dominant diffusing species is dilute. In this special case, it is convenient to represent the Stefan-Maxwell equations in terms of the molar flux defined by

$$\mathbf{N}_A = c_A\mathbf{v}_A\,, \qquad A = 1, 2, ..., N \tag{142}$$

which allows us to express Eqs. (59) as

$$0 = -\nabla x_A + \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{x_A \mathbf{N}_B - x_B \mathbf{N}_A}{c\mathscr{D}_{AB}}, \quad A = 1, 2, ..., N-1 \quad (143)$$

At this point we separate the second term to obtain

$$0 = -c\nabla x_A + x_A \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{\mathbf{N}_B}{\mathscr{D}_{AB}} - \mathbf{N}_A \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{x_B}{\mathscr{D}_{AB}}, \quad A = 1, 2, ..., N-1 \quad (144)$$

and we define the mixture diffusivity by

$$\frac{1}{\mathscr{D}_{Am}} = \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{x_B}{\mathrm{D}_{AB}}, \qquad A = 1, 2, ..., N-1 \quad (145)$$

so that the Stefan-Maxwell equations can be expressed as

$$0 = -c\mathscr{D}_{Am}\nabla x_A + x_A \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{\mathscr{D}_{Am}}{\mathscr{D}_{AB}} \mathbf{N}_B - \mathbf{N}_A, \quad A = 1, 2, ..., N-1 \quad (146)$$

For some processes, such as diffusion in porous media (Whitaker, 1999) in which the flux of all the species is driven by heterogeneous reaction or by adsorption/desorption, we can impose the simplification

$$x_A \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{\mathscr{D}_{Am}}{\mathscr{D}_{AB}} \mathbf{N}_B << \mathbf{N}_A, \quad A = 1, 2, ..., G, \quad G < N \quad (147)$$

when the following two conditions are satisfied:

$$\text{Constraint: } (x_A)_{\max} << 1, \quad A = 1, 2, ..., G < N \quad (148a)$$

$$\text{Restriction: } \mathbf{N}_B = \mathbf{O}(\mathbf{N}_A), \qquad B = 1, 2, ..., N \quad (148b)$$

The first of Eqs. (148) is identified as a *constraint* since the maximum values of the mole fractions are generally known *a priori*, while the second inequality is identified as a *restriction* since it is not expressed in terms of quantities that are known *a priori*. Equation 148b should be interpreted to mean that $\mathbf{N}_B$ is not significantly larger than $\mathbf{N}_A$ and if species *B* is stagnant, $\mathbf{N}_B$ would be zero.

In Eqs. (147) and (148a) we have indicated that our *N*-component system contains *G* components that are dilute. For example, if we may have a five-component mixture in which three components have mole fractions that are small compared to one, we have $G = 3$ and Eqs. (147) and (148a) applies to these three components. Use of Eq. (147) allows us to express the dilute forms of Eqs. (146) as

$$\mathbf{N}_A = -c\mathscr{D}_{Am}\nabla x_A, \quad A = 1, 2, ..., G < N \quad (149)$$

At this point we recognize that Eqs. (72) can be expressed in terms of $\mathbf{N}_A$ to obtain

$$\frac{\partial c_A}{\partial t} + \nabla \cdot \mathbf{N}_A = R_A, \quad A = 1, 2, ..., N-1 \quad (150)$$

and that Eq. (149) can be used to obtain a *dilute solution diffusion equation* given by

$$\frac{\partial c_A}{\partial t} = \nabla \cdot \left(c\mathscr{D}_{Am}\nabla x_A \right) + R_A, \quad A = 1, 2, ..., G < N \quad (151)$$

We are still confronted with the complexity of the transport equation for the total molar concentration given by Eq. (87), and this difficulty is classically avoided by assuming that the total molar concentration is a constant in order to obtain

$$\frac{\partial c_A}{\partial t} = \nabla \cdot \left(\mathscr{D}_{Am}\nabla c_A \right) + R_A, \quad A = 1, 2, ..., G, \begin{cases} G < N \\ \text{other conditions} \end{cases} \quad (152)$$

in which the other conditions associated with this result are given by

$$\text{Assumption:} \qquad c = \text{constant} \quad (153a)$$

$$\text{Restriction: } \mathbf{N}_B = \mathbf{O}(\mathbf{N}_A), \qquad B = 1, 2, ..., N \quad (153b)$$

$$\text{Constraint: } (x_A)_{\max} << 1, \qquad A = 1, 2, ..., G < N \quad (153c)$$

The constraint identified by Eq. (153c) is generally available in terms of the problem statement, and when this constraint is satisfied it is probable that the assumption given by Eq. (153a) and the restriction given by Eq. (153b) are also valid.

6.2 Dilute solution convective-diffusion equation using $\mathbf{J}_A^*$

In order to develop the convective-diffusion version of Eqs. (152), we begin with the generally valid form given by Eqs. (84) and repeated here as

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = -\nabla \cdot \left(\mathbf{J}_A^* - x_A \sum_{B=1}^{B=N} \frac{M_B}{\bar{M}} \mathbf{J}_B^* \right) + R_A, \quad A = 1, 2, ..., N \quad (154)$$

The Stefan-Maxwell equations can be expressed as

$$0 = -\nabla x_A + \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{x_A \mathbf{J}_B^* - x_B \mathbf{J}_A^*}{c\mathscr{D}_{AB}}, \quad A = 1, 2, ..., N-1 \quad (155)$$

and the summation can be separated leading to

$$0 = -c\nabla x_A + x_A \sum_{\substack{B=1\\B\neq A}}^{B=N} \frac{\mathbf{J}_B^*}{\mathscr{D}_{AB}} - \mathbf{J}_A^* \sum_{\substack{B=1\\B\neq A}}^{B=N} \frac{x_B}{\mathscr{D}_{AB}}, \quad A = 1, 2, ..., N-1 \tag{156}$$

The definition of the mixture diffusivity given by Eq. (145) can be used to express this result in the form

$$0 = -c\,\mathscr{D}_{Am}\nabla x_A + x_A \sum_{\substack{B=1\\B\neq A}}^{B=N} \frac{\mathscr{D}_{Am}}{\mathscr{D}_{AB}} \mathbf{J}_B^* - \mathbf{J}_A^*, \quad A = 1, 2, ..., N-1 \tag{157}$$

In making judgments about this result, we need to remember that the diffusive fluxes are constrained by

$$\sum_{B=1}^{B=N} \mathbf{J}_B^* = 0 \tag{158}$$

indicating that the diffusive fluxes tend to be the same order of magnitude. This means that the following inequality

Restriction:

$$x_A \sum_{\substack{B=1\\B\neq A}}^{B=N} \frac{\mathscr{D}_{Am}}{\mathscr{D}_{AB}} \mathbf{J}_B^* << \mathbf{J}_A^*, \quad A = 1, 2, ..., G < N \tag{159}$$

has considerable appeal when the mole fraction of species *A* is *small compared to one* as indicated by

Restriction: $x_A << 1, \quad A = 1, 2, ..., G < N$ (160)

Use of the inequality given by Eq. (159) in the Stefan-Maxwell equations given by Eqs. (157) leads to the multi-component form of Fick's Law

"Fick's Law"

$$\mathbf{J}_A^* = -c\,\mathscr{D}_{Am}\nabla x_A, \quad A = 1, 2, ..., G, \begin{cases} G < N \\ x_A << 1 \end{cases} \tag{161}$$

which is analogous to the result for binary systems given by Eq. (121).

We now turn our attention to the species continuity equation given by Eq. (154). Use of the dilute solution condition indicated by Eq. (160) and the constraint on the diffusive fluxes given by Eq. (158) leads to the restriction

Restriction: $$x_A \sum_{B=1}^{B=N} \frac{M_B}{\bar{M}} \mathbf{J}_B^* << \mathbf{J}_A^* \tag{162}$$

Use of this inequality along with the multi-component form of Fick's Law given by Eq. (161) in Eq. (154) leads to the following form of the convective-diffusion equation

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\mathbf{v}) = \nabla\cdot\left(c\,\mathscr{D}_{Am}\nabla x_A\right) + R_A, \quad A = 1, 2, ..., G < N \tag{163}$$

In addition to the inequalities given by Eqs. (160) and (162), we assume that the total molar concentration is constant in order to obtain the classic linear convective-diffusion equation for species *A*.

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\mathbf{v}) = \nabla\cdot\left(\mathscr{D}_{Am}\nabla c_A\right) + R_A, A = 1, 2, ..., G, \begin{cases} G < N \\ c = \text{constant} \\ x_A << 1 \end{cases} \tag{164}$$

This special form of the species continuity equation is ubiquitous in the chemical engineering literature; however, the simplifications associated with this result are generally not made clear. In addition to the dominant restrictions listed in Eq. (164), one should keep in mind the restriction given by Eq. (162) that would appear to be automatically satisfied by Eqs. (158) and (160) unless there is a serious disparity in the molecular masses.

6.3 Dilute solution convective-diffusion equation using $\mathbf{J}_A$

In this case we begin with Eq. (91)

$$\frac{\partial c_A}{\partial t} + \nabla\cdot(c_A\mathbf{v}) = -\nabla\cdot\mathbf{J}_A + R_A, \quad A = 1, 2, ..., N-1 \tag{165}$$

and note that the Stefan-Maxwell equations can be expressed as

$$0 = -\nabla x_A + \sum_{\substack{B=1\\B\neq A}}^{B=N} \frac{x_A\mathbf{J}_B - x_B\mathbf{J}_A}{c\,\mathscr{D}_{AB}}, A = 1, 2, ..., N-1 \tag{166}$$

Separating the terms in the sum leads to

$$0 = -c\nabla x_A + x_A \sum_{\substack{B=1\\B\neq A}}^{B=N} \frac{\mathbf{J}_B}{\mathscr{D}_{AB}} - \mathbf{J}_A \sum_{\substack{B=1\\B\neq A}}^{B=N} \frac{x_B}{\mathscr{D}_{AB}}, \quad A = 1, 2, ..., N-1 \tag{167}$$

and use of the definition of the mixture diffusivity given by Eq. (145) provides

$$0 = -c\,\mathscr{D}_{Am}\nabla x_A + x_A \sum_{\substack{B=1\\B\neq A}}^{B=N} \frac{\mathscr{D}_{Am}}{\mathscr{D}_{AB}} \mathbf{J}_B - \mathbf{J}_A, \quad A = 1, 2, ..., N-1 \tag{168}$$

In making judgments about this result we need to remember that the diffusive fluxes are constrained by

$$\sum_{A=1}^{A=N} M_A \mathbf{J}_A = 0 \qquad (169)$$

thus if the mole fraction of species *A* is small compared to one, we can make use of the restriction given by

Restriction:

$$x_A \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{\mathscr{D}_{Am}}{\mathscr{D}_{AB}} \mathbf{J}_B << \mathbf{J}_A \,, \qquad A = 1, 2, ..., G < N \qquad (170)$$

Under these circumstances, the Stefan-Maxwell equation for species *A* takes the form

"Fick's Law":

$$\mathbf{J}_A = -c\mathscr{D}_{Am} \nabla x_A \,, \qquad A = 1, 2, ..., G < N \qquad (171)$$

Use of this result in Eq. (165) leads to the following form of the convective-diffusion equation

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = \nabla \cdot \left(c\mathscr{D}_{Am} \nabla x_A \right) + R_A \qquad (172)$$

This result, based on the *single restriction* given by Eq. (170), is identical to that given earlier by Eq. (163). To complete the analysis of the mixed-mode diffusive flux, we assume that the total molar concentration is constant so that Eq. (172) takes the form

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = \nabla \cdot \left(\mathscr{D}_{Am} \nabla c_A \right) + R_A \,,$$
$$A = 1, 2, ..., G \,, \quad \begin{cases} G < N \\ c \;=\; \text{constant} \\ x_A \;<<\; 1 \end{cases} \qquad (173)$$

Certainly the route to Eq. (173) is simpler than that followed in the development of Eq. (164); however, the preferred approach might still be considered to be a matter of choice.

6.4 Diffusion through stagnant species

The case of binary transport of species *A* through a stagnant species *B* has been treated in terms of the classic Stefan diffusion tube (Whitaker, 2009b, Sec. 2.7). Moving beyond the binary system, we consider the case in which species *A* is diffusing and all other species are stagnant. Under these circumstances, the Stefan-Maxwell equation for species *A* reduces to

$$0 = -\nabla x_A - \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{x_A x_B \mathbf{v}_A}{\mathscr{D}_{AB}} \qquad (174)$$

and this can be arranged in the form

$$0 = -c\nabla x_A - \sum_{\substack{B=1 \\ B\neq A}}^{B=N} \frac{x_B}{\mathscr{D}_{AB}} \mathbf{N}_A \qquad (175)$$

Use of the definition of the mixture diffusivity given by Eq. (145) immediately leads to

$$\mathbf{N}_A = -c\mathscr{D}_{Am} \nabla x_A \qquad (176)$$

Note that this result is *not restricted* to a dilute solution; however, we have imposed the condition on the velocities given by

Assumption: $\mathbf{v}_B = \mathbf{v}_C = ... = \mathbf{v}_N = 0 \qquad (177)$

This assumption could be replaced with the restriction

Restriction: $\mathbf{v}_B << \mathbf{v}_A, \mathbf{v}_C << \mathbf{v}_A, ..., \mathbf{v}_N << \mathbf{v}_A \qquad (178)$

in which the use of the absolute values of the velocities is understood. Here one should remember that we are repeatedly relying on Birkhoff's (1960) plausible intuitive hypothesis that small causes give rise to small effects. Use of Eq. (176) in Eq. (150) leads to

$$\frac{\partial c_A}{\partial t} = \nabla \cdot \left(c\mathscr{D}_{Am} \nabla x_A \right) + R_A \qquad (179)$$

and we can assume that the total molar concentration is constant to obtain

$$\frac{\partial c_A}{\partial t} = \nabla \cdot \left(\mathscr{D}_{Am} \nabla c_A \right) + R_A \,, \quad \begin{cases} c \;=\; \text{constant} \\ \text{other conditions} \end{cases} \qquad (180)$$

where the other conditions are those indicated by Eqs. (178). This result is identical to Eq. (152) except for the fact that there is only a single component that could satisfy this equation. As a reminder of the difference between Eq. (180) and Eq. (152) we summarize the conditions upon which it is based

Restriction: $\mathbf{v}_B << \mathbf{v}_A, \mathbf{v}_C << \mathbf{v}_A, ..., \mathbf{v}_N << \mathbf{v}_A \qquad (181)$

Restriction: $x_A \nabla c << \nabla c_A \qquad (182)$

Comparing these two restrictions with Eqs. (153) indicates that Eqs. (152) and (180) describe rather different physical phenomena even though the two equations are *identical*. In reality, it seems unlikely that a process restricted by Eq. (181) could involve significant homogeneous reaction, thus a more realistic version of Eq. (180) would require that we set R_A equal to zero. Nevertheless, the fact that Eq. (152) and Eq. (180) are identical in form suggests that we must be very careful to understand the precise meaning of the special forms of Eq. (68).

7. General solution for *N*-component systems: Constant total molar concentration

From the analysis in previous sections, it seems clear that the most efficient route to the determination of the molar concentration is via the mixed-mode

continuity equation described in Sec. 4. This is especially true for the case in which we develop an exact solution of the Stefan-Maxwell equations. In this section we consider the case of constant total molar concentration and in the next section we examine the case of constant total mass density. The completely general case for which neither ρ nor c is constant remains as a challenge.

In this treatment we make use of Eq. (91) repeated here as

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = -\nabla \cdot \mathbf{J}_A + R_A \,, \qquad A = 1, 2, ..., N-1 \tag{183}$$

along with the constraint on the mixed-mode diffusive flux given by

$$\sum_{A=1}^{A=N} M_A \mathbf{J}_A = 0 \tag{184}$$

For N-component systems, it is convenient to work in terms of matrices, thus we define the following column matrices that will be used in subsequent paragraphs.

$$[c] = \begin{bmatrix} c_A \\ c_B \\ c_C \\ ... \\ ... \\ c_{N-1} \end{bmatrix}, \quad [\nabla c] = \begin{bmatrix} \nabla c_A \\ \nabla c_B \\ \nabla c_C \\ ... \\ ... \\ \nabla c_{N-1} \end{bmatrix},$$

$$[\nabla x] = \begin{bmatrix} \nabla x_A \\ \nabla x_B \\ \nabla x_C \\ ... \\ ... \\ \nabla x_{N-1} \end{bmatrix}, \quad [\mathbf{J}] = \begin{bmatrix} \mathbf{J}_A \\ \mathbf{J}_B \\ \mathbf{J}_C \\ ... \\ ... \\ \mathbf{J}_{N-1} \end{bmatrix},$$

$$[R] = \begin{bmatrix} R_A \\ R_B \\ R_C \\ ... \\ ... \\ R_{N-1} \end{bmatrix} \tag{185}$$

Use of the first, fourth and fifth of these matrices allows us to express Eq. (183) as

$$\frac{\partial [c]}{\partial t} + \nabla \cdot ([c]\mathbf{v}) = -\nabla \cdot [\mathbf{J}] + [R] \tag{186}$$

and our single objective at this point is to develop a useful representation for $[\mathbf{J}]$. A similar approach using $\mathbf{v}^*$ and $\mathbf{J}_A^*$ with $A = 1, 2, ..., N-1$ is given by Bird *et al*. (2002, Sec. 22.9). In addition, Quintard *et al*. (2006) have studied the formulation and the numerical solution for this problem using both the molar forms, $\mathbf{v}^*$ and $\mathbf{J}_A^*$, and the mass forms, $\mathbf{v}$ and $\mathbf{j}_A$.

We begin our analysis of the diffusive flux with the Stefan-Maxwell equations given by Eq. (166), and we make use of the mixture diffusivity defined by Eq. (145) to obtain

$$\mathbf{J}_A = -c\,\mathscr{D}_{Am} \nabla x_A + x_A \sum_{\substack{B=1 \\ B \neq A}}^{B=N} \frac{\mathscr{D}_{Am}}{\mathscr{D}_{AB}} \mathbf{J}_B \,, \qquad A = 1, 2, ..., N-1 \tag{187}$$

We want to use Eq. (184) to eliminate $\mathbf{J}_N$ and it will be convenient to express that constraint on the mixed-mode diffusive fluxes in the alternate form given by

$$\sum_{A=1}^{A=N} \mathbf{J}_A \left(M_A / M_N \right) = 0 \tag{188}$$

At this point we extract $\mathbf{J}_N$ from the sum in Eq. (187) in order to obtain

$$\mathbf{J}_A = -c\,\mathscr{D}_{Am} \nabla x_A + x_A \sum_{\substack{B=1 \\ B \neq A}}^{B=N-1} \frac{\mathscr{D}_{Am}}{\mathscr{D}_{AB}} \mathbf{J}_B + x_A \frac{\mathscr{D}_{Am}}{\mathscr{D}_{AN}} \mathbf{J}_N \,, \qquad A = 1, 2, ..., N-1 \tag{189}$$

and from Eq. (188) we have the following representation for $\mathbf{J}_N$

$$\mathbf{J}_N = -\sum_{B=1}^{B=N-1} \mathbf{J}_B \left(M_B / M_N \right) \tag{190}$$

In order to use this result with Eq. (189), we need to condition the sum with the constraint indicated by $B \neq A$ and this leads to

$$\mathbf{J}_N = -\sum_{\substack{B=1 \\ B \neq A}}^{B=N-1} \mathbf{J}_B \left(M_B / M_N \right) - \mathbf{J}_A \left(M_A / M_N \right) \tag{191}$$

Use of this result in Eq. (189) provides the following form of the Stefan-Maxell equations

$$\mathbf{J}_A \left(1 + x_A \frac{M_A \mathscr{D}_{Am}}{M_N \mathscr{D}_{AN}} \right) + x_A \sum_{\substack{B=1 \\ B \neq A}}^{B=N-1} \left(\frac{M_B \mathscr{D}_{Am}}{M_N \mathscr{D}_{AN}} - \frac{\mathscr{D}_{Am}}{\mathscr{D}_{AB}} \right) \mathbf{J}_B = -c\,\mathscr{D}_{Am} \nabla x_A, A = 1, 2, ..., N-1 \tag{192}$$

This can be expressed in compact form according to

$$\left[H\right]\begin{bmatrix}\mathbf{J}_A\\ \mathbf{J}_B\\ \mathbf{J}_C\\ \cdots\\ \cdots\\ \mathbf{J}_{N-1}\end{bmatrix} = -\ c\begin{bmatrix}\mathrm{D}_{Am}\nabla x_A\\ \mathrm{D}_{Bm}\nabla x_B\\ \mathrm{D}_{Cm}\nabla x_C\\ \cdots\\ \cdots\\ \mathrm{D}_{N-1m}\nabla x_{N-1}\end{bmatrix} \tag{193}$$

in which $\left[H\right]$ is an $(N-1)\times(N-1)$ square matrix

$$[H]=\begin{bmatrix}H_{AA} & H_{AB} & . & . & . & H_{AN-1}\\ H_{BA} & H_{BB} & . & . & . & H_{BN-1}\\ H_{CA} & . & . & . & . & .\\ . & . & . & . & . & .\\ . & . & . & . & . & .\\ H_{N-1A} & . & . & . & . & H_{N-1N-1}\end{bmatrix}. \tag{194}$$

having the elements defined by

$$H_{AA}=1+x_A\frac{M_A\mathscr{D}_{Am}}{M_N\mathscr{D}_{AN}}, \qquad A\ =\ 1,2,...,N-1 \tag{195a}$$

$$H_{AB}=x_A\left(\frac{M_B\mathscr{D}_{Am}}{M_N\mathscr{D}_{AN}}-\frac{\mathscr{D}_{Am}}{\mathscr{D}_{AB}}\right), \qquad A,B\ =\ 1,2,..,N-1,\ \ A\neq B \tag{195b}$$

We assume that the inverse of $[H]$ exists in order to express the column matrix of the mixed-mode diffusive flux vectors in the form

$$\begin{bmatrix}\mathbf{J}_A\\ \mathbf{J}_B\\ \mathbf{J}_C\\ \cdots\\ \cdots\\ \mathbf{J}_{N-1}\end{bmatrix} = -\ c\left[H\right]^{-1}\begin{bmatrix}\mathscr{D}_{Am}\nabla x_A\\ \mathscr{D}_{Bm}\nabla x_B\\ \mathscr{D}_{Cm}\nabla x_C\\ \cdots\\ \cdots\\ \mathscr{D}_{N-1m}\nabla x_{N-1}\end{bmatrix} \tag{196}$$

The column matrix on the right hand side of this result can be expressed as

$$\begin{bmatrix}\mathscr{D}_{Am}\nabla x_A\\ \mathscr{D}_{Bm}\nabla x_B\\ \mathscr{D}_{Cm}\nabla x_C\\ \cdots\\ \mathscr{D}_{N-1m}\nabla x_{N-1}\end{bmatrix} = \begin{bmatrix}\mathscr{D}_{Am} & 0 & 0 & \cdots & 0\\ 0 & \mathscr{D}_{Bm} & 0 & \cdots & 0\\ 0 & 0 & \mathscr{D}_{Cm} & \cdots & 0\\ \cdot & \cdot & \cdot & \cdots & \cdot\\ 0 & 0 & 0 & \cdots & \mathscr{D}_{N-1m}\end{bmatrix}\begin{bmatrix}\nabla x_A\\ \nabla x_B\\ \nabla x_C\\ \cdot\cdot\\ \nabla x_{N-1}\end{bmatrix} \tag{197}$$

so that the matrix representation for the mixed-mode diffusive flux becomes

$$\begin{bmatrix}\mathbf{J}_A\\ \mathbf{J}_B\\ \mathbf{J}_C\\ \cdots\\ \cdots\\ \mathbf{J}_{N-1}\end{bmatrix} = -c\left[H\right]^{-1}\begin{bmatrix}\mathscr{D}_{Am} & 0 & 0 & \cdots & 0\\ 0 & \mathscr{D}_{Bm} & 0 & \cdots & 0\\ 0 & 0 & \mathscr{D}_{Cm} & \cdots & 0\\ \cdot & \cdot & \cdot & \cdots & \cdot\\ 0 & 0 & 0 & \cdots & \mathscr{D}_{N-1m}\end{bmatrix}\begin{bmatrix}\nabla x_A\\ \nabla x_B\\ \nabla x_C\\ \cdot\cdot\\ \nabla x_{N-1}\end{bmatrix} \tag{198}$$

The *diffusivity matrix* is now defined by

$$[D]=[H]^{-1}\begin{bmatrix}\mathscr{D}_{Am} & 0 & 0 & \cdots & 0\\ 0 & \mathscr{D}_{Bm} & 0 & \cdots & 0\\ 0 & 0 & \mathscr{D}_{Cm} & \cdots & 0\\ \cdot & \cdot & \cdot & \cdots & \cdot\\ 0 & 0 & 0 & \cdots & \mathscr{D}_{N-1m}\end{bmatrix} \tag{199}$$

and this allows us to express Eq. (198) as

$$\begin{bmatrix}\mathbf{J}_A\\ \mathbf{J}_B\\ \mathbf{J}_C\\ \cdots\\ \cdots\\ \mathbf{J}_{N-1}\end{bmatrix} = -\ c[D]\begin{bmatrix}\nabla x_A\\ \nabla x_B\\ \nabla x_C\\ \cdots\\ \cdots\\ \nabla x_{N-1}\end{bmatrix} \tag{200}$$

with the compact form given by

$$\left[\mathbf{J}\right]=-\ c[D]\left[\nabla x\right] \tag{201}$$

This represents the *N*-component analog of Fick's Law given by Eq. (135) that we recall here as

$$\text{Fick's Law:}\quad \mathbf{J}_A=-c\left[\left(M_B/\bar{M}\right)\mathscr{D}_{AB}\right]\nabla x_A \tag{202}$$

Use of Eq. (201) in Eq. (186) leads to

$$\frac{\partial[c]}{\partial t}+\nabla\cdot\left([c]\mathbf{v}\right)=\nabla\cdot\left(c[D]\left[\nabla x\right]\right)+\left[R\right] \tag{203}$$

Once again we may be faced with the difficult task of determining the total molar concentration on the basis of Eq. (93), and to avoid this problem we restrict Eq. (203) to the case of constant total molar concentration. This leads to

$$\frac{\partial[c]}{\partial t}+\nabla\cdot\left([c]\mathbf{v}\right)=\nabla\cdot\left([D]\left[\nabla c\right]\right)+\left[R\right] \qquad \begin{cases} c\ =\ \text{constant}\\ N-\text{component system}\end{cases} \tag{204}$$

Here it is important to remember that $[D]$ depends explicitly on the mole fractions, as indicated by the

definitions given in Eq. 195 and implicitly as indicated by the definition of the mixture diffusivity given by Eq. (145). This means that a trial-and-error numerical solution will be necessary in which the assumed values used for the mole fractions are upgraded after each iteration. The solution for $[c]$ will provide values of $c_A, c_B, ..., c_{N-1}$ and the concentration c_N can be determined by the first of Eqs. (71). Similarly, the solution for $[R]$ will provide values of $R_A, R_B, ..., R_{N-1}$ and the reaction rate R_N can be determined by Eq. (69). In the case of complex kinetics, the column matrix of reaction rates will need to be expressed as

$$[R] = [\mathscr{F}(c_A, c_A, ..., c_N)] \qquad (205)$$

and the trial-and-error procedure will be more complex.

8. General solution for *N*-component systems: Constant total mass density

In addition to the *N*-component form of the species continuity equation based on the assumption of a *constant total molar concentration*, it would be useful to develop the analogous form for *constant total density*. Our starting point for this analysis is Eq. (203) and the analysis requires that we express $[\nabla x]$ in terms of the gradient of the mass fractions, $\nabla\omega_A$, $\nabla\omega_B$, etc. We begin the analysis with Eq. (105) repeated here as

$$x_A = \frac{\bar{M}}{M_A}\omega_A, \quad A = 1,2,...N \qquad (206)$$

in which the mean molecular mass can be expressed as in terms of the mass fractions in order to obtain (see Eq. C11 in the Appendix C)

$$\frac{1}{\bar{M}} = \frac{\omega_A}{M_A} + \frac{\omega_B}{M_B} + \frac{\omega_C}{M_C} + ... + \frac{\omega_N}{M_N} \qquad (207)$$

We can use Eq. (206) to express the gradient of the mole fraction as

$$\nabla x_A = \frac{\nabla\bar{M}}{M_A}\omega_A + \frac{\bar{M}}{M_A}\nabla\omega_A, \qquad A = 1,2,...N \quad (208)$$

while the gradient of the mean molecular mass is given by

$$\nabla\bar{M} = -\bar{M}^2\sum_{B=1}^{B=N}\frac{\nabla\omega_B}{M_B} \qquad (209)$$

Use of Eq. (209) in Eq. (208) leads to

$$\nabla x_A = \frac{\bar{M}}{M_A}\left[\nabla\omega_A - \omega_A\sum_{B=1}^{B=N}\frac{\bar{M}}{M_B}\nabla\omega_B\right], \qquad A = 1,2,...N \qquad (210)$$

At this point we can make use of the fact that the sum of the mass fractions is equal to one so that the gradients are related by

$$\nabla\omega_N = -\left(\nabla\omega_A + \nabla\omega_B + \nabla\omega_C + ...+ \nabla\omega_{N-1}\right) \quad (211)$$

This allows us to eliminate $\nabla\omega_N$ from Eq. (210) and express that result in the form

$$\nabla x_A = \frac{\bar{M}}{M_A}\left[\nabla\omega_A - \omega_A\sum_{B=1}^{B=N-1}\left(\frac{\bar{M}}{M_B} - \frac{\bar{M}}{M_N}\right)\nabla\omega_B\right], \qquad A = 1,2,...N-1 \qquad (212)$$

Here we need to condition the sum with the constraint indicated by $B \neq A$ and this leads to

$$\nabla x_A = \frac{\bar{M}}{M_A}\left\{\left[1 + \omega_A\left(\frac{\bar{M}}{M_N} - \frac{\bar{M}}{M_A}\right)\right]\nabla\omega_A + \omega_A\sum_{\substack{B=1\\B\neq A}}^{B=N-1}\left(\frac{\bar{M}}{M_N} - \frac{\bar{M}}{M_B}\right)\nabla\omega_B\right\}, A = 1,2,...N-1 \qquad (213)$$

which can be expressed as a matrix equation given by

$$\begin{bmatrix}\nabla x_A\\ \nabla x_B\\ \nabla x_C\\ .\\ .\\ \nabla x_{N-1}\end{bmatrix} = \begin{bmatrix} W_{AA} & W_{AB} & W_{AC} & . & . & W_{AN-1}\\ W_{BA} & W_{BB} & . & . & . & W_{BN-1}\\ W_{CA} & . & . & . & . & .\\ . & . & . & . & . & .\\ . & . & . & . & . & .\\ W_{N-1A} & W_{N-1B} & . & . & . & W_{N-1N-1}\end{bmatrix}\begin{bmatrix}\nabla\omega_A\\ \nabla\omega_B\\ \nabla\omega_C\\ .\\ .\\ \nabla\omega_{N-1}\end{bmatrix} \qquad (214)$$

Here the elements of this $(N-1)\times(N-1)$ square matrix are defined as

$$W_{AA} = \frac{\bar{M}}{M_A} + \omega_A\frac{\bar{M}}{M_A}\left(\frac{\bar{M}}{M_N} - \frac{\bar{M}}{M_A}\right), \qquad A = 1,2,...,N-1 \qquad (215a)$$

$$W_{AB} = \omega_A\frac{\bar{M}}{M_A}\left(\frac{\bar{M}}{M_N} - \frac{\bar{M}}{M_A}\right), \qquad A,B = 1,2,...,N-1, \quad A \neq B \qquad (215b)$$

At this point we recall Eq. (200) and make use of Eq. (214) to obtain

$$\begin{bmatrix} \mathbf{J}_A \\ \mathbf{J}_B \\ \mathbf{J}_C \\ \cdots \\ \cdots \\ \mathbf{J}_{N-1} \end{bmatrix} = -c[D][W] \begin{bmatrix} \nabla\omega_A \\ \nabla\omega_B \\ \nabla\omega_C \\ . \\ . \\ \nabla\omega_{N-1} \end{bmatrix} \tag{216}$$

in which the square matrix $[W]$ is defined explicitly by

$$[W] = \begin{bmatrix} W_{AA} & W_{AB} & W_{AC} & . & . & W_{AN-1} \\ W_{BA} & W_{BB} & . & . & . & W_{BN-1} \\ W_{CA} & . & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ W_{N-1A} & W_{N-1B} & . & . & . & W_{N-1N-1} \end{bmatrix} \tag{217}$$

Use of the third of Eqs. (104) leads to the total mass density as a multiplier and Eq. (216) takes the form

$$\begin{bmatrix} \mathbf{J}_A \\ \mathbf{J}_B \\ \mathbf{J}_C \\ \cdots \\ \cdots \\ \mathbf{J}_{N-1} \end{bmatrix} = -\rho\,\bar{M}^{-1}[D][W] \begin{bmatrix} \nabla\omega_A \\ \nabla\omega_B \\ \nabla\omega_C \\ . \\ . \\ \nabla\omega_{N-1} \end{bmatrix} \tag{218}$$

We are now in a position to impose the condition that the total mass density is a constant in order to express the mixed-mode fluxes in the form

$$\begin{bmatrix} \mathbf{J}_A \\ \mathbf{J}_B \\ \mathbf{J}_C \\ \cdots \\ \cdots \\ \mathbf{J}_{N-1} \end{bmatrix} = -\bar{M}^{-1}[D][W] \begin{bmatrix} \nabla\rho_A \\ \nabla\rho_B \\ \nabla\rho_C \\ . \\ . \\ \nabla\rho_{N-1} \end{bmatrix}, \quad \rho = \text{constant} \tag{219}$$

At this point we make use of the first of Eqs. (104) to express the column matrix of the gradients of the species densities as

$$\begin{bmatrix} \nabla\rho_A \\ \nabla\rho_B \\ \nabla\rho_C \\ . \\ . \\ \nabla\rho_{N-1} \end{bmatrix} = \begin{bmatrix} M_A & 0 & 0 & . & . & 0 \\ 0 & M_B & 0 & . & . & 0 \\ 0 & 0 & M_C & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ 0 & 0 & . & . & . & M_{N-1} \end{bmatrix} \begin{bmatrix} \nabla c_A \\ \nabla c_B \\ \nabla c_C \\ . \\ . \\ \nabla c_{N-1} \end{bmatrix} \tag{220}$$

Substitution of this result into Eq. (219) leads to

$$\begin{bmatrix} \mathbf{J}_A \\ \mathbf{J}_B \\ \mathbf{J}_C \\ \cdots \\ \cdots \\ \mathbf{J}_{N-1} \end{bmatrix} = -\bar{M}^{-1}[D][W] \begin{bmatrix} M_A & 0 & 0 & . & . & 0 \\ 0 & M_B & 0 & . & . & 0 \\ 0 & 0 & M_C & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ 0 & 0 & . & . & . & M_{N-1} \end{bmatrix} \begin{bmatrix} \nabla c_A \\ \nabla c_B \\ \nabla c_C \\ . \\ . \\ \nabla c_{N-1} \end{bmatrix} \tag{221}$$

in which it is understood that the total mass density is assumed to be constant. We can represent this result in compact form

$$[\mathbf{J}] = -[\mathbb{D}][\nabla c] \tag{222}$$

in which the new *diffusivity matrix* is given by

$$[\mathbb{D}] = -[D][W] \begin{bmatrix} M_A/\bar{M} & 0 & 0 & . & . & 0 \\ 0 & M_B/\bar{M} & 0 & . & . & 0 \\ 0 & 0 & M_C/\bar{M} & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ 0 & 0 & . & . & . & M_{N-1}/\bar{M} \end{bmatrix} \tag{223}$$

Use of Eq. (222) in Eq. (186) yields

$$\frac{\partial[c]}{\partial t} + \nabla\cdot([c]\mathbf{v}) = \nabla\cdot([\mathbb{D}][\nabla c]) + [R] \tag{224}$$

$$\begin{cases} \rho = \text{constant} \\ N - \text{component system} \end{cases}$$

In the trial-and-error solution of this transport equation, values of the mole fractions will be required as in the solution of Eq. (204); however, in this case it is the total mass density, ρ, that is a specified constant and not the total molar concentration, c. This requires that we first determine ρ_N and then c_N according to

$$\rho_N = \rho - \sum_{A=1}^{A=N-1} c_A M_A, \quad c_N = \rho_N / M_N \tag{225}$$

The mole fractions required for the evaluation of $[D]$ would then be determined by

$$x_A = c_A \Big/ \sum_{B=1}^{B=N} c_B \tag{226}$$

while the mass fractions required for the evaluation of $[W]$ would be calculated according to

$$\omega_A = c_A M_A \Big/ \sum_{B=1}^{B=N} c_B M_B \tag{227}$$

The result for constant total density given by Eq. (224), along with that for constant total molar

concentration given by Eq. (204), should prove to be useful for a wide range of mass transfer problems, provided that the Stefan-Maxwell equations are an acceptable representation for the diffusive fluxes. A discussion of the conditions for which the total molar concentration and total mass density may be treated as constants is given in Appendix E.

9. Conclusions

In this study we have examined the derivation of the Stefan-Maxwell equations and we have explored the structure of these equations in terms of the mass diffusive flux, the molar diffusive flux, and the mixed-mode diffusive flux. Several classic special cases have been examined and the assumptions, restrictions and constraints have been identified whenever possible. A general method of solution of the Stefan-Maxwell equations has been presented in terms of the mixed-mode diffusive flux.

Nomenclature

$\mathscr{A}_A(t)$	surface area of a species *A* material volume, m^2
$\mathbf{b}_A$	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/m3
c	total molar concentration, moles/m^3
$\mathbf{d}_A$	driving force for diffusion of species *A* in an ideal solution, m^{-1}
$\mathscr{D}_{AB}$	$\mathscr{D}_{BA}$, binary diffusion coefficient for species *A* and *B*, m^2/s
$\mathscr{D}_{Am}$	mixture diffusivity for species *A*, m^2/s
$[D]$	diffusivity matrix used with constant total molar concentration, m^2/s
$[\mathbb{D}]$	diffusivity matrix used with constant total mass density, m^2/s
D_A^T	thermal diffusion coefficient for species *A*, kg/m^2s
G	number of molecular species that are dilute
$\mathbf{g}$	gravitational body force per unit mass, N/kg
$\mathbf{j}_A$	$\rho_A \mathbf{u}_A$, mass diffusive flux of species *A*, kg/ m^2s
$\mathbf{J}_A^*$	$c_A \mathbf{u}_A^*$, molar diffusive flux of species *A*, moles/ m^2s
$\mathbf{J}_A$	$c_A \mathbf{u}_A$, mixed-mode diffusive flux of species *A*, moles/ m^2s
M_A	molecular mass of species *A*, g/mole
$\bar{M}$	mean molecular mass of a mixture, g/mole
N	total number of molecular species
$\mathbf{N}_A$	$c_A \mathbf{v}_A$, molar flux of species *A*, mole/m^2s
$\mathbf{n}$	unit normal vector
$\mathbf{P}_{AB}$	force per unit volume exerted by species *B* on species *A*, N/m^3
p	$\sum_{A=1}^{A=N} p_A$, total pressure, N/m^2
p_A	partial pressure of species *A*, N/m^2
r_A	*net* mass rate of production of species *A* owing to homogeneous reactions, kg/m^3s
R_A	*net* molar rate of production of species *A* owing to homogeneous reactions, moles/m^3s
R	gas constant, J/mol K
t	time, s
$\mathbf{t}_{A(\mathbf{n})}$	stress vector for species *A*, N/m^2
$\mathbf{T}_A$	stress tensor for species *A*, N/m^2
U	total internal energy in a volume *V*, J
$\mathbf{u}_A$	$\mathbf{v}_A - \mathbf{v}$, mass diffusion velocity, m/s
$\mathbf{u}_A^*$	$\mathbf{v}_A - \mathbf{v}^*$, molar diffusion velocity, m/s
$\mathbf{v}_A$	velocity of species *A*, m/s
$\mathbf{v}$	$\sum_{A=1}^{A=N} \omega_A \mathbf{v}_A$, mass average velocity, m/s
$\mathbf{v}^*$	$\sum_{A=1}^{A=N} x_A \mathbf{v}_A$, molar 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
$\mathscr{V}_A(t)$	volume of a species *A* body, m^3
x_A	c_A / c, mole fraction of species *A*

Greek Letters

ρ_A	mass density of species *A*, kg/m^3
ρ	total mass density, kg/m^3
μ	viscosity, N/m^2s
$\boldsymbol{\tau}$	viscous stress tensor, N/m^2
$\boldsymbol{\tau}_A$	viscous stress tensor for species *A*, N/m^2
ω_A	ρ_A / ρ, mass fraction of species *A*

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Appendix A: Chemical Reaction and Linear Momentum

The rate of change of linear momentum of species *A* owing to chemical reaction, $r_A \mathbf{v}_A^*$, can be caused either by the increase of species *A* (*production*) or by the decrease of species *A* (*consumption*). If species *A* is consumed by chemical reaction, it seems plausible

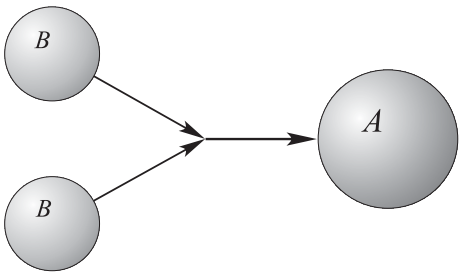

Fig. A1. Reaction of species *B* to form species *A*

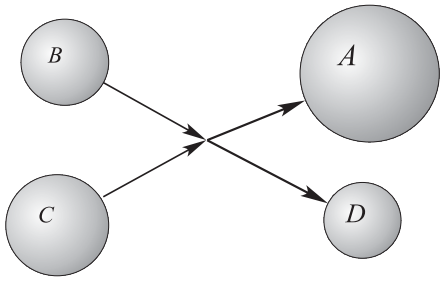

Fig. A2. Reaction of *B* and *C* to produce *A* and *D*

that the rate of change of linear momentum is given by $r_A \mathbf{v}_A$. Here we need to note that the molecular velocity (Hirschfelder *et al*., 1954, page 453) of species *A* is much larger than the continuum velocity, $\mathbf{v}_A$; however, the average velocity associated with the *consumption* of species *A* should be adequately represented by $\mathbf{v}_A$. If species *A* is produced by a chemical reaction, the rate of change of linear momentum depends on the velocities of the species that react to form species *A*.

The simple reaction illustrated in Fig. A1 can be described as $2B \rightarrow A$, and we assume that the loss of momentum by species *B* is equal to the gain of momentum of species *A*. We express this idea as [see Eq. (21)]

$$\underbrace{r_B \mathbf{v}_B^*}_{\text{loss}} + \underbrace{r_A \mathbf{v}_A^*}_{\text{gain}} = 0 \qquad \text{(A1)}$$

and note that conservation of mass [see Eq. 2] requires

$$\underbrace{r_B}_{\text{loss}} + \underbrace{r_A}_{\text{gain}} = 0 \qquad \text{(A2)}$$

On the basis of the argument given above, we assume that

$$\mathbf{v}_B^* = \mathbf{v}_B \qquad \text{(A3)}$$

and Eq. (A1) takes the form

$$\underbrace{r_B \mathbf{v}_B}_{\text{loss}} + \underbrace{r_A \mathbf{v}_A^*}_{\text{gain}} = 0 \qquad \text{(A4)}$$

When Eq. (A2) is used with this result we find that $\mathbf{v}_A^*$ is given by

$$\mathbf{v}_A^* = \mathbf{v}_B \qquad \text{(A5)}$$

and the rate of change of linear momentum of species *A* can be expressed as

$$\left\{ \begin{array}{c} \text{rate of change of} \\ \text{linear momentum} \\ \text{of species } A \end{array} \right\} = r_A \mathbf{v}_A^* = r_A \mathbf{v}_A + r_A \left(\mathbf{v}_B - \mathbf{v}_A \right) \qquad \text{(A6)}$$

The species velocities can be expressed in terms of the mass average velocity and the diffusion velocity to obtain

$$\mathbf{v}_A = \mathbf{v} + \mathbf{u}_A \,, \qquad \mathbf{v}_B = \mathbf{v} + \mathbf{u}_B \qquad \text{(A7)}$$

and these results can be used in Eq. (A6) so that the rate of change of momentum of species *A* takes the form

$$\left\{ \begin{array}{c} \text{rate of change of} \\ \text{linear momentum} \\ \text{of species } A \end{array} \right\} = r_A \mathbf{v}_A + r_A \left(\mathbf{u}_B - \mathbf{u}_A \right) \qquad \text{(A8)}$$

This leads to the estimate

$$\left\{ \begin{array}{c} \text{rate of change of} \\ \text{linear momentum} \\ \text{of species } A \end{array} \right\} = r_A \mathbf{v}_A + \mathbf{O}\left(r_A \mathbf{u}_A \right) \qquad \text{(A9)}$$

suggested by Whitaker (1986, Eqs. 1-19 and 1-55).

If we consider the slightly more complex reaction illustrated in Fig. A2, the concepts illustrated in Eqs. (A2) and (A4) take the form

$$\underbrace{r_B + r_C}_{\text{loss}} + \underbrace{r_A}_{\text{gain}} + \underbrace{r_D}_{\text{gain}} = 0 \qquad \text{(A10)}$$

$$\underbrace{r_B \mathbf{v}_B + r_C \mathbf{v}_C}_{\text{loss}} + \underbrace{r_A \mathbf{v}_A^*}_{\text{gain}} + \underbrace{r_D \mathbf{v}_D^*}_{\text{gain}} = 0 \qquad \text{(A11)}$$

In this case constructing a value for $\mathbf{v}_A^*$ is not as simple as the result illustrated by Eq. (A5). In terms of molar rates of reaction, we have

$$\begin{array}{l} r_B = M_B R_B \,, \quad r_B = M_B R_B \,, \\ r_B = M_B R_B \,, \quad r_B = M_B R_B \end{array} \qquad \text{(A12)}$$

in which M_B represents the molecular mass of species *B* and R_B represents the molar rate of

reaction for species *B*. In terms of molecular masses and molar rates of reaction, we can express Eq. (A11) as

$$\underbrace{M_B R_B \mathbf{v}_B}_{\text{loss}} + \underbrace{M_C R_C \mathbf{v}_C}_{\text{loss}} + \underbrace{M_A R_A \mathbf{v}_A^*}_{\text{gain}} + \underbrace{M_D R_D \mathbf{v}_D^*}_{\text{gain}} = 0 \tag{A13}$$

and Eq.(A10) can be replaced by

$$R_B = R_C\,, \quad R_C = -R_A\,, \quad R_A = R_D$$

Use of this constraint on the molar rates of reaction in Eq. (A13) leads to

$$M_B \mathbf{v}_B + M_C \mathbf{v}_C = M_A \mathbf{v}_A^* + M_D \mathbf{v}_D^* \tag{A14}$$

We now express the species velocities in terms of the mass average velocity and the diffusion velocities in order to obtain

$$\mathbf{v}_A = \mathbf{v} + \mathbf{u}_A\,, \quad \mathbf{v}_B = \mathbf{v} + \mathbf{u}_B\,, \quad \mathbf{v}_C = \mathbf{v} + \mathbf{u}_C \tag{A15}$$

Use of these relations in Eq. (A14) provides

$$M_B \mathbf{u}_B + M_C \mathbf{u}_C + (M_B + M_C)\mathbf{v} = M_A(\mathbf{v}_A^* - \mathbf{v}_A) + M_D(\mathbf{v}_D^* - \mathbf{v}_D) + M_A \mathbf{u}_A + M_D \mathbf{u}_D + (M_A + M_D)\mathbf{v} \tag{A16}$$

that can be simplified to

$$M_A(\mathbf{v}_A^* - \mathbf{v}_A) + M_D(\mathbf{v}_D^* - \mathbf{v}_D) = (M_B \mathbf{u}_B + M_C \mathbf{u}_C) - (M_A \mathbf{u}_A + M_D \mathbf{u}_D) \tag{A17}$$

Provided that the molecular masses are all the same order of magnitude, this result suggests that the difference, $\mathbf{v}_A^* - \mathbf{v}_A$, is on the order of the diffusion velocities. Given the general constraint on the diffusion velocities [see Eq. (14)], the result given by Eq. (A17) suggests that

$$\mathbf{v}_A^* = \mathbf{v}_A + \mathbf{O}(\mathbf{u}_A) \tag{A18}$$

which is equivalent to Eq. (A9).

The two cases represented in Figs. A1 and A2 are especially simple; however, most chemical reactions are likely to be binary in nature, thus Eq. (A18) represents a plausible estimate of the velocity $\mathbf{v}_A^*$.

Appendix B: Thermodynamic pressure

The decomposition given by Eq. (42) indicates that $\mathbf{T}_A$ is represented in terms of the partial pressure, p_A, and the viscous stress tensor, $\boldsymbol{\tau}_A$. The partial pressure of species *A* can be defined by (Whitaker, 1989, Chapter 10)

$$p_A = \rho_A^2 \left(\partial e_A / \partial \rho_A\right)_{s, \rho_B, \rho_C, \ldots\ldots} \tag{B1}$$

in which e_A is the internal energy of species *A* per unit mass of species *A*, and ρ_A is the mass density of species *A*. We defined the total pressure in terms of the partial pressures according to

$$p = \sum_{A=1}^{A=N} p_A \tag{B2}$$

However, the total pressure, *p*, can also be expressed as

$$p = \rho^2 \left(\partial e / \partial \rho\right)_{s, \rho_B, \rho_C, \ldots, \rho_N} \tag{B3}$$

in which *e* is the total internal energy defined by

$$e = \sum_{A=1}^{A=N} \omega_A e_A \tag{B4}$$

In this appendix we wish to show that there is no conflict between Eqs. (B1), (B2) and (B3), and this requires that we demonstrate the following:

$$\sum_{A=1}^{A=N} \rho_A^2 \left(\frac{\partial e_A}{\partial \rho_A}\right)_{s, \rho_B, \rho_C, \ldots, \rho_N} = \rho^2 \left(\frac{\partial e}{\partial \rho}\right)_{s, \rho_B, \rho_C, \ldots, \rho_N} \tag{B5}$$

In order to illustrate how the thermodynamic definition of the *partial pressure* is related to the thermodynamic definition of the *total pressure*, we need the following theorem:

Theorem: $$\sum_{A=1}^{A=N} \rho_A \frac{\partial \Lambda_A}{\partial \eta} = \rho \frac{\partial \Lambda}{\partial \eta} \tag{B6}$$

Here Λ_A is a *partial* mass quantity such as the species internal energy represented in Eq. (B1), while Λ is a *total* mass quantity defined by

$$\Lambda = \sum_{A=1}^{A=N} \omega_A \Lambda_A \tag{B7}$$

In Eq. (B6) we have used η to represent some thermodynamic state variable such as the temperature, the total mass density, etc.

We begin this proof with some variable Ω that can be represented as

$$\rho\Omega = \rho_A \Omega_A + \rho_B \Omega_B + \ldots + \rho_N \Omega_N \tag{B8}$$

or in a manner identical to Eq. (B7)

$$\Omega = \omega_A \Omega_A + \omega_B \Omega_B + \ldots + \omega_N \Omega_N \tag{B9}$$

Here the mass fractions are defined by the second of Eqs. (11) and they are constrained by

$$\omega_A + \omega_B + \ldots + \omega_N = 1 \tag{B10}$$

Because of this constraint all the mass fractions are not independent and the functional representation for Ω is given by

$$\Omega = \Omega(\rho, T, \omega_A, \omega_B, \ldots, \omega_{N-1}) \tag{B11}$$

If we differentiate Ω with respect to ω_A we can hold all the mass fractions constant except one. For convenience we choose this one to be ω_N and write (Slattery, 1999, page 447)

$$\left(\partial \Omega / \partial \omega_A\right)_{\rho, T, \omega_B (B \neq A, N)} = \Omega_A - \Omega_N \tag{B12}$$

This allows us to express Ω_A as

$$\Omega_A = \left(\partial \Omega / \partial \omega_A\right)_{\rho, T, \omega_B (B \neq A, N)} + \Omega_N \tag{B13}$$

and Eq. (B8) can be used to obtain

$$\rho\Omega = \sum_{A=1}^{A=N} \rho_A \Omega_A = \sum_{A=1}^{A=N} \rho_A \left(\frac{\partial \Omega}{\partial \omega_A} \right)_{\rho, T, \omega_B (B \neq A, N)} + \rho \Omega_N \tag{B14}$$

Subsequently we will use this result in the form

$$\sum_{A=1}^{A=N} \rho_A \left(\frac{\partial \Omega}{\partial \omega_A} \right)_{\rho, T, \omega_B (B \neq A, N)} = \rho\Omega - \rho \Omega_N \tag{B15}$$

At this point we consider the special case in which

$$\Omega = \frac{\partial \Lambda}{\partial \eta}, \quad \Omega_A = \frac{\partial \Lambda_A}{\partial \eta}, A = 1, 2, ..., N \tag{B16}$$

Use of this result in Eq. (B15) yields

$$\sum_{A=1}^{A=N} \rho_A \left. \frac{\partial (\partial \Lambda / \partial \eta)}{\partial \omega_A} \right|_{\rho, T, \omega_B (B \neq A, N)} = \rho \frac{\partial \Lambda}{\partial \eta} - \rho \frac{\partial \Lambda_N}{\partial \eta} \tag{B17}$$

Here we write Eq. (B13) for the variables Λ_A and Λ to obtain

$$\Lambda_A = \left(\partial \Lambda / \partial \omega_A \right)_{\rho, T, \omega_B (B \neq A, N)} + \Lambda_N \tag{B18}$$

Use of this result in the left hand side of the theorem we wish to prove leads to

$$\sum_{A=1}^{A=N} \rho_A \frac{\partial \Lambda_A}{\partial \eta} = \sum_{A=1}^{A=N} \rho_A \left[\frac{\partial}{\partial \eta} \left(\frac{\partial \Lambda}{\partial \omega_A} \right)_{\rho, T, \omega_B (B \neq A, N)} + \frac{\partial \Lambda_N}{\partial \eta} \right] \tag{B19}$$

Changing the order of differentiation in the first term and carrying out the summation with the second term provides

$$\sum_{A=1}^{A=N} \rho_A \frac{\partial \Lambda_A}{\partial \eta} = \sum_{A=1}^{A=N} \rho_A \left. \frac{\partial (\partial \Lambda / \partial \eta)}{\partial \omega_A} \right|_{\rho, T, \omega_B (B \neq A, N)} + \rho \frac{\partial \Lambda_N}{\partial \eta} \tag{B20}$$

Substitution of this result in Eq. (B17) provides the desired proof given by

Theorem:
$$\sum_{A=1}^{A=N} \rho_A \frac{\partial \Lambda_A}{\partial \eta} = \rho \frac{\partial \Lambda}{\partial \eta} \tag{B21}$$

At this point we want to verify the relations contained in Eq. (B5), and we begin with the following representation of the partial pressure

$$p_A = \rho_A^2 \left(\partial e_A / \partial \rho_A \right)_{s, \rho_B, \rho_C, ...} \tag{B22}$$

which can be summed over all species to obtain

$$\sum_{A=1}^{A=N} p_A = \sum_{A=1}^{A=N} \rho_A^2 \left(\partial e_A / \partial \rho_A \right)_{s, \rho_B, \rho_C, ..., \rho_N} \tag{B23}$$

Our objective now is to represent the right hand side of this result in terms of the total thermal energy. We begin with Eq. (B21)in the form

$$\sum_{A=1}^{A=N} \rho_A \left(\frac{\partial e_A}{\partial \rho} \right)_{s, \rho_B, \rho_C, ..., \rho_N} = \rho \left(\frac{\partial e}{\partial \rho} \right)_{s, \rho_B, \rho_C, ..., \rho_N} \tag{B24}$$

and multiply by the total density to obtain

$$\sum_{A=1}^{A=N} \rho \rho_A \left(\frac{\partial e_A}{\partial \rho} \right)_{s, \rho_B, \rho_C, ..., \rho_N} = \rho^2 \left(\frac{\partial e}{\partial \rho} \right)_{s, \rho_B, \rho_C, ..., \rho_N} \tag{B25}$$

The functional dependence of e_A can be represented in terms of the mass fractions or the species densities as indicated by

$$e_A = e_A \left(\rho, s, \omega_A, \omega_B, ..., \omega_{N-1} \right) \tag{B26a}$$

$$e_A = e_A \left(s, \rho_A, \rho_B, ..., \rho_N \right) \tag{B26b}$$

In addition, the density of species *A*, for example, can be expressed as

$$\rho_A = \rho - \left(\rho_B + \rho_C + ... + \rho_N \right) \tag{B27}$$

or in the functional form given by

$$\rho_A = \rho_A \left(\rho, \rho_B, ..., \rho_N \right) \tag{B28}$$

On the basis of this representation for ρ_A we can express Eq. (B26b) as a *composite function* given by

$$e_A = e_A \left[s, \rho_A \left(\rho, \rho_B, ..., \rho_N \right), \rho_B, ..., \rho_N \right] \tag{B29}$$

Directing our attention to the derivative on the left hand side of Eq. (B24) we note that it can be expressed as (Stein and Barcellos, 1992, page 149)

$$\left(\frac{\partial e_A}{\partial \rho} \right)_{s, \rho_B, \rho_C, ... \rho_N} = \left(\frac{\partial e_A}{\partial \rho_A} \right)_{s, \rho_B, \rho_C, ... \rho_N} \left(\frac{\partial \rho_A}{\partial \rho} \right)_{\rho_B, \rho_C, ... \rho_N} \tag{B30}$$

Since the mass density for species *A* can be expressed as

$$\rho_A = \omega_A \, \rho \tag{B31}$$

we have

$$\left(\partial \rho_A / \partial \rho \right)_{\rho_B, \rho_C, ... \rho_N} = \omega_A \tag{B32}$$

and Eq. (B30) takes the form

$$\left(\partial e_A / \partial \rho \right)_{s, \rho_B, \rho_C, ... \rho_N} = \omega_A \left(\partial e_A / \partial \rho_A \right)_{s, \rho_B, \rho_C, ... \rho_N} \tag{B33}$$

Use of this relation in Eq. (B25) leads to

$$\sum_{A=1}^{A=N} \rho_A^2 \left(\frac{\partial e_A}{\partial \rho} \right)_{s, \rho_B, \rho_C, ... \rho_N} = \rho^2 \left(\frac{\partial e}{\partial \rho} \right)_{s, \rho_B, \rho_C, ..., \rho_N} \tag{B34}$$

and on the basis of the definition of the partial pressure, this takes the form

$$\sum_{A=1}^{A=N} p_A = \rho^2 \left(\frac{\partial e}{\partial \rho} \right)_{s, \rho_B, \rho_C, ..., \rho_N} \tag{B35}$$

We now define the total pressure according to [see Eq. (B2)]

$$p = \sum_{A=1}^{A=N} p_A \tag{B36}$$

which leads to

$$p = \rho^2 \left(\frac{\partial e}{\partial \rho} \right)_{s, \rho_B, \rho_C, ..., \rho_N} \tag{B37}$$

At this point we have proved Eq. (B5).

To complete this discussion we need to indicate how this representation of the total pressure is related to the classic description for equilibrium systems. If we represent the *volume per unit mass* as

$$v = 1 / \rho \tag{B38}$$

we see that Eq. (B37) leads to the following expression for the total pressure

$$p = - \left(\frac{\partial e}{\partial v} \right)_{s, \rho_B, \rho_C, ..., \rho_N} \tag{B39}$$

In terms of thermo-statics (Truesdell, 1971), we consider a system at *equilibrium* having a mass *m* with the volume and internal energy given by

$$V = m \, v, \qquad U = m \, e \tag{B40}$$

Under these circumstances the equilibrium pressure takes the classic form (Gibbs, 1928, page 33) given by

$$p = -\left(\partial U/\partial V\right)_S \qquad \text{(B41)}$$

Appendix C. Useful algebraic relations

We begin by noting that the total mass density and total molar concentration for a *N*-component system are given by

$$\rho = \rho_A + \rho_B + \rho_C + ... + \rho_N \qquad \text{(C1a)}$$

$$c = c_A + c_B + c_C + ... + c_N \qquad \text{(C1b)}$$

The mass fractions and mole fractions take the form

$$\omega_A = \frac{\rho_A}{\rho}, \qquad x_A = \frac{c_A}{c}, \qquad A = 1,2,...,N \qquad \text{(C2)}$$

and the constraints on these quantities are given by

$$\sum_{B=1}^{B=N} \omega_A = 1, \quad \sum_{B=1}^{B=N} x_A = 1 \qquad \text{(C3)}$$

The mean molecular mass is defined by

$$\bar{M} = x_A M_A + x_B M_B + x_C M_C + ... + x_N M_N \qquad \text{(C4)}$$

and multiplication by the total molar concentration gives

$$c\,\bar{M} = c_A M_A + c_B M_B + c_C M_C + ... + c_N M_N \qquad \text{(C5)}$$

The species molar concentration and the species mass density are related by

$$\rho_A = c_A M_A, \quad c_A = \rho_A / M_A \qquad \text{(C6)}$$

and the use of the first of these in Eq. (C5) provides

$$c\,\bar{M} = \rho_A + \rho_B + \rho_C + ... + \rho_N \qquad \text{(C7)}$$

Use of Eq. (C1a) allows us to express this result as

$$c\,\bar{M} = \rho \qquad \text{(C8)}$$

We can use Eq. (C1b) and the second of Eqs. (C6) to obtain

$$c = \frac{\rho_A}{M_A} + \frac{\rho_B}{M_B} + \frac{\rho_C}{M_C} + ... + \frac{\rho_N}{M_N} \qquad \text{(C9)}$$

Dividing both sides by the total mass density provides the following result

$$c/\rho = \frac{\omega_A}{M_A} + \frac{\omega_B}{M_B} + \frac{\omega_C}{M_C} + ... + \frac{\omega_N}{M_N} \qquad \text{(C10)}$$

and on the basis of Eq. (C8) we have

$$\frac{1}{\bar{M}} = \frac{\omega_A}{M_A} + \frac{\omega_B}{M_B} + \frac{\omega_C}{M_C} + ... + \frac{\omega_N}{M_N} \qquad \text{(C11)}$$

For a *N*-component system, the mole fraction of species *A* is given by

$$x_A = \frac{c_A}{c} = \frac{c_A \bar{M}}{\rho} = \frac{\left(\rho_A/M_A\right)\bar{M}}{\rho} = \frac{\bar{M}}{M_A}\omega_A, \qquad A = 1,2,...,N \qquad \text{(C12)}$$

and in compact form we express this result as

$$x_A = \frac{\bar{M}}{M_A}\omega_A, \qquad A = 1,2,...,N \qquad \text{(C13)}$$

For use in the Stefan-Maxwell equations we need the product form of this result that is given by

$$x_A x_B = \frac{\bar{M}^2}{M_A M_B}\omega_A \omega_B, \qquad A,B = 1,2,...,N \qquad \text{(C14)}$$

In order to develop a relation between the gradient of the mole fraction, ∇x_A, and the gradient of the mass fraction, $\nabla \omega_A$, for a binary system we begin with Eq. (C13) and take the gradient to obtain

$$\nabla x_A = \frac{\nabla \bar{M}}{M_A}\omega_A + \frac{\bar{M}}{M_A}\nabla \omega_A, \quad A = 1,2,...,N \qquad \text{(C15)}$$

In terms of *binary systems*, the gradient of the mean molecular mass takes the form

$$\nabla \bar{M} = \left(\nabla x_A\right) M_A + \left(\nabla x_B\right) M_B = \left(M_A - M_B\right)\nabla x_A \qquad \text{(C16)}$$

and use of this result in the *binary form* of Eq. (C15) provides

$$\nabla x_A = \frac{\omega_A}{M_A}\left(M_A - M_B\right)\nabla x_A + \frac{\bar{M}}{M_A}\nabla \omega_A, \qquad A = 1,2 \qquad \text{(C17)}$$

Collecting terms leads to

$$\nabla x_A \left[1 - \frac{\omega_A}{M_A}\left(M_A - M_B\right)\right] = \frac{\bar{M}}{M_A}\nabla \omega_A, \qquad A = 1,2 \qquad \text{(C18)}$$

which can be simplified to the form

$$\nabla x_A \left(\omega_B M_A + \omega_A M_B\right) = \bar{M}\,\nabla \omega_A, \qquad A = 1,2 \qquad \text{(C19)}$$

At this point we use Eq. (C13) to obtain

$$\nabla x_A \left[\frac{x_B M_B M_A}{\bar{M}} + \frac{x_A M_A M_B}{\bar{M}}\right] = \bar{M}\,\nabla \omega_A, \qquad A = 1,2 \qquad \text{(C20)}$$

which can be simplified to (Bird, 2009)

$$\nabla x_A = \frac{\bar{M}^2}{M_A M_B}\nabla \omega_A, \qquad A = 1,2 \qquad \text{(C21)}$$

This result is Eq. (107) in the section on binary systems.

Appendix D: Assumptions, restrictions and constraints

Throughout this paper we have imposed various assumptions associated with the analysis. The most frequent of these concerned the total mass density and the total molar concentration, and an example concerning the total mass density is given in Eq. (63). In engineering analysis there is a logical sequence of events that begins with a simplifying assumption, or an *idea*, and leads to a theory with an identifiable *domain of validity*. In this section we wish to illustrate this sequence of events with an example from fluid mechanics where the path from an *assumption* to a *constraint* is well known (Whitaker, 1988)

A large class of fluid mechanical problems can be described by the continuity equation for incompressible flow

$$\nabla \cdot \mathbf{v} = 0 \qquad \text{(D1)}$$

and the Navier-Stokes equations

$$\rho\left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v}\right) = -\nabla p + \rho\mathbf{g} + \mu\nabla^2\mathbf{v} \qquad \text{(D2)}$$

The development of these two equations requires *assumptions* that may be supported by *restrictions* or reinforced by *constraints*; however, we will simply accept Eq. (D1) and Eq. (D2) without inquiring into their limitations.

As an illustration of the development of assumptions, restrictions and constraints, we consider Eq. (D2) and *assume* that the convective inertial effects are negligible in order to obtain

$$\rho\frac{\partial \mathbf{v}}{\partial t} = -\nabla p + \rho\mathbf{g} + \mu\nabla^2\mathbf{v} \qquad \text{(D3)}$$

This linear form can be easily solved for a wide variety of initial and boundary conditions, whereas the general form given by Eq. (D2) represents a difficult problem. It is important to clearly identify the assumption that leads one from Eq. (D2) to Eq. (D3) , and one way to express this is

Assumption: $\rho\mathbf{v}\cdot\nabla\mathbf{v} = 0$ (D4)

Equation (D4) indicates exactly what is being done in a *mathematical sense*, but it is not necessarily a precise description of the physics of any particular fluid mechanical process. Strictly speaking, Eq. (D4) can only be true when the velocity vector is a constant and this is not likely to occur in any real flow.

From a physical point of view, the simplification of Eq. (D2) to Eq. (D3) is based on the idea that the convective inertial term, $\rho\mathbf{v}\cdot\nabla\mathbf{v}$, is *negligible*. This immediately raises the question: "Negligible relative to what?" and one answer is that the convective inertial term is negligible relative to the viscous term. This represents the second level in our process of simplification, and in this case we express our simplification as a *restriction*.

Restriction: $\rho\mathbf{v}\cdot\nabla\mathbf{v} << \mu\nabla^2\mathbf{v}$ (D5)

In writing inequalities of this type, it is understood that the comparison is being made between the absolute values of the vectors under consideration. If we apply the idea represented by Eq. (D5) to the Navier-Stokes equations, we again obtain Eq. (D3) *provided* we are willing to assume that *small causes give rise to small effects* (Birkhoff, 1960). Equation (D5) has a definite advantage over Eq. (D4) since it indicates what is required in a *physical sense*; however, neither Eq. (D4) nor Eq. (D5) indicate *when* Eq. (D3) will be valid in terms of parameters that are known *a priori*. In order to determine precisely under what circumstances Eq. (D3) will be valid, one must be able to estimate the magnitude of the terms in Eq. (D2).

We begin our analysis of the inertial term by expressing the velocity in terms of a unit vector and the magnitude according to

$$\mathbf{v} = \mathrm{v}\boldsymbol{\lambda} \qquad \text{(D6)}$$

Here $\boldsymbol{\lambda}$ is a unit tangent vector to a streamline and v is the magnitude defined by

$$\mathrm{v} = \sqrt{\mathbf{v}\cdot\mathbf{v}} \qquad \text{(D7)}$$

The representation given by Eq. (D6) allows us to express the inertial term as

$$\rho\mathbf{v}\cdot\nabla\mathbf{v} = \mathrm{v}\boldsymbol{\lambda}\cdot\nabla\mathbf{v} \qquad \text{(D8)}$$

in which $\boldsymbol{\lambda}\cdot\nabla$ is known as the directional derivative (Stein and Barcellos, 1992, Sec. 14.7). The directional derivative can be expressed as

$$\boldsymbol{\lambda}\cdot\nabla = \frac{d}{ds} \qquad \text{(D9)}$$

where s represents the arc length measured along a streamline. Use of Eq. (D9) in Eq. (D8) provides the following *exact* representation of the inertial term

$$\rho\mathbf{v}\cdot\nabla\mathbf{v} = \rho\,\mathrm{v}\frac{d\mathbf{v}}{ds} \qquad \text{(D10)}$$

While this form is not often used in the development of solutions of the Navier-Stokes equations, it is extremely useful in the development of an estimate of the magnitude of the inertial term. To do so, we need only think about how the velocity vector changes as we proceed along a streamline and this suggests that we define an *inertial length*, L_ρ, by the estimate

$$\frac{d\mathbf{v}}{ds} = \mathbf{O}\left(\mathbf{v}/L_\rho\right) \qquad \text{(D11)}$$

One should think of the inertial length as being the distance, *along a streamline*, over which significant changes in the velocity take place. A little thought will indicate that the estimate of L_ρ requires an intuitive knowledge of the flow field, and this intuitive knowledge is based primarily on a knowledge of the no-slip condition. Use of Eq. (D11) allows us to estimate the inertial term as

$$\rho\mathbf{v}\cdot\nabla\mathbf{v} = \rho\,\mathrm{v}\frac{d\mathbf{v}}{ds} = \mathbf{O}\left(\rho\mathrm{v}^2/L_\rho\right) \qquad \text{(D12)}$$

and we need only develop an estimate of the viscous term in Eq. (D5) to complete our analysis.

We begin developing an estimate of the magnitude of the viscous term by expanding the Laplacian in rectangular, Cartesian coordinates to obtain

$$\nabla^2\mathbf{v} = \frac{\partial^2\mathbf{v}}{\partial x^2} + \frac{\partial^2\mathbf{v}}{\partial y^2} + \frac{\partial^2\mathbf{v}}{\partial z^2} \qquad \text{(D13)}$$

In terms of order of magnitude estimates, we express this result as

$$\nabla^2\mathbf{v} = \mathbf{O}\left(\frac{\Delta\mathbf{v}\big|_x}{L_x^2}\right) + \mathbf{O}\left(\frac{\Delta\mathbf{v}\big|_y}{L_y^2}\right) + \mathbf{O}\left(\frac{\Delta\mathbf{v}\big|_z}{L_z^2}\right) \qquad \text{(D14)}$$

Here $\Delta\mathbf{v}\big|_x$ represents the change of $\mathbf{v}$ that takes place over the distance L_x, and the meaning of $\Delta\mathbf{v}\big|_y$ and $\Delta\mathbf{v}\big|_z$ is analogous for the *y* and *z*-directions. We now represent the *largest* of the three terms on the right

hand side of Eq. as $\Delta\mathbf{v}/L_\mu^2$ so that our estimate of the viscous term becomes

$$\nabla^2\mathbf{v} = \mathbf{O}\left(\Delta\mathbf{v}/L_\mu^2\right) \qquad \text{(D15)}$$

We refer to L_μ as the *viscous length* and note that in general it is quite different than the inertial length. Once again we note that knowledge of the no-slip condition is crucial for the determination of a reliable estimate of the viscous length. For a large class of problems, $\Delta\mathbf{v}$ in Eq. (D15) is on the order of the velocity itself because of the no-slip condition, i.e.,

$$\Delta\mathbf{v} \approx \mathbf{v}\,, \quad \textit{because of the no-slip condition} \qquad \text{(D16)}$$

and this allows us to estimate the viscous term in Eq. (D5) as

$$\mu\nabla^2\mathbf{v} = \mathbf{O}\left(\mu\,\mathrm{v}/L_\mu^2\right) \qquad \text{(D17)}$$

Use of this result, along with the estimate of the inertial term, in the restriction given by Eq. (D5) leads to the inequality

$$\frac{\rho\mathrm{v}^2}{L_\rho} << \frac{\mu\mathrm{v}}{L_\mu^2} \qquad \text{(D18)}$$

It is traditional to define the Reynolds number in terms of the viscous length

$$Re = \frac{\rho\mathrm{v}L_\mu}{\mu} \qquad \text{(D19)}$$

and this allows us to express Eq. (D18) as a constraint that takes the form

Constraint: $$Re\left(L_\mu/L_\rho\right) << 1 \qquad \text{(D20)}$$

We refer to this as a *constraint* with the thought that the Reynolds number, the viscous length, and the inertial length will all be known, at least in an approximate sense. This means that the *domain of validity* of Eq. (D3) is established by Eq. (D20), and this is something that is not done by either the *assumption* given by Eq. (D4) or the *restriction* given by Eq. (D5).

Appendix E: Constraints for constant total molar concentration

Throughout this paper we have imposed the condition of *constant* total molar concentration and *constant* total mass density in order to obtain transport equations that could be used to determine the species molar concentration or the species mass density. In general the assumption of constant total molar concentration is associated with gas-phase diffusion processes, and the assumption of constant total mass density is associated with liquid-phase diffusion processes. In this appendix we will treat only the first of these two cases with the thought that the second case can be explored on the basis of our analysis of the first.

The assumption that the total molar concentration is constant can be expressed as

Assumption: $$c = \text{constant} \qquad \text{(E1)}$$

however, nothing is constant and what is meant by Eq. (E1) is that the variations of the total molar concentration are *small enough* so that they can be neglected. The general application of the Stefan-Maxwell equations requires that we replace $c\nabla x_A$ with ∇c_A and this leads to the restriction given by

Restriction: $$x_A\nabla c << c\nabla x_A \qquad \text{(E2)}$$

If small causes give rise to small effects (Birkhoff, 1960), the condition represented by Eq. (E2) will lead to the multi-component transport equation given by Eq. (204) and the binary form given by Eq. (124).

In order to identify the conditions under which Eq. (E2) is valid, we need to express this inequality in terms of parameters that are known a priori and to achieve this we follow the approach outlined in Appendix D. While that approach has led to an established success, the problem under consideration in this appendix is more difficult and further study is in order.

As an example we consider the process illustrated in Fig. E1 in which the γ-phase represents a flowing fluid. The κ–γ interface might be an interface at which adsorption or desorption occurs, or an interface at which a catalytic reaction occurs, or an interface at which mass transfer between the κ-phase and the γ-phase occurs. This could occur because the κ-phase is a porous catalyst phase or because of a difference in the chemical potential of species *A* between the κ-phase and the γ-phase. The direction of mean flow is indicated by the unit vector $\bar{\boldsymbol{\lambda}}$, and the direction orthogonal to the mean flow is indicated by the unit vector $\bar{\mathbf{n}}$.

Directing our attention to Eq. (E2) we express that result in the form

Restriction: $$c^{-1}\nabla c << x_A^{-1}\nabla x_A \qquad \text{(E3)}$$

And note that we need to consider the gradients in the direction of flow (the $\bar{\boldsymbol{\lambda}}$-direction indicated in Fig. 1E) and the direction orthogonal to the direction of flow (the $\bar{\mathbf{n}}$-direction indicated in Fig. 1E). We represent the two inequalities associated with Eq. (E3) as

Restriction: $$c^{-1}\bar{\boldsymbol{\lambda}}\cdot\nabla c << x_A^{-1}\bar{\boldsymbol{\lambda}}\cdot\nabla x_A \qquad \text{(E4a)}$$

Restriction: $$c^{-1}\bar{\mathbf{n}}\cdot\nabla c << x_A^{-1}\bar{\mathbf{n}}\cdot\nabla x_A \qquad \text{(E4b)}$$

and note that the second of these is likely to be the most important restriction. We limit our analysis to ideal gases so that the equation of state is given by

$$pV = nRT\,, \quad \text{ideal gas} \qquad \text{(E5)}$$

and the total molar concentration can be expressed as

$$c = p/RT \qquad \text{(E6)}$$

For an ideal gas, the left hand side of Eq. (E3) takes the form

$$c^{-1}\nabla c = p^{-1}\nabla p - T^{-1}\nabla T \qquad \text{(E7)}$$

and this yields two restrictions associated with Eq. (E3) that are given by

Restrictions:

$$p^{-1}\nabla p << x_A^{-1}\nabla x_A\,, \quad T^{-1}\nabla T << x_A^{-1}\nabla x_A \qquad \text{(E8)}$$

In this appendix we will consider only the first of these restrictions and that requires an analysis of the

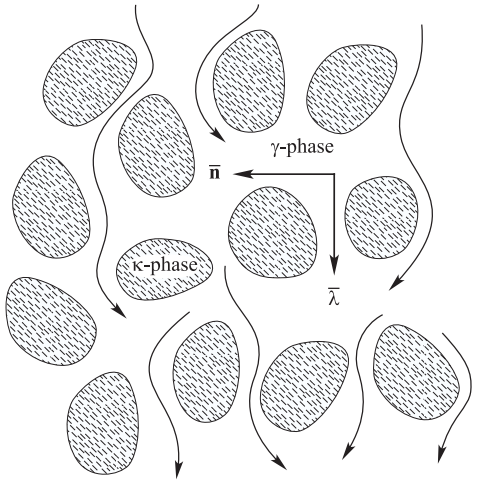

Fig. E1. Mass transfer in a two-phase system

Navier-Stokes equations. The second restriction requires an analysis of the thermal energy equation, and in many cases it would be appropriate to include the rate of chemical reaction and the heat of reaction.

We begin our analysis of the first of Eqs. (E8) by considering the direction of the mean flow illustrated in Fig. E1. This leads to a restriction given by

Restriction: $$p^{-1}\,\bar{\boldsymbol{\lambda}}\cdot\nabla p << x_A^{-1}\,\bar{\boldsymbol{\lambda}}\cdot\nabla x_A \tag{E9}$$

and we can make use of Eq. (D2) to obtain

$$p^{-1}\,\bar{\boldsymbol{\lambda}}\cdot\nabla p = \frac{1}{p}\mathbf{O}\left[\rho\frac{\partial(\mathbf{v}\cdot\bar{\boldsymbol{\lambda}})}{\partial t}\right] + \frac{1}{p}\mathbf{O}\left[\mathbf{v}\cdot\nabla(\mathbf{v}\cdot\bar{\boldsymbol{\lambda}})\right] + \frac{1}{p}\mathbf{O}\left[\rho\mathbf{g}\cdot\bar{\boldsymbol{\lambda}}\right] + \frac{1}{p}\mathbf{O}\left[\mu\nabla^2(\mathbf{v}\cdot\bar{\boldsymbol{\lambda}})\right] \tag{E10}$$

The magnitude of the velocity in the direction of the mean flow is given by

$$\mathrm{v} = \mathbf{v}\cdot\bar{\boldsymbol{\lambda}} \tag{E11}$$

and this allows us to express Eq. (E10) in the form

$$p^{-1}\,\bar{\boldsymbol{\lambda}}\cdot\nabla p = \frac{1}{p}\mathbf{O}\left(\rho\frac{\partial \mathrm{v}}{\partial t}\right) + \frac{1}{p}\mathbf{O}\left(\rho\mathbf{v}\cdot\nabla\mathrm{v}\right) + \frac{1}{p}\mathbf{O}\left(\rho\mathbf{g}\cdot\bar{\boldsymbol{\lambda}}\right) + \frac{1}{p}\mathbf{O}\left(\mu\nabla^2\mathrm{v}\right) \tag{E12}$$

Following the development given in Appendix D, we estimate the inertial and viscous terms according to

$$\rho\mathbf{v}\cdot\nabla\mathrm{v} = \mathbf{O}\left(\rho\mathrm{v}^2/L_\rho\right), \quad \mu\nabla^2\mathrm{v} = \mathbf{O}\left(\mu\Delta\mathrm{v}/L_\mu^2\right) \tag{E13}$$

and we estimate the local acceleration as

$$\rho\frac{\partial \mathrm{v}}{\partial t} = \mathbf{O}\left(\frac{\rho\mathrm{v}}{t^*}\right) \tag{E14}$$

in which t^* is a characteristic process time. Use of Eqs. (E13) and (E14) in Eq. (E12) leads to the following estimate for the pressure gradient in the direction of the mean flow:

$$p^{-1}\,\bar{\boldsymbol{\lambda}}\cdot\nabla p = \frac{1}{p}\mathbf{O}\left(\rho\,\mathrm{v}/t^*\right) + \frac{1}{p}\mathbf{O}\left(\rho\mathrm{v}^2/L_\rho\right) + \frac{1}{p}\mathbf{O}\left(\rho\mathbf{g}\cdot\bar{\boldsymbol{\lambda}}\right) + \frac{1}{p}\mathbf{O}\left(\mu\,\mathrm{v}/L_\mu^2\right) \tag{E15}$$

Here we have assumed that the no-slip condition is valid at the γ–κ interface, thus $\Delta\mathrm{v}$ can be replaced with v.

The magnitude of the pressure can be estimated as

$$p = \mathbf{O}\left(\rho C^2\right) \tag{E16}$$

where C is the speed of sound (Whitaker, 1981, Sec. 10.3). Use of this result in Eq. (E15) leads to

$$p^{-1}\,\bar{\boldsymbol{\lambda}}\cdot\nabla p = \mathbf{O}\left(\frac{M}{Ct^*}\right) + \mathbf{O}\left(\frac{M^2}{L_\rho}\right) + \mathbf{O}\left(\frac{M^2}{\mathrm{Fr}}\frac{1}{L_\mu}\right) + \mathbf{O}\left(\frac{M^2}{\mathrm{Re}}\frac{1}{L_\mu}\right) \tag{E17}$$

in which the following dimensionless quantities have been used:

$$M = \text{Mach number} = \mathrm{v}/C$$
$$\mathrm{Fr} = \text{Froude number} = \mathrm{v}^2/\mathbf{g}\cdot\bar{\boldsymbol{\lambda}}L_\mu \tag{E18}$$
$$\mathrm{Re} = \text{Reynolds number} = \rho\mathrm{v}L_\mu/\mu$$

Directing our attention to the right hand side of Eq. (E9) we estimate the gradient as

$$\bar{\boldsymbol{\lambda}}\cdot\nabla x_A = \mathbf{O}\left(\Delta x_A/L_c\right) \tag{E19}$$

in which L_c represents the *convective length scale* for the transport of species *A*. Use of this result along with Eq. (E17) in Eq. (E9) leads to the constraint given by

$$\mathbf{O}\left(\frac{M}{Ct^*}\right) + \mathbf{O}\left(\frac{M^2}{L_\rho}\right) + \mathbf{O}\left(\frac{M^2}{\mathrm{Fr}}\frac{1}{L_\mu}\right) + \mathbf{O}\left(\frac{M^2}{\mathrm{Re}}\frac{1}{L_\mu}\right) << \mathbf{O}\left(\frac{\Delta x_A}{x_A}\frac{1}{L_c}\right) \tag{E20}$$

Since $\Delta x_A/x_A$ will be less than or on the order of one, a conservative representation of this constraint is given by

$$\mathbf{O}\left(\frac{M\,L_c}{Ct^*}\right) + \mathbf{O}\left(\frac{M^2L_c}{L_\rho}\right) + \mathbf{O}\left(\frac{M^2}{\mathrm{Fr}}\frac{L_c}{L_\mu}\right) + \mathbf{O}\left(\frac{M^2}{\mathrm{Re}}\frac{L_c}{L_\mu}\right) << 1 \tag{E21}$$

For Mach numbers small compared to one, it will be difficult to violate this constraint; however, one must remember that this constraint is based on Eq. (E9) and we also need to consider the restriction given by

Restriction: $$p^{-1}\,\bar{\mathbf{n}}\cdot\nabla p << x_A^{-1}\,\bar{\mathbf{n}}\cdot\nabla x_A \tag{(E22)}$$

To explore this restriction, we express Eq. (E10) in the form

$$p^{-1}\,\bar{\mathbf{n}}\cdot\nabla p = \frac{1}{p}\mathbf{O}\left[\rho\frac{\partial(\mathbf{v}\cdot\bar{\mathbf{n}})}{\partial t}\right] + \frac{1}{p}\mathbf{O}\left[\rho\mathbf{v}\cdot\nabla(\mathbf{v}\cdot\bar{\mathbf{n}})\right] + \frac{1}{p}\mathbf{O}\left[\rho\mathbf{g}\cdot\bar{\mathbf{n}}\right] + \frac{1}{p}\mathbf{O}\left[\mu\nabla^2(\mathbf{v}\cdot\bar{\mathbf{n}})\right] \tag{E23}$$

For the special case in which $\bar{\mathbf{n}}$ is replaced by the unit normal vector to a streamline, the inertial term takes the form (Whitaker, Sec.7.4, 1968)

$$\rho\mathbf{v}\cdot\nabla(\mathbf{v}\cdot\bar{\mathbf{n}}) = \rho\mathbf{v}\cdot\nabla\mathbf{v}\cdot\mathbf{n} = \rho v^2\kappa \tag{E24}$$

in which κ is the curvature (Stein & Barcellos, Sec. 13.4, 1992). Here it is important to keep in mind that $\bar{\mathbf{n}}$ is a constant unit vector as indicated in Fig. E1 while the unit normal to a streamline will be a function of position. Equation (E24) helps us to estimate the inertial term in Eq. (E23) as

$$\frac{1}{p}\mathbf{O}\left[\rho\mathbf{v}\cdot\nabla(\mathbf{v}\cdot\bar{\mathbf{n}})\right] = \frac{1}{p}\rho v^2\,\bar{\kappa} \tag{E25}$$

in which $\bar{\kappa}$ represents some appropriate mean curvature associated with the system illustrated in Fig. E1. About the other terms in Eq. (E23) we can only say that they will be smaller than the analogous terms in Eq. (E10). This means that we can *over estimate* $p^{-1}\,\bar{\mathbf{n}}\cdot\nabla p$ as

$$p^{-1}\,\bar{\mathbf{n}}\cdot\nabla p = \frac{1}{p}\mathbf{O}\left[\rho\frac{\partial(\mathbf{v}\cdot\bar{\boldsymbol{\lambda}})}{\partial t}\right] + \frac{1}{p}\mathbf{O}\left[\rho v^2\,\bar{\kappa}\right] + \frac{1}{p}\mathbf{O}\left[\rho\mathbf{g}\cdot\bar{\mathbf{n}}\right] + \frac{1}{p}\mathbf{O}\left[\mu\nabla^2(\mathbf{v}\cdot\bar{\boldsymbol{\lambda}})\right] \tag{E26}$$

and follow our earlier development to obtain

$$p^{-1}\,\bar{\mathbf{n}}\cdot\nabla p = \mathbf{O}\left(\frac{M}{Ct^*}\right) + \mathbf{O}\left[M^2\,\bar{\kappa}\right] + \mathbf{O}\left(\frac{M^2}{\mathrm{Fr}}\frac{1}{L_\mu}\right) + \left(\frac{M^2}{\mathrm{Re}}\frac{1}{L_\mu}\right) \tag{E27}$$

In this case the Froude number is defined by

$$\mathrm{Fr} = \text{Froude number} = v^2/\mathbf{g}\cdot\bar{\mathbf{n}}\,L_\mu \tag{E28}$$

Directing our attention to the right hand side of Eq. (E22) we estimate the gradient as

$$\bar{\mathbf{n}}\cdot\nabla x_A = \mathbf{O}\left(\Delta x_A/L_{\mathscr{D}}\right) \qquad ((\mathrm{E29}))$$

in which $L_{\mathscr{D}}$ represents the *diffusive length scale* for the transport of species *A*. Use of this result along with Eq. (E27) in Eq. (E22) leads to the constraint

$$\mathbf{O}\left(\frac{M}{Ct^*}\right) + \mathbf{O}\left[M^2\,\bar{\kappa}\right] + \mathbf{O}\left(\frac{M^2}{\mathrm{Fr}}\frac{1}{L_\mu}\right) + \left(\frac{M^2}{\mathrm{Re}}\frac{1}{L_\mu}\right) << \mathbf{O}\left(\frac{\Delta x_A}{x_A}\frac{1}{L_\mathrm{D}}\right) \tag{E30}$$

Since $\Delta x_A/x_A$ will be less than or on the order of one, a conservative representation of this constraint is given by

$$\mathbf{O}\left(\frac{M\,L_{\mathscr{D}}}{Ct^*}\right) + \mathbf{O}\left[M^2\,L_{\mathscr{D}}\bar{\kappa}\right] + \mathbf{O}\left(\frac{M^2}{\mathrm{Fr}}\frac{L_{\mathscr{D}}}{L_\mu}\right) + \left(\frac{M^2}{\mathrm{Re}}\frac{L_{\mathscr{D}}}{L_\mu}\right) << 1 \tag{E31}$$

Once again, it will be difficult to violate this constraint whenever the Mach number is small compared to one.

At this point we have developed a constraint associated with the restriction given by the first of Eqs. (E8); however, the second restriction given by

$$\text{Restriction:} \qquad T^{-1}\nabla T << x_A^{-1}\nabla x_A \tag{E32}$$

still needs to be explored. This will require an analysis of the thermal energy equation and for most realistic systems the thermal energy equation will be coupled to a mass transfer and reaction process. In addition, the constraints associated with non-ideal gases need to be developed along with the constraints associated with the assumption for liquid phase mass transfer processes given by

$$\text{Assumption:} \qquad \rho = \text{constant} \tag{E33}$$

The constraints associated with this assumption will be much more difficult to obtain than those given by Eqs. (E21) and (E31); however, the developments presented in this appendix should provide guidance for the attack on Eq. (E33).