A Few Basic Facts About Isothermal Mass Transfer in a Binary Mixture

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Table of Contents

Introduction	1
I. Problem Formulation in Terms of Mass	2
II. Problem Formulation in Terms of Moles	7
III. Problem Formulation in Terms of Hybrid Mass/Moles Reference	12
IV. Steady State Analysis (constant center-of-mass velocity)	13
V. Steady State Analysis (variable center-of-mass velocity)	16

Introduction

The purpose of these notes is to provide a complete analysis of a very simple system, namely isothermal mass transfer in a binary mixture. As engineers, we often think of a diffusion process as a membrane separating a reservoir with a high-concentration of solute from that with a low-concentration of solute. We recall that the steady-state solution is a linear profile from one boundary concentration to the next. This picture is over-simplified and contains numerous assuptions. It is not the general case.

A correct formulation of this problem is essential in obtaining a rigorous, generalized solution. Part of the confusion associated with mass transfer is that there are many degrees of freedom in formulating the problem, resulting in potentially an infinity of problem formulations. Each of these formulations, if solved in a manner consistent with the arbitrary choices that went into the problem formulation will yield results consistent with any other formulation. In sections I and II of this hand-out, we present two common formulations of isothermal mass transfer in a binary mixture. In section III, we present a third, uncommon formulation to illustrate the arbitrary nature of the choices as well as the ability to rectify the results from different formulations.

In section IV, we examine the steady-state solution of the evolution equations for a simple system (an inviscid, ideal gas) under the assumption that the center-of-mass velocity is constant. We would like to make this assumption because it allows us to decouple the momentum balance and the mass balances. If this assumption is not true then we have to solve the momentum and mass balances simultaneously. In the solution of the evolution equations, we come upon a contradiction that indicates that the assumption that the center-of-mass velocity is constant is an unphysical assumption.

In section V, we examine the steady-state solution of the evolution equations for a simple system (an inviscid, ideal gas) without the assumption that the center-of-mass velocity is constant. We find that the coupled mass and momentum balances cannot be solved analytically but can be solved numerically. We provide plots of the numerical solution for different conditions.

In this hand-out, we attempt to follow the notation used in “Transport Phenomena” by Bird, Stewart & Lightfoot, Second Edition, in terms of nomenclature, capitalization, subscripts, and asterisks.

I. Problem Formulation in Terms of Mass

In this section of the document, we formulate the problem of isothermal mass transfer in a binary system completely in terms of mass and mass related variables, such as the mass density, mass fraction, mass-averaged velocity, and mass fluxes. We provide (A) variable definitions, (B) evolution equations, (C) constitutive relations, (D) assumptions, and (E) conclusions. Parts of the text refers back to Molecular Dynamics (MD) simulations because this work was initially prompted by a desire to have a macroscopic description that would serve as a coarse-grained theory upon which molecular simulations could be mapped.

I.A. variable definitions

mass density

ρ

In an MD simulation ρ has an unambiguous definition:

$$\rho = \frac{N_A m_A + N_B m_B}{V} \tag{I.1}$$

where N_A and N_B are the number of molecules of A and B in the simulation, and m_A and m_B are the masses of a molecule of A and B respectively.

mass fractions

w_A and w_B

In an MD simulation w_A and w_B have unambiguous definitions:

$$w_A = \frac{N_A m_A}{N_A m_A + N_B m_B} \qquad w_B = \frac{N_B m_B}{N_A m_A + N_B m_B} \tag{I.2}$$

component mass densities

ρ_A and ρ_B

In an MD simulation ρ_A and ρ_B have unambiguous definitions:

$$\rho_A = w_A \rho \qquad \rho_B = w_B \rho \tag{I.3}$$

component velocities relative to stationary laboratory frame of reference

$\mathbf{v}_A$ and $\mathbf{v}_B$

In an MD simulation $\mathbf{v}_A$ and $\mathbf{v}_B$ have unambiguous definitions:

$$\mathbf{v}_A = \frac{1}{N_A}\sum_{i=1}^{N_A} \mathbf{v}_{A,i} \qquad \mathbf{v}_B = \frac{1}{N_B}\sum_{i=1}^{N_B} \mathbf{v}_{B,i} \tag{I.4}$$

where $\mathbf{v}_{A,i}$ is the velocity of the ith molecule of component A relative to the laboratory frame of reference.

total mass flux of each component relative to stationary laboratory frame of reference

$\mathbf{n}_A$ and $\mathbf{n}_B$

The total flux of each component can be unambiguously determined as

$$\mathbf{n}_A = \rho w_A \mathbf{v}_A \qquad\qquad \mathbf{n}_B = \rho w_B \mathbf{v}_B \tag{I.5}$$

mass-averaged (or center-of-mass) velocity relative to laboratory frame of reference

$\mathbf{v}$

The mass-averaged velocity is defined as

$$\mathbf{v} = w_A \mathbf{v}_A + w_B \mathbf{v}_B \tag{I.6}$$

convective mass flux of each component relative to stationary laboratory frame of reference

χ_A and χ_B

The convective flux of each component (carried by the mass-averaged velocity) can be unambiguously determined as

$$\chi_A = \rho w_A \mathbf{v} \qquad\qquad \chi_B = \rho w_B \mathbf{v} \tag{I.7}$$

diffusive flux of each component relative to mass-averaged velocity

$\mathbf{j}_A$ and $\mathbf{j}_B$

The diffusive flux of each component can be unambiguously determined because the total flux is defined as the sum of the convective and diffusive flux.

$$\mathbf{j}_A = \mathbf{n}_A - \chi_A \qquad\qquad \mathbf{j}_B = \mathbf{n}_B - \chi_B \tag{I.8}$$

Substituting equations (5) and (7) into equation (8) yields

$$\mathbf{j}_A = \rho w_A (\mathbf{v}_A - \mathbf{v}) \qquad\qquad \mathbf{j}_B = \rho w_B (\mathbf{v}_B - \mathbf{v}) \tag{I.9}$$

Substituting equations (6) into equation (9) yields

$$\mathbf{j}_A = \rho w_A w_B (\mathbf{v}_A - \mathbf{v}_B) \qquad\qquad \mathbf{j}_B = \rho w_A w_B (\mathbf{v}_B - \mathbf{v}_A) \tag{I.10}$$

Comments:

1. You can see that the diffusive mass flux is defined without ever introducing any constitutive relation such as Fick’s law.
2. You can also see from equation (10) that there is no total center of mass motion due to the diffusive fluxes.

$$\mathbf{j}_A + \mathbf{j}_B = 0 \tag{I.11}$$

I.B. evolution equations

We assume here that there is no reaction.

evolution equation on total mass (continuity equation)

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \left(\mathbf{n}_A + \mathbf{n}_B\right) \tag{I.12}$$

$$\begin{aligned}\frac{\partial \rho}{\partial t} &= -\nabla \cdot \left(\boldsymbol{\chi}_A + \mathbf{j}_A + \boldsymbol{\chi}_B + \mathbf{j}_B\right) = -\nabla \cdot \left(\boldsymbol{\chi}_A + \boldsymbol{\chi}_B\right) = -\nabla \cdot \left(\rho w_A \mathbf{v} + \rho w_B \mathbf{v}\right) \\ &= -\nabla \cdot \left(\rho \mathbf{v}\right)\end{aligned} \tag{I.13}$$

Because the diffusive flux has no net mass transport, it drops out of the overall mass balance.

evolution equation on mass of component A

$$\frac{\partial \rho w_A}{\partial t} = -\nabla \cdot \mathbf{n}_A \tag{I.14}$$

$$\frac{\partial \rho w_A}{\partial t} = -\nabla \cdot \left(\boldsymbol{\chi}_A + \mathbf{j}_A\right) = -\nabla \cdot \left(\rho w_A \mathbf{v}\right) - \nabla \cdot \mathbf{j}_A \tag{I.15}$$

We can use the product rule on the accumulation term and the convection term in equation (15) and we can substitute in equation (13) into (15) to obtain

$$w_A \frac{\partial \rho}{\partial t} + \rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - w_A \nabla \cdot \left(\rho \mathbf{v}\right) - \nabla \cdot \mathbf{j}_A \tag{I.16}$$

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - \nabla \cdot \mathbf{j}_A \tag{I.17}$$

Equation (17) is the expression typically used as the evolution equation for the mass of component A. It is only true in the absence of reaction. An analogous expression can be written for component B.

I.C. constitutive relations

One can write Fick's law in a virtual infinity of forms. However, given our decisions to (i) define material transport in terms of mass fluxes and (ii) define diffusion relative to the mass-averaged velocity, there is only one intelligent choice for Fick's law, namely one where (iii) the driving force is given in terms of the gradient of the mass fraction.

$$\mathbf{j}_A = -\rho D_{AB} \nabla w_A \qquad\qquad \mathbf{j}_B = -\rho D_{BA} \nabla w_B \tag{I.18}$$

Given this choice

$$D_{AB} = D_{BA} = D \tag{I.19}$$

Comments:
1. For any other choice of driving force, these two diffusivities will not be the same.
2. Since there is only one independent variable in an isothermal binary diffusion process, regardless of the choice of gradient, there will always be some relation between D_{AB} and D_{BA}.

With this constitutive relation, the evolution equation for the mass fraction of A, equation (17) becomes

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A + \nabla \cdot \left(\rho D \nabla w_A \right) \tag{I.20}$$

We can use the triple product rule on the diffusive term.

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A + \rho D \nabla^2 w_A + \rho \nabla D \cdot \nabla w_A + D \nabla \rho \cdot \nabla w_A \tag{I.21}$$

If the diffusivity is not a function of ρ and w_A, then equation (21) drops one term and becomes

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A + \rho D \nabla^2 w_A + D \nabla \rho \cdot \nabla w_A \qquad \text{for constant } D \tag{I.22}$$

If in addition to a constant diffusivity, we also have an incompressible fluid, equation (22) becomes

$$\frac{\partial w_A}{\partial t} = -\mathbf{v} \cdot \nabla w_A + D \nabla^2 w_A \qquad \text{for constant } D \text{ and incompressible fluid} \tag{I.23}$$

I.D. assumptions

Aside from the definition of the system being binary, isothermal, and free of chemical reaction, there are three important assumptions in this derivation.

1. We assumed that we would work the problem with mass fluxes.
2. We assumed that we would measure the diffusive flux relative to the mass-averaged velocity. This assumption was totally arbitrary, but is a good choice because equation (11) is not satisfied without other choices of reference velocity.
3. We assumed that the driving force in Fick's was expressed as a gradient in mass fraction.

These three assumptions define our diffusivity. If we change any of these assumptions, then we will have to compute a different numerical value of the diffusivity.

I.E. conclusions

There is no ambiguity in a well-defined description of isothermal binary mass transport.
It is important to realize what assumptions are made.
There is only one independent diffusivity in this system.
The diffusive flux is defined before the introduction of the constitutive relation, Fick's law. All Fick's law does is define the diffusivity.

II. Problem Formulation in Terms of Moles

In this section of the document, we formulate the problem of isothermal mass transfer in a binary system completely in terms of moles and mole-related variables, such as the molar density, mole fraction, molar-averaged velocity, and molar fluxes. In a precisely analogous procedure to what was done in section I., we provide (A) variable definitions, (B) evolution equations, (C) constitutive relations, (D) assumptions, and (E) conclusions. Additionally, we relate the diffusivity from section I to the diffusivity from section II.

II.A. variable definitions

molar density

c

In an MD simulation c has an unambiguous definition:

$$c = \frac{N_A + N_B}{V} \qquad \text{(II.1)}$$

where N_A and N_B are the number of molecules of A and B in the simulation.

mole fractions

x_A and x_B

In an MD simulation x_A and x_B have unambiguous definitions:

$$x_A = \frac{N_A}{N_A + N_B} \qquad x_B = \frac{N_B}{N_A + N_B} \qquad \text{(II.2)}$$

component molar densities

c_A and c_B

In an MD simulation c_A and c_B have unambiguous definitions:

$$c_A = x_A c \qquad c_B = x_B c \qquad \text{(II.3)}$$

component velocities relative to stationary laboratory frame of reference

$\mathbf{v}_A$ and $\mathbf{v}_B$

In an MD simulation $\mathbf{v}_A$ and $\mathbf{v}_B$ have unambiguous definitions:

$$\mathbf{v}_A = \frac{1}{N_A}\sum_{i=1}^{N_A}\mathbf{v}_{A,i} \qquad \mathbf{v}_B = \frac{1}{N_B}\sum_{i=1}^{N_B}\mathbf{v}_{B,i} \qquad \text{(II.4)}$$

where $\mathbf{v}_{A,i}$ is the velocity of the i^{th} molecule of component A. relative to the laboratory frame of reference. These are the same definitions as were used in the mass-referenced case.

total molar flux of each component relative to stationary laboratory frame of reference

$\mathbf{N}_A$ and $\mathbf{N}_B$

The total flux of each component can be unambiguously determined as

$$\mathbf{N}_A = cx_A\mathbf{v}_A \qquad \mathbf{N}_B = cx_B\mathbf{v}_B \tag{II.5}$$

molar-averaged (or center-of-moles) velocity relative to laboratory frame of reference

$\mathbf{v}^*$

The molar-averaged velocity is defined as

$$\mathbf{v}^* = x_A\mathbf{v}_A + x_B\mathbf{v}_B \tag{II.6}$$

convective molar flux of each component relative to stationary laboratory frame of reference

X_A and X_B

The convective flux of each component (carried by the molar-averaged velocity) can be unambiguously determined as

$$\mathrm{X}_A = cx_A\mathbf{v}^* \qquad \mathrm{X}_B = cx_B\mathbf{v}^* \tag{II.7}$$

diffusive molar flux of each component relative to molar-averaged velocity

$\mathbf{J}^*_A$ and $\mathbf{J}^*_B$

The diffusive flux of each component can be unambiguously determined because the total flux is defined as the sum of the convective and diffusive flux.

$$\mathbf{J}^*_A = \mathbf{N}_A - \mathrm{X}_A \qquad \mathbf{J}^*_B = \mathbf{N}_B - \mathrm{X}_B \tag{II.8}$$

Substituting equations (5) and (7) into equation (8) yields

$$\mathbf{J}^*_A = cx_A\left(\mathbf{v}_A - \mathbf{v}^*\right) \qquad \mathbf{J}^*_B = cx_B\left(\mathbf{v}_B - \mathbf{v}^*\right) \tag{II.9}$$

Substituting equations (6) into equation (9) yields

$$\mathbf{J}^*_A = cx_Ax_B\left(\mathbf{v}_A - \mathbf{v}_B\right) \qquad \mathbf{J}^*_B = cx_Ax_B\left(\mathbf{v}_B - \mathbf{v}_A\right) \tag{II.10}$$

Comments:

1. You can see that the diffusive molar flux is defined without ever introducing any constitutive relation such as Fick’s law.
2. You can also see from equation (10) that there is no total molar-averaged motion due to the diffusive fluxes.

$$\mathbf{J}^*_A + \mathbf{J}^*_B = 0 \tag{II.11}$$

II.B. evolution equations

We assume here that there is no reaction.

evolution equation on total moles (continuity equation)

$$\frac{\partial c}{\partial t} = -\nabla \cdot (\mathbf{N}_A + \mathbf{N}_B) \qquad \text{(II.12)}$$

$$\begin{aligned}\frac{\partial c}{\partial t} &= -\nabla \cdot (\mathrm{X}_A + \mathbf{J}^*_A + \mathrm{X}_B + \mathbf{J}^*_B) = -\nabla \cdot (\mathrm{X}_A + \mathrm{X}_B) = -\nabla \cdot (c x_A \mathbf{v}^* + c x_B \mathbf{v}^*) \\ &= -\nabla \cdot (c\mathbf{v}^*)\end{aligned} \qquad \text{(II.13)}$$

Because the diffusive flux has no net mass transport, it drops out of the overall mass balance.

evolution equation on moles of component A

$$\frac{\partial c x_A}{\partial t} = -\nabla \cdot \mathbf{N}_A \qquad \text{(II.14)}$$

$$\frac{\partial c x_A}{\partial t} = -\nabla \cdot (\mathrm{X}_A + \mathbf{J}^*_A) = -\nabla \cdot (c x_A \mathbf{v}^*) - \nabla \cdot \mathbf{J}^*_A \qquad \text{(II.15)}$$

We can use the product rule on the accumulation term and the convection term in equation (15) and we can substitute in equation (13) into (15) to obtain

$$x_A \frac{\partial c}{\partial t} + c\frac{\partial x_A}{\partial t} = -c\mathbf{v}^* \cdot \nabla x_A - x_A \nabla \cdot (c\mathbf{v}^*) - \nabla \cdot \mathbf{J}^*_A \qquad \text{(II.16)}$$

$$c\frac{\partial x_A}{\partial t} = -c\mathbf{v}^* \cdot \nabla x_A - \nabla \cdot \mathbf{J}^*_A \qquad \text{(II.17)}$$

Equation (17) is the expression typically used as the evolution equation for the moles of component A. It is only true in the absence of reaction. An analogous expression can be written for component B.

II.C. constitutive relations

One can write Fick's law in a virtual infinity of forms. However, given our decisions to (i) define material transport in terms of molar fluxes and (ii) define diffusion relative to the molar-averaged velocity, there is only one intelligent choice for Fick's law, namely one where (iii) the driving force is given in terms of the gradient of the mole fraction.

$$\mathbf{J}^*_A = -cD^*_{AB} \nabla x_A \qquad \mathbf{J}^*_B = -cD^*_{BA} \nabla x_B \qquad \text{(II.18)}$$

Given this choice

$$D^*_{AB} = D^*_{BA} = D^* \qquad \text{(II.19)}$$

Comments:
1. For any other choice of driving force, these two diffusivities will not be the same.
2. Since there is only one independent variable in an isothermal binary diffusion process, regardless of the choice of gradient, there will always be some relation between D^*_{AB} and D^*_{BA}.

With this constitutive relation, the evolution equation for the mole fraction of A, equation (17) becomes

$$c\frac{\partial x_A}{\partial t} = -c\mathbf{v}^* \cdot \nabla x_A + \nabla \cdot \left(cD^* \nabla x_A\right) \qquad \text{(II.20)}$$

We can use the triple product rule on the diffusive term.

$$c\frac{\partial x_A}{\partial t} = -c\mathbf{v}^* \cdot \nabla x_A + cD^* \nabla^2 x_A + c\nabla D^* \cdot \nabla x_A + D^* \nabla c \cdot \nabla x_A \qquad \text{(II.21)}$$

If the diffusivity is not a function of c and x_A, then equation (21) drops one term and becomes

$$c\frac{\partial x_A}{\partial t} = -c\mathbf{v}^* \cdot \nabla x_A + cD^* \nabla^2 x_A + D^* \nabla c \cdot \nabla x_A \qquad \text{for constant } D^* \qquad \text{(II.22)}$$

If in addition to a constant diffusivity, we also have a fluid with constant molar density, equation (22) becomes

$$\frac{\partial x_A}{\partial t} = -\mathbf{v}^* \cdot \nabla x_A + D^* \nabla^2 x_A \qquad \text{for constant } D^* \text{ and } c \qquad \text{(II.23)}$$

II.D. assumptions

Aside from the definition of the system being binary, isothermal, and free of chemical reaction, there are three important assumptions in this derivation.

1. We assumed that we would work the problem with molar fluxes.
2. We assumed that we would measure the diffusive flux relative to the molar-averaged velocity. This assumption was totally arbitrary, but is a good choice because equation (11) is not satisfied without other choices of reference velocity.
3. We assumed that the driving force in Fick's was expressed as a gradient in mole fraction.

These three assumptions define our diffusivity. If we change any of these assumptions, then we will have to compute a different numerical value of the diffusivity.

II.E. conclusions

We have the same conclusions as those for the mass-referenced system.

II.F. relationship between diffusivities

In Case I, we had a single diffusivity, *D*, and in Case II, we had a single diffusivity, $D*$. These diffusivities are related. The easiest way to see the relation is to recall that the definitions of $\mathbf{v}_A$ and $\mathbf{v}_B$ are the same in both cases. As a result, if we can express, each diffusivity in terms of these velocities, then we can obtain a relation between the two diffusvities.

First combine equations (10), (18), and (19) for both cases:

$$\mathbf{j}_A = \rho w_A w_B \left(\mathbf{v}_A - \mathbf{v}_B\right) = -\rho D \nabla w_A \qquad \mathbf{j}_B = \rho w_A w_B \left(\mathbf{v}_B - \mathbf{v}_A\right) = -\rho D \nabla w_B \tag{II.24}$$

$$\mathbf{J*}_A = c x_A x_B \left(\mathbf{v}_A - \mathbf{v}_B\right) = -cD*\nabla x_A \qquad \mathbf{J*}_B = c x_A x_B \left(\mathbf{v}_B - \mathbf{v}_A\right) = -cD*\nabla x_B \tag{II.25}$$

In each case (for either species) solve for the difference in velocities and equate.

$$\left(\mathbf{v}_A - \mathbf{v}_B\right) = \frac{-D\nabla w_A}{w_A w_B} = \frac{-D*\nabla x_A}{x_A x_B} \tag{II.26}$$

Solving for the ratio of diffusivities we have:

$$\frac{D}{D*} = \frac{w_A w_B}{x_A x_B}\frac{\nabla x_A}{\nabla w_A} = \frac{w_A w_B}{x_A x_B}\left(\frac{\partial x_A}{\partial w_A}\right) \tag{II.27}$$

We can analytically evalute the partial derivative

$$\left(\frac{\partial x_A}{\partial w_A}\right) = \frac{x_A x_B}{w_A w_B} \tag{II.28}$$

As a result,

$$D = D* \tag{II.29}$$

The diffusivity from the mass-referenced case and the diffusivity from the molar-referenced case turn out to be the same diffusivity.

III. Problem Formulation in terms of hybrid mass/moles reference

The purpose of this demonstration is to indicate that one can choose any arbitrary formulation of a diffusive process. It also demonstrates that some choices are more easy to live with than others. In this case we again limit ourselves to a binary, isothermal system free of reaction. Additionally, we assume that our description of mass transport will use mass fluxes. These mass fluxes will be references relative to the mass-average velocity. As a result our derivation, will be the same up to equation (I.17). Now we choose a different form of Fick's law, which employs the gradient of the mole fraction.

$$\mathbf{j}_A = -\rho D^{\bullet}_{AB} \nabla x_A \qquad \mathbf{j}_B = -\rho D^{\bullet}_{BA} \nabla x_B \tag{III.1}$$

The fluxes are still equal and opposite, so we can solve for the relationship between the two diffusivities, $D^{\bullet}_{AB}$ and $D^{\bullet}_{BA}$.

$$D^{\bullet}_{AB} = D^{\bullet}_{BA} = D^{\bullet} \tag{III.2}$$

We can equate the fluxes in equation (I.18) and (III.1) to obtain

$$\mathbf{j}_A = -\rho D \nabla w_A = -\rho D^{\bullet} \nabla x_A \qquad \mathbf{j}_B = -\rho D \nabla w_B = -\rho D^{\bullet} \nabla x_B \tag{III.3}$$

Solving either species for the ratio of diffusivities, we have:

$$\frac{D^{\bullet}}{D} = \frac{\partial w_A}{\partial x_A} = \frac{w_A w_B}{x_A x_B} \tag{III.4}$$

Therefore, if we know either of the diffusivities, we can obtain the other.

IV. Problem Formulation in terms of a density driving force

One commonly sees Fick's law written where the driving force is not the gradient of the mass fraction but rather the gradient of the mass density,

$$\mathbf{j}_A = -D_{AB}^{\circ}\nabla\rho_A \qquad \mathbf{j}_B = -D_{BA}^{\circ}\nabla\rho_B \tag{IV.1}$$

The fluxes are still equal and opposite, so we can solve for the relationship between the two diffusivities, D_{AB}° and D_{BA}°.

$$-D_{AB}^{\circ}\nabla\rho_A = D_{BA}^{\circ}\nabla\rho_B \tag{IV.2}$$

$$D_{AB}^{\circ} = -D_{BA}^{\circ}\left(\frac{\partial\rho_B}{\partial\rho_A}\right) \tag{IV.3}$$

The partial derivative that appears in equation (IV.3) does not vanish as it did in case I, which is because $\nabla w_A = -\nabla w_B$ but, in general, $\nabla\rho_A \neq \nabla\rho_B$. We will further discuss this factor momentarily. Regardless, we can can equate the fluxes in equation (I.18) and (IV.1) to obtain

$$\mathbf{j}_A = -\rho D\nabla w_A = -D_{AB}^{\circ}\nabla\rho_A \qquad \mathbf{j}_B = -\rho D\nabla w_B = -D_{BA}^{\circ}\nabla\rho_B \tag{IV.4}$$

Solving for the ratio of diffusivities, we have:

$$\frac{D_{AB}^{\circ}}{D} = \rho\left(\frac{\partial w_A}{\partial\rho_A}\right) \qquad \frac{D_{BA}^{\circ}}{D} = \rho\left(\frac{\partial w_B}{\partial\rho_B}\right) \tag{IV.5}$$

Therefore, if we knew the diffusivity, *D*, and had a thermodynamic description of the fluid, we could obtain the diffusivities, D_{AB}° and D_{BA}°. In other words, they are not independent.