

Mass Transfer

*Fundamentals
and
Applications*

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Fundamentals and Applications

ANTHONY L. HINES

Oklahoma State University

ROBERT N. MADDOX

Oklahoma State University

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Preface

Although mass transfer processes are encountered by each of us in our daily lives, we seldom consider the actual transfer process. As an example, both macroscopic and microscopic mass transfer are involved in the simple act of breathing. When we inhale, air is transported into the lungs by macroscopic mass transfer. The air that enters the lungs has a higher concentration of oxygen than does the blood that flows through the lungs. Because of the concentration difference, oxygen diffuses through the walls of the lungs and into the blood, which distributes it throughout the body. Similarly, because the blood has a higher concentration of carbon dioxide than does the lungs, the carbon dioxide diffuses from the blood and into the lungs, where it is exhaled. If we are to properly understand the breathing process, we need information regarding the surface area available for mass transfer, the thickness of the cell walls through which the oxygen is transferred, the concentration difference across the walls of the lungs, and diffusion coefficients for oxygen and carbon dioxide through the walls of the lungs.

In addition to having an interest in understanding diffusional processes such as the one described above, the chemical engineer traditionally has been involved in the design of macroscopic separation processes such as distillation, absorption extraction, and adsorption. The design of these processes requires that we have a thorough understanding of mass transfer fundamentals. Subsequently, we have arranged this textbook to familiarize the student first with concentration units and flux rates, followed by methods to predict diffusion and mass transfer coefficients in a variety of materials.

The recent trend in the teaching of mass transfer has been to introduce the

student to mass transfer from the point of view of transport phenomena followed by macroscopic separation processes. To achieve this goal two textbooks are frequently required. Our goal in writing this book is to introduce the student to the fundamentals of both microscopic and macroscopic mass transfer in a single text.

The first part of this book covers the microscopic diffusional processes and the prediction and use of transport coefficients. In Chapter 1, concentration units, flux relationships, and coupled transport processes are discussed. This chapter provides the student with the background necessary to understand the portion of the text that deals with macroscopic separation processes. Chapter 2 introduces the student to diffusion coefficients for gases, liquids, and solids. An attempt is made to expand the discussion of diffusion coefficients as compared to other mass transfer textbooks. In Chapter 3 we present the formulation of macroscopic problems and the formulation of diffusional mass transfer problems by the differential shell balance method (transport method). The differential formulation of diffusion problems is further pursued in Chapter 4 by reducing the equations of change. The major emphasis in Chapter 4, however, is to present methods for solving these problems with several methods of solution discussed. The concept of a convective mass transfer coefficient is introduced in Chapter 5. Theoretical models that describe mass transfer at a fluid–fluid interface are presented. These models include a discussion of the film theory, surface renewal theory, and penetration theory. Interfacial mass transfer and the use of overall mass transfer coefficients are discussed. In Chapter 6, methods for predicting convective mass transfer coefficients for various geometries are presented. The analogies between heat, momentum, and mass transfer are discussed. Boundary layer theory and its application to mass transfer from a solid surface is introduced.

The remainder of the book deals primarily with macroscopic separation processes, including absorption, distillation, and extraction in both tray and packed towers. In Chapter 7 a brief presentation of thermodynamic fundamentals is included to introduce the student to phase equilibrium as applied to mass transfer processes. An interpretation of phase diagrams for liquid–liquid and gas–liquid systems is given in this chapter.

Absorption and stripping calculations for single-component and multicomponent systems are presented in Chapter 8. The student is first introduced to the standard graphical procedures that are applicable to transfer of a single solute. The more complicated multicomponent calculational procedures are then studied. A discussion of distillation of binary systems is given in Chapter 9. The simple graphical McCabe–Thiele and enthalpy–composition methods are presented in this chapter. Distillation of the more complicated multicomponent systems is discussed in Chapter 10. Both the shortcut methods and the more detailed tray-by-tray methods are introduced. Liquid extraction of ternary systems is introduced in Chapter 11. Ternary diagrams are used to determine

the number of equilibrium stages for both countercurrent and crosscurrent processes. A discussion of column internals and the sizing of tray-type towers is presented in Chapter 13. Following the discussion of equilibrium-stage calculational methods, absorption and distillation in packed columns is introduced in Chapter 12. The determination of packing heights and column diameters is discussed. A chapter discussing adsorption is presented. Both equilibrium adsorption and adsorption in packed towers are discussed. Methods for designing packed adsorbers are presented in Chapter 14.

The text is intended for both undergraduate and graduate students in chemical engineering, although much of the material can be used as a refresher by practicing engineers. Parts of Chapters 3, 4, and 6 are of an advanced nature and are better suited for a graduate course. The material presented in Chapters 10 and 14 is also typically reserved for the graduate student or the practicing engineer.

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Anthony L. Hines
Robert N. Maddox

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Mass Transfer Fundamentals

1

1.1 Introduction

Thermal and momentum diffusion are frequently encountered by students throughout their undergraduate careers. These are adequately dealt with by Fourier's law of heat conduction, which relates the flow of heat to a thermal gradient, and Newton's law, which relates the flow of momentum to a velocity gradient.

The molecular transport of matter, often denoted as *ordinary diffusion*, can be described in a manner similar to conductive heat transfer by using Fick's equation. His analogy states that the mass flux of component i per unit cross-sectional area perpendicular to the direction of flow is proportional to its concentration gradient. It can be expressed as

$$j_i = -\rho D \frac{d\omega_i}{dz} \quad (1-1)$$

where j_i is the mass flux of i in the Z direction with respect to the system moving with the mass average velocity, ρ is the mass concentration, ω_i the mass fraction or driving force, and D a constant of proportionality defined as the diffusion coefficient with the units (length²/time). From this expression we observe that species i diffuses in the direction of decreasing concentration of i . The analogy is thus made with Fourier's law of heat conduction, which relates the flow of heat from a high- to a low-temperature region. The diffusion coefficient in the presence of a concentration gradient as given by Eq. (1-1) is denoted as an *intrinsic* or *interdiffusion coefficient*. Although most intrinsic diffusion coefficients

are defined in terms of a concentration gradient, it will be shown later that a gradient of the chemical potential is responsible for the net flux of any species.

The discussion above implies that a gradient must exist before diffusion will take place. On the basis of past studies, this has been shown not to be the case. This is demonstrated by the random motion of a single molecule of species i through gas i . Although this is a diffusion process, in this case a net mass transfer of i will not occur. The diffusion coefficient for i into itself is termed *self-diffusion*. Measurements of this type of coefficient can be made by using radioisotope techniques.

1.2 Concentration and Flux Relationships

Concentrations

The concentration gradient may be expressed in a variety of ways, and before proceeding further, the more popular ones encountered in the literature will be formally defined.

The mass concentration of species i has the same units as density and is expressed as ρ_i with the units (mass i /unit volume). The sum of all mass concentrations within a mixture is equal simply to the overall density and can be expressed as

$$\rho = \sum_{i=1}^n \rho_i \quad (1-2)$$

From the mass concentration, the mass fraction of species i can be obtained by dividing the mass concentration of i in the mixture by the total mass density:

$$\omega_i = \frac{\rho_i}{\rho} \quad (1-3)$$

From Eqs. (1-2) and (1-3) it is seen that

$$\sum_{i=1}^n \frac{\rho_i}{\rho} = \sum_{i=1}^n \omega_i = 1 \quad (1-4)$$

The molar concentration of component i is represented as C_i and has the units (moles i /unit volume). The sum of all molar concentrations for all species can be summed to give the total number of moles or concentration in the system:

$$C = \sum_{i=1}^n C_i \quad (1-5)$$

The mole fraction of species i is thus found by dividing the molar concentration of i by C , which gives

$$x_i = \frac{C_i}{C} \quad (1-6)$$

If we sum over all species, then

$$\frac{\sum_{i=1}^n C_i}{C} = \sum_{i=1}^n x_i = 1 \quad (1-7)$$

It is often necessary to convert from mass to molar concentration. This is accomplished by dividing the mass concentration of i by the molecular weight of that species:

$$C_i = \frac{\rho_i}{M_i} \quad (1-8)$$

Flux relationships

To calculate the flux of a species, it frequently proves convenient to describe the transfer with respect to a fixed set of coordinates. The molar flux of species i can then be expressed as

$$N_i = C_i U_i \quad (1-9)$$

where N_i is the molar flux of i with the units (moles/length²-time) and U_i is the velocity of i with respect to a fixed reference frame. Analogously, the mass flux may be expressed as

$$n_i = \rho_i U_i \quad (1-10)$$

where n_i has the units (mass/length²-time).

In some cases it is more convenient to write the total flux of i with respect to some reference other than a fixed set of coordinates. In general we can reference the flux of i to an arbitrary reference velocity U^0 as

$${}_0j_i = \rho_i(U_i - U^0) \quad (1-11)$$

or

$${}_0J_i = C_i(U_i - U^0) \quad (1-12)$$

where ${}_0j_i$ and ${}_0J_i$ represent the mass and molar fluxes of i with respect to the reference velocity U^0 . The reference velocity U^0 is chosen such that the following relations are valid:

$$U^0 = \sum_{i=1}^n x_i U_i \quad (1-13)$$

and

$$\sum_{i=1}^n x_i = 1 \quad (1-14)$$

In the expressions above, values of x_i are normalized weighting factors which relate the contribution of each species to the reference velocity. Note that

$$\sum_{i=1}^n \frac{x_i}{C_i} {}_0J_i = 0 \quad (1-15)$$

Since a system may contain several molecular species, each having a different average velocity, a frame of reference must be chosen before a discussion is undertaken of the transport of a particular component. This may be a fixed axis or the velocity of any other species in the system. The more important and more widely used moving references are the mass average, molar average, and

volume average velocities. Relations will be developed using lower case letters for mass fluxes and upper case letters for molar fluxes.

Mass average velocity

The mass average velocity, U^m , can be written in terms of the mass concentration, ρ_i , and the velocity of i with respect to a fixed coordinate axis, U_i , as

$$U^m \sum_{i=1}^n \rho_i = \sum_{i=1}^n \rho_i U_i \quad (1-16)$$

$$\text{or} \quad U^m = \frac{\sum_{i=1}^n \rho_i U_i}{\sum_{i=1}^n \rho_i} \quad (1-17)$$

Substituting Eq. (1-4) into Eq. (1-17) gives

$$U^m = \sum_{i=1}^n \omega_i U_i \quad (1-18)$$

Thus we see that the weighting factor for the mass average velocity is simply the weight fraction (i.e., $\chi_i = \omega_i$). If we substitute the mass average velocity into Eq. (1-11), the mass flux of i with respect to the mass average velocity results.

$${}_m j_i = \rho_i (U_i - U^m) \quad (1-19)$$

Similarly, by substituting the mass average velocity into Eq. (1-12), we have the molar flux of i with respect to the mass average velocity.

$${}_m J_i = C_i (U_i - U^m) \quad (1-20)$$

Molar average velocity

The molar average velocity is defined by an expression analogous to the mass average velocity.

$$U^M = \frac{\sum_{i=1}^n C_i U_i}{\sum_{i=1}^n C_i} \quad (1-21)$$

$$\text{or} \quad U^M = \sum_{i=1}^n x_i U_i \quad (1-22)$$

Upon substituting the molar average velocity defined by the equations above for the arbitrary reference velocity of Eq. (1-12), we obtain the molar flux of i with respect to the molar average velocity.

$${}_M J_i = C_i (U_i - U^M) \quad (1-23)$$

An equation for the mass flux of i with respect to the molar average velocity results if the molar average velocity is substituted for the arbitrary reference velocity in Eq. (1-11).

$${}_M j_i = \rho_i (U_i - U^M) \quad (1-24)$$

Volume average velocity

The volume average velocity is probably the most important reference velocity for obtaining experimental data, since for a fixed system of constant volume, this velocity is identically equal to zero. The volume average velocity is defined by

$$\mathbf{U}^v = \sum_{i=1}^n \bar{V}_i C_i \mathbf{U}_i \quad (1-25)$$

where \bar{V}_i is defined as the partial molar volume. The molar flux of i with respect to the volume average velocity thus is written as

$${}_v \mathbf{J}_i = C_i (\mathbf{U}_i - \mathbf{U}^v) \quad (1-26)$$

Example 1.1

- (a) Based on the definition of \bar{V}_i and $\sum_{i=1}^n \bar{V}_i C_i = 1$, prove that $\sum_{i=1}^n {}_v \mathbf{J}_i \bar{V}_i = 0$.
 (b) Show that $\sum_{i=1}^n {}_M \mathbf{J}_i = 0$.

Solution:

- (a) Beginning with Eq. (1-26) and multiplying both sides of the equation by \bar{V}_i gives

$${}_v \mathbf{J}_i \bar{V}_i = C_i \bar{V}_i (\mathbf{U}_i - \mathbf{U}^v)$$

Expanding the expression above and summing over all species, we have

$$\begin{aligned} \sum_{i=1}^n {}_v \mathbf{J}_i \bar{V}_i &= \sum_{i=1}^n (C_i \bar{V}_i \mathbf{U}_i - C_i \bar{V}_i \mathbf{U}^v) \\ &= \mathbf{U}^v - \mathbf{U}^v \underbrace{\sum_{i=1}^n C_i \bar{V}_i}_{=1} \\ &= \mathbf{U}^v (1 - \sum_{i=1}^n C_i \bar{V}_i) \end{aligned}$$

Since $\sum_{i=1}^n C_i \bar{V}_i = 1$, we have $\sum_{i=1}^n {}_v \mathbf{J}_i \bar{V}_i = 0$.

- (b) Starting with Eq. (1-23), we obtain

$$\begin{aligned} \sum_{i=1}^n {}_M \mathbf{J}_i &= \sum_{i=1}^n C_i (\mathbf{U}_i - \mathbf{U}^M) \\ &= \sum_{i=1}^n C_i \mathbf{U}_i - \mathbf{U}^M \sum_{i=1}^n C_i \end{aligned}$$

Introducing the definition of the molar average velocity, we have

$$\sum_{i=1}^n {}_M \mathbf{J}_i = \sum_{i=1}^n C_i \mathbf{U}_i - \frac{\sum_{i=1}^n C_i \mathbf{U}_i}{\sum_{i=1}^n C_i} \sum_{i=1}^n C_i = 0$$