ThirdEdition

PRINCIPLES AND MODERN APPLICATIONS OF

Mass Transfer Operations

JAIME BENÍTEZ



PRINCIPLES AND MODERN APPLICATIONS OF MASS TRANSFER OPERATIONS

PRINCIPLES AND MODERN APPLICATIONS OF MASS TRANSFER OPERATIONS

Third Edition

Jaime Benitez

WILEY

Copyright © 2017 by John Wiley & Sons, Inc. All rights reserved

Published by John Wiley & Sons, Inc., Hoboken, New Jersey Published simultaneously in Canada

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permission.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data:

Names: Benitez, Jaime, 1948- author.

Title: Principles and modern applications of mass transfer operations / Jaime Benitez. Description: Third edition. | Hoboken, New Jersey : Wiley, 2016. | Includes bibliographical references and index.

Identifiers: LCCN 2016031563 | ISBN 9781119042730 (hardback) | ISBN 9781119276944 (ePub) | ISBN 9781119276951 (Adobe PDF)

Subjects: LCSH: Mass transfer. | Chemical engineering. | BISAC: TECHNOLOGY & ENGINEERING / Chemical & Biochemical.

 $\label{eq:Classification: LCC TP156.M3 B44 2016 | DDC 660/.28423-dc23 LC record available at https://lccn.loc.gov/2016031563$

Printed in the United States of America

 $10 \hspace{0.2cm} 9 \hspace{0.2cm} 8 \hspace{0.2cm} 7 \hspace{0.2cm} 6 \hspace{0.2cm} 5 \hspace{0.2cm} 4 \hspace{0.2cm} 3 \hspace{0.2cm} 2 \hspace{0.2cm} 1$

A mis tres Teresas, Ivette, Humberto, y Jaime: mi hermosa familia.

Table of Contents

Preface to the Third Editionxvii
Preface to the Second Edition xix
Preface to the First Editionxxi
Nomenclaturexxiii
1. FUNDAMENTALS OF MASS TRANSFER
1.1 INTRODUCTION 1
1.2 MOLECULAR MASS TRANSFER
1.2.1 Concentrations
1.2.2 Velocities and Fluxes
1.2.3 The Maxwell–Stefan Relations
1.2.4 Fick's First Law for Binary Mixtures16
1.3 THE DIFFUSION COEFFICIENT 17
1.3.1 Diffusion Coefficients for Binary Ideal Gas Systems
1.3.2 Diffusion Coefficients for Dilute Liquids
1.3.3 Diffusion Coefficients for Concentrated Liquids
1.3.4 Effective Diffusivities in Multicomponent Mixtures
1.4 STEADY-STATE MOLECULAR DIFFUSION IN FLUIDS
1 4 1 Molar Flux and the Equation of Continuity 37
1.4.2 Steady-State Molecular Diffusion in Gases
1.4.3 Steady-State Molecular Diffusion in Liquids
1.5 STEADY-STATE DIFFUSION IN SOLIDS
1.5.1 Steady-State Binary Molecular Diffusion in
Porous Solids
1.5.2 Knudsen Diffusion in Porous Solids
1.5.3 Hydrodynamic Flow of Gases in Porous Solids

1.5.4 "Dusty Gas" Model for Multicomponent Diffusion	64
1.6 DIFFUSION WITH HOMOGENEOUS CHEMICAL REACTION	65
1.7 ANALOGIES AMONG MOLECULAR TRANSFER PHENOMENA	71
PROBLEMS	73
REFERENCES	89
2. CONVECTIVE MASS TRANSFER	91
2.1 INTRODUCTION	91
2.2 MASS-TRANSFER COEFFICIENTS	92
2.2.1 Diffusion of A Through Stagnant B ($N_B = 0$, $\Psi_A = 1$) 2.2.2 Equimolar Counterdiffusion ($N_B = -N_A$, Ψ_A = undefined)	93 95
2.3 DIMENSIONAL ANALYSIS	97
2.3.1 The Buckingham Method	97
2.4 FLOW PAST FLAT PLATE IN LAMINAR FLOW; BOUNDARY LAYER THEORY	103
2.5 MASS- AND HEAT-TRANSFER ANALOGIES	110
2.6 CONVECTIVE MASS-TRANSFER CORRELATIONS	119
 2.6.1 Mass-Transfer Coefficients for Flat Plates	120 121 126 127 133
2.6.6 Mass Transfer in Hollow-Fiber Membrane Modules	136

2.7 ESTIMATION OF MULTICOMPONENT MASS-TRANSFER COEFFICIENTS	140
PROBLEMS	142
REFERENCES	156
3. INTERPHASE MASS TRANSFER	158
3.1 INTRODUCTION	158
3.2 EQUILIBRIUM	158
3.3 DIFFUSION BETWEEN PHASES	163
 3.3.1 Two-Resistance Theory 3.3.2 Overall Mass-Transfer Coefficients	164 166 171
3.4 MATERIAL BALANCES	179
	179
3.4.1 Countercurrent Flow. 3.4.2 Cocurrent Flow. 3.4.3 Batch Processes.	194 197
3.4.1 Countercurrent Flow	194 197 198
3.4.1 Countercurrent Flow	194 197 198 206

4. EQUIPMENT FOR GAS-LIQUID MASS-TRANSFER	
OPERATIONS	 221
4.1 INTRODUCTION	221
4.2 GAS-LIQUID OPERATIONS: LIQUID DISPERSED	221
4.2.1 Types of Packing	222
4.2.2 Liquid Distribution	225
4.2.3 Liquid Holdup	227
4.2.4 Pressure Drop	234
4.2.5 Mass-Transfer Coefficients	237
4.3 GAS-LIQUID OPERATIONS: GAS DISPERSED	242
4.3.1 Sparged Vessels (Bubble Columns)	242
4.3.2 Tray Towers	248
4.3.3 Tray Diameter	252
4.3.4 Tray Gas-Pressure Drop	255
4.3.5 Weeping and Entrainment	257
4.3.6 Tray Efficiency	259
PROBLEMS	266
REFERENCES	279
5. ABSORPTION AND STRIPPING	 281
51 INTRODUCTION	281
5.2 COUNTERCURRENT MULTISTAGE EQUIPMENT	282
5.2.1 Graphical Determination of the Number of Ideal Trays	282
5.2.2 Tray Efficiencies and Real Trays by Graphical Methods	283
5.2.3 Dilute Mixtures	284
5.3 COUNTERCURRENT CONTINUOUS-CONTACT EQUIPMENT	290
5.3.1 Dilute Solutions; Henry's Law	296

Contents

5.4 THERMAL EFFECTS DURING ABSORPTION AND STRIPPING	299
5.4.1 Adiabatic Operation of a Tray Absorber	299
5.4.2 Adiabatic Operation of a Packed-Bed Absorber	.302
PROBLEMS	.306
REFERENCES	318
6. DISTILLATION	.319
6.1 INTRODUCTION	.319
6.2 SINGLE-STAGE OPERATION-FLASH VAPORIZATION	320
6.3 DIFFERENTIAL DISTILLATION	.325
6.4 CONTINUOUS RECTIFICATION-BINARY SYSTEMS	328
6.5 McCABE-THIELE METHOD FOR TRAYED TOWERS	.328
6.5.1 Rectifying Section. 6.5.2 Stripping Section. 6.5.3 Feed Stage.	.330 .331 333
6.5.4 Number of Equilibrium Stages and Feed-Stage Location 6.5.5 Limiting Conditions	.335 .336
6.5.6 Optimum Reflux Ratio	339
6.5.7 Large Number of Stages	345
6.5.8 Use of Open Steam 6.5.9 Tray Efficiencies	.349 .350
6.6 BINARY DISTILLATION IN PACKED TOWERS	.358
6.7 MULTICOMPONENT DISTILLATION	.363

6.8 FENSKE-UNDERWOOD-GILLILAND METHOD
6.8.1 Total Reflux: Fenske Equation
6.9 RIGOROUS CALCULATION PROCEDURES FOR MULTICOMPONENT DISTILLATION
6.9.1 Equilibrium Stage Model
6.10 BATCH DISTILLATION
6.10.1 Binary Batch Distillation with Constant Reflux
PROBLEMS
REFERENCES
7. LIQUID-LIQUID EXTRACTION
7.1 INTRODUCTION 406
7.2 LIQUID EQUILIBRIA
7.3 STAGEWISE LIQUID-LIQUID EXTRACTION413
7.3.1 Single-Stage Extraction

Contents

7.3.3 Countercurrent Extraction Cascades
7.3.5 Continuous Countercurrent Extraction with Reflux
7.4 EQUIPMENT FOR LIQUID-LIQUID EXTRACTION
7.4.1 Mixer-Settler Cascades
7.4.2 Multicompartment Columns
PROBLEMS
REFERENCES
8. HUMIDIFICATION OPERATIONS
8.1 INTRODUCTION
8.2 EQUILIBRIUM CONSIDERATIONS
8.2.1 Saturated Gas–Vapor Mixtures
8.2.2 Unsaturated Gas–Vapor Mixtures
8.2.3 Adiabatic-Saturation Curves
8.2.4 Wet-Bulb Temperature
8.3 ADIABATIC GAS-LIQUID CONTACT OPERATIONS
8.3.1 Fundamental Relationships
8.3.2 Water Cooling with Air
8.3.3 Dehumidification of Air–Water Vapor479
PROBLEMS
REFERENCES

9. MEMBRANES AND OTHER SOLID SORPTION AGENTS485
9.1 INTRODUCTION
9.2 MASS TRANSFER IN MEMBRANES
9.2.1 Solution-Diffusion for Liquid Mixtures.4889.2.2 Solution-Diffusion for Gas Mixtures.4899.2.3 Module Flow Patterns.492
9.3 EQUILIBRIUM CONSIDERATIONS IN POROUS SORBENTS
9.3.1 Adsorption and Chromatography Equilibria
9.4 MASS TRANSFER IN FIXED BEDS OF POROUS SORBENTS
9.4.1 Basic Equations for Adsorption
9.5 APPLICATIONS OF MEMBRANE-SEPARATION PROCESSES520
9.5.1 Dialysis
9.6 APPLICATIONS OF SORPTION-SEPARATION PROCESSES
PROBLEMS
REFERENCES
Appendix A Binary Diffusion Coefficients
Appendix B Lennard–Jones Constants

Appendix C Maxwell–Stefan Equations	550
Appendix D Packed-Column Design Program	552
Appendix E Sieve-Tray Design Program	558
Appendix F-1 McCabe–Thiele: Liquid Feed	564
Appendix F-2 McCabe–Thiele: Vapor Feed	568
Appendix G-1 Single-Stage Extraction	572
Appendix G-2 Multistage Crosscurrent Extraction	574
Appendix H Constants and Unit Conversions	578
Index	

Preface to the Third Edition

The most significant difference between the first two editions and the third edition is the adoption in the latter of PTC Mathcad Prime most recent version (version 3.1 as of this writing). PTC Mathcad Prime—one of the world's leading tools for technical computing in the context of engineering, science, and math applications—is a significant departure from the previous versions of Mathcad. There is a definite learning curve associated with making the switch from Mathcad to Mathcad Prime. However, the new features included in Mathcad Prime make switching from Mathcad worthwhile. Besides, programs written for the previous versions of Mathcad will not run in Mathcad Prime. Other differences in this edition are listed in the following paragraphs.

In Chapter 3 of the third edition, the material covered in Problems 3.14 and 3.15 of the second edition to determine analytically minimum flow rates in absorbers and strippers is incorporated in the theoretical presentation of Section 3.4 (Material Balances), and the corresponding Mathcad Prime code for solving these problems is given. In Section 3.5 of the third edition, Mathcad Prime code is given to determine analytically the number of ideal stages required for absorbers and strippers.

Section 4.2 of the third edition use, exclusively, the updated Billet and Schultes correlations for estimating the loading and flooding points in packed beds, and the corresponding gas-pressure drop for operation between these limits. The Generalized Pressure Drop Correlation (GPDC) is not included. The updated Billet and Schultes correlations are also used to estimate the volumetric mass-transfer coefficients in both liquid and gas phases. New end-of-chapter problems have been added throughout this third edition.

I want to acknowledge the extraordinarily thorough editing job that Katrina Maceda, Production Editor at Wiley, and Baljinder Kaur, Project Manager at Aptara did on this edition. The book is much better now because of them. It was a pleasure working with both of you. Ludo de Wolf, a physical therapist with gifted hands and a delightful sense of humor, literally removed from my shoulders the heavy load of completing this edition. Thanks to my wife Teresa for her unconditional love and support. I know it is not easy!

> Jaime Benítez Gainesville, Florida

Preface to the Second Edition

The idea for the first edition of this book was born out of my experience teaching a course on mass-transfer operations at the Chemical Engineering Department of the University of Puerto Rico during the previous 25 years. This course is the third in a three-course unit operations sequence. The first course covers momentum transfer (fluid mechanics), and the second course covers heat transfer. Besides these two courses, another prerequisite of the mass-transfer course is a two-semester sequence of chemical engineering thermodynamics.

I decided to write a textbook for a first course on mass-transfer operations with a level of presentation that was easy to follow by the reader, but with enough depth of coverage to guarantee that students using the book will, upon successful completion of the course, be able to specify preliminary designs of the most common mass-transfer equipment (such as absorbers, strippers, distillation columns, liquid extractors, etc.). I decided also to incorporate, from the very beginning of the book, the use of Mathcad, a computational tool that is, in my opinion, very helpful and friendly. The first edition of this book was the result of that effort.

Part of my objective was achieved, as evidenced by the following excerpt from a very thorough review of the first edition of my book, written by Professor Mark J. McCready, a well-known expert in chemical engineering education: "If the topics that are needed for a given course are included in this text, I would expect the educational experience to go smoothly for both student and instructor. I think that students will like this book, because the explanations are clear, the level of difficulty is appropriate, and the examples and included data give the book very much of a 'handbook' flavor. Instructors will find that, overall, the topics are presented in a logical order and the discussion makes sense; there are many examples and lots of homework problems" (McCready, M. J., *AIChE J.*, Vol. 49, No. 1, January 2003).

"Each major section of the book has learning objectives which certainly benefit the students and perhaps the instructor. A key feature of the book, which separates it from the other texts mentioned above, is the incorporation of Mathcad for both example problems and homework questions. A library of Mathcad programs for solving the Maxwell-Stefan equations, packed column calculations, sieve-tray design, binary distillation problems by McCabe-Thiele method, and multistage crosscurrent extraction is given in the appendices. These programs enable students to obtain useful solutions with less effort, as well as allow them to explore the different variables or parameters. The wide availability, low cost, and ease of use of Mathcad allow it to be the modern equivalent of 'back of the envelope' calculations, which can be refined, if necessary, using full-scale process simulators" (McCready, 2003). However, the same reviewer also points out some limitations of the book. One of the main objectives of this second edition is to remedy those shortcomings of the first edition to make it more attractive as a textbook to a broader audience. Another important objective of the second edition is to incorporate material related to mass-transfer phenomena in biological systems. Many chemical engineering departments all over the world are changing their names and curricula to include the area of biochemical engineering in their offerings. The second edition includes pertinent examples such as convection and diffusion of oxygen through the body's circulatory system, bio-artificial kidneys, separation of sugars by chromatography, and purification of monoclonal antibodies by affinity adsorption.

As with the first edition, the first four chapters of the book present a basic framework for analysis that is applicable to most mass-transfer operations. Chapters 5 to 7 apply this common methodology to the analysis and design of some of the most popular types of mass-transfer operations. Chapter 5 covers gas absorption and stripping; Chapter 6 covers distillation; and Chapter 7 covers liquid extraction. Chapter 8, new to the second edition, covers humidification operations in general, and detailed design of packed cooling towers specifically. These operations—in particular, cooling towers—are very common in industry. Also, from the didactic point of view, their analysis and design involve simultaneous mass- and heat-transfer considerations. Therefore, the reader is exposed in detail to the similarities and differences between these two transport phenomena. Chapter 9, also new, covers mass-transfer processes using barriers (membranes) and solid sorption agents (adsorption, ion exchange, and chromatography).

In response to suggestions by Professor McCready and other reviewers, some other revisions and additions to the second edition are:

• In Chapter 1, the Maxwell-Stefan equations (augmented by the steady-state continuity equation for each component) are solved numerically using a combination of a Runge-Kutta-based differential equation solver (*Rkfixed*) and an algebraic equation solver (*Given-Find*), both included in Mathcad. This methodology is much more flexible than the one presented in the first edition (orthogonal collocation), and its theoretical justification is well within the scope of the mathematical background required for a first course in mass-transfer operations.

• Chapter 1 includes a section on diffusion in solids.

• Chapter 2 includes a section on boundary-layer theory and an example on simultaneous mass and heat transfer during air humidification.

• Chapter 6 includes a section on multistage batch distillation.

I wish to acknowledge gratefully the contribution of the University of Puerto Rico at Mayagüez to this project. My students in the course INQU 4002 reviewed the material in the book, found quite a few errors, and gave excellent suggestions on ways to improve its content and presentation. My students are my source of motivation; they make all the effort to prepare this book worthwhile!

> Jaime Benítez Mayagüez, Puerto Rico

Preface to the First Edition

The importance of the mass-transfer operations in chemical processes is profound. There is scarcely any industrial process that does not require a preliminary purification of raw materials or final separation of products. This is the realm of mass-transfer operations. Frequently, the major part of the cost of a process is that for the separations accomplished in the mass-transfer operations, a good reason for process engineers and designers to master this subject. The mass-transfer operations are largely the responsibility of chemical engineers, but increasingly practitioners of other engineering disciplines are finding them necessary for their work. This is especially true for those engaged in environmental engineering, where separation processes predominate.

My objective in writing this book is to provide a means to teach undergraduate chemical engineering students the basic principles of mass transfer and to apply these principles, aided by modern computational tools, to the design of equipment used in separation processes. The idea for it was born out of my experiences during the last 25 years teaching mass-transfer operations courses at the University of Puerto Rico.

The material treated in the book can be covered in a one-semester course. Chapters are divided into sections with clearly stated objectives at the beginning. Numerous detailed examples follow each brief section of text. Abundant end-of-chapter problems are included, and problem degree of difficulty is clearly labeled for each. Most of the problems are accompanied by their answers. Computer solution is emphasized, both in the examples and in the endof-chapter problems. The book uses mostly SI units, which virtually eliminates the tedious task of unit conversions and makes it "readable" to the international scientific and technical community.

Following the lead of other authors in the chemical engineering field and related technical disciplines, I decided to incorporate the use of Mathcad into this book. Most readers will probably have a working knowledge of Mathcad. (Even if they don't, my experience is that the basic knowledge needed to begin using Mathcad effectively can be easily taught in a two-hour workshop.) The use of Mathcad simplifies mass-transfer calculations to a point that it allows the instructor and the student to readily try many different combinations of the design variables, a vital experience for the amateur designer.

The Mathcad environment can be used as a sophisticated scientific calculator, can be easily programed to perform a complicated sequence of calculations (for example, to check the design of a sieve-plate column for flooding, pressure drop, entrainment, weeping, and calculating Murphree plate efficiencies), can be used to plot results, and as a word processor to neatly present homework problems. Mathcad can perform calculations using a variety of unit systems, and will give a warning signal when calculations that are not dimensionally consistent are tried. This is a most powerful didactic tool, since dimensional consistency in calculations is one of the most fundamental concepts in chemical engineering education.

The first four chapters of the book present a basic framework of analysis that is applicable to any mass-transfer operation. Chapters 5 to 7 apply this common methodology to the analysis and design of the most popular types of masstransfer operations. Chapter 5 covers gas absorption and stripping, chapter 6 distillation columns, and chapter 7 liquid extraction. This choice is somewhat arbitrary, and based on my own perception of the relevance of these operations. However, application of the general framework of analysis developed in the first four chapters should allow the reader to master, with relative ease, the peculiarities of any other type of mass-transfer operation.

I wish to acknowledge gratefully the contribution of the University of Puerto Rico at Mayagüez to this project. My students in the course INQU 4002 reviewed the material presented in the book, found quite a few errors, and gave excellent suggestions on ways to improve it. My special gratitude goes to Teresa, my wife, and my four children who were always around lifting my spirits during the long, arduous hours of work devoted to this volume. They make it all worthwhile!

> Jaime Benítez Mayagüez, Puerto Rico

Nomenclature

LATIN LETTERS

Α absorption factor; dimensionless. Α mass flow rate of species A; kg/s. A_a active area of a sieve tray; m². A_d area taken by the downspout in a sieve tray; m². A_h area taken by the perforations on a sieve tray; m². A_M membrane area; m². A_n net cross-section area between trays inside a tray column; m². A_t total cross-section area, m². mass-transfer surface area per unit volume; m⁻¹. a hydraulic, or effective, specific surface area of packing; m⁻¹. a_h В mass flow rate of species B; kg/s. viscous flow parameter; m². B_0 total molar concentration; mol/m³. с c_i, C_i molar concentration of species i; mol/m³. Ctotal number of components in multicomponent distillation. C_p specific heat at constant pressure; J/kg·K. C_S humid heat; J/kg·K. C_D drag coefficient; dimensionless. Da Damkohler number for first-order reaction; dimensionless. D_{ii} Maxwell–Stefan diffusivity for pair i-j; m²/s. Fick diffusivity or diffusion coefficient for pair *i*-*j*; m²/s. D_{ii} $D_{K,i}$ Knudsen diffusivity for component *i*; m^2/s . d_e equivalent diameter; m. driving force for mass diffusion of species i; m⁻¹. \mathbf{d}_i d_i inside diameter; m. d_{o} outside diameter; m. d_o perforation diameter in a sieve plate; m. d_p particle size; m. Sauter mean drop diameter defined in equation (7-48); m. d_{vs} DM dimensional matrix. tube diameter; m. D D distillate flow rate; moles/s. E fractional entrainment; liquid mass flow rate/gas mass flow rate. Eextract mass flow rate, kg/s. E_m mechanical efficiency of a motor-fan system; dimensionless. Eo Eotvos number defined in equation (7-53); dimensionless. EFextraction factor defined in equation (7-19); dimensionless. \mathbf{E}_{ME} Murphree stage efficiency in terms of extract composition. Murphree gas-phase tray efficiency; dimensionless. \mathbf{E}_{MG} \mathbf{E}_{MGE} Murphree gas-phase tray efficiency corrected for entrainment. \mathbf{E}_{O} overall tray efficiency of a cascade; equilibrium trays/real trays. \mathbf{E}_{OG} point gas-phase tray efficiency; dimensionless.

f_{12}	proportionality coefficient in equation (1-21).
f	friction factor; dimensionless.
, f	fractional approach to flooding velocity; dimensionless.
f _{ert}	fractional extraction; dimensionless.
F	mass-transfer coefficient; mol/m ² ·s.
F	molar flow rate of the feed to a distillation column; mol/s.
F	mass flow rate of the feed to a liquid extraction process: kg/s.
FR_{iD}	fractional recovery of component i in the distillate: dimensionless.
FR_{iW}	fractional recovery of component i in the residue; dimensionless.
\mathbf{Fr}_{7}	liquid Froude number: dimensionless.
Ga	Galileo number: dimensionless.
G_M	superficial molar velocity: mol/m ² ·s.
G_{Mr}	superficial liquid-phase molar velocity; mol/m ² ·s.
$G_{M_{\mathcal{H}}}$	superficial gas-phase molar velocity; mol/m ² ·s.
G_r	superficial liquid-phase mass velocity: kg/m ² ·s.
G_{ν}	superficial gas-phase mass velocity: kg/m ² ·s.
Gr	Grashof number for mass transfer: dimensionless.
Gr_H	Grashof number for heat transfer: dimensionless.
Gz	Graetz number: dimensionless.
g	acceleration due to gravity: 9.8 m/s^2 .
g,	dimensional conversion factor: 1 kg·m/N·s ² .
H	Henry's law constant: atm. kPa. Pa.
H	molar enthalpy; J/mol.
H	height of mixing vessel; m.
Η´	enthalpy of gas-vapor mixture; J/kg.
HETS	height equivalent to a theoretical stage in staged liquid extraction
	columns; m.
HK	heavy-key component in multicomponent distillation.
ΔH_S	heat of solution; J/mol of solution.
H_{tL}	height of a liquid-phase transfer unit; m.
H_{tG}	height of a gas-phase transfer unit; m.
H_{tOG}	overall height of a gas-phase transfer unit; m.
H_{tOL}	overall height of a liquid-phase transfer unit; m.
h	convective heat-transfer coefficient, W/m ² ·K.
h_d	dry-tray head loss; cm of liquid.
h_l	equivalent head of clear liquid on tray; cm of liquid.
h_L	specific liquid holdup; m ³ holdup/m ³ packed bed.
h_t	total head loss/tray; cm of liquid.
h_w	weir height; m.
h_{σ}	head loss due to surface tension; cm of liquid.
$h_{2\phi}$	height of two-phase region on a tray; m.
i	number of dimensionless groups needed to describe a situation.
.İn	Chilton–Colburn <i>j</i> -factor for mass transfer; dimensionless.
jн	Chilton–Colburn <i>j</i> -factor for heat transfer; dimensionless.
\mathbf{j}_i	mass diffusion flux of species <i>i</i> with respect to the mass-average
	velocity; kg/m ² ·s.
\mathbf{J}_i	molar diffusion flux of species <i>i</i> with respect to the molar-average
	velocity; mol/m ² ·s.

Nomenclature

- J_0 Bessel function of the first kind and order zero; dimensionless.
- J_1 Bessel function of the first kind and order one; dimensionless.
- *K* distribution coefficient; dimensionless.
- K Krogh diffusion coefficient; cm³ O₂/cm·s·torr.
- K parameter in Langmuir adsorption isotherm; Pa⁻¹.
- K_{AB} molar selectivity parameter in ion exchange; dimensionless.
- K_W wall factor in Billet–Schultes pressure-drop correlations; dimensionless. k thermal conductivity, W/m·K.
- k_c convective mass-transfer coefficient for diffusion of A through stagnant B in dilute gas-phase solution with driving force in terms of molar concentrations; m/s.
- k'_c convective mass-transfer coefficient for equimolar counterdiffusion in gas-phase solution with driving force in molar concentrations; m/s.
- k_G convective mass-transfer coefficient for diffusion of A through stagnant B in dilute gas-phase solution with driving force in terms of partial pressure; mol/m²·s·Pa.
- K_G overall convective mass-transfer coefficient for diffusion of A through stagnant B in dilute solutions with driving force in terms of partial pressures; mol/m²·s·Pa.
- k'_G convective mass-transfer coefficient for equimolar counterdiffusion in gas-phase solution with driving force in terms of partial pressure; mol/m²·s·Pa.
- k_L convective mass-transfer coefficient for diffusion of A through stagnant B in dilute liquid-phase solution with driving force in terms of molar concentrations; m/s.
- k_L convective mass-transfer coefficient for equimolar counterdiffusion in liquid-phase solution with driving force in terms of molar concentrations; m/s.
- Kn Knudsen number, dimensionless.
- k_r reaction rate constant; mol/m²·s·mol fraction.
- K_r restrictive factor for diffusion of liquids in porous solids; dimensionless.
- k_x convective mass-transfer coefficient for diffusion of A through stagnant B in dilute liquid-phase solution with driving force in terms of mol fractions; mol/m².s.
- K_x overall convective mass-transfer coefficient for diffusion of A through stagnant B in dilute solutions with driving force in terms of liquid-phase mol fractions; mol/m²·s.
- k'_x convective mass-transfer coefficient for equimolar counterdiffusion in liquid-phase solution with driving force in terms of mol fractions; mol/m²·s.
- k_y convective mass-transfer coefficient for diffusion of A through stagnant B in dilute gas-phase solution with driving force in terms of mol fractions; mol/m²·s.
- K_y overall convective mass-transfer coefficient for diffusion of A through stagnant B in dilute solutions with driving force in terms of gas-phase mol fractions; mol/m²·s.
- k'_y convective mass-transfer coefficient for equimolar counterdiffusion in gas-phase solution with driving force in terms of mol fractions; mol/m²·s.

L	characteristic length, m.
L	molar flow rate of the L-phase: mol/s.
L	length of settling vessel; m.
LK	light-key component in multicomponent distillation.
L_S	molar flow rate of the nondiffusing solvent in the <i>L</i> -phase; mol/s.
Ľ	mass flow rate of the <i>L</i> -phase; kg/s.
L'_{S}	mass flow rate of the nondiffusing solvent in the <i>L</i> -phase; kg/s.
L_e	entrainment mass flow rate, kg/s.
L_w	weir length; m.
l	characteristic length, m.
l	tray thickness; m.
l_M	membrane thickness; m.
Le	Lewis number; dimensionless.
M_i	molecular weight of species <i>i</i> .
M_0	oxygen demand; cm ³ O ₂ /cm ³ ·min.
MTZ	width of the mass-transfer zone in fixed-bed adsorption; m.
т	amount of mass; kg.
т	slope of the equilibrium distribution curve; dimensionless.
n	total mass flux with respect to fixed coordinates; kg/m ² ·s.
\mathbf{n}_i	mass flux of species i with respect to fixed coordinates; kg/m ² ·s.
n	number of variables significant to dimensional analysis of a given
	problem.
n	rate of mass transfer from the dispersed to the continuous phase
	in liquid extraction; kg/s.
n	number of species in a mixture.
Ν	total molar flux with respect to fixed coordinates; mol/m ² -s.
\mathbf{N}_i	molar flux of species i with respect to fixed coordinates; mol/m ² -s.
N	number of equilibrium stages in a cascade; dimensionless.
N_E	mass of B/(mass of A + mass of C) in the extract liquids.
N_R	number of stages in rectifying section; dimensionless.
N_R	mass of B/(mass of A + mass of C) in the raffinate liquids.
N_S	number of stages in stripping section; dimensionless.
N_{tL}	number of liquid-phase transfer units; dimensionless.
N_{tG}	number of gas-phase transfer units; dimensionless.
N_{tOD}	overall number of dispersed-phase transfer units; dimensionless.
N_{tOG}	overall number of gas-phase transfer units; dimensionless.
N_{tOL}	overall number of liquid-phase transfer units; dimensionless.
Nu	Nusselt number; dimensionless.
O_t	molar oxygen concentration in the air leaving an aeration tank; percent.
O_{eff}	oxygen transfer efficiency; mass of oxygen absorbed by water/total mass
,	of oxygen supplied.
p	pitch, distance between centers of perforations in a sieve plate; m.
p_i	partial pressure of species <i>l</i> ; atm, Pa, KPa, bar.
$p_{B,M}$	logarithmic mean partial pressure of component B; atm, Pa, kPa, bar.
P	total pressure; atm, Pa, kPa, bar.
r D	permeate now through a memorane; mol/s.
r D	mpener power; KW.
P_c	critical pressure, Fa, KPa, bar.
re_D	reciet number for mass transfer.

Nomenclature

xxvii

- Pe_H Peclet number for heat transfer.
- P_i vapor pressure of species *i*; atm, Pa, kPa, bar.
- Po power number defined in equation (7-37); dimensionless.
- Pr Prandtl number; dimensionless.
- Q volumetric flow rate; m³/s.
- Q net rate of heating; J/s.
- *Q* membrane permeance; m/s.
- q membrane permeability; barrer, m²/s.
- *q* parameter defined by equation (6-27); dimensionless.
- q_m parameter in Langmuir adsorption isotherm; g/g.
- *r* rank of the dimensional matrix, **DM**; dimensionless.
- r_A solute particle radius; m.
- R radius; m.
- R ideal gas constant; J/mol·K.
- *R* reflux ratio; mol of reflux/mol of distillate.
- *R* raffinate mass flow rate; kg/s.
- R_A volumetric rate of formation of A; mol per unit volume per unit time.
- R_m retentate flow in a membrane; mol/s.
- Re Reynolds number; dimensionless.
- R_i volumetric rate of formation of component *i*; mol/m³.s.
- S surface area, cross-sectional area; m².
- *S* stripping factor, reciprocal of absorption factor (*A*); dimensionless.
- *S* mass flow rate of the solvent entering a liquid extraction process; kg/s.
- Sc Schmidt number; dimensionless.
- Sh Sherwood number; dimensionless.
- SR salt rejection; dimensionless.
- St_D Stanton number for mass transfer; dimensionless.
- St_H Stanton number for heat transfer; dimensionless.
- t tray spacing; m.
- t time; s, h.
- t_b breakthrough time in fixed-bed adsorption; s.
- t_{res} residence time; min.
- T temperature; K.
- T_{as} adiabatic saturation temperature; K.
- T_b normal boiling point temperature; K.
- T_c critical temperature, K.
- T_w wet-bulb temperature; K.
- *u* fluid velocity past a stationary flat plate, parallel to the surface; m/s.
- v mass-average velocity for multicomponent mixture; m/s.
- \mathbf{v}_i velocity of species *i*; m/s.
- v_t terminal velocity of a particle; m/s.
- **V** molar-average velocity for multicomponent mixture; m/s.
- V volume; m³.
- V molar flow rate of the V-phase; mol/s.
- V_S molar flow rate of the nondiffusing solvent in the V-phase; mol/s.
- V' mass flow rate of the V-phase; kg/s.
- V_S mass flow rate of the nondiffusing solvent in the V-phase; kg/s.
- V_A molar volume of a solute as liquid at its normal boiling point; cm³/mol.
- V_B boilup ratio; mol of boilup/mol of residue.

xxviii

V_b	molar volume of a substance as liquid at its normal boiling point;
V	critical volume: cm ³ /mol
V _C	mass flow rate: kg/s
W	work por unit mass. I/kg
VV 147	work per unit mass, 5/kg.
W	motar now rate of the residue from a distination column; mot/s.
we	weber number defined in equation (7-49); dimensionless.
x_i	mol fraction of species t in either figure or solid phase.
x_i	mass fraction of species i in raffinate (liquid extraction).
$x_{B,M}$	logarithmic mean mol fraction of component B in liquid or solid phase.
<i>x</i>	rectangular coordinate.
<i>x</i>	mass of C/mass of A in raffinate liquids.
X	mol ratio in phase <i>L</i> ; mol of A/mol of A-free <i>L</i> .
X	flow parameter; dimensionless.
X	parameter in Gilliland's correlation, see equation (6-87); dimensionless.
X	mass of $C/(mass of A + mass of C)$ in the raffinate liquids.
X'	mass ratio in phase <i>L</i> ; kg of A/kg of A-free <i>L</i> .
У	rectangular coordinate.
у́	mass of C/mass of B in extract liquids.
$\mathcal{Y}_{B,M}$	logarithmic mean mol fraction of component B in gas phase.
y_i	mol fraction of species <i>i</i> in the gas phase.
y_i	mass fraction of species <i>i</i> in extract (liquid extraction).
Y	mol ratio in phase V; mol of A/mol of A-free V.
Y	parameter in Gilliland's correlation, see equation (6-86); dimensionless.
Y	mass of C/(mass of A + mass of C) in the extract liquids.
Y	molal absolute humidity; mol A/mol B.
Y'	absolute humidity; kg A/kg B´
Y'	mass ratio in phase V; kg of A/kg of A-free V.
z	rectangular coordinate.
z_i	average mol fraction of component <i>i</i> in a solution or multiphase mixture.
Z	total height; m.
Z_c	compressibility factor at critical conditions; dimensionless.
Z_R	total height of the rectifying section of a packed fractionator; m.
Z_S	total height of the stripping section of a packed fractionator; m.

GREEK LETTERS

- $\begin{array}{ll} \alpha & \mbox{thermal diffusivity; } m^2/s. \\ \alpha & \mbox{relative volatility; dimensionless.} \end{array}$
- $\alpha_m,\,\alpha_{\!A\!B}\,$ membrane separation factor; dimensionless.
- β volume coefficient of thermal expansion; K⁻¹.
- Γ matrix of thermodynamic factors defined by equation (1-32).
- Γ concentration polarization factor; dimensionless.
- γ_i activity coefficient of species *i* in solution.
- $\delta \qquad \qquad \text{length of the diffusion path; m.}$
- $\delta \qquad \ \ \, velocity \ \ boundary-layer \ thickness; m.$
- δ_{ij} Kronecker delta; 1 if i = k, 0 otherwise.

Nomenclature

- Δ_R difference in flow rate, equation (7-12); kg/s.
- ε porosity or void fraction; dimensionless.
- ϵ_{AB} Lennard–Jones parameter; erg.
- θ membrane cut; mol of permeate/mol of feed.
- κ Boltzmann constant; 1.38 × 10⁻¹⁶ erg/K.
- κ constant in equation (4-50), defined in equation (4-52); dimensionless.
- λ_i molar latent heat of vaporization of component *i*; J/mol.
- λ similar to the stripping factor, *S*, in equations (4-61) to (4-66).
- $\lambda \qquad \text{mean free path in gases; m.}$
- μ_i chemical potential of species *i*; J/mol.
- μ_B solvent viscosity; cP.
- ν momentum diffusivity, or kinematic viscosity; m²/s.
- v_i stoichiometric number of species *i*.
- ϵ reduced inverse viscosity in Lucas method; (μP)⁻¹.
- π constant; 3.1416
- π Pi groups in dimensional analysis.
- π osmotic pressure; Pa.
- ρ mass density; kg/m³.
- ρ_i mass density of species *i*; kg/m³.
- σ_{AB} Lennard–Jones parameter; Å.
- σ surface tension, dyn/cm, N/m.
- τ shear stress; N/m^{2.}
- τ pore-path tortuosity; dimensionless.
- Φ_B association factor of solvent B; dimensionless.
- φ packing fraction in hollow-fiber membrane module; dimensionless.
- ϕ root of equation (6-82); dimensionless.
- ϕ_e effective relative froth density; height of clear liquid/froth height.
- ϕ_C fractional holdup of the continuous liquid phase.
- ϕ_D fractional holdup of the dispersed liquid phase.
- ϕ_G specific gas holdup; m³ holdup/m³ total volume.
- ω_i mass fraction of species *i*.
- Ω_D diffusion collision integral; dimensionless.
- Ω impeller rate of rotation; rpm.
- Ψ stream function; m²/s.
- Ψ_A molar flux fraction of component A; dimensionless.
- Ψ_0 dry-packing resistance coefficient in Billet–Schultes pressure-drop correlations; dimensionless.

1

Fundamentals of Mass Transfer

1.1 INTRODUCTION

When a system contains two or more components whose concentrations vary from point to point, there is a natural tendency for mass to be transferred, minimizing the concentration differences within the system and moving it toward equilibrium. The transport of one component from a region of higher concentration to that of a lower concentration is called *mass transfer*.

Many of our daily experiences involve mass-transfer phenomena. The invigorating aroma of a cup of freshly brewed coffee and the sensuous scent of a delicate perfume both reach our nostrils from the source by diffusion through air. A lump of sugar added to the cup of coffee eventually dissolves and then diffuses uniformly throughout the beverage. Laundry hanging under the sun during a breezy day dries fast because the moisture evaporates and diffuses easily into the relatively dry moving air.

Mass transfer plays an important role in many industrial processes. A group of operations for separating the components of mixtures is based on the transfer of material from one homogeneous phase to another. These methods—covered by the term mass-transfer operations—include such techniques as distillation, gas absorption, humidification, liquid extraction, adsorption, membrane separations, and others. The driving force for transfer in these operations is a concentration gradient, much as a temperature gradient provides the driving force for heat transfer.

Distillation separates, by partial vaporization, a liquid mixture of miscible and volatile substances into individual components or, in some cases, into groups of components. The separation of a mixture of methanol and water into its components; of liquid air into oxygen, nitrogen, and argon; and of crude petroleum into gasoline, kerosene, fuel oil, and lubricating stock are examples of distillation.

Principles and Modern Applications of Mass-Transfer Operations, Third Edition, Jaime Benitez. © 2017 John Wiley & Sons, Inc. Published 2017 by John Wiley & Sons, Inc.

Fundamentals of Mass Transfer

In *gas absorption*, a soluble vapor is absorbed by means of a liquid in which the solute gas is more or less soluble, from its mixture with an inert gas. The washing of ammonia from a mixture of ammonia and air by means of liquid water is a typical example. The solute is subsequently recovered from the liquid by distillation, and the absorbing liquid can be either discarded or reused. When a solute is transferred from the solvent liquid to the gas phase, the operation is known as *desorption or stripping*.

In *humidification* or *dehumidification* (depending upon the direction of transfer), the liquid phase is a pure liquid containing but one component while the gas phase contains two or more substances. Usually the inert or carrier gas is virtually insoluble in the liquid. Removal of water vapor from air by condensation on a cold surface and the condensation of an organic vapor, such as carbon tetrachloride out of a stream of nitrogen, are examples of dehumidification. In humidification operations, the direction of transfer is from the liquid to the gas phase.

The *adsorption* operations exploit the ability of certain solids preferentially to concentrate specific substances from solution onto their surfaces. In this manner, the components of either gaseous or liquid solutions can be separated from each other. A few examples will illustrate the great variety of practical applications of adsorption. It is used to dehumidify air and other gases, to remove objectionable odors and impurities from industrial gases, to recover valuable solvent vapors from dilute mixtures with air and other gases, to remove objectionable taste and odor from drinking water, and many other applications.

Liquid extraction is the separation of the constituents of a liquid solution by contact with another insoluble liquid. If the substances constituting the original solution distribute themselves differently between the two liquid phases, a certain degree of separation will result. The solution which is to be extracted is called the *feed*, and the liquid with which the feed is contacted is called the *solvent*. The solvent-rich product of the operation is called the *extract*, and the residual liquid from which the solute has been removed is called the *raffinate*.

Membrane separations are rapidly increasing in importance. In general, the membranes serve to prevent intermingling of two miscible phases. They also prevent ordinary hydrodynamic flow, and movement of substances through them is by diffusion. Separation of the components of the original solution takes place by selectively controlling their passage from one side of the membrane to the other. An example of a membrane-mediated, liquid–liquid separation process is *dialysis*. In this process, a colloid is removed from a liquid solution by contacting the solution with a solvent through an intervening membrane which is permeable to the solution, but not to the larger colloidal particles. For example, aqueous beet-sugar solutions containing undesired colloidal material are freed of the latter by contact with water through a semipermeable membrane. Sugar and water diffuse through the membrane, but not the colloid.

1.2 Molecular Mass Transfer

Returning to the lump of sugar added to the cup of coffee, it is evident that the time required for the sugar to distribute uniformly depends upon whether the liquid is quiescent, or whether it is mechanically agitated by a spoon. In general, the mechanism of mass transfer depends upon the dynamics of the system in which it occurs. Mass can be transferred by random molecular motion in quiescent fluids, or it can be transferred from a surface into a moving fluid, aided by the dynamic characteristics of the flow. These two distinct modes of transport, *molecular mass transfer* and *convective mass transfer*, are analogous to conduction heat transfer and convective heat transfer. Each of these modes of mass transfer will be described and analyzed. The two mechanisms often act simultaneously. Frequently, when this happens, one mechanism can dominate quantitatively so that approximate solutions involving only the dominant mode can be used.

1.2 MOLECULAR MASS TRANSFER

As early as 1815, it was observed qualitatively that whenever a gas mixture contains two or more molecular species, whose relative concentrations vary from point to point, an apparently natural process results which tends to diminish any inequalities in composition. This macroscopic transport of mass, independent of any convection effects within the system, is defined as *molecular diffusion*.

In the specific case of a gaseous mixtures, a logical explanation of this transport phenomenon can be deduced from the kinetic theory of gases. At any temperature above absolute zero, individual molecules are in a state of continual yet random motion. Within dilute gas mixtures, each solute molecule behaves independently of the other solute molecules, since it seldom encounters them. Collisions between the solute and the solvent molecules are continually occurring. As a result of the collisions, the solute molecules move along a zigzag path, sometimes toward a region of higher concentration, sometimes toward a region of lower concentration.

Consider a hypothetical section passing normal to the concentration gradient within an isothermal, isobaric gaseous mixture containing solute and solvent molecules. The two thin, equal elements of volume above and below the section will contain the same number of molecules, as stipulated by Avogadro's law (Welty et al., 1984).

Although it is not possible to state which way any particular molecule will travel in a given interval of time, a definite number of the molecules in the lower element of volume will cross the hypothetical section from below, and the same number of molecules will leave the upper element and cross the section from above. With the existence of a concentration gradient, there are more solute molecules in one of the elements of volume than in the other; accordingly, an overall net transfer from a region of higher concentration to one of lower concentration will result. The net flow of each molecular species occurs in the direction of a negative concentration gradient. The laws of mass transfer show the relation between the flux of the diffusing substance and the concentration gradient responsible for this mass transfer. Since diffusion occurs only in mixtures, its evaluation must involve an examination of the effect of each component. For example, it is often desired to know the diffusion rate of a specific component relative to the velocity of the mixture in which it is moving. Since each component may possess a different mobility, the mixture velocity must be evaluated by averaging the velocities of all the components present.

In order to establish a common basis for future discussions, definitions and relations which are often used to explain the role of components within a mixture are considered next.

1.2.1 Concentrations

Your objectives in studying this section are to be able to:

- 1. Convert a composition given in mass fraction to mole fraction, and the reverse.
- 2. Transform a material from one measure of concentration to another, including mass/volume and moles/volume.

In a multicomponent mixture, the concentration of particular species can be expressed in many ways. A mass concentration for each species, as well as for the mixture, can be defined. For species A, the mass concentration, ρ_A , is defined as the mass of A per unit volume of the mixture. The total mass concentration, or density, ρ , is the total mass of the mixture contained in a unit volume; that is,

$$\rho = \sum_{i=1}^{n} \rho_i \tag{1-1}$$

where *n* is the number of species in the mixture. The *mass fraction*, ω_A , is the mass concentration of species A divided by the total mass density,

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

The sum of the mass fractions, by definition, must be 1:

$$\sum_{i=1}^{n} \omega_i = 1 \tag{1-3}$$

1.2 Molecular Mass Transfer

The *molar concentration* of species A, c_A , is defined as the number of moles of A present per unit volume of the mixture. By definition, one mol of any species contains a mass equivalent to its molecular weight; therefore, the mass concentration and the molar concentration are related by

$$c_A = \frac{\rho_A}{M_A} \tag{1-4}$$

where M_A is the molecular weight of species A. When dealing with a gas phase under conditions in which the ideal gas law applies, the molar concentration is given by

$$c_A = \frac{p_A}{RT} \tag{1-5}$$

where p_A is the partial pressure of the species A in the mixture, T is the absolute temperature, and R is the gas constant. The total molar concentration, c, is the total moles of mixture contained in a unit volume; that is,

$$c = \sum_{i=1}^{n} c_i \tag{1-6}$$

For a gaseous mixture that obeys the ideal gas law,

$$c = \frac{P}{RT} \tag{1-7}$$

where *P* is the total pressure. The *mol fraction* for liquid or solid mixtures, x_A , and for gaseous mixtures, y_A , are the molar concentrations of species A divided by the total molar concentration:

$$\begin{aligned} x_A &= \frac{c_A}{c} \quad \text{(liquids and solids)} \\ y_A &= \frac{c_A}{c} \quad \text{(gases)} \end{aligned} \tag{1-8}$$

For a gaseous mixture that obeys the ideal gas law, the mol fraction, y_A , can be written in terms of pressures:

$$y_A = \frac{c_A}{c} = \frac{p_A}{P} \tag{1-9}$$

Equation (1-9) is an algebraic representation of Dalton's law for gas mixtures. The sum of the mol fractions, by definition, must be 1.

$$\sum_{i=1}^{n} y_i = \sum_{i=1}^{n} x_i = 1.0$$
 (1-10)

Example 1.1 Concentration of Feed to a Gas Absorber

A gas containing 88% (by volume) CH_4 , 4% C_2H_6 , 5% $n-C_3H_8$, and 3% $n-C_4H_{10}$ at 300 K and 500 kPa will be scrubbed by contact with a nonvolatile oil in a gas absorber. The objective of the process is to recover in the liquid effluent as much as possible of the heavier hydrocarbons in the feed (see Figure 1.1). Calculate:

- (a) Total molar concentration in the gas feed.
- (b) Density of the gas feed.
- (c) Composition of the gas feed, expressed in terms of mass fractions.



Solution

(a) Use Equation (1-7) to calculate the total molar concentration:

$$c = \frac{P}{RT} = \frac{500}{8.314 \times 300} = 0.20 \frac{\text{kmol}}{\text{m}^3}$$

1.2 Molecular Mass Transfer

(b) Calculate the gas average molecular weight, M_{av} :

Component	kmol	Molecular weight	Mass, kg
CH_4	88	16.04	1411.52
$C_2 H_6$	4	30.07	120.28
$\tilde{n-C_3H_8}$	5	44.09	220.45
$n-C_4H_{10}$	3	58.12	174.36
Total	100		1926.61

Basis: 100 kmol of gas mixture

$$M_{av} = \frac{1926.61}{100} = 19.26 \ \frac{\text{kg}}{\text{kmol}}$$

To calculate the mixture mass density:

$$\rho = cM_{av} = 0.20 \times 19.26 = 3.85 \frac{\text{kg}}{\text{m}^3}$$

(c)	Calculate	the	mass	fraction	of	each	component	in	the	gas	mixture	from	the
int	ermediate	rest	ilts of	part (b):									

Component	Mass, kg	Mass fraction
CH4	1411.52	(1411.52/1926.61) = 0.733
$C_2 H_6$	120.28	0.062
$n-C_3H_8$	220.45	0.114
$n-C_4H_{10}$	174.36	0.091
Total	1926.61	1.000

Example 1.2 Concentration of Potassium Nitrate Wash Solution

In the manufacture of potassium nitrate, potassium chloride reacts with a hot aqueous solution of sodium nitrate according to

$$\mathrm{KCl}{+}\mathrm{NaNO}_{3} \twoheadrightarrow \mathrm{KNO}_{3}{+}\mathrm{NaCl}$$

The reaction mixture is cooled down to 293 K and pure KNO_3 crystallizes. The resulting slurry contains the KNO_3 crystals and an aqueous solution of both KNO_3 and NaCl. The crystals in the slurry are washed in a multistage process with a saturated KNO_3 solution to free them of NaCl (see Figure 1.2). The equilibrium solubility of KNO_3 in water at 293 K is 24% (by weight); the density of the saturated solution is 1162 kg/m³ (Perry and Chilton, 1973). Calculate:

(a) Total molar density of the fresh wash solution.

(b) Composition of the fresh wash solution, expressed in terms of molar fractions.



Figure 1.2 Schematic diagram of the washing process in Example 1.2.

Solution

(a) Calculate the average molecular weight, $M_{av}\!,$ of the wash solution, and then its total molar density.

Component	Mass, kg	Molecular weight	kmol
KNO3	24	101.10	0.237
H_2O	76	18.02	4.218
Total	100		4.455

Basis: 100 kg of fresh wash solution

Therefore,

$$M_{av} = \frac{100}{4.455} = 22.45 \ \frac{\text{kg}}{\text{kmol}}$$

$$c = \frac{\rho}{M_{av}} = \frac{1162}{22.45} = 51.77 \frac{\text{kmol}}{\text{m}^3}$$

(b) Calculate the mol fractions from intermediate results in part (a):

Component	kmol	Mol fraction
$\frac{\mathrm{KNO}_3}{\mathrm{H}_2\mathrm{O}}$	$0.237 \\ 4.218$	(0.237/4.455) = 0.053 0.947
Total	4.455	1.000

Example 1.3 Material Balances on a Bio-Artificial Kidney (Montgomery et al., 1998)

The primary functions of the kidneys are to remove waste products (such as urea, uric acid, and creatinine), and to maintain the fluid and salt balance in the blood. Blood consists of two parts: blood cells, mostly red (45% by volume), and plasma (55% by volume). Urea, uric acid, creatinine, and water are all found in the plasma. If the kidneys fail, wastes start to accumulate and the body becomes overloaded with fluid. Fortunately, patients with renal failure can use an external dialysis machine, also known as an artificial kidney, to clean the blood. The cleaning of the blood in the artificial kidney is due to the difference in toxin concentrations between the blood and the dialysis fluid. Semi-permeable membranes in the machine selectively allow toxins to pass from the blood to the dialysis fluid.

During a dialysis procedure, a patient was connected to the machine for 4 hours. The blood was pumped through the artificial kidney at the rate of 1200 mL/min. The partially cleansed blood was returned to the patient's body, and the wastes removed were collected in the used dialysis fluid. During the procedure, the patient's kidneys were completely inactive. A total of 1540 g of urine was collected with an urea concentration of 1.3% by weight. A sample of the blood plasma was analyzed before the dialysis and found to contain 155.3 mg/dL of urea. The specific gravity of the plasma was measured at 1.0245. Calculate:

(a) The urea removal efficiency by the artificial kidney.

(b) The urea concentration in the plasma of the cleansed blood, in mg/dL.

Solution

(a) Write a material balance for urea on the artificial kidney.

Basis: 4 hours

Assuming that the rate of formation and decomposition of urea during the procedure is negligible, and that no urea is removed by the patient's kidneys:

urea in "clean" blood = urea in "dirty" blood - urea in urine

The mass of urea in the urine is simply $1540 \times 0.013 = 20.0$ g. Calculate the mass of urea in the "dirty" blood by the following procedure:

• Calculate the total volume of plasma that flows through the artificial kidney in 4 hours:

$$\frac{1200 \text{ mL of blood}}{\text{min}} \left| \frac{60 \text{ min}}{\text{h}} \right| \frac{0.55 \text{ mL of plasma}}{\text{mL of blood}} \left| \frac{1 \text{ dL}}{100 \text{ mL}} \right| \frac{4 \text{ h}}{\text{mL of blood}} = 1584 \text{ dL}$$

• Calculate the urea in the "dirty" blood from the given plasma concentration:

 $\frac{155.3 \text{ mg of urea}}{\text{dL of plasma}} \left| \frac{1.0 \text{ g}}{1000 \text{ mg}} \right| \frac{1584 \text{ dL of plasma}}{246 \text{ g of urea}} = 246 \text{ g of urea}$

The urea removal efficiency is then $(20/246) \times 100 = 8.1\%$.

(b) Substituting in the material balance, the mass of urea in the clean blood is found to be 246 - 20 = 226 g. To calculate the corresponding concentration, the volume of plasma remaining after dialysis must be calculated. Assuming that no cells are removed by the machine during the procedure, the mass of plasma remaining is the difference between the mass of plasma entering the artificial kidney and the mass of urine removed. The mass of plasma entering is given by

 $\frac{1.0245 \text{ g of plasma}}{\text{mL of plasma}} \frac{100 \text{ mL}}{1.0 \text{ dL}} \frac{1584 \text{ dL of plasma}}{1.0 \text{ dL}} = 162,280 \text{ g of plasma}$

The mass of plasma remaining is 162,280 - 1540 = 160,740 g. The volume of plasma remaining is $(160,740/(1.0245 \times 100) = 1569$ dL of plasma. Therefore, the urea concentration in the remaining plasma is $(226 \times 1000)/1569 = 144$ mg/dL.

Notice that in the artificial kidney the removal efficiency of all the wastes must be kept relatively low because of the need to maintain homeostasis in the patient's body at all times. If too many wastes are removed at one time, death may occur.

1.2.2 Velocities and Fluxes

Your objectives in studying this section are to be able to:

- 1. Define the following terms: mass-average velocity, molar-average velocity, mass (or molar) flux, and diffusion mass (or molar) flux.
- 2. Write down an expression to calculate the mass (or molar) flux relative to a fixed coordinate system in terms of the diffusion mass (or molar) flux and the bulk motion contribution.

The basic empirical relation to estimate the rate of molecular diffusion, first postulated by Fick (1855) and, accordingly, often referred to as Fick's first law, quantifies the diffusion of component A in an isothermal, isobaric system. According to Fick's law, a species can have a velocity relative to the mass or molar-average velocity (called *diffusion velocity*) only if gradients in the concentration exist. In a multicomponent system, the various species will normally move at dif-

1.2 Molecular Mass Transfer

ferent velocities; for that reason, an evaluation of a characteristic velocity for the gas mixture requires the averaging of the velocities of each species present.

The *mass-average velocity* for a multicomponent mixture is defined in terms of the mass densities

$$\mathbf{v} = \frac{\sum_{i=1}^{n} \rho_i \mathbf{v}_i}{\sum_{i=1}^{n} \rho_i} = \frac{\sum_{i=1}^{n} \rho_i \mathbf{v}_i}{\rho} = \sum_{i=1}^{n} \omega_i \mathbf{v}_i$$
(1-11)

where \mathbf{v}_i denotes the absolute velocity of species i relative to stationary coordinate axis. The mass-average velocity is the velocity that would be measured by a pitot tube. On the other hand, the molar-average velocity for a multicomponent mixture is defined in terms of the molar concentrations of all components by

n

$$\mathbf{V} = \frac{\sum_{i=1}^{n} c_i \mathbf{v}_i}{\sum_{i=1}^{n} c_i} = \frac{\sum_{i=1}^{n} c_i \mathbf{v}_i}{c} = \sum_{i=1}^{n} x_i \mathbf{v}_i$$
(1-12)

Diffusion rates are most conveniently described in terms of fluxes. The mass (or molar) flux of a given species is a vector quantity denoting the amount of the particular species, in either mass or molar units, that passes per given unit time through a unit area normal to the vector. The flux may be defined with reference to coordinates that are fixed in space, coordinates which are moving with the mass-average velocity, or coordinates which are moving with the molar-average velocity.

The mass flux of species i with respect to coordinates that are fixed in space is defined by

$$\mathbf{n}_{i} = \boldsymbol{\rho}_{i} \mathbf{v}_{i} \tag{1-13}$$

If we sum the component fluxes, we obtain the *total mass flux*

$$\mathbf{n} = \rho \mathbf{v} \tag{1-14}$$

The molar flux of species i with respect to coordinates that are fixed in space is given by

$$\mathbf{N}_i = c_i \mathbf{v}_i \tag{1-15}$$

The *total molar flux* is the sum of these quantities:

$$\mathbf{N} = c\mathbf{V} \tag{1-16}$$

The mass diffusion flux of species i with respect to the mass-average velocity is given by

$$\mathbf{j}_i = \boldsymbol{\rho}_i \left(\mathbf{v}_i - \mathbf{v} \right)$$
 and $\sum_{i=1}^n \mathbf{j}_i = 0$ (1-17)

The *molar diffusion flux* of species i with respect to the molar-average velocity is given by

$$\mathbf{J}_{i} = c_{i} \left(\mathbf{v}_{i} - \mathbf{V} \right) \quad \text{and} \quad \sum_{i=1}^{n} \mathbf{J}_{i} = 0$$
(1-18)

The mass flux \mathbf{n}_i is related to the mass diffusion flux as

$$\mathbf{n}_{i} = \mathbf{j}_{i} + \boldsymbol{\rho}_{i} \mathbf{v} = \mathbf{j}_{i} + \boldsymbol{\omega}_{i} \mathbf{n}$$
(1-19)

The molar flux N_i is related to the molar diffusion flux as

$$\mathbf{N}_{i} = \mathbf{J}_{i} + c_{i}\mathbf{V} = \mathbf{J}_{i} + y_{i}\mathbf{N}$$
(1-20)

.

It is important to note that the molar flux, N_i , described by equation (1-20) is a resultant of the two vector quantities:

$$\mathbf{J}_{i}$$
 the molar diffusion flux, \mathbf{J}_{i} , resulting from the con-
centration gradient; this term is referred to as the
concentration gradient contribution;

and

$$y_i \mathbf{N} = c_i \mathbf{V}$$
 the molar flux resulting as component *i* is carried in the bulk flow of the fluid; this flux term is designated the *bulk motion contribution*.

Either or both quantities can be a significant part of the total molar flux, N_{i} . Whenever equation (1-20) is applied to describe molar diffusion, the vector nature of the individual fluxes, N_i , must be considered. The same applies for the mass fluxes in equation (1-19).

Example 1.4 Oxygen Transport in the Human Body

. .

Oxygen is important for living organisms, since metabolic processes in the body involve oxygen. The transport of oxygen in the body is therefore crucial to life. The blood in the human circulatory system transports oxygen from the lungs to every single cell in the body. In the larger blood vessels, most of the oxygen transport is due to the bulk motion contribution, while the concentration gradient contribution is more important in smaller blood vessels and capillaries. In the larger vessels, blood flow is rapid and unimpeded, and the oxygen concentration in the fluid

1.2 Molecular Mass Transfer

remains relatively constant. On the other hand, in smaller vessels oxygen diffuses out of the veins into the surrounding tissue, resulting in decreasing concentrations in the blood.

When referring to the oxygen concentration in the blood, both oxygen bound to hemoglobin and aqueous oxygen dissolved in the plasma are included. Each molecule of hemoglobin, a protein in red blood cells, can bind four oxygen molecules. The vast majority of the blood oxygen is coupled to hemoglobin. In the larger blood vessels, any dissolved oxygen lost to the surrounding tissues by diffusion is replaced by oxygen dissociating from the hemoglobin into the plasma to maintain its constant concentration.

1.2.3 The Maxwell-Stefan Relations

Your objectives in studying this section are to be able to:

- 1. Write down the Maxwell–Stefan (MS) equations for a binary system, and for multicomponent systems.
- 2. Define the concepts MS diffusivity, and thermodynamic factor.
- 3. Express the driving force for mass transfer in terms of mole fraction gradients for ideal and nonideal systems.

Consider a binary mixture of ideal gases 1 and 2 at constant temperature and pressure. From a momentum balance describing collisions between molecules of species 1 and molecules of species 2, we obtain (Taylor and Krishna, 1993)

$$\nabla p_1 = -f_{12}y_1y_2\left(\mathbf{v}_1 - \mathbf{v}_2\right) \tag{1-21}$$

where f_{12} is an empirical parameter analogous to a friction factor or a drag coefficient. For convenience, we define an inverse drag coefficient $D_{12} = P/f_{12}$ and rewrite equation (1-21) as

$$\mathbf{d}_1 = \frac{\nabla p_1}{P} = -\frac{y_1 y_2 \left(\mathbf{v}_1 - \mathbf{v}_2\right)}{D_{12}}$$
(1-22)

where \mathbf{d}_1 is the driving force for diffusion of species 1 in an ideal gas mixture at constant temperature and pressure.

Equation (1-22) is the MS equation for the diffusion of species 1 in a binary ideal gas mixture. The symbol D_{12} is the MS diffusivity. From a similar analysis for species 2,

$$\mathbf{d}_{2} = \frac{\nabla p_{2}}{P} = -\frac{y_{1}y_{2}(\mathbf{v}_{2} - \mathbf{v}_{1})}{D_{21}}$$
(1-23)

For all the applications considered in this book the system pressure is constant across the diffusion path. Then, equations (1-22) and (1-23) simplify to

$$\begin{aligned} \frac{\nabla y_1}{P} &= -\frac{y_1 y_2 \left(\mathbf{v}_1 - \mathbf{v}_2\right)}{D_{12}} \\ \frac{\nabla y_2}{P} &= -\frac{y_1 y_2 \left(\mathbf{v}_2 - \mathbf{v}_1\right)}{D_{21}} \end{aligned} \tag{1-24}$$

Example 1.5 Diffusivities in Binary Mixtures

Show that, for a binary mixture, $D_{12} = D_{21}$.

Solution

Since for a binary mixture $(y_1 + y_2) = 1.0$,

$$\nabla y_1 = -\nabla y_2$$

Then, from equation (1-24)

$$-\frac{y_1y_2(\mathbf{v}_1 - \mathbf{v}_2)}{D_{12}} = \frac{y_1y_2(\mathbf{v}_2 - \mathbf{v}_1)}{D_{21}}$$

which can be true only if $D_{12} = D_{21}$.

For multicomponent mixtures, equation (1-22) can be generalized to (Taylor and Krishna, 1993)

$$\mathbf{d}_{i} = -\sum_{j=1}^{n} \frac{y_{i}y_{j}\left(\mathbf{v}_{i} - \mathbf{v}_{j}\right)}{D_{ij}} \qquad i = 1, 2, \dots, n-1$$

$$(1-25)$$

Equations (1-25) can be written in terms of the molar fluxes $\mathbf{N}_i = c_i \mathbf{v}_i$ to get

1.2 Molecular Mass Transfer

$$\mathbf{d}_{i} = -\sum_{j=1}^{n} \frac{y_{i} \mathbf{N}_{j} - y_{j} \mathbf{N}_{i}}{c D_{ij}} \qquad i = 1, 2, \dots, n-1$$
(1-26)

or, in terms of the diffusion fluxes, \mathbf{J}_i

$$\mathbf{d}_{i} = -\sum_{j=1}^{n} \frac{y_{i} \mathbf{J}_{j} - y_{j} \mathbf{J}_{i}}{c D_{ij}} \qquad i = 1, 2, \dots, n-1$$
(1-27)

These are the MS diffusion equations for multicomponent systems. They are named after the Scottish physicist James Clerk Maxwell and the Austrian scientist Josef Stefan who were primarily responsible for their development around 1870. It is important to point out that only (n - 1) of the MS equations are independent because the \mathbf{d}_i must sum to zero. Also, for a multicomponent ideal gas mixture, a more elaborate analysis than that of Example 1.5 is needed to show that (Taylor and Krishna, 1993)

$$D_{ij} = D_{ji} \tag{1-28}$$

It is easy to show, for a binary mixture of ideal gases where the driving force for diffusion is the mol fraction gradient, equation (1-27) reduces to

$$\mathbf{J}_{1} = -cD_{12}\mathbf{d}_{1} = -cD_{12}\nabla y_{1}$$
(1-29)

For nonideal fluids the driving force for diffusion must be defined in terms of chemical potential gradients as

$$\mathbf{d}_i = \frac{x_i}{RT} \nabla_{T,P} \boldsymbol{\mu}_i \tag{1-30}$$

The subscripts T,P are to emphasize that the gradient is to be calculated under constant temperature and pressure conditions. We may express equation (1-30) in terms of activity coefficients, γ_i , and mol fraction gradients as

$$\mathbf{d}_{i} = \sum_{j=1}^{n-1} \Gamma_{ij} \nabla x_{j} = \Gamma \nabla x_{i}$$
(1-31)

where the *thermodynamic factor matrix* Γ is given by

$$\Gamma_{ij} = \delta_{ij} + \frac{\partial \ln \gamma_i}{\partial x_j} \bigg|_{T,P,\Sigma}$$
(1-32)

where δ_{ij} is the *Kronecker delta* defined as

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases}$$
(1-33)

The symbol Σ is used in equation (1-32) to indicate that the differentiation with respect to mol fraction is to be carried out in such a manner that the mol fractions always add up to 1.0. Combining equations (1-26), (1-27), and (1-31) we obtain

$$\Gamma \nabla x_i = \sum_{j=1}^n \frac{x_i \mathbf{J}_j - x_j \mathbf{J}_i}{cD_{ij}} = \sum_{j=1}^n \frac{x_i \mathbf{N}_j - x_j \mathbf{N}_i}{cD_{ij}} \quad i = 1, 2, \dots, n-1$$
(1-34)

For a multicomponent mixture of ideal gases, equation (1-34) becomes

$$\nabla y_{i} = \sum_{j=1}^{n} \frac{y_{i} \mathbf{J}_{j} - y_{j} \mathbf{J}_{i}}{c D_{ij}} = \sum_{j=1}^{n} \frac{y_{i} \mathbf{N}_{j} - y_{j} \mathbf{N}_{i}}{c D_{ij}} \quad i = 1, 2, \dots, n-1$$
(1-35)

For a binary mixture, equation (1-34) reduces to

$$\mathbf{J}_{1} = -cD_{12}\boldsymbol{\Gamma}\boldsymbol{\nabla}\boldsymbol{x}_{1} \tag{1-36}$$

where the *thermodynamic factor* Γ is given by

$$\Gamma = 1 + x_1 \frac{\partial \ln \gamma_1}{\partial x_1} \tag{1-37}$$

The thermodynamic factor is evaluated for liquid mixtures from activity coefficient models. For a *regular solution*, for example,

$$\ln \gamma_1 = A \left(1 - x_1 \right)^2 \tag{1-38}$$

therefore, equation (1-37) yields

$$\Gamma = 1 - 2Ax_1x_2 \tag{1-39}$$

1.2.4 Fick's First Law for Binary Mixtures

Your objectives in studying this section are to be able to:

- 1. Write down Fick's first law for diffusion in a binary, isothermal, isobaric mixture.
- 2. Define the Fick diffusivity, and establish the relation between the Fick diffusivity and the MS diffusivity for a binary system.

1.2 Molecular Mass Transfer

At about the same time that Maxwell and Stefan were developing their ideas of diffusion in multicomponent mixtures, Adolf Fick and others were attempting to uncover the basic diffusion equations through experimental studies involving binary mixtures (Fick, 1855). The result of Fick's work was the "law" that bears his name. The Fick equation for a binary mixture in an isothermal, isobaric system is

$$\mathbf{J}_{1} = -c\mathbf{D}_{12}\nabla x_{1} \tag{1-40}$$

where D_{12} is the *Fick diffusivity or diffusion coefficient*. Comparing equations (1-36) and (1-40) we see that, for a binary system, the Fick diffusivity D and the MS diffusivity D are related by

$$D_{12} = D_{12}\Gamma$$
 (1-41)

For ideal systems, Γ is unity and the diffusivities are identical.

$$D_{12} = D_{12}$$
 for ideal systems (1-42)

The correlation and prediction of Fick and MS diffusion coefficients are discussed in the section that follows. The Fick diffusivity incorporates two aspects: (1) the significance of an inverse drag coefficient (D), and (2) thermodynamic nonideality (Γ). Consequently, the physical interpretation of the Fick diffusion coefficient is less transparent than for the MS diffusivity.

1.3 THE DIFFUSION COEFFICIENT

Fick's law proportionality factor, D_{12} , is known as the diffusion coefficient or diffusivity. Its fundamental dimensions, which are obtained from equation (1-40),

$$\mathbf{D}_{12} = -\frac{\mathbf{J}_1}{c \boldsymbol{\nabla} x_1} = \left(\frac{\mathbf{M}}{\mathbf{L}^2 \mathbf{t}}\right) \left(\frac{1}{\mathbf{M}/\mathbf{L}^3 \times 1/\mathbf{L}}\right) = \frac{\mathbf{L}^2}{\mathbf{t}}$$

are identical to the fundamental dimensions of the other transport properties: kinematic viscosity, ν , and thermal diffusivity, α . The mass diffusivity is usually reported in units of cm²/s; the SI units are m²/s, which is a factor 10⁻⁴ smaller.

The diffusion coefficient depends upon the pressure, temperature, and composition of the system. Experimental values for the diffusivities of gases, liquids, and solids are tabulated in Appendix A. As one might expect from consideration of the mobility of the molecules, the diffusivities are generally higher for gases (in the range of 0.5×10^{-5} to 1.0×10^{-5} m²/s) than for liquids (in the range of 10^{-10} to 10^{-9} m²/s) which are higher than the values reported for solids (in the range of 10^{-14} to 10^{-10} m²/s). In the absence of experimental data, semitheoretical expressions have been developed which give approximations, sometimes as valid as experimental values due to the difficulties encountered in their measurement.

1.3.1 Diffusion Coefficients for Binary Ideal Gas Systems

Your objectives in studying this section are to be able to:

- 1. Estimate diffusion coefficients for binary gas systems using the Wilke-Lee equation with tabulated values of the Lennard-Jones parameters.
- 2. Estimate diffusion coefficients for binary gas systems using the Wilke–Lee equation with values of the Lennard–Jones parameters estimated from empirical correlations.
- 3. Use a Mathcad® routine to implement calculation of diffusion coefficients for binary gas systems using the Wilke–Lee equation.

The theory describing diffusion in binary gas mixtures at low to moderate pressures has been well developed. Modern versions of the kinetic theory of gases have attempted to account for the forces of attraction and repulsion between molecules. Hirschfelder et al. (1949), using the Lennard–Jones potential to evaluate the influence of intermolecular forces, presented the following equation to estimate the diffusion coefficient for gas pairs of nonpolar, nonreacting molecules:

$$D_{AB} = \frac{0.00266T^{1.5}}{PM_{AB}^{0.5}\sigma_{AB}^2\Omega_D}$$
(1-43)

where

$$M_{AB} = \frac{2M_A M_B}{M_A + M_B}$$

D_{AB}	= diffusion coefficient, cm ² /s
M_A, M_B	= molecular weights of A and B
T	= temperature, K
Р	= pressure, bar
σ_{AB}	= "collision diameter," a Lennard–Jones parameter, Å
Ω_D	= diffusion collision integral, dimensionless

The collision integral, Ω_D , is a function of the temperature and of the intermolecular potential field for one molecule of A and one molecule of B. It is usually tabulated as a function of $T^* = \kappa T/\epsilon AB$, where κ is the Boltzmann constant (1.38 × 10⁻¹⁶ erg/K) and ϵ_{AB} is the energy of molecular interaction for the binary system A and B—a Lennard–Jones parameter—in erg. A very accurate approximation of Ω_D can be obtained from (Neufield et al., 1972)

1.3 The Diffusion Coefficient

(1-44)

$$\begin{array}{ll} \mbox{where} & T^* = \mbox{kT}/ \ensuremath{\varepsilon_{AB}}, & a = 1.06036 & b = 0.15610 \\ c = 0.19300 & d = 0.47635 & e1 = 1.03587 \\ f = 1.52996 & g = 1.76474 & h = 3.89411 \\ \end{array}$$

For a binary system composed of nonpolar molecular pairs, the Lennard-Jones parameters of the pure components may be combined empirically by the following relations:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \qquad \epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B} \qquad (1-45)$$

These relations must be modified for polar–polar and polar–nonpolar molecular pairs; the proposed modifications are discussed by Hirschfelder et al. (1954).

The Lennard–Jones parameters for the pure components are usually obtained from viscosity data. Appendix B tabulates some of the data available. In the absence of experimental data, the values of the parameters for pure components may be estimated from the following empirical correlations:

$$\sigma = 1.18 V_{\iota}^{1/3} \tag{1-46}$$

$$\varepsilon / \kappa = 1.15T_b \tag{1-47}$$

where V_b is the molar volume of the substance as liquid at its normal boiling point, in cm³/gmol, and T_b is the normal boiling point temperature. Molar volumes at normal boiling point for some commonly encountered compounds are listed in Table 1.1. For other compounds not listed in Table 1.1, if a reliable value of the critical volume (V_c) is available, the Tyn and Calus (1975) method is recommended:

$$V_{\mu} = 0.285 V_{\mu}^{1.048} \tag{1-48}$$

Otherwise, the atomic volume of each element present are added together as per the molecular formula of the compound. Table 1.2 lists the contributions for each of the constituent atoms.

Several proposed methods for estimating D_{AB} in low-pressure binary gas systems retain the general form of equation (1-43), with empirical constants based on experimental data. One of the most widely used methods, shown to be quite general and reliable, was proposed by Wilke and Lee (1955):

$$\mathbf{D}_{AB} = \frac{\left[3.03 - \left(\frac{0.98}{M_{AB}^{0.5}}\right)\right] \left(10^{-3}\right) T^{1.5}}{P M_{AB}^{0.5} \sigma_{AB}^2 \Omega_D}$$
(1-49)

where all the symbols are as defined under equation (1-43). The use of the Wilke–Lee equation is illustrated in the following examples.

Compound	Volume (cm ³ /gmol)	Compound	Volume (cm ³ /gmol)
Hydrogen, H ₂	14.3	Nitric oxide, NO	23.6
Oxygen, O_2	25.6	Nitrous oxide, N_2O	36.4
Nitrogen, \bar{N}_2	31.2	Ammonia, NH ₃	25.8
Air	29.9	Water, H_2O	18.9
Carbon monoxide, CO	30.7	Hydrogen sulfide, H ₂ S	32.9
Carbon dioxide, CO_2	34.0	Bromine, Br_2	53.2
Carbonyl sulfide, CÕS	51.5	Chlorine, Cl_2	48.4
Sulfur dioxide, SO_2	44.8	Iodine, I_2	71.5

Table 1.1 Molar Volumes at Normal Boiling Point

Source: Data from Welty et al. (1984).

Element	Volume (cm ³ /gmol)	Element	Volume (cm ³ /gmol)		
Bromine	27.0	Oxygen, except as			
Carbon	14.8	noted below	7.4		
Chlorine	24.6	Oxygen, in methyl			
Hydrogen	3.7	esters	9.1		
Iodine	37.0	Oxygen, in methyl			
Nitrogen	15.6	ethers	9.9		
Nitrogen, in		Oxygen, in higher			
primary amines	10.5	ethers and other esters	11.0		
Nitrogen, in		Oxygen, in acids	12.0		
secondary amines	12.0	Sulfur	25.6		
For three-membered ri	ng, such as ethyl	ene oxide, subtract 6.0			
For four-membered rin	g, such as cyclob	utane, subtract 8.5			
For five-membered rin	g, such as furan,	subtract 11.5			
For pyridine, subtract					
For benzene ring, subt					
For naphthalene ring,	For naphthalene ring, subtract 30.0				
For anthracene ring, subtract 47.5					

 Table 1.2 Atomic Volume Contributions of the Elements

Source: Data from Welty et al. (1984).

Example 1.6 Calculation of Diffusivity by the Wilke-Lee Equation with Known Values of the Lennard-Jones Parameters

Estimate the diffusivity of carbon disulfide vapor in air at 273 K and 1 bar using the Wilke–Lee equation (1-49). Compare this estimate with the experimental value reported in Appendix A.

Solution

Values of the Lennard–Jones parameters (σ and $\epsilon/\kappa)$ are obtained from Appendix B:

	σ, in Å	ϵ/κ , in K	M, g/mol
$\overline{\mathrm{CS}_2}$	4.483	467	76
Air	3.620	97	29

Evaluate the various parameters of equation (1-49) as follows:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} = 4.052 \text{ Å}$$

$$\frac{\varepsilon_{_{AB}}}{\kappa} = \sqrt{\frac{\varepsilon_{_A}}{\kappa} \times \frac{\varepsilon_{_B}}{\kappa}} = \sqrt{467 \times 97} = 212.8 \text{ K}$$

$$\frac{\kappa T}{\varepsilon_{_{AB}}} = \frac{273.0}{212.8} = 1.283 \qquad \Omega_{_D} = 1.282 \quad \left[\text{from equation (1-44)} \right]$$

$$M_{_{AB}} = 2\left[\frac{M_{_{A}}M_{_{B}}}{M_{_{A}} + M_{_{B}}}\right] = \frac{2 \times 76 \times 29}{76 + 29} = 41.981$$

Substituting these values into the Wilke-Lee equation yields

$$D_{AB} = \frac{0.001 \left(3.03 - \frac{0.98}{\sqrt{41.981}}\right) \left(273\right)^{1.5}}{\left(1.0\right) \left(4.052\right)^2 \left(1.282\right) \sqrt{41.981}} = 0.0952 \frac{\text{cm}^2}{\text{s}}$$
$$D_{AB} = 9.52 \times 10^{-6} \frac{\text{m}^2}{\text{s}}$$

As evidenced by this example, estimation of binary diffusivities can be quite tedious. Most mass-transfer problems involve the calculation of one or more values of diffusivities. Convenience therefore suggests the use of a computer software package for technical calculations, such as Mathcad, for that purpose. Figure 1.3 shows a Mathcad routine to estimate the gas phase binary diffusivity using the Wilke-Lee equation and the conditions for this example. For any other set of conditions, only the two lines of the program following the "Enter Data" expression must be modified accordingly. The experimental value for this example is obtained from Appendix A:

$$\begin{split} \mathbf{D}_{AB} P &= 0.894 \quad \frac{\mathbf{m}^2 \times \mathbf{Pa}}{\mathbf{s}} \\ \mathbf{D}_{AB} &= 0.894 \quad \frac{\mathbf{m}^2 \times \mathbf{Pa} \times 1 \mathbf{bar}}{\mathbf{s} \times 1 \mathbf{bar} \times 10^5 \mathbf{Pa}} \\ \mathbf{D}_{AB} &= 8.94 \times 10^{-6} \quad \frac{\mathbf{m}^2}{\mathbf{s}} \end{split}$$

The error of the estimate, compared to the experimental value, is 6.5%.

Example 1.7 Calculation of Diffusivity by the Wilke-Lee Equation with Estimated Values of the Lennard-Jones Parameters

Estimate the diffusivity of allyl chloride (C_3H_5Cl) in air at 298 K and 1 bar using the Wilke-Lee equation (1-49). The experimental value reported by Lugg (1968) is 0.098 cm²/s.

Solution

Values of the Lennard-Jones parameters for allyl chloride (A) are not available in Appendix B. Therefore, they must be estimated from equations (1-46) and (1-47). From Table 1.2,

$$V_b = (3)(14.8) + (5)(3.7) + 24.6 = 87.5 \text{ cm}^3/\text{mol}$$

An alternate method to estimate V_b for allyl chloride is using equation (1-48) with a value of $V_c = 234$ cm³/mol (Reid et al., 1987).

$$V_b = (0.285)(234)1.048 = 86.7 \text{ cm}^3/\text{mol}$$

The two estimates are virtually identical. From equation (1-46), $\sigma_A = 5.24$ Å. The normal boiling point temperature for allyl chloride is $T_b = 318.3$ K (Reid et al., 1987). From equation (1-47), $\varepsilon_A/\kappa = 366$ K. The molecular weight of allyl chloride is 76.5 g/mol. The corresponding values for air are $\sigma_B = 3.62$ Å, $\varepsilon_B/\kappa = 97$ K, and $M_B = 29$ g/mol. Substituting these values into the Mathcad routine of Figure 1.3 yields

$$D_{AB} = 0.0992 \text{ cm}^2/\text{s}$$

The error of this estimate, compared to the experimental value, is 1.2%.

1.3 The Diffusion Coefficient

It must be emphasized that, for low-pressure binary gas systems, the diffusivity does not depend on the composition of the mixture. Either component can be chosen as component A or component B. As the next section will show, the estimation of diffusivities in liquid mixtures is much more complex.

In the Wilke-Lee equation, *T* is temperature in K, *P* is absolute
pressure in bar, *M* is molecular weight in g/mol, the Lennard-Jones
parameters are from Appendix B with the units specified there. The
data presented here are from Example 1.6.
Enter Data:
$$T := 273$$
 $P := 1.0$ $M_A := 76$ $M_B := 29$
 $\sigma_A := 4.483$ $\sigma_B := 3.620$ $\varepsilon_{Ak} := 467$ $\varepsilon_{Bk} := 97$
 $\sigma_{AB} := \frac{(\sigma_A + \sigma_B)}{2} = 4.052$
 $\varepsilon_{ABk} := \sqrt{\varepsilon_{Ak} \cdot \varepsilon_{Bk}} = 212.836$ $x := \frac{T}{\varepsilon_{ABk}} = 1.283$
 $a := 1.06026$ $b := 0.15610$ $c := 0.19300$
 $d := 0.47635$ $e1 := 1.03587$ $f := 1.52996$
 $g := 1.76474$ $h := 3.89411$
 $M_{AB} := 2 \cdot \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{-1} = 41.981$
 $\Omega := \frac{a}{x^b} + \frac{c}{e^{d \cdot x}} + \frac{e1}{e^{f \cdot x}} + \frac{g}{e^{h \cdot x}} = 1.282$
 $D_{AB} := \frac{0.001 \cdot \left(3.03 - \frac{0.98}{\sqrt{M_{AB}}}\right) \cdot T^{1.5}}{P \cdot \sigma_{AB}^2 \cdot \Omega \cdot \sqrt{M_{AB}}} \cdot \frac{\mathrm{cm}^2}{\mathrm{s}} = 0.0952 \frac{\mathrm{cm}^2}{\mathrm{s}}$

Figure 1.3 Mathcad routine to estimate gas-phase mass diffusivities using the Wilke-Lee equation.

1.3.2 Diffusion Coefficients for Dilute Liquids

Your objectives in studying this section are to be able to:

- 1. Estimate diffusion coefficients for binary dilute liquid systems using the Wilke and Chang equation.
- 2. Estimate diffusion coefficients for binary dilute liquid systems using the Hayduk and Minhas correlations.
- 3. Use a Mathcad routine to implement calculation of diffusion coefficients for binary dilute liquid systems using the Hayduk and Minhas equation.

In contrast to the case for gases, where an advanced kinetic theory to explain molecular motion is available, theories of the structure of liquids and their transport characteristics are still inadequate to allow a rigorous treatment. Liquid diffusion coefficients are several orders of magnitude smaller than gas diffusivities, and depend on concentration due to the changes in viscosity with concentration and changes in the degree of ideality of the solution. As the mol fraction of either component in a binary mixture approaches unity, the thermodynamic factor Γ approaches unity and the Fick diffusivity and the MS diffusivity are equal. The diffusion coefficients obtained under these conditions are the infinite dilution diffusion coefficients and are given the symbol D^0 .

The Stokes–Einstein equation is a theoretical method of estimating D^0 ,

$$D_{AB}^{0} = \frac{\kappa T}{6\pi r_{A}\mu_{B}}$$
(1-50)

where r_A is the solute particle radius, and μ_B is the solvent viscosity. This equation has been fairly successful in describing diffusion of colloidal particles or large round molecules through a solvent which behaves as a continuum relative to the diffusing species.

Equation (1-50) has provided a useful starting point for a number of semiempirical correlations arranged into the general form

$$\frac{D_{AB}^{0}\boldsymbol{\mu}_{B}}{\kappa T} = f\left(V_{bA}\right)$$
(1-51)

in which $f(V_{bA})$ is a function of the molecular volume of the diffusing solute. Empirical correlations using the general form of equation (1-51) have been developed which attempt to predict the liquid diffusion coefficient in terms of the solute and solvent properties. Wilke and Chang (1955) have proposed the following still widely used correlation for nonelectrolytes in an infinitely dilute solution:

1.3 The Diffusion Coefficient

$$\frac{D_{AB}^{0}\boldsymbol{\mu}_{B}}{T} = \frac{7.4 \times 10^{-8} \left(\boldsymbol{\Phi}_{B} \boldsymbol{M}_{B}\right)^{0.5}}{V_{bA}^{0.6}}$$
(1-52)

where

- 0

100	
D_{AB}	= diffusivity of A in very dilute solution in solvent B, cm ² /s
M_B	= molecular weight of solvent B
\overline{T}	= temperature, K
μ B	= viscosity of solvent B, cP
V_{bA}	= solute molar volume at its normal boiling point, cm ³ /mol
	= 75.6 cm^3/mol for water as solute
Φ_{B}	= association factor of solvent B, dimensionless
2	= 2.26 for water as solvent
	= 1.9 for methanol as solvent
	= 1.5 for ethanol as solvent
	= 1.0 for unassociated solvents, e.g., benzene, ether, heptane

The value of V_{bA} may be the true value or, if necessary, estimated from equation (1-48), or from the data of Table 1.2, except when water is the diffusing solute, as noted above. The association factor for a solvent can be estimated only when diffusivities in that solvent have been experimentally measured. There is also some doubt about the ability of the Wilke–Chang equation to handle solvents of very high viscosity, say 100 cP or more.

Hayduk and Minhas (1982) considered many correlations for the infinite dilution binary diffusion coefficient. By regression analysis, they proposed several correlations depending on the type of solute–solvent system:

(a) For solutes in aqueous solutions:

$$D_{AB}^{0} = 1.25 \times 10^{-8} \left(V_{bA}^{-0.19} - 0.292 \right) T^{1.52} \mu_{B}^{\epsilon}$$

$$\epsilon = \frac{9.58}{V_{bA}} - 1.12$$
(1-53)

where

D^0	
D_{AB}	= diffusivity of A in very dilute aqueous solution , cm ² /s
T	= temperature, K
μ_B	= viscosity of water, cP
V_{bA}	= solute molar volume at its normal boiling point, cm3/mol

(b) For nonaqueous (nonelectrolyte) solutions:

$$D_{AB}^{0} = 1.55 \times 10^{-8} \frac{V_{bB}^{0.27} T^{1.29} \sigma_{B}^{1.25}}{V_{bA}^{0.42} \mu_{B}^{0.92} \sigma_{A}^{0.105}}$$
(1-54)

where σ is surface tension at the normal boiling point temperature, in dyn/cm. If values of the surface tension are not known, they may be estimated by the Brock and Bird (1955) corresponding states method (limited to nonpolar liquids):

$$\sigma(T_b) = P_c^{2/3} T_c^{1/3} \left(0.132\alpha_c - 0.278 \right) \left(1 - T_{br} \right)$$

$$T_{br} = \frac{T_b}{T_c}$$

$$\alpha_c = 0.9076 \left[1 + \frac{T_{br} \ln \left(P_c / 1.013 \right)}{1 - T_{br}} \right]$$
(1-55)

where

 $\sigma(T_{\rm h})$ = surface tension at the normal boiling point temperature, dyn/cm

 P_c = critical pressure, bar T_c = critical temperature, K

When using the correlation shown in equation (1-54), the authors note several restrictions:

- 1. The method should not be used for diffusion in viscous solvents. Values of μ_{B} above about 20 cP would classify the solvent as viscous.
- 2.If the solute is water, a dimer value of V_{bA} should be used (V_{bA} = 37.4 cm³/mol).
- 3. If the solute is an organic acid and the solvent is other than water, methanol, or butanol, the acid should be considered a dimer with twice the expected value of V_{bA} .
- For nonpolar solutes diffusing into monohydroxy alcohols, the values of V_{bB} 4. should be multiplied by a factor equal to $8\mu_B$ where μ_B is the solvent viscosity in cP.

Example 1.8 Calculation of Liquid Diffusivity in Aqueous Solution

Estimate the diffusivity of ethanol (C₂H₆O) in a dilute solution in water at 288 K. Compare your estimate with the experimental value reported in Appendix A.

Solution

(a) Use the Wilke-Chang correlation, equation (1-52). Calculate the molar volume of ethanol using equation (1-48) with $V_c = 167.1 \text{ cm}^3/\text{mol}$ (Reid et al., 1987):

$$V_{bA} = 0.285 (167.1)^{1.048} = 60.9 \frac{\text{cm}^3}{\text{mol}}$$

The viscosity of liquid water at 288 K is $\mu_B = 1.153$ cP (Reid et al., 1987). Substituting in equation (1-52) gives

1.3 The Diffusion Coefficient

$$D_{AB}^{0} = \frac{\left(7.4 \times 10^{-8}\right) \left(288\right) \left[\left(2.26\right) \left(18\right)\right]^{1/2}}{\left(1.153\right) \left(60.9\right)^{0.6}} = 1.002 \times 10^{-5} \frac{\mathrm{cm}^{2}}{\mathrm{s}}$$

The experimental value reported in Appendix A is 1.0×10^{-5} cm²/s. Therefore, the error of the estimate is only 0.2%. (This is not typical!)

(b) Using the Hayduk and Minhas correlation for aqueous solutions:

$$\varepsilon = \frac{9.58}{60.9} - 1.12 = -0.963$$
$$D_{AB}^{0} = 1.25 \times 10^{-8} \left[60.9^{-0.19} - 0.292 \right] \left(288 \right)^{1.52} \left(1.153 \right)^{-0.693}$$
$$= 0.991 \times 10^{-5} \frac{\text{cm}^{2}}{\text{s}}$$

The error of the estimate in this case is -0.9%.

Example 1.9 Calculation of Liquid Diffusivity in Dilute Nonaqueous Solution

Estimate the diffusivity of acetic acid $(\rm C_2H_4O_2)$ in a dilute solution in acetone $(\rm C_3H_6O)$ at 313 K. Compare your estimate with the experimental value reported in Appendix A. The following data are available (Reid et al., 1987):

Parameter	Acetic acid	Acetone
T_h , K	390.4	329.2
T_c° , K	594.8	508.0
P_c , bars	57.9	47.0
V_c , cm ³ /mol	171	209
μ, cP		0.264
M	60	58

Solution

(a) Use the Wilke–Chang correlation, equation (1-52). Calculate the molar volume of acetic acid using equation (1-48) with $V_c = 171 \text{ cm}^3/\text{mol}$: $V_{bA} = 62.4 \text{ cm}^3/\text{mol}$. The association factor for acetone is $\Phi = 1.0$. From equation (1-52),

$$D_{AB}^{0} = \frac{\left(7.4 \times 10^{-8}\right) \left(313\right) \left[\left(1\right) \left(58\right)\right]^{1/2}}{\left(0.264\right) \left(62.4\right)^{0.6}} = 5.595 \times 10^{-5} \frac{\mathrm{cm}^{2}}{\mathrm{s}}$$

From Appendix A, the experimental value is 4.04×10^{-5} cm²/s. Therefore, the error of the estimate is 38.5%.

(b) Use the Hayduk and Minhas correlation for nonaqueous solutions. According to restriction 3 mentioned above, the molar volume of the acetic acid to be used in equation (1-54) should be $V_{bA} = 2 \times 62.4 = 124.8 \text{ cm}^3/\text{mol}$. The molar volume of acetone is calculated from equation (1-48): $V_{bB} = 77.0 \text{ cm}^3/\text{mol}$. Estimates of the surface tension at the normal boiling point of each component are calculated from equation (1-55) as follows:

For acetone (B):

$$\begin{split} T_{br} &= \frac{329.2}{508} = 0.648 \\ \alpha_c &= 7.319 \\ \sigma_B &= 20.0 ~\mathrm{dyn/cm} \end{split}$$

For acetic acid (A):

$$T_{br} = \frac{390.4}{594.8} = 0.656$$

 $\alpha_c = 7.910$
 $\sigma_p = 26.2 \text{ dyn/cm}$

Substituting numerical values in equation (1-54):

$$\begin{split} D^0_{AB} &= 1.55 \times 10^{-8} \, \frac{\left(77\right)^{0.27} \left(313\right)^{1.29} \left(20\right)^{0.125}}{\left(124.8\right)^{0.42} \left(0.264\right)^{0.92} \left(26.2\right)^{0.105}} \\ D^0_{AB} &= 3.84 \times 10^{-5} \ \frac{\mathrm{cm}^2}{\mathrm{s}} \end{split}$$

From Appendix A, the experimental value is 4.04×10^{-5} cm²/s. Therefore, the error of the estimate is -5.0%.

Figure 1.4 shows a Mathcad routine to estimate liquid-phase binary diffusivities for nonaqueous solutions using the Hayduk and Minhas equation and the conditions for this example. For any other set of conditions, only the four lines of the program following the "Enter Data" expression must be modified accordingly.

In this equation, temperatures are in K, pressures in bar, molar volumes in cc/mol, and viscosity of the solvent in cP. Enter Data: $T_{brA} := \frac{T_{bA}}{T_{cA}} = 0.656 \qquad \qquad T_{brB} := \frac{T_{bB}}{T_{cB}} = 0.648$ $\alpha_{cA} := 0.9076 \cdot \left(1 + \frac{T_{brA} \cdot \ln\left(\frac{P_{cA}}{1.013}\right)}{1 - T_{brA}} \right) = 7.921$ $\alpha_{cB} \coloneqq 0.9076 \cdot \left(1 + \frac{T_{brB} \cdot \ln\left(\frac{P_{cB}}{1.013}\right)}{1 - T_{brB}} \right) = 7.32$ $\sigma_{A} \coloneqq P_{cA}^{\frac{2}{3}} \cdot T_{cA}^{\frac{1}{3}} \cdot \left[0.132 \cdot \alpha_{cA} - 0.278\right] \cdot \left[1 - T_{brA}\right]^{\frac{11}{9}} = 26.185$ $\sigma_{B} \coloneqq P_{cB}^{\frac{2}{3}} \cdot T_{cB}^{\frac{1}{3}} \cdot \left[0.132 \cdot \alpha_{cB} - 0.278\right] \cdot \left[1 - T_{brB}\right]^{\frac{11}{9}} = 19.959$ $D_{L0} \coloneqq \frac{1.55 \cdot 10^{-8} \cdot V_{bB}^{0.27} \cdot T^{1.29} \cdot \sigma_{B}^{0.125}}{V_{bA}^{0.42} \cdot \mu_{B}^{0.92} \cdot \sigma_{A}^{0.105}} \cdot \frac{\text{cm}^{2}}{\text{s}} = (3.839 \cdot 10^{-5}) \frac{\text{cm}^{2}}{\text{s}}$

Figure 1.4 Mathcad routine to estimate liquid-phase mass diffusivities in dilute nonaqueous solutions using the Hayduk and Minhas equation.

1.3.3 Diffusion Coefficients for Concentrated Liquids

Most methods for predicting D in concentrated liquid solutions attempt to combine the infinite dilution diffusion coefficients $(D_{12})^0$ and $(D_{21})^0$ in a single function of composition. The Vignes formula is recommended by Reid et al. (1987):

$$D_{12} = \left(D_{12}^{0}\right)^{*_{2}} \left(D_{21}^{0}\right)^{*_{1}}$$
(1-56)
$$D_{12} = D_{12}\Gamma$$

Example 1.10 Diffusion Coefficients for Acetone-Benzene (Taylor and Krishna, 1993)

Estimate the MS and Fick diffusion coefficients for an acetone(1)–benzene(2) mixture of composition $x_1 = 0.7808$ at 298 K. The infinite dilution diffusivities are:

$$\begin{split} D_{12}^0 &= 2.75 \times 10^{-9} \ \frac{\text{m}^2}{\text{s}} \\ D_{21}^0 &= 4.15 \times 10^{-9} \ \frac{\text{m}^2}{\text{s}} \end{split}$$

From the non–random–two–liquid (NRTL) equation, for this system at the given temperature and concentration, the thermodynamic correction factor Γ = 0.871. The experimental value of D_{12} at this concentration is 3.35 \times 10⁻⁹ m²/s.

Solution

Substituting in equation (1-56):

$$\begin{split} D_{12} &= \left(2.75 \times 10^{-9}\right)^{0.2192} \times \left(4.155 \times 10^{-9}\right)^{0.7808} \\ D_{12} &= 3.792 \times 10^{-9} \ \frac{\mathrm{m}^2}{\mathrm{s}} \\ D_{12} &= 3.792 \times 10^{-9} \times 0.871 \\ D_{12} &= 3.30 \times 10^{-9} \ \frac{\mathrm{m}^2}{\mathrm{s}} \end{split}$$

The predicted value of the Fick diffusivity is in excellent agreement with the experimental result.