

Mass Transfer in Multicomponent Mixtures



**J.A. Wesselingh
R. Krishna**

Mass Transfer in Multicomponent Mixtures

Mass Transfer in Multicomponent Mixtures

J.A. Wesselingh

R. Krishna

© **VSSD**

First edition 2000-2006

Published by:

VSSD

Leeghwaterstraat 42, 2628 CA Delft, The Netherlands

tel. +31 15 2782124, telefax +31 15 2787585, e-mail: hlf@vssd.nl

internet: <http://www.vssd.nl/hlf>

URL on this book and for downloading auxiliary files:

<http://www.vssd.nl/hlf/d004.htm>

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photo-copying, recording, or otherwise, without the prior written permission of the publisher.

NUR 952

Printed version ISBN: 978-90-71301-58-2 Ebook: ISBN: 978-90-6562-224-2

Keywords: mass transfer, multicomponent mixtures

Foreword

It was twenty years ago. A little before that, I had left the Equipment Engineering Department of Shell Research in Amsterdam for a less hectic job at Delft University. At least, so I thought at that moment. In my former section at Shell we had worked on catalytic crackers, on polymerisation reactors, on cleaning of oil tankers and other exciting developments, but I had found managing this a bit too much. There I was, with a lower salary, teaching separation processes to second year students, and running the undergraduate laboratory with one hundredth of my Shell budget. I had written a little book on Separation Processes, and sent it to friends in Amsterdam.

One of the pieces of equipment that we had in Shell Research was (what was then) the largest distillation test column in the world. It was two and a half metres in diameter and some twenty metres high. The column was so big that we could only run it in the summer: the reboiler used the complete capacity of our boiler house. The operating pressure could be varied between vacuum and fifteen atmospheres. We had a beautiful time trying out all kinds of trays and packings. In time we started to get interested in trying to understand not only distillation of binary mixtures, but also of mixtures with more components. We started to gather measurements and to try to understand them. However, much of what we saw was baffling, to say the least. Only gradually did we realise that our binary mass transfer tools were not adequate; that we needed to try something different. That something was a young graduate from Manchester who had picked up wild ideas on mass transfer doing his PhD. His name was Krishna. I left Shell just after he arrived.

One day, Krishna came along at home to visit me. He had read my book and told me politely that my approach to mass transfer was not all that good. I was a little vexed because I was professor, he was not, and besides, I had copied my ideas from well-known handbooks. Even so, I did try to listen, and three weeks later went back to him for more explanation. It was all about *multicomponent* mass transfer, it had connections with thermodynamics and was quite different from anything I knew.. I had difficulties in following what he was telling me, and I can remember: 'Hans, if you really want to understand this, we should give a course together.' That is where this book started.

We are now twenty years, fifteen PhD students, twenty-three courses and some thousand participants further. The course has evolved and so has the book. It now has examples from membrane technology, reaction engineering, sorption processes, biotechnology; from mixtures of gases or liquids, but also porous media and

polymers. The basics have not changed: they are still almost the same as presented by James Clerk Maxwell in 1866 and (more clearly) by Josef Stefan in 1872. (Maxwell is the one of the theory of electrical and magnetic fields, and Stefan the one associated with the name of Boltzmann.) I am a little ashamed when I look in editions of the *Encyclopaedia Britannica* from around 1900 and see how well diffusion was then understood. It feels as if it has taken me more than a century to pick up the brilliant but simple ideas of these two long-dead scientists. Krish and I hope this book will help you to do that a bit more quickly.

Hans Wesselingh
Groningen, May 2000

Contents

| | |
|---|----|
| FOREWORD | 5 |
| 1 BEGINNING... | 13 |
| 1.1 Who should read this Book? | 13 |
| 1.2 What this Book covers | 14 |
| 1.3 Structure of the Book | 15 |
| 1.4 Guidelines to the Reader | 16 |
| 1.5 Guidelines to the Teacher | 17 |
| 1.6 Symbols | 18 |
| 1.7 Conventions | 21 |
| 2 IS SOMETHING WRONG? | 24 |
| 2.1 The Starting Point | 24 |
| 2.2 Three Gases | 26 |
| 2.3 Two Cations | 28 |
| 2.4 Two Gases and a Porous Plug | 28 |
| 2.5 Summary | 30 |
| 2.6 Further Reading | 30 |
| 2.7 Exercises | 30 |
| PART 1. MASS TRANSFER IN GASES AND LIQUIDS | 33 |
| 3 DRIVING FORCES | 34 |
| 3.1 Potentials, Forces and Momentum | 34 |
| 3.2 Momentum (Force) Balance of a Species | 36 |
| 3.3 The Driving Force: a Potential Gradient | 38 |
| 3.4 The Maxwell-Stefan Equation | 39 |
| 3.5 Simplifying the Mathematics | 40 |
| 3.6 The Film Model | 41 |
| 3.7 Difference Form of the Driving Force | 42 |
| 3.8 Summary | 44 |
| 3.9 Further Reading | 44 |
| 3.10 Exercises | 45 |
| 4 FRICTION | 46 |
| 4.1 Friction Coefficients and Diffusivities | 46 |
| 4.2 Velocities and the Bootstrap | 48 |
| 4.3 Velocities and Fluxes | 50 |
| 4.4 The Difference Equation | 50 |
| 4.5 Mass Transfer Coefficients | 52 |
| 4.6 Summary | 53 |
| 4.7 Further Reading | 53 |
| 4.8 Exercises | 53 |
| 5 BINARY EXAMPLES | 55 |
| 5.1 Stripping | 55 |
| 5.2 Polarisation | 56 |

| | | |
|------|---|-----|
| 5.3 | Vaporisation | 56 |
| 5.4 | Gasification of a Carbon Particle | 58 |
| 5.5 | Binary Distillation | 59 |
| 5.6 | Summary | 60 |
| 5.7 | Further Reading | 60 |
| 5.8 | Exercises | 61 |
| 6 | TERNARY EXAMPLES | 63 |
| 6.1 | From Binary to Ternary | 63 |
| 6.2 | A Condenser | 64 |
| 6.3 | A Ternary Distillation | 65 |
| 6.4 | A Ternary Reaction | 68 |
| 6.5 | Binary Approximation of a Ternary | 68 |
| 6.6 | Summary | 70 |
| 6.7 | Further Reading | 70 |
| 6.8 | Exercises | 71 |
| 7 | MASS AND HEAT TRANSFER | 74 |
| 7.1 | Temperature Gradients | 74 |
| 7.2 | Enthalpy | 75 |
| 7.3 | Mass Transfer Relation | 76 |
| 7.4 | Energy Transfer Relation | 77 |
| 7.5 | Condensation in Presence of an Inert Gas | 79 |
| 7.6 | Heterogeneous Reacting Systems | 80 |
| 7.7 | An Ammonia Absorber | 80 |
| 7.8 | Summary | 81 |
| 7.9 | Further Reading | 81 |
| 7.10 | Exercises | 82 |
| 8 | NON-IDEALITIES | 84 |
| 8.1 | Chemical Potential and Activity | 84 |
| 8.2 | Non-ideal Binary Distillation | 84 |
| 8.3 | A Simple Model of Non-idealities | 85 |
| 8.4 | Large Non-Idealities: Demixing | 87 |
| 8.5 | Maxwell-Stefan versus Fick | 88 |
| 8.6 | When can we neglect Non-ideality? | 89 |
| 8.7 | Mass Transfer in Liquid-Liquid Extraction | 90 |
| 8.8 | Summary | 92 |
| 8.9 | Further Reading | 92 |
| 8.10 | Exercises | 92 |
| 9 | DIFFUSION COEFFICIENTS | 95 |
| 9.1 | Diffusivities in Gases | 95 |
| 9.2 | Diffusivities in Liquids | 97 |
| 9.3 | How do you measure diffusivities? | 100 |
| 9.4 | Summary | 102 |
| 9.5 | Further Reading | 102 |
| 9.6 | Exercises | 103 |
| 10 | TRANSFER COEFFICIENTS | 106 |
| 10.1 | Introduction | 106 |
| 10.2 | Dimensionless Groups | 106 |

| | |
|---|-----|
| 10.3 Tubes and Packed Beds | 108 |
| 10.4 Packed Gas-Liquid Columns | 110 |
| 10.5 Single Particles, Bubbles and Drops | 111 |
| 10.6 Using 'Single' Coefficients for Swarms | 117 |
| 10.7 Using Binary Coefficients in Multicomponent Calculations | 118 |
| 10.8 Summary | 118 |
| 10.9 Further Reading | 119 |
| 10.10 Exercises | 120 |
| 11 ELECTRICAL FORCES AND ELECTROLYTES | 122 |
| 11.1 Electrolytes | 122 |
| 11.2 The Electroneutrality Relation | 123 |
| 11.3 Electrical Forces | 124 |
| 11.4 Transport Relations | 124 |
| 11.5 Diffusion of Hydrochloric Acid | 125 |
| 11.6 Plus a Trace of Sodium Chloride | 126 |
| 11.7 Diffusion of Proteins | 126 |
| 11.8 Conduction and Friction between Ions | 128 |
| 11.9 Diffusivities in Electrolyte Solutions | 130 |
| 11.10 Summary | 132 |
| 11.11 Further Reading | 133 |
| 11.12 Exercises | 134 |
| 12 CENTRIFUGAL AND PRESSURE FORCES | 137 |
| 12.1 Volumetric Properties | 137 |
| 12.2 The Pressure Gradient | 138 |
| 12.3 Gravitational Force | 138 |
| 12.4 Centrifuges | 139 |
| 12.5 Gas and Protein Centrifugation | 140 |
| 12.6 Difference Equation for the Pressure Force | 141 |
| 12.7 The Maxwell-Stefan Equations (again) | 142 |
| 12.8 Summary | 143 |
| 12.9 Further Reading | 143 |
| 12.10 Exercises | 143 |
| 13 WHY WE USE THE MS-EQUATIONS | 146 |
| 13.1 Three Ways | 146 |
| 13.2 A Mixture of Three Gases | 147 |
| 13.3 The Fick Description | 148 |
| 13.4 Thermodynamics of Irreversible Processes | 150 |
| 13.5 The Maxwell-Stefan Description | 150 |
| 13.6 Units | 152 |
| 13.7 Further Reading | 152 |
| 13.8 Exercises | 153 |
| PART 2. MASS TRANSFER THROUGH A SOLID MATRIX | 155 |
| 14 SOLID MATRICES | 156 |
| 14.1 The Applications | 156 |
| 14.2 Membrane Processes | 156 |
| 14.3 Adsorption and Chromatography | 158 |
| 14.4 Heterogeneous Catalysis | 160 |

| | | |
|-------|---|-----|
| 14.5 | Structured and Non-structured Matrices | 161 |
| 14.6 | Effects of a Matrix on Mass Transfer | 162 |
| 14.7 | Compositions with a Matrix | 163 |
| 14.8 | How Further? | 164 |
| 14.9 | Further Reading | 165 |
| 14.10 | Exercises | 165 |
| 15 | PROPERTIES OF POLYMERS | 167 |
| 15.1 | A Few Words on Polymers | 167 |
| 15.2 | Thermodynamics of Mixtures in a Polymer | 171 |
| 15.3 | Summary | 177 |
| 15.4 | Further Reading | 177 |
| 15.5 | Exercises | 177 |
| 16 | DIFFUSION IN POLYMERS | 180 |
| 16.1 | Behaviour of Diffusivities | 180 |
| 16.2 | The Free Volume Theory | 182 |
| 16.3 | Summary | 188 |
| 16.4 | Further Reading | 189 |
| 16.5 | Exercises | 189 |
| 17 | DIALYSIS AND GAS SEPARATION | 191 |
| 17.1 | Dialysis | 191 |
| 17.2 | Gas Separation | 194 |
| 17.3 | Summary | 197 |
| 17.4 | Further Reading | 197 |
| 17.5 | Exercises | 198 |
| 18 | PERVAPORATION AND REVERSE OSMOSIS | 200 |
| 18.1 | Pervaporation | 200 |
| 18.2 | Reverse Osmosis | 204 |
| 18.3 | Summary | 208 |
| 18.4 | Further Reading | 208 |
| 18.5 | Exercises | 209 |
| 19 | ELECTROLYSIS AND ELECTRODIALYSIS | 211 |
| 19.1 | Introduction | 211 |
| 19.2 | Polarisation in Electrolysis | 212 |
| 19.3 | Electrodialysis | 214 |
| 19.4 | Summary | 220 |
| 19.5 | Further Reading | 220 |
| 19.6 | Exercises | 221 |
| 20 | ION EXCHANGE | 223 |
| 20.1 | Fixed-Bed Processes | 223 |
| 20.2 | Ion Exchange Equilibria | 224 |
| 20.3 | Linear Driving Force Model | 225 |
| 20.4 | Ion Exchange (Film Limited) | 227 |
| 20.5 | Ion Exchange (Particle Limited) | 228 |
| 20.6 | Summary | 230 |
| 20.7 | Further Reading | 230 |
| 20.8 | Exercises | 231 |

| | | |
|----|--|-----|
| 21 | GAS PERMEATION | 233 |
| | 21.1 Transport in Cylindrical Pores | 233 |
| | 21.2 The Diffusion Coefficients | 233 |
| | 21.3 Looking Back | 235 |
| | 21.4 Transport in a Bed of Spheres | 236 |
| | 21.5 The Dusty Gas Model | 238 |
| | 21.6 Summary | 240 |
| | 21.7 Further Reading | 240 |
| | 21.8 Exercises | 241 |
| 22 | IN POROUS CATALYSTS | 242 |
| | 22.1 Introduction | 242 |
| | 22.2 Pressure gradients inside a particle | 243 |
| | 22.3 Separate Transport Equations | 245 |
| | 22.4 Single-variable Pressure and Rate Expressions | 245 |
| | 22.5 Solution for a Slab | 247 |
| | 22.6 Summary | 249 |
| | 22.7 Further Reading | 249 |
| | 22.8 Exercises | 250 |
| 23 | IN ADSORBENTS | 252 |
| | 23.1 Adsorption | 252 |
| | 23.2 Equilibria – Langmuir Isotherm | 253 |
| | 23.3 Maxwell-Stefan and Fick Diffusivities | 254 |
| | 23.4 Macropore Diffusion | 257 |
| | 23.5 Transport Equations | 258 |
| | 23.6 Transient Adsorption of a Binary | 259 |
| | 23.7 Membrane Applications | 260 |
| | 23.8 Summary | 261 |
| | 23.9 Further Reading | 261 |
| | 23.10 Exercises | 262 |
| 24 | ULTRAFILTRATION | 264 |
| | 24.1 The Module | 264 |
| | 24.2 Membrane and Permeants | 265 |
| | 24.3 Osmotic Pressure (No Ions, no Charge) | 266 |
| | 24.4 Size Exclusion | 266 |
| | 24.5 Polarisation | 267 |
| | 24.6 Transport Equations | 269 |
| | 24.7 Inside the Membrane | 272 |
| | 24.8 Electrical Effects | 273 |
| | 24.9 Summary | 275 |
| | 24.10 Further Reading | 276 |
| | 24.11 Exercises | 277 |
| 25 |ENDING | 279 |
| | 25.1 Looking Back | 279 |
| | 25.2 Thermodynamic Models – the Potentials | 279 |
| | 25.3 Driving Forces | 281 |
| | 25.4 Friction Terms | 281 |
| | 25.5 Friction Coefficients | 282 |

| | |
|--|-----|
| 25.6 Additional Relations (Bootstraps) | 283 |
| 25.7 The Many Variants | 285 |
| 25.8 Goodbye | 286 |
| 25.9 Further Reading | 287 |
| 25.10 Last Exercise | 287 |
| THANKS | 289 |
| APPENDIX 1. READING MATHCAD | 293 |
| APPENDIX 2. UNITS | 296 |
| A2-1 Molar basis | 296 |
| A2-2 Mass basis | 297 |
| A2-3 Volume basis | 297 |
| A2-4 Molar and mass diffusivities | 298 |
| A2-5 Molar and volume diffusivities | 299 |
| A2-6 Molar and mass driving force | 300 |
| A2-7 Molar and volume driving forces | 300 |
| A2-8 Difference equation for a 'film' | 301 |
| A2-9 Difference equation, molar basis | 301 |
| A2-10 Difference equation, mass basis | 302 |
| A2-11 Difference equation, volume basis | 302 |
| A2-12 Summary | 303 |
| APPENDIX 3. PORING OVER PORES | 304 |
| A3-1 Introduction | 304 |
| A3-2 The System | 305 |
| A3-3 Forces and Velocities | 305 |
| A3-4 The Two Transport equations | 308 |
| A3-5 Comparing the Two Models | 310 |
| A3-6 Summary | 313 |
| A3-7 Further Reading | 314 |
| A3-8 Exercises | 314 |
| ANSWERS | 317 |
| INDEX | 326 |
| AUXILIARY FILES FOR 'MASS TRANSFER IN MULTICOMPONENT MIXTURES' | 329 |

1

Beginning...

1.1 Who should read this Book?

This book is about the diffusion and mass transfer processes that are really important, but which are neglected in most textbooks:

- those with three or more species, the ‘multicomponent’ mixtures,
- those with more than one driving force, including electrical or pressure gradients, and
- those with a solid matrix such as a polymer or a porous medium.

If you want to know more about these subjects, but find existing texts too difficult, then this is the book for you. Also, if you already understand the intricacies of multi-component mass transfer, you may find it enjoyable to see how far you can get with simple means.

We are assuming that you are interested in processes or products. This may be in an academic or industrial setting: in chemicals, water treatment, food, biotechnology, pharmaceuticals ... you name it. The book assumes that you have a working knowledge of:

- thermodynamics and phase equilibria: chemical potentials, enthalpies, activity coefficients, partial molar volumes and distribution coefficients,
- transport phenomena: simple mass balances, binary diffusion and mass transfer coefficients, and
- fluid flow, especially around particles and in porous media.

If you are not too sure, do not despair. We will repeat all important concepts in a leisurely manner. However, this is not a book for a complete beginner in mass transfer; you must have heard of the above concepts. Because there are many new ideas to get used to, we have tried to avoid mathematical complexity. For the greater part of the text you do not need more than the ability to solve three linear equations with three unknowns. You can even do a fair bit with pencil, paper and a calculator. Of course you will need a computer for larger problems, but not to obtain a first understanding.

1.2 What this Book covers

This book takes motion in a mixture to be governed by forces on the individual species. There are two kinds of forces:

- driving forces, which stem from the potential gradient of a species, and
- friction forces between the species, which arise from their velocity differences.

Maxwell and Stefan already used this method more than a century ago. This mechanical viewpoint is much more general than Fick's law, which is usually taken as the basis of diffusion theory. It has not caught on, probably because the mathematics is thought to be difficult. This is not really a problem however:

- There are simple approximations to the solutions of the equations.
- The computer and numerical techniques now make 'exact' calculations much easier.

Using potential gradients allows the incorporation of different driving forces:

- composition gradients (or more precisely: activity gradients),
- electrical potential gradients,
- pressure gradients,
- centrifugal fields and others.

The friction approach to interaction between the species allows a consistent handling of any number of components. Working with force balances makes it easy to link the subject of mass transfer to other parts of science. Thermodynamics and transport processes become neighbours: equilibrium is simply the situation where driving forces have disappeared. The use of forces on the species in a mixture fits in the way of thinking of engineers: it is a logical extension of mechanics of a single species. For friction coefficients we can make use of the many relations for hydrodynamics of particles or porous media. These show that flow and diffusion are two sides of the same coin.

With our starting points we can describe almost any mass transfer process. Examples in this book cover:

- multicomponent distillation, absorption and extraction,
- multicomponent evaporation and condensation,
- sedimentation and ultracentrifugation,
- dialysis and gas separations,
- pervaporation and reverse osmosis,
- electrolysis and electrodialysis,
- ion exchange and adsorption
- heterogeneous catalysis and
- ultrafiltration.

The examples treat diffusion in gases, in liquids, in electrolyte solutions, in swollen polymers and in porous media. The book includes methods for estimating multi-component diffusivities and mass transfer coefficients.

A major limitation of the book is that it mainly covers examples with a single transfer resistance, not complete pieces of equipment. Such a resistance will be a building block for the simulation of separation columns, membrane modules or chemical reactors. The reader must be prepared to incorporate the equations into his own simulations. The approximations used should be sufficiently accurate for most engineering applications.

With this book, we hope to make you feel at home in the equations of multi-component mass transfer. However, we do not *derive* these equations. If you are inquisitive and have some perseverance, you will be able to retrace the fundamentals in the references that we give.

1.3 Structure of the Book

This book has twenty-five chapters, covering a range of subjects. You may feel that it is a jumble of facts and problems, but there is an underlying structure. The theme is the development of the Maxwell-Stefan equations.

There are two main parts: on transfer in gases and liquids (Chapters 3... 13), and on transfer through a solid matrix (Chapters 14...24). Chapters 3 and 4 introduce the two sides of the Maxwell-Stefan equations: the driving forces for mass transfer and the frictional forces between moving species. Chapters 5 and 6 apply the equations to simple binary and ternary examples. Chapters 8, 11 and 12 complete the description of the driving forces by including the effects of non-ideality in a mixture (8), electrical forces (11) and centrifugal and pressure forces (12). Chapters 9 and 10 consider parameters in the friction terms: diffusivities or mass transfer coefficients. Chapter 13 discusses the relation between the MS-equations and other ways of describing mass transfer.

You may wonder what has happened to Chapter 7. It introduces the effects of a temperature gradient, and does not quite fit into the structure. We could have put it almost anywhere.

The second part of the book considers mass transfer through solid matrices. Chapter 14 gives a preview of the subject and discusses the two types of matrix:

- polymer matrices (Chapters 15...20) and
- structures with defined pores (Chapters 21...24).

Chapters 15 and 16 give a brief description of polymers and of the behaviour of diffusion coefficients in polymers. These chapters are a sideline, introducing concepts that we need further on. We continue with a series of examples with

different driving forces: composition gradients (Chapter 17), pressure gradients (Chapters 17 and 18) and electrical gradients (Chapters 19 and 20).

In the chapters on porous media, we mainly focus on the friction side of the MS-equations. Chapter 21 covers transport of non-adsorbing gases and introduces the effects of viscous flow. Chapter 22 shows how the Maxwell-Stefan equations are applied when chemical reactions are taking place. Chapter 23 considers diffusion of species which *do* adsorb, such as in microporous adsorbents. In Chapter 24 we consider an example where viscous flow is very important: ultrafiltration.

We finish by looking back at the many different aspects of the MS-equations in Chapter 25.

1.4 Guidelines to the Reader

The text was written to accompany overhead transparencies in a full week's course on multi-component mass transfer. Most transparencies have found their way into the figures: they are important, not just illustrations. The figures contain all formulae and much of the other information. Not all chapters are equally important. As a minimum, we recommend that you work through Chapters 3, 4, 5, 6, 14, 17 and 21. Together, these will give you a working idea of multicomponent mass transfer theory for about two day's work.

Other comments:

- If you are convinced that you know all about mass transfer (as we used to be!) you should read Chapter 2. It may contain a few surprises.
- Chapters 7, 8 and 12 cover subjects which, although important, can be omitted on first reading.
- The Chapters 9, 10, 11 (second half), 15 and 16 are on the estimation of properties and model parameters such as diffusivities and mass transfer coefficients. You can skip these on first reading.
- If you are not interested in ions, electrolytes and electrical fields you can skip Chapters 11, 19, 20 and parts of 24. (However, do note that electrical fields are much more prevalent than thought by most chemical engineers!)
- If you never encounter polymers, you will not need Chapters 15...20.
- When porous media play no role in your life, you can omit Chapters 21...24.

It is all up to you.

Chapters 2...6 contain a number of questions and small sums in the text. We recommend that you try these. The answers are buried in the text or figures. Behind each chapter is a series of exercises. These are to help you to go through the material more thoroughly than you will with a single reading. There are short questions, discussions and additions to the material of the main text. The answers are given at the end of the book.

Beginning with Chapter 5, there are assignments in Mathcad – a fairly accessible programming language. There are two kinds: short ones, which you are to program yourself and longer files, which are demonstrations of more complicated problems. Our students very much favour the first type. We have marked them with ★ and we hope that you will try a fair number of these. The second kind of files is for you to use for your own problems, to look at, to play with, to modify or to criticise. We leave it to you. Many of these files work out examples given in the text. The Mathcad assignments can be downloaded from the website <http://www.vssd.nl/hlf/d004.htm>. Appendix 1 contains an introduction to Mathcad: enough to allow you to read the files. At the website you will find files with only the questions, and those with complete answers. They are in three forms: for Mathcad 8 and later, for Mathcad 13 and later and for Acrobat Reader 7 and later. The pdf files in the Acrobat directory are read-only: you cannot play with the files as you can in Mathcad.

The regular text of the book continues in Chapter 2. However, you should glance through the list of symbols, and the list of conventions at the end of this chapter. You may not understand all details on first reading, but you should know where they are so you can look back later.

1.5 Guidelines to the Teacher

This book has evolved in a series of twenty-three courses that we have given at different universities since 1982. The participants were mainly PhD and Masters students, but we have also had many participants from industry and a fair number of our colleagues: together about nine hundred of them. Most have been from chemical engineering, but we have also had mathematicians, chemists, physicists, mechanical engineers, and the occasional pharmacy or biology student.

Because we always have an audience coming from many different places, our courses have mostly been in five days consecutively. In such a course we have about 36 hours for lectures and computer assignments. We divide these into (roughly) 16 hours of lecturing and 20 hours of computer assignments in changing groups of two. Except for Chapters 1 and 25 (which require no lecturing time) and 2 and 14 (which take less than half an hour), all chapters need about an hour. This means that you will have to make a choice of about 15 chapters from the 19 others that we provide. The ‘Guidelines to the Reader’ above should help you in making a choice.

As a minimum for a course we recommend Chapters 3, 4, 5, 6, 14, 17 and 21. Together, these will give participants a working idea of multicomponent mass transfer theory for about two day’s work.

You can download auxiliary files from the website <http://www.vssd.nl/hlf/d004.htm>. These also contain a complete set of PowerPoint 2003 files of the colour slides that

we use in our course. You can use and edit these freely for your own teaching, but you are not allowed to use them for commercial purposes. They are our property! On assessing the knowledge of students. You can of course do that in the traditional way. We also have good experience with giving each student some article on a mass transfer problem and asking him or her to construct a new Mathcad example. Our students find this difficult but instructive. Success!

1.6 Symbols

Symbols used only at one or two points, are defined there and not listed here.

| | | |
|---------------|-----------------------------------|------------------------------------|
| \mathcal{A} | Avogadro constant | $\# \text{ mol}^{-1}$ |
| A | non-ideality parameter | - |
| a | activity | - |
| c | molar concentration | mol m^{-3} |
| c_p | molar heat capacity | J mol^{-1} |
| D | Fick diffusivity | $\text{m}^2 \text{ s}^{-1}$ |
| d | diameter | m |
| \mathcal{D} | Maxwell-Stefan diffusivity | $\text{m}^2 \text{ s}^{-1}$ |
| E | energy flux | $\text{J m}^{-2} \text{ s}^{-1}$ |
| E | activation energy | J mol^{-1} |
| F | force per mole | N mol^{-1} |
| \mathcal{F} | Faraday constant | C mol^{-1} |
| g | acceleration of gravity | m s^{-2} |
| H | enthalpy | J mol^{-1} |
| h | heat transfer coefficient | $\text{W m}^{-2} \text{ K}^{-1}$ |
| I | electrical current density | A m^{-2} |
| J | flux with respect to the mixture | $\text{mol m}^{-2} \text{ s}^{-1}$ |
| k | mass transfer coefficient | m s^{-1} |
| K | equilibrium constant | - |
| M | molar mass | kg mol^{-1} |
| m | mass | kg |
| N | flux with respect to an interface | $\text{mol m}^{-2} \text{ s}^{-1}$ |
| n | number of moles | mol |
| p | pressure | N m^{-2} |
| R | gas constant | $\text{J mol}^{-1} \text{ K}^{-1}$ |
| R | retention | - |
| r | radius | m |

| | | |
|-------|------------------------------|-----------------------------------|
| r | reaction rate | $\text{mol m}^{-3} \text{s}^{-1}$ |
| T | temperature | K |
| t | time | s |
| T_g | glass transition temperature | K |
| u | diffusive velocity | m s^{-1} |
| v | viscous velocity | m s^{-1} |
| V | molar volume | $\text{m}^3 \text{mol}^{-1}$ |
| w | whole (overall) velocity | m s^{-1} |
| x | mole fraction | - |
| y | mole fraction | - |
| z | distance (position) | m |
| z | charge number | - |

Greek symbols

| | | |
|---------------|------------------------------------|-------------------------------------|
| α | viscous selectivity | - |
| Δ | increase of... | - |
| ε | volume (void) fraction | - |
| ϕ | electrical potential | V |
| γ | activity coefficient | - |
| η | viscosity | Pa s |
| λ | thermal conductivity | $\text{J m}^{-1} \text{K}^{-1}$ |
| μ | chemical potential | J mol^{-1} |
| ν | stoichiometric coefficient | - |
| π | osmotic pressure | N m^{-2} |
| ρ | density | kg m^{-3} |
| σ | interfacial tension | N m^{-1} |
| τ | stress | N m^{-2} |
| τ | tortuosity | - |
| υ | diffusion volume | $\text{m}^3 \text{mol}^{-1}$ |
| ω | angular speed | rad s^{-1} |
| ξ | friction coefficient, structured | $\text{N s mol}^{-1} \text{m}^{-1}$ |
| ψ | potential of a species | J mol^{-1} |
| ζ | friction coefficient, unstructured | $\text{N s mol}^{-1} \text{m}^{-1}$ |

Superscripts

| | |
|-------------------|--|
| \bar{x} | <u>average</u> of x in a film |
| p_1^* | * pressure of <u>pure</u> '1' (vapour pressure) |
| V_1^* | * volume of <u>pure</u> '1' |
| $D_{1,2}^0$ | <u>0</u> in <u>free space</u> |
| $D_{1,2}^d$ | in the <u>dispersed</u> phase |
| p_1^b | <u>boiling</u> pressure |
| $D_{1,2}^{x_1=1}$ | $D_{1,2}$ <u>at</u> $x_1 = 1$ |
| p_1^{eq} | pressure of '1' if a reaction were to go to <u>equilibrium</u> |
| T_{ref} | <u>reference</u> |
| v^T | <u>thermal</u> velocity |
| \bar{u}_1 | velocity of '1' <u>at the average composition</u> |
| x', x'' | x in two <u>different phases</u> |

Subscripts

| | |
|---------------------------|---|
| c_w | concentration of <u>water</u> |
| d_p | diameter of <u>particle</u> or <u>pore</u> |
| $D_{1,eff}$ | <u>effective</u> Fick diffusivity of '1' |
| V_f | <u>free</u> volume |
| $\zeta_{1,M}$ | friction coefficient between '1' and the <u>matrix</u> |
| V_C | molar volume of a <u>chain</u> element |
| $x_{1\alpha}, x_{1\beta}$ | species '1' at different <u>positions</u> $\alpha, \beta, \gamma, \delta$ |
| T_{ref} | <u>reference</u> temperature |
| u_1, u_2 | <u>species</u> '1' and '2' |
| $u_{1\bullet}$ | <u>tracer</u> with properties equal to species '1' |
| u_i | species i <u>under consideration</u> |
| u_j | species j <u>other</u> than that under consideration |
| ζ_V | <u>viscous</u> friction coefficient |

Abbreviations

| | |
|----|-----------------|
| ED | electrodialysis |
| FH | Flory-Huggins |
| MS | Maxwell-Stefan |
| RO | Reverse Osmosis |
| UF | Ultrafiltration |

1.7 Conventions

Below are a few notes on the conventions used in this book. You may want to look back at this list occasionally while you are reading the book; do not expect to understand every detail on first reading.

(1) In the drawings and sketches, the positive direction is from left to right. Velocities and fluxes in that direction are also positive.

(2) A force is directed down a potential gradient. Examples are:

$$F_1 = -\frac{d\mu_1}{dz} \quad \text{or} \quad F_i = -Fz_i \frac{\Delta\phi}{\Delta z}$$

This convention holds both for differential and for difference equations.

(3) When computing a difference, we begin with the value at the most positive position (the right hand value) and subtract the other:

$$\Delta x_2 = x_{2\beta} - x_{2\alpha}$$

(4) Examples may consider compositions in many positions; these are denoted by Greek subscripts. If the problem considers different phases, these are distinguished by accents (Figure 1.1).

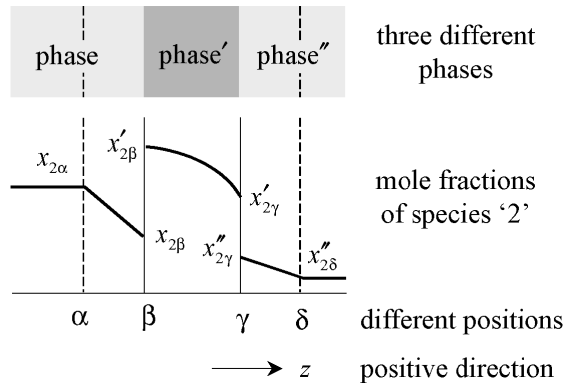


Fig. 1.1 Three different phases

(5) A 'property' can mean several different things in a mixture. We illustrate this for the molar volumes in a ternary mixture. (Figure 1.2)

molar volumes of the pure species V_1^*, V_2^*, V_3^*
 molar volumes of the species as in the mixture (partial molar volumes) V_1, V_2, V_3
 molar volume of the mixture $V = x_1V_1 + x_2V_2 + x_3V_3$

Fig.1.2 Component volumes: pure and in a mixture

In an ideal mixture, the species volumes are the same as those of the pure species, but only then. Note that a property of the mixture has no separate subscript or superscript.

(6) A mixture moving through a solid matrix can be described in several ways. As an example, we consider the movement of two permeants ‘1’ and ‘2’ through a membrane. We can regard the membrane material as a third component ‘3’, or as something separate – the matrix ‘M’ – which is not part of the mixture (Figure 1.3). The friction forces exerted on component ‘1’ in the two notations are:

$$\begin{array}{l}
 (a) \quad \boxed{x_2 \zeta_{1,2}(u_1 - u_2)} + \boxed{x_3 \zeta_{1,3}(u_1 - u_3)} \\
 (b) \quad \boxed{x_2 \zeta_{1,2}(u_1 - u_2)} + \boxed{\zeta_{1,M}(u_1 - u_M)}
 \end{array}$$




friction exerted by ‘2’ on ‘1’ friction exerted by the matrix on ‘1’

Fig.1.3 Two notations:
 (a) the matrix is part of the mixture,
 (b) the matrix is separate

Each of the terms separately has the same size in both notations. Also the velocities are identical (including $u_3 = u_M$). However, the numerical values of both the mole fractions and the friction coefficients differ.

(7) We will be describing porous media in two ways. In the first, we consider the effects of the structure of the medium: effects of pore or particle sizes, or the effect of the void fraction. In this model it is also common to distinguish between two species velocities: diffusive and viscous (or convective) velocities. Viscous flow is governed by hydrodynamics. The sum of the two velocities is the whole (or overall velocity). Note how the symbols for the velocities are contained in the letters of their names (Figure 1.4).

Structured model

| | | | |
|---|------------------|---|-------------------|
|  | <i>diffusive</i> | $F_1 = x_2 \zeta_{1,2} (u_1 - u_2) + \zeta_{1,M} u_1$ $F_2 = x_1 \zeta_{1,2} (u_2 - u_1) + \zeta_{2,M} u_2$ | ζ (zeta) |
|  | <i>viscous</i> | $F = \zeta_V v \quad v_1 = \alpha_1 v \quad v_2 = \alpha_2 v$ | |
|  | <i>whole</i> | $w_1 = u_1 + v_1 \quad w_2 = u_2 + v_2$ | |

Non-structured model


| | | |
|---|---|----------------|
|  | $F_1 = x_2 \xi_{1,2} (w_1 - w_2) + \xi_{1,M} w_1$ $F_2 = x_1 \xi_{2,1} (w_2 - w_1) + \xi_{2,M} w_2$ | ξ (ksi) |
|---|---|----------------|

Fig. 1.4 Notation in the structured and non-structured models

In the non-structured model, the effects of the structure are built into the friction coefficients. This kind of model only considers the whole velocities. The two models give the same result when applied properly. However, the friction coefficients can behave quite differently. The relations between the two sets of coefficients are complicated.

2

Is Something Wrong?

In this chapter, we look back at how we have learned mass transfer. We see that Fick's law is incomplete and that it leads to wrong predictions, even in simple multicomponent problems.

2.1 The Starting Point

We expect your working knowledge of mass transfer to be something like that summarised in Figure 2.1. Once these were also the only tools we had. So let us have a look at them. The upper part of the figure shows two 'laws' which govern motion of a species i in a mixture, with respect to that mixture:

- the flux of a species is proportional to its diffusivity and concentration gradient, and
- the flux is proportional to a concentration difference times a mass transfer coefficient.

The flux is defined relative to some 'frame of reference', for example one that moves with the average molar velocity of the mixture.

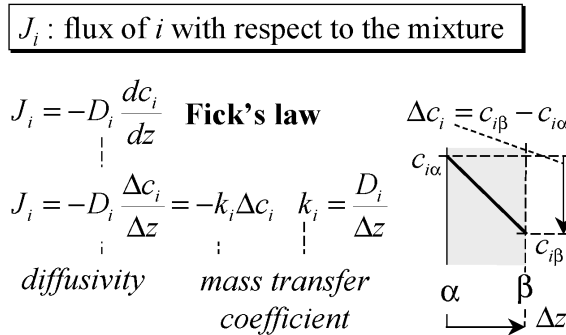


Fig. 2.1 Mass transfer as you have learned it

The first law (Fick's law) tells us that a species should move down its concentration gradient. You may regard the second 'law' as a difference form of the first, which is applicable to a thin film. A film is a rough model for a mass transfer resistance. The two laws are handy little formulae for describing simple mass transfer problems. In passing we note that the fluxes and concentrations used here are in molar units

($\text{mol m}^{-2} \text{s}^{-1}$ and mol m^{-3}). This implies that the diffusivity has units of $\text{m}^2 \text{s}^{-1}$ and the mass transfer coefficient of m s^{-1} (a velocity).

We are usually interested not in the fluxes with respect to the mixture, but in the fluxes with respect to some boundary or interface. We give these the symbol N_i (Figure 2.2). Only if the flux N of the mixture (as a whole) is zero, are the fluxes J_i and N_i equal. Otherwise, we must add a *drift flux* to the *diffusion flux*. Also here, we can write the flux relation as either a differential equation or a difference equation. The last is simpler, but approximate. We can force the difference equation into a simple looking form by including a *Stefan* or *drift* correction. Unfortunately, this correction can have *any* value and sign; the result is not as useful as it looks.

| | |
|--|---|
| N_i : flux with respect to an interface | |
| differential equation | <i>flux of mixture</i> |
| $N_i = -D_i \frac{dc_i}{dz} + N\bar{x}_i$ | $N = \sum_i N_i$ |
| difference equation | |
| $N_i = -\underbrace{k_i \Delta c_i}_{\substack{\text{diffusion} \\ \text{flux}}} + \underbrace{N\bar{x}_i}_{\substack{\text{drift} \\ \text{flux}}}$ | $\rightarrow -\underbrace{k_i s_i \Delta c_i}_{\substack{\text{Stefan or drift} \\ \text{correction}}}$ |

Fig. 2.2 The flux with respect to an interface

In most of the examples that we consider in this chapter, drift is not important. So you should expect both fluxes J_i and N_i to be equal, and directed down the concentration gradient of i . The only exception will be in the very last example, where drift *is* important.

Conventional mass transfer in a binary mixture of gases (Figure 2.3) is especially simple. If pressure and temperature in the gas are assumed constant, the total molar concentration is also constant. By definition the sum of the fluxes with respect to the mixture is zero. If you then write down the flux equations for the two components it is immediately clear that there is only one binary diffusion coefficient. Also experiment (and the kinetic theory of gases) tells us that this diffusivity is a constant (that is: independent of composition, not of pressure and temperature).

There is more to be said about conventional mass transfer theory, but this should be enough for the moment.

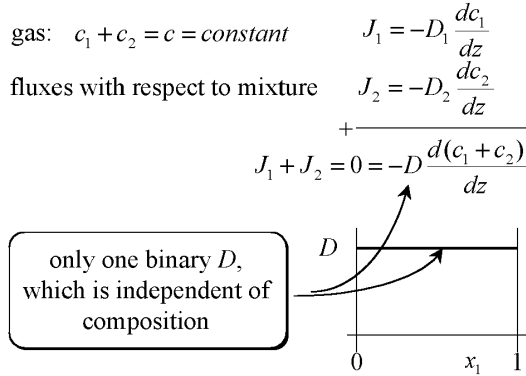


Fig. 2.3 A binary gas is simple

2.2 Three Gases

Look at the experiment in Figure 2.4. There are two equal glass bulbs filled with mixtures of ideal gases. The left bulb consists of hydrogen and nitrogen, and the right bulb of carbon dioxide and nitrogen. The amounts of nitrogen in the two bulbs only differ slightly. Both bulbs are at the same pressure and temperature. At a certain moment we connect them by a capillary; this is fairly narrow, say with a diameter of one millimetre, but otherwise nothing special. Gases start diffusing from one bulb to the other. Before you read on we would like to ask you to think a moment about the questions given in the figure, and to make your own decision on which answer you choose.

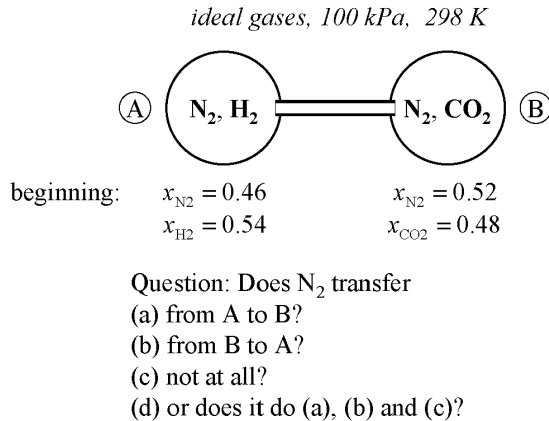


Fig. 2.4 A 'simple' experiment, with some questions

Have you answered the questions?

The results of the experiment are shown in Figure 2.5. The behaviours of hydrogen and carbon dioxide (bottom part of the figure) are as expected. Their compositions change monotonically in such a way that after a few days the amounts in the two bulbs will have become equal. Hydrogen (which is the smaller molecule) moves more rapidly than carbon dioxide. Nitrogen (note the difference in the composition scale) behaves quite differently. Initially it diffuses from the high concentration (bulb B) to the low concentration, and the two concentrations become equal after about one hour. However, nitrogen keeps on diffusing in the same direction, now *against* its concentration gradient. The gradient keeps increasing up to about eight hours after the start of the experiment. Only after that, do the two bulbs gradually go back to equal compositions.

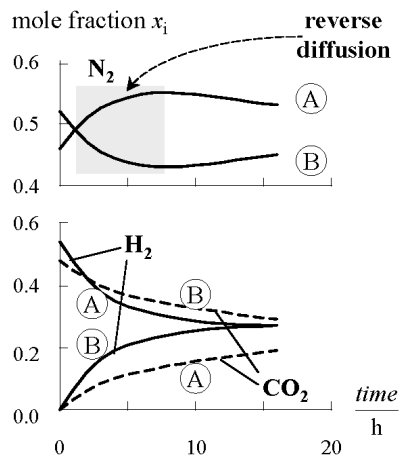


Fig. 2.5 The strange behaviour of nitrogen

With the conventional mass transfer theory of the first two figures in mind you will probably find it difficult to understand what is happening. So just try to forget these for a moment and try a different viewpoint. It is fairly obvious why hydrogen is going from left to right. There is far more hydrogen in the left bulb than in the right one; the random thermal motions of the molecules will on average cause them to move to the right. The same mechanism causes carbon dioxide to move to the left. Now it looks as if nitrogen is being dragged along by the carbon dioxide. This is understandable: you would expect more friction between the heavy carbon dioxide molecules and nitrogen than between nitrogen and hydrogen. At least initially, the movement of nitrogen is mainly determined by the carbon dioxide and hydrogen gradients, and not by its own gradient (which is rather small).

You can extend conventional mass transfer theory to explain the results, but the result is much more complicated and less convincing than that above.

2.3 Two Cations

This experiment involves a membrane that is permeable to cations, but not to anions (Figure 2.6). We bring a dilute solution of sodium chloride in the right compartment and a much more concentrated solution of hydrochloric acid in the left compartment. You would expect the sodium ions to diffuse from the right to the left until the two concentrations have become equal. They do indeed go in that direction. However, they may go on until their concentration in the left compartment is many times higher than in the right one!

The experiment has similarities with the previous one. The explanation, however, is rather different. Hydrogen ions diffuse through the membrane to the right. (Remember that the chloride ions cannot.) This causes a small positive excess charge in the right compartment. The resulting electrical gradient forces the sodium ions to the left and restricts the amount of hydrogen that can be transferred. There is no such mechanism in conventional mass transfer.

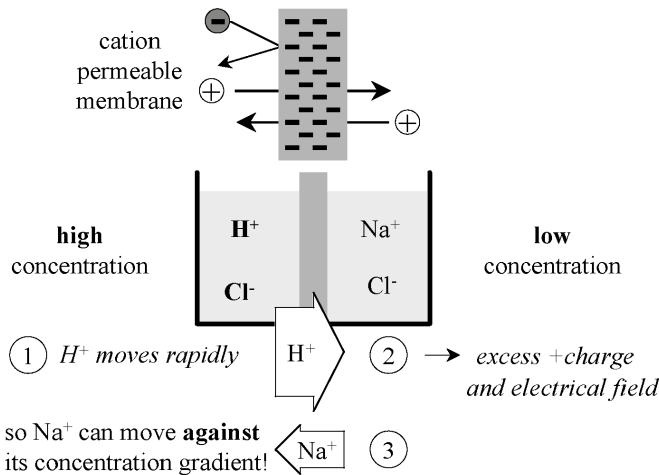


Fig. 2.6 Sodium moves against its gradient

2.4 Two Gases and a Porous Plug

As a last example (Figure 2.7) we consider a porous plug. It is a plug with fine openings (you might think of compressed cotton wool), but otherwise inert. On one side there is helium, on the other argon, both at exactly the same pressure and temperature. Such a situation can be maintained by having flows of pure helium and pure argon past the ends of the plug, passing out into the open. The concentration gradients of the two gases are equal. A careless application of Figure 2.3 might let you expect that the fluxes should also be equal.

In reality, experiment shows that the helium flux is about three times higher¹ than the argon flux! If you want to understand this you should realise that Figure 2.3 only tells you something about the movement of helium and argon with respect to each other. Figure 2.3 tells you nothing about the movement of the mixture with respect to the plug. This movement is balanced by friction between the two gases and the plug. To let the two friction terms cancel, helium must have the higher velocity. There is no interaction with any plug in the conventional analysis of mass transfer; clearly you should take the plug as a component of the mass transfer system.

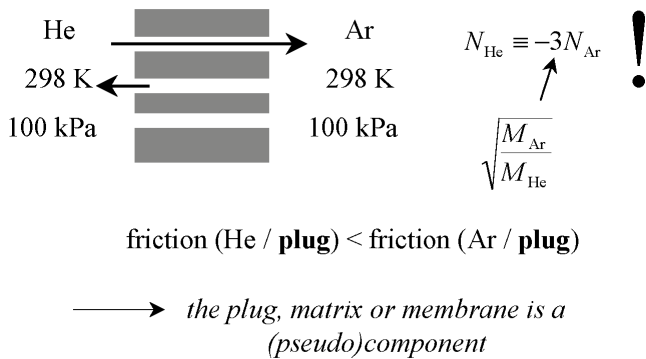


Fig. 2.7 The fluxes need not be equal-but-opposite

By applying a pressure difference (Figure 2.8) you can equalise the two fluxes. The viscous flow due to the pressure gradient increases the argon flux and decreases the helium flux. This is analogous to the effect of the electrical gradient in the previous example. The pressure difference required depends on the structure of the plug: the finer the pores, the larger the pressure difference.

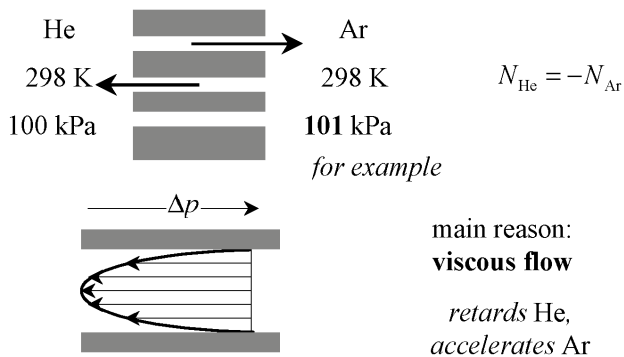


Fig. 2.8 Equal fluxes with a small pressure difference

¹ The ratio is equal to the square root of the ratio of the molar masses.

In the three-gases problem we saw earlier, the capillary is much wider. Even so, rapid diffusion of hydrogen does cause a minute pressure difference. The transport of nitrogen against its gradient is in small part due to the resulting viscous flow.

2.5 Summary

In this second chapter we have briefly reviewed conventional mass transfer. We have then applied it to a few examples and seen that it does not work well. The examples suggest that a better approach to mass transfer would have to take the following phenomena into account:

- friction between each pair of components, including any solid matrix,
- the occurrence of other driving forces than only composition gradients. You can think of electrical and pressure gradients, and
- viscous flow in heterogeneous media (solid matrices).

We will be working these ideas out in the rest of this book.

2.6 Further Reading

Cussler, E. L. (1997) *Diffusion, Mass Transfer in Fluid Systems*, 2nd edition, Cambridge University Press, Cambridge, 1997.

A lively book and a good primer. If you decide not to proceed into the subject of multicomponent mass transfer, Cussler will give you a few excuses.

Duncan, J.B. and Toor, H.L. (1962) An experimental study of three component gas diffusion. *A.I.Ch.E.J.* **8**, 38-41. *This describes the two-bulb diffusion experiment.*

2.7 Exercises

2.1 The concentrations of oxygen and nitrogen in the atmosphere change with altitude. At the top of the Mount Everest their values are about one half of those at sea level. According to Fick's law, air should be diffusing away into outer space; rough estimates show that the half-life of the atmosphere should be about ten thousand years. This is incorrect; the atmosphere is several hundred times older. Which force counteracts the diffusion and is neglected by Fick's law?

2.2 Consider a glass of water. The concentration of water in the liquid is $55\,000\text{ mol m}^{-3}$; that in the surrounding air 1 mol m^{-3} . So a large concentration difference exists across the water/air interface, which is thought to be a few molecules thick. It may not seem to be surprising that water is vaporising. Now we put a lid on the glass. The air in the glass becomes saturated; the water concentration might go up to 2 mol m^{-3} . We still have the concentration gradient in the interface, yet vaporisation stops. (This is obviously at variance with Fick's law, although few people seem to notice.)

In the next chapter we will take the driving force for mass transfer to be the chemical potential gradient. What does this theory tell when we put the lid on?

2.3 We fill the two compartments of the cell in Figure 2.6 with the same aqueous solution of NaCl. There are no concentration differences, so there is no driving force for either water or for the ions. If we now apply an electrical potential difference across the membrane, sodium will be forced through. This is not surprising: there is a driving force on the sodium, be it one that is not incorporated in Fick's law. What is surprising, is that the electrical force leads to a considerable flux of water. Water is not charged, and there is no obvious driving force. How can this be?

2.4 Flow is quite important in gas and water pipelines, in the airing of clothes, in the wetting of toilet paper... in just about everything in daily life. However, transport in media with extremely small pores, such as cellophane, seems to be dominated by diffusion. Why would this be?

2.5 Study the introduction to the review of Krishna and Wesselingh (1997), 'The Maxwell-Stefan approach to mass transfer' *Chem.Eng.Sci.* **73**, 861-911. Here the limitations of conventional approaches to mass transfer are shown using several other examples.