

# Mass Transfer in Multicomponent Mixtures



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# 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

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# 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



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

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

*Greek symbols*

$\alpha$	viscous selectivity	-
$\Delta$	increase of...	-
$\varepsilon$	volume (void) fraction	-
$\phi$	electrical potential	V
$\gamma$	activity coefficient	-
$\eta$	viscosity	Pa s
$\lambda$	thermal conductivity	$\text{J m}^{-1} \text{K}^{-1}$
$\mu$	chemical potential	$\text{J mol}^{-1}$
$\nu$	stoichiometric coefficient	-
$\pi$	osmotic pressure	$\text{N m}^{-2}$
$\rho$	density	$\text{kg m}^{-3}$
$\sigma$	interfacial tension	$\text{N m}^{-1}$
$\tau$	stress	$\text{N m}^{-2}$
$\tau$	tortuosity	-
$\upsilon$	diffusion volume	$\text{m}^3 \text{mol}^{-1}$
$\omega$	angular speed	$\text{rad s}^{-1}$
$\xi$	friction coefficient, structured	$\text{N s mol}^{-1} \text{m}^{-1}$
$\psi$	potential of a species	$\text{J mol}^{-1}$
$\zeta$	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
$\zeta_V$	<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).

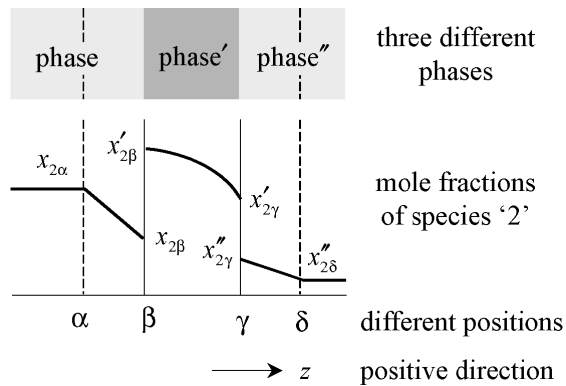


Fig. 1.1 Three different phases

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


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

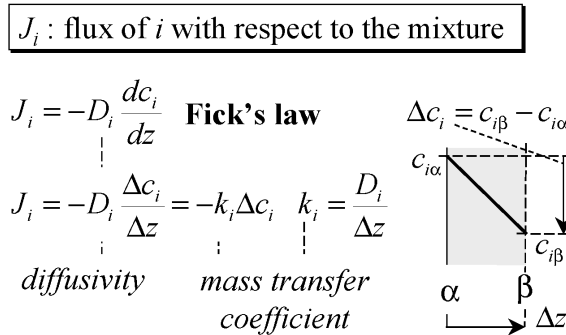


Fig. 2.1 Mass transfer as you have learned it

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