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 are in the folder Exercises/Questions on the CD-ROM. Completed Mathcad files are in the folder Exercises/Answers on the CD-ROM. You can read these, and change their parameters, using the free program Mathcad Explorer which is also on the CD-ROM as a self extracting file in Mathcad/Explorer. Appendix 1 in the book contains an introduction to Mathcad; enough to allow you to read the files. You can further improve your Mathcad skills with the tutorial in Mathcad Explorer. To make full use of the Mathcad exercises, you will need Mathcad 7.0, Student Edition or higher. Before our courses, we give students a short self-instruction course in Mathcad. You will find this in the Mathcad/Tutor7 folder. It consists of ten Mathcad files; they should help you to get a good start in Mathcad in less than half a day.

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.

The CD-ROM that accompanies this book contains a complete set of PowerPoint 7.0 files of the colour transparencies that we use in the course. They are in the folder Transparencies. 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!