MASS TRANSFER

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Beginning . . .

WHO SHOULD READ THIS BOOK?

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

- those with three or more species and
- those with more than one driving force, such as centrifugal, electrical or pressure gradients.

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 multicomponent mass transfer, you may find it enjoyable to see how far you can get with simple means.

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.

If you are not too sure, do not despair. We will introduce these concepts in a fairly leisurely manner. 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. Indeed, we hope to show that a large part of multicomponent mass transfer can be applied with pencil, paper and a calculator. Of course you will need a computer for larger problems, but not to obtain a first understanding.

WHAT THIS BOOK COVERS

Textbook treatments of mass transfer traditionally start with binary mixtures . . . and stop there. However, there are few real processes involving only binary mass transfer. Even a distillation usually has

more components. In membrane processes the simplest cases involve three species: the two to be separated and the membrane itself. Unfortunately, multicomponent mixtures possess properties which are not found even qualitatively in binary mixtures. Also the binary approach cannot be extended easily to mixtures with more than two components. The binary start is a dead-end alley.

This book takes the approach that species move with respect to each other owing to their potential gradients. The rate of movement is restricted by friction between the species. This method was already brought forward by Maxwell and Stefan more than a century ago. It has not caught on, probably because the mathematics are thought to be difficult. This is not really a problem however:

- there are simple approximations to the solutions of the equations. This is the approach taken in this book.
- the computer and numerical techniques now make 'exact' calculations much easier.

Taking potential gradients allows the incorporation of different driving forces:

- composition (or more precisely activity) gradients,
- electrical potential gradients,
- pressure gradients,
- centrifugal fields

and so on. Also thermodynamics and transport phenomena now become one subject. Equilibrium is simply the situation where the driving forces have disappeared.

The friction approach to interactions between the species allows any number of components to be handled in a consistent manner. More components only means more and longer equations.

With these starting points almost any mass transfer process can be described. Examples in this book cover:

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

The examples treat diffusion in gases, in liquids, in electrolyte

solutions, in porous media and in swollen polymers. The book includes some data for estimating multicomponent diffusivities and mass transfer coefficients.

A major limitation of the book is that it only covers situations with a transfer resistance in one of the phases. Such a resistance will be a building block for the simulation of separation or reactor equipment. The reader must be prepared to incorporate the equations into his own simulations. The approximations used should be sufficiently accurate for most engineering applications.

GUIDELINES TO THE READER

This text was written to accompany overhead transparencies in a course on multicomponent mass transfer. So the figures are quite important. Indeed you can get a fair impression of the contents by glancing through the figures and reading the summaries after every chapter (except Chapters 14 and 15). Not all chapters are equally important. If you are convinced that you know everything about mass transfer (as we used to be!) you should read Chapter 2. It may contain a few surprises. Chapters 3 and 4 are the basis for the rest and are essential. Binary examples to start with are given in Chapter 5. Your first multicomponent calculations are at the beginning of Chapter 6. At that point you should know enough to start making your own choices. Of course not every reading sequence is equally handy. For example, if you want to study electrodialysis you should take Chapters 11 (electrolyte solutions) and 12 (membrane processes) first. Otherwise it is up to you.

We have given exercises at several points in the text. Most of these are small and only require pencil, paper and a calculator. We advise you to try them. A set of worked examples is also included. Many of these are much larger; they may require several hours work. We have solved them using 'MathCAD', but other packages should do a similar job.

2

Is something wrong?

THE STARTING POINT

We expect your working knowledge of mass transfer to be something like that summarized in Fig. 2.1. Once these were also the only tools

$$\text{mass transfer,}$$
$$\text{as you have learned it}$$

$$J_i = -D \frac{dc_i}{dz}$$

flux diffusivity

$$N_i = k(c_{i0} - c_{is})$$

$$k = \frac{D}{\delta} \quad \text{mass transfer coefficient}$$

- - - - - - - - - - - - - - -

$$\text{fluxes with respect to...?}$$
$$J \ ... \ \text{mixture.}$$
$$N \ ... \ \text{interface.}$$

Fig. 2.1

we had. So let us have a look at them. There are two 'laws':

- the flux of a species is proportional to its concentration gradient and

- the flux is proportional to a concentration difference times a mass transfer coefficient.

You may regard the second 'law' as an integration of the first over a thin film. It 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 (mol m^{-2} s^{-1} and mol m^{-3}). This implies that the diffusivity has units of m^2 s^{-1} and the mass transfer coefficient of m s^{-1} (a velocity). We distinguish two kinds of fluxes. One (J) with respect to the (moving) mixture. The other (N) with respect to an interface. 'J' is the more fundamental of the two, but 'N' is the one usually required by the engineer. More about this later.

Conventional mass transfer in a binary mixture of gases (Fig. 2.2)

classic mass transfer in gases

gas : $c_1 + c_2 = c = $ constant

fluxes with respect to mixture

$$J_1 = -D_1 \frac{dc_1}{dz}$$

$$J_2 = -D_2 \frac{dc_2}{dz}$$

only one binary D

$$+ \overline{\qquad\qquad\qquad}$$

$$(J_1 + J_2) = 0 = -D \frac{d(c_1 + c_2)}{dz}$$
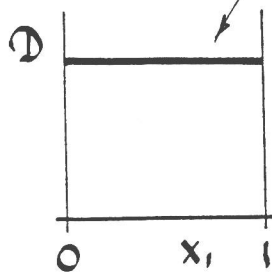
independent of composition, ...

so life is nice and simple ...

HOWEVER....

Fig. 2.2

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). The simplicity of the above rules might lead you to believe that this is all there is to mass transfer. However, that is not so as we shall see in the following examples.

THREE GASES

Look at the experiment in Fig. 2.3. There are two equal glass bulbs

three gases'

100 kPa

A   298 K   B
N_2, H_2 N_2, CO_2

mixtures of ideal gases

$X_{N_2} = 0,46$ $X_{N_2} = 0,52$

$X_{H_2} = 0,54$ $X_{CO_2} = 0,48$

does N_2 flow
a) from A to B ?
b) from B to A ?
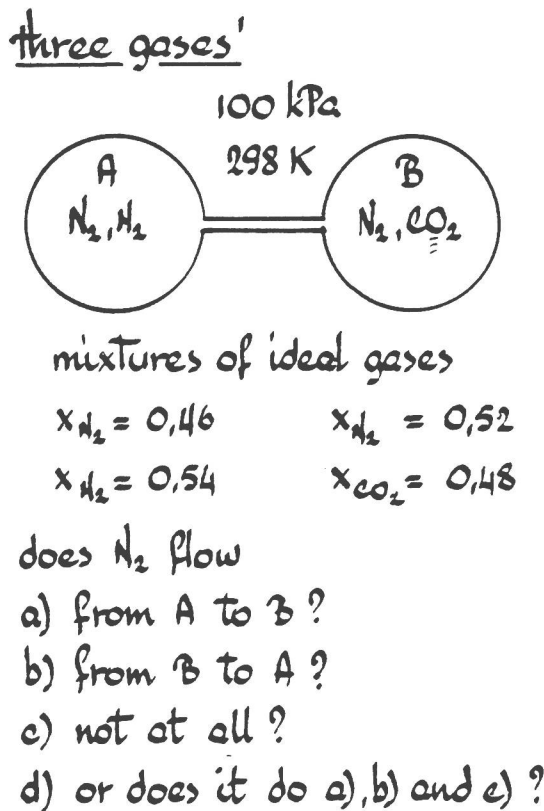c) not at all ?
d) or does it do a), b) and c) ?

Fig. 2.3

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 they are connected by a capillary. The capillary 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.

— Have you answered the questions? —

The results of the experiment are shown in Fig. 2.4. The behaviour of

three gases[2]
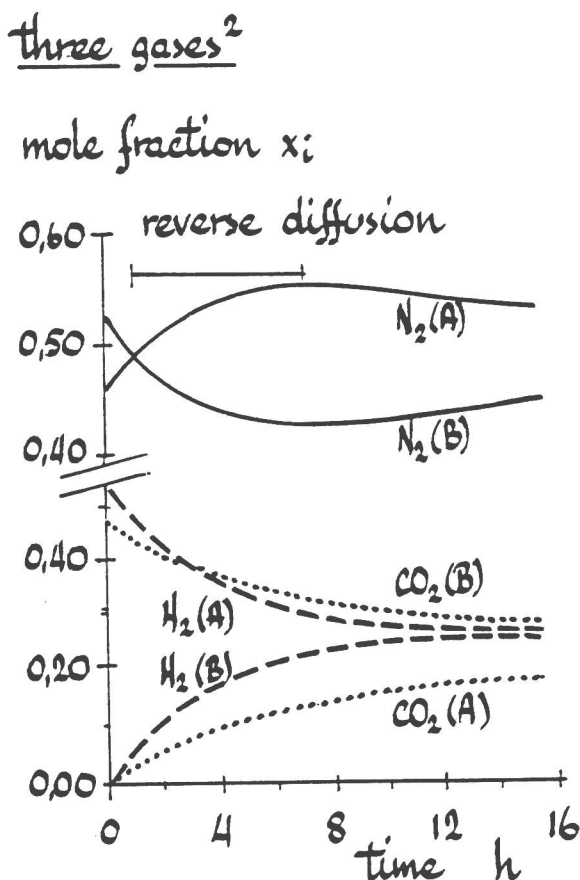
mole fraction x_i

Fig. 2.4

hydrogen and carbon dioxide (bottom part of the figure) is 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 moves more rapidly than carbon dioxide. Nitrogen (note the difference in the composition scale) behaves quite differ-

ently. 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.

With the conventional mass transfer theory of the first two figures in mind you will probably find it very difficult to understand what is going on. 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, and 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). There is no such mechanism in the conventional laws of mass transfer.

TWO CATIONS

This experiment involves a membrane which is permeable to cations, but not to anions and water (Fig. 2.5). 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. Again there is no such mechanism in conventional mass transfer.

TWO GASES AND A POROUS PLUG

As a last example (Fig. 2.6) 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