

6

Ternary Examples

This is an important chapter. After finishing it you should have done your first multicomponent calculations.

6.1 From Binary to Ternary

The extension of the transport relations from binary to three components is straightforward (Figure 6.1). There are now two independent transport relations. In each relation there are two friction terms: for component 1:

- that between (1 and 2), and
- that between (1 and 3).

The forces in these equations are forces per mole of the component considered.

$$\begin{array}{l} F_1 = \zeta_{1,2}x_2(u_1 - u_2) + \zeta_{1,3}x_3(u_1 - u_3) \\ F_2 = \zeta_{2,1}x_1(u_2 - u_1) + \zeta_{2,3}x_3(u_2 - u_3) \end{array} \left. \begin{array}{l} \text{forces per mole of '1'} \\ \text{forces per mole of '2'} \end{array} \right\}$$

Fig. 6.1 From binary to ternary ...

If we multiply the first equation with x_1 , and the second with x_2 , we obtain the forces per mole of mixture (Figure 6.2). In the mixture, friction between (1 and 2) must balance the friction between (2 and 1). A look at the equations then shows that the friction coefficients between (1 and 2) and between (2 and 1) must be equal. (This a form of the *Onsager relation*). So, although there are four friction terms in the two equations, there are only three friction coefficients. The same holds for Maxwell-Stefan diffusivities and mass transfer coefficients.

$$\begin{array}{l} -x_1F_1 = \left[\zeta_{1,2}x_1x_2(u_1 - u_2) \right] + \zeta_{1,3}x_1x_3(u_1 - u_3) \\ -x_2F_2 = \left[\zeta_{2,1}x_1x_2(u_2 - u_1) \right] + \zeta_{2,3}x_2x_3(u_2 - u_3) \end{array} \left. \begin{array}{l} \text{forces per mole} \\ \text{of mixture} \end{array} \right\}$$

these should cancel: $\zeta_{2,1} \equiv \zeta_{1,2}$ $D_{2,1} \equiv D_{1,2}$ $k_{2,1} \equiv k_{1,2}$

Fig. 6.2 Forces per mole of mixture and the equality of two friction coefficients

Also the difference form of the Maxwell-Stefan equations is just an extension of the binary case. Figure 6.3 shows the flux form that you will need many times. Further extensions, to quaternary and so on, only require more equations with more terms.

	binary	ternary	quaternary
$-\Delta x_1 =$	$\frac{x_2 N_1 - x_1 N_2}{k_{1,2} c}$	$+$	$\frac{x_3 N_1 - x_1 N_3}{k_{1,3} c} + \dots$
$-\Delta x_2 =$	$\frac{x_1 N_2 - x_2 N_1}{k_{1,2} c}$	$+$	$\frac{x_3 N_2 - x_2 N_3}{k_{2,3} c} + \dots$

Fig. 6.3 Difference equations, binary, ternary, quaternary...

6.2 A Condenser

Your first multicomponent exercise concerns a condenser (Figure 6.4). The tubes of the condenser are cooled internally, and water and ammonia condense from a vapour mixture of ammonia, water and hydrogen. The hydrogen is insoluble and does not condense. You are to find the fluxes through the gas film.

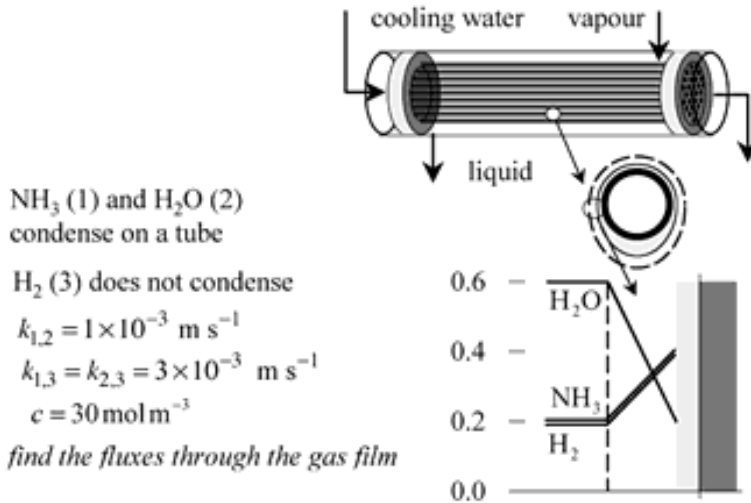


Fig. 6.4 Condensation of a ternary mixture

It is important that you try this exercise yourself. Further on in this book there will be many more examples of multicomponent transfer (usually more complicated). Once you have the idea you will be able to glance over them and you will recognise the same things coming back, again and again. But you must first try yourself. All data for the exercise are given in the figure. So go ahead. Write down the transport equations and the bootstrap relations and solve the fluxes. It may cost you a quarter of an hour, but once you have done it you will see how simple it is. The exercise is

worked out in Figure 6.5. If you write out the equations you have a set of three linear equations in the three fluxes. In this example the bootstrap relation is so simple that you can immediately reduce the system to two equations and solve them.

transport (MS) relations:

$$\text{NH}_3 \quad -0.2 = \frac{0.4N_1 - 0.3N_2}{(1 \times 10^{-3})30} + \frac{0.3N_1 - 0.4N_3}{(3 \times 10^{-3})30}$$

$$\text{H}_2\text{O} \quad 0.4 = \frac{0.4N_2 - 0.3N_1}{(1 \times 10^{-3})30} + \frac{0.3N_2 - 0.3N_3}{(3 \times 10^{-3})30}$$

bootstrap $N_3 = 0$

three linear equations, three unknowns

$$\longrightarrow N_1 = 0.015 \quad N_2 = 0.045 \text{ mol m}^{-2} \text{ s}^{-1}$$

exact solutions:

$$N_1 = 0.013 \quad N_2 = 0.049 \text{ mol m}^{-2} \text{ s}^{-1}$$

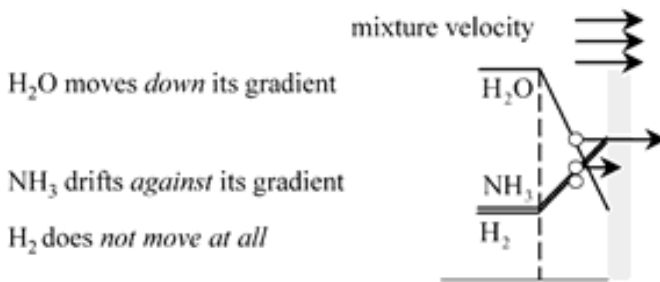


Fig. 6.5 The solution to the condenser

The mixture moves towards the liquid. The driving force on water is in the same direction and it moves more rapidly. Ammonia is retarded by a driving force in the opposite direction. Hydrogen does not move at all even though it has a concentration gradient. Its driving force cancels against friction with the other components. If you know the driving forces, the theory here always gives a linear set of equations for the fluxes or velocities. The problems arise when you do not know the driving forces. You then usually have to solve the equations by trial and error. Even then, the fact that the MS-equations are linear in the fluxes or velocities is a distinct advantage.

6.3 A Ternary Distillation

We now turn to another multicomponent problem: the prediction of tray efficiencies in distillation. Doing this completely would require setting up a complete model of a tray and this is outside the scope of this book. We can, however, obtain a qualitative idea of the problems by looking at our transport relations.

The (Murphree) efficiency of a tray is defined as the ratio of two quantities (Figure 6.6). The first is the change of the vapour composition on a real tray for a certain component. The second is the change that would occur in an equilibrium stage. Such a stage is an ideal concept: you may regard it as a tray with both phases well mixed and with no mass transfer resistances. In binary distillation, efficiencies are very useful. They are always positive, and usually have a value somewhat below one. They tend to be fairly constant throughout a column, and are easily incorporated in distillation design. Can analogous concepts be used in multicomponent distillation? We think not and will try to explain this.

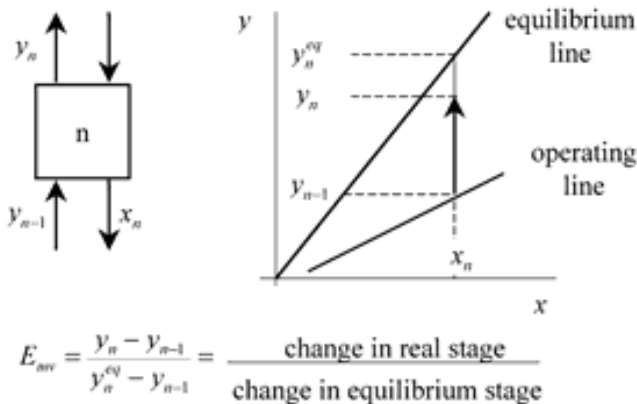


Fig. 6.6 The Murphree efficiency of a tray

Look at the vapour film of the distillation column given in Figure 6.7. (We will neglect any mass transfer resistance in the liquid). There are three components: ethanol, water and a trace of butanol. Ethanol is vaporising; it has a gradient from the liquid down to the gas. Water has an opposite gradient and is condensing. The butanol compositions have been chosen equal at both sides of the film: butanol has no gradient. The transfer coefficients involving water are much higher than those involving the alcohols are. The bootstrap relation is that of *equimolar exchange*, as already discussed. The friction between butanol and ethanol is much larger than that between butanol and water. Now the usual question: will butanol be moving, and in which direction? Of course butanol will be dragged along by the ethanol: it will be vaporising. However, butanol has no driving force: its vapour compositions on the two sides of the film are in equilibrium. So the butanol efficiency must be *unity*.

We look at a few small variations of the butanol gradient (Figure 6.8). Suppose that we increase the bulk concentration of butanol a little to give it a gradient towards the interface. At a certain point the driving force and the drag on butanol will cancel. There will be no flux and no change in the butanol mole fractions on the tray. The efficiency will be *zero*. In between these two points, the denominator in the Murphree efficiency goes to zero. (This is not obvious; you have to believe this for

the moment). The Murhpree efficiency of butanol is then undetermined: plus or minus infinity.

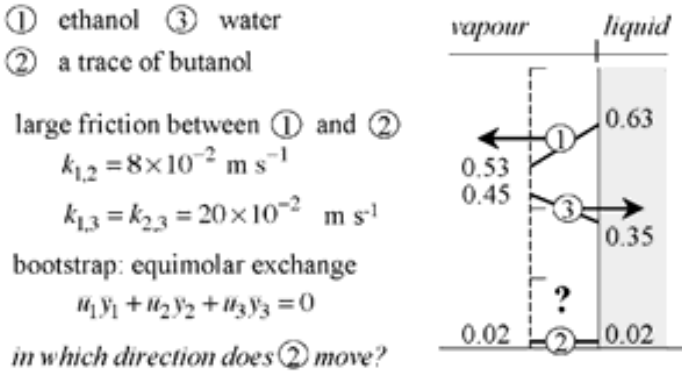


Fig. 6.7 The vapour film on a ternary distillation tray

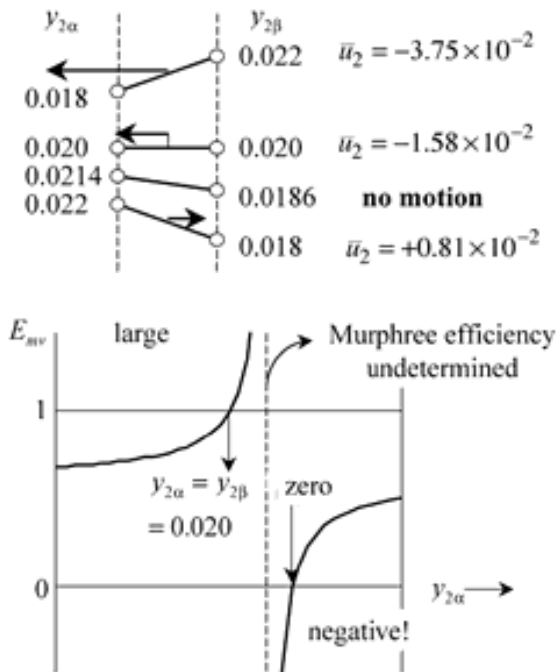


Fig. 6.8 Murphree efficiency of butanol versus composition

More complete calculations confirm the picture found here. Murphree efficiencies in multi-component mixtures are not the simple well-behaved functions of binary systems. The binary concept is useless. Please note that the problems are not due to non-idealities. In this case they are due to interactions between molecules in ideal gas mixtures! We believe efficiency approaches to multicomponent distillation to be a

dead-end alley. They only increase confusion. We prefer models that compute the mass transfer fluxes directly.

It may be remarked at this point that the three-gases problem from Chapter 2 is formally identical to the problem we have just considered. It can be described almost quantitatively with the same equations.

6.4 A Ternary Reaction

As a third example, we consider a reaction of gases on a catalytic surface. The gases are nitrogen and hydrogen, and they react to form ammonia (Figure 6.9). The reaction causes differences in composition between the bulk and the surface. As a result hydrogen and nitrogen diffuse to the right, and ammonia diffuses to the left. You must expect the mass transfer coefficients involving hydrogen to be larger than the nitrogen-ammonia coefficient.

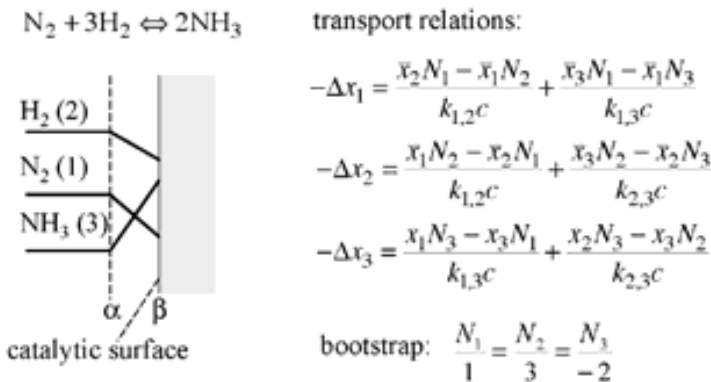


Fig. 6.9 Ammonia reaction on a catalytic surface

The reaction stoichiometry provides the bootstrap relation. Because much hydrogen is consumed, there is a large drift flux towards the catalytic surface. You will notice that we have written all equations in the flux form; this is always handiest when dealing with chemical reactions. In the following figure, it is easy to get the symbols for nitrogen (N_2) and the flux of hydrogen (N_2) mixed up. So look carefully.

With these complications, you might expect considerable multicomponent effects. We come back to this in a moment.

6.5 Binary Approximation of a Ternary

Engineers often use binary mass transfer relations for ternary mixtures. From the previous examples you might obtain the impression that this should lead to disaster. This is not so: in most cases the problems are not spectacular.

When can we approximate ternaries as ‘effective’ binaries? That is when the two friction terms can be taken together. Figure 6.10 shows three cases.

a ternary can be approximated as a binary when

$$-\frac{\Delta x_1}{x_1} = x_2 \frac{u_1 - u_2}{k_{1,2}} + x_3 \frac{u_1 - u_3}{k_{1,3}} \rightarrow \dots = \bar{x}_{eff} \frac{\bar{u}_1 - \bar{u}_{eff}}{k_{1,eff}}$$

- ① one friction term dominates:

$$\boxed{\frac{x_3}{k_{1,3}} \gg \frac{x_2}{k_{1,2}}} \rightarrow x_3 \frac{\bar{u}_1 - \bar{u}_3}{k_{1,3}} \quad \begin{array}{l} \bar{x}_{eff} = x_3 \\ k_{1,eff} = k_{1,3} \end{array}$$

examples: mobile species in many membranes
solutes in a solvent

- ② equal velocity of two species:

$$\boxed{\bar{u}_2 = \bar{u}_3} \rightarrow \left(\frac{x_2}{k_{1,2}} + \frac{x_3}{k_{1,3}} \right) (\bar{u}_1 - \bar{u}_2) \quad \frac{\bar{x}_{eff}}{k_{1,eff}} = \left(\frac{x_2}{k_{1,2}} + \frac{x_3}{k_{1,3}} \right)$$

example: Na^+ and Cl^- in water

- ③ equal diffusivities:

$$\boxed{k_{1,2} = k_{1,3}} \rightarrow \frac{(x_2 + x_3)u_1 - (x_2u_2 + x_3u_3)}{k_{1,2}} \quad \begin{array}{l} \bar{x}_{eff} = x_2 + x_3 \\ \bar{u}_{eff} = \frac{x_2u_2 + x_3u_3}{x_2 + x_3} \end{array}$$

example: ‘I’ in *o*- and *m*-xylene

Fig. 6.10 When a ternary behaves as a binary

- In the first case, one friction term disappears in both equations. This might happen when friction with a membrane or a solvent dominates.
- When two components have the same velocity, they behave as a single component. This happens when hydrogen diffuses through stagnant air (nitrogen and oxygen). The two ions of a salt may also behave as a single component. (However, with three ions, the situation is completely different, as we shall see in Chapter 11.)
- In the third case, two species are similar and two mass transfer coefficients are identical. We can now group the species into an effective binary.

Many problems are approximately described by these situations. Their behaviour is then similar to that of a binary. You should not, however, take this as an excuse for not learning the multicomponent approach. If you use the binary viewpoint you cannot see when multicomponent effects do become important.

There is another important case where multicomponent mixtures behave as binaries. This happens when all fluxes are coupled by the stoichiometry of a single chemical reaction. An example is the ammonia reaction from the previous section. If we take

the transport equation for nitrogen, we can eliminate the hydrogen and ammonia fluxes with the stoichiometry relations (Figure 6.11). The result is an effective binary relation and we can obtain similar ones for the other components. So – possibly to your surprise – this reacting multicomponent mixture shows a simple behaviour! We will make use of this when we discuss heterogeneous catalysis in Chapter 22.

simplifying the transport equation of N_2 in Fig 6.9:
 eliminate N_2 and N_3 with $N_2 = 3N_1$ $N_3 = -2N_1$
 $\longrightarrow N_1 = -k_{1,eff}c\Delta x_1$ with $\frac{1}{k_{1,eff}} = \frac{x_2 - 3x_1}{k_{1,2}} + \frac{x_3 + 2x_1}{k_{1,3}}$
 similarly for H_2 and NH_3

Fig. 6.11 Effective binary relation in the ammonia reaction

6.6 Summary

- In the driving force and friction description of mass transfer, multicomponent systems are a straightforward extension of binary systems.
- You need one mass transfer coefficient for each pair of interactions. So one for a binary, three for a ternary, six for a quaternary, and ten for a five-component mixture.
- For given boundary conditions of the film the transport and bootstrap relations are linear equations in the velocity. You can solve these easily.
- In multicomponent systems, friction can well cause a component to move against its gradient. This is why certain binary concepts, such as that of a tray efficiency, are not always transferable to multicomponent systems.
- Binary theory can be used to approximate multicomponent systems when all mass transfer coefficients are equal, and when all components are dilute except for the solvent.
- When all fluxes are coupled by the stoichiometry of a single chemical reaction, we can describe a mixture as a set of pseudo binaries.

6.7 Further Reading

Krishna, R. and Standart, G. (1976) A multicomponent film model incorporating an exact matrix method of solution to the Maxwell-Stefan equations. *A.I.Ch.E.J.*, **22**, 383-389.

Presents an exact analytic solution to the Maxwell-Stefan equations for ideal gas mixtures. This approach is often used as a benchmark to test simpler approximate solutions.

Taylor, R. and Krishna, R. (1993) *Multicomponent Mass Transfer*. Wiley, New York.

Gives several worked examples to show the differences between binary and ternary mass transfer. Comprehensive treatment of mass transfer in ternary distillation and condensation of mixed vapours. Pseudo-binary treatment of multicomponent mixtures using the effective diffusivity approach is discussed critically.

Toor, H.L. (1957) Diffusion in three component gas mixtures. *A.I.Ch.E.J.*, **3**, 198-207.

A classic paper which emphasises the peculiarities of ternary mass transfer.

6.8 Exercises

6.1 In Figure 6.1 we have written the forces per mole of each of the species. How do you modify the driving force terms to obtain forces per unit mass? In Figure 6.2 we have written the forces per mole of mixture. How do you obtain the driving forces per unit mass of the mixture? Using different units is explored systematically in the Appendix 2 on Units.

6.2 We consider the ternary mixture of Figure 6.1. Although there are only two independent transport relations, we can write out all three relations. We have put the friction coefficients for these equations in a matrix below:

$$\begin{array}{cc} & \zeta_{1,2} & \zeta_{1,3} \\ \zeta_{2,1} & & \zeta_{2,3} \\ \zeta_{3,1} & \zeta_{3,2} & \end{array}$$

The coefficients in the first two rows are the same as those in the figure. Check that you understand those of the last row for component '3'. Note that there are no diagonal terms in the matrix: a component does not exert any friction on itself. The Onsager relation tells us that all three coefficients in the lower left triangle are equal to the corresponding values in the upper right triangle. So there are three different friction coefficients, not six. Extend this reasoning to obtain the number of coefficients in a mixture of four components.

6.3★ Ternary Diffusion in a Stefan Tube (Mathcad). Your first real multicomponent exercise. You are to set up the transport relations for two gases diffusing through stagnant air in a tube. You can use the same Given...Find blocks as before, but now with more equations (two or three; you can solve this problem in several ways).

6.4★ Diffusional Distillation (Mathcad). An exercise on a surprisingly simple way of breaking an azeotrope. As in the previous example, you know the compositions on

both sides of a film beforehand. This makes the problem relatively easy. 6.3 and 6.4 are important exercises; they show the structure of most future calculations.

6.5 Accuracy of the Difference Equation (a Condenser) (Mathcad). This is a large file (which took several days to construct). It considers the problem of the condenser in Figures 6.4 and 6.5. It first solves the simple difference equations that we use (the 'one step' approximation). It then subdivides the film into four thin layers; this should approximate the differential equation quite accurately. Comparing the two solutions allows you to see what the accuracy is of the one-step method. The four-step method also gives composition profiles in the film. You will spend most of your time reading the file and only little in making a few modifications.

6.6 Efficiency on a Distillation Tray (Mathcad). We have built a model of a distillation tray for you to play with. Have a look at it and check that the behaviour of the efficiencies of a trace component is like that shown in Figure 6.8.

6.7 The Maxwell-Stefan equations for ternary diffusion can be solved analytically without making the difference approximation; the solution is given by Krishna and Standart (1976). This exact analytic solution can also be programmed without great difficulty using MathCad. For the diffusional distillation example 6.4, try to compare these results with those obtained using the difference approximation.

Hint. You may look at Chapter 8 of Taylor and Krishna (1993) for help, if needed.

6.8 In the distillation tray efficiency example 6.6 we took the vapour phase to be well mixed. In actual distillation tray operations, a better model is to assume that the vapour phase is in plug flow. Try to work out the component efficiencies for the plug flow vapour situation. Can you explain the differences in the efficiency values for the two sets of assumptions?

Hint. You may consult Chapter 13 of Taylor and Krishna (1993) for help.

6.9 Air consists of a mole fraction of 0.21 of oxygen; the rest is nitrogen. In many problems the two components do not move with respect to each other and so behave as a single component. The diffusivities of hydrogen-in-oxygen and hydrogen-in-nitrogen are estimated as 3.22×10^{-5} and $3.41 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. Write down the Maxwell-Stefan equation for hydrogen, and from this determine the effective diffusivity of hydrogen in air.

6.10 A species '1' is diffusing through a mixture where all other species have the same velocity. The friction side of the MS-equation then has the form:

$$x_2\zeta_{1,2}(u_1 - u_m) + x_3\zeta_{1,3}(u_1 - u_m) + x_4\zeta_{1,4}(u_1 - u_m) + \dots = \zeta_{1,eff}(u_1 - u_m)$$

- (a) Write the general formula for the effective friction coefficient of a species i moving through other species j which all have the same velocity. Do this also for Maxwell-Stefan diffusivities and mass transfer coefficients.
- (b) Could you also use an effective friction coefficient when the velocities of the other species are not equal?
- (c) Can you think of any special cases, where the velocities of the other components are not equal, but where an effective coefficient is still handy.