

Part 1

Mass Transfer in Gases and Liquids

3

Driving Forces

In this chapter we introduce a new way at looking at mass transfer. We look at the individual species in a mixture, at the forces working on them, and at their resulting motion. There are two kinds of forces: driving forces and friction forces. Their balance is the Maxwell-Stefan equation, which is the basis of this book. We end with a simplified form of the MS-equation and an estimate of the driving force.

3.1 Potentials, Forces and Momentum

Before we consider motion in mixtures, we briefly repeat a few concepts from mechanics and thermodynamics.

Our first concept is that of a *potential*. Consider the mass in Figure 3.1 and suppose you raise it slowly (reversibly) in the earth's gravity field. The work you perform is equal to the increase of potential of the mass. If you increase the height by one metre, the potential increases by almost ten Joules. The mass could – potentially – return the same amount of work if its motion were to be reversed. In this book, we will mostly consider not the mass of a species, but the number of moles. We obtain the potential per mole by multiplying our first result by the molar mass.

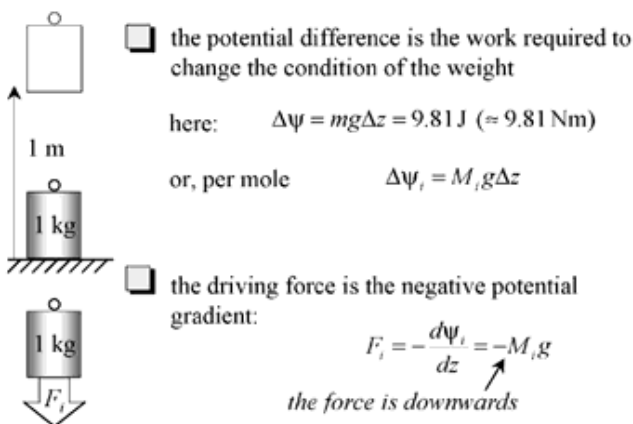


Fig. 3.1 Gravity: a simple example of a potential gradient

The gravitational *force* on the mass is the negative of the *potential gradient*. It has a value of about ten Newton per kilogram; for a simple chemical this might be one

Newton per mole. We will see that this is a very small force when considering molecular motion. The negative sign shows that it is directed downwards. There are other more important forces, such as those due to electrical fields and pressure fields, those in centrifuges, and the support forces in solid matrices such as membranes. We will come back to these in Chapter 11 (electrical forces), Chapter 12 (centrifugal and pressure forces) and Chapter 14 (solid matrices).

Our second concept is that of the *chemical potential*. Consider a separation of one mole of i from a large amount of a mixture (Figure 3.2). The work required to do this reversibly is the change of the chemical potential. It typically has a value of a few thousand Joules per mole. The chemical potential is related to composition; it usually increases with the concentration of the species. As you can see, the chemical potential is a logarithmic function of the *activity* of the species. This activity is the product of the *activity coefficient* and the mole fraction.

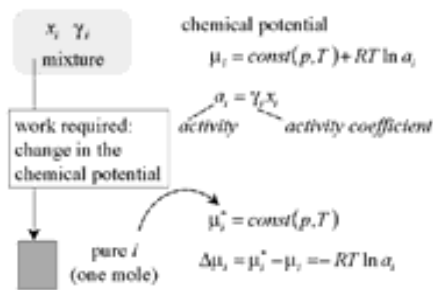


Fig. 3.2 An important potential: the chemical potential

Gases, and liquid mixtures of similar components, form *ideal solutions* (Figure 3.3). The activity is then the same as the mole fraction. This simplifies formulae, and we will often assume ideality in our examples. Note that the chemical potential of a gas can be written in terms of a partial pressure.

chemical potential in
 an ideal solution

$$\mu_i = \text{const}(p, T) + RT \ln(x_i)$$

in an ideal gas

$$\mu_i = \text{const}(p, T) + RT \ln\left(\frac{p_i}{p}\right)$$

partial pressure

Fig. 3.3 Chemical potentials in ideal solutions

In a moment we shall see that also the gradient of the chemical potential causes a force, in a manner analogous to gravity.

Our last concept is that of *momentum*. The momentum of a particle – which is sometimes called its ‘amount of motion’ – is the product of the mass and velocity of

the particle. The momentum of a system is the sum of that of all parts. The momentum of the system can change due to flows carrying momentum in, out, or by forces working on the system (Figure 3.4). The momentum balance shown is the one-dimensional form of a more general relation. The symbol v in this equation stands for ‘some velocity’; it does not have the special meaning that it has in the rest of the book. You can regard the momentum balance as a generalisation of the Newton law of mechanics. For a closed system with a single force it reads $F = ma$.

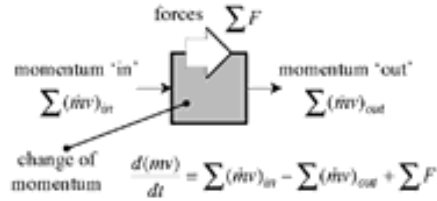


Fig. 3.4 The momentum balance

This ends our repetition of mechanics and thermodynamics: we now go back to mass transfer.

3.2 Momentum (Force) Balance of a Species

The previous chapter has indicated that we need to look at mass transfer in a different way. As a start, we consider a simple experiment with two glass bulbs connected by a capillary (Figure 3.5). The bulb at the left contains hydrogen (species ‘1’); that at the right carbon dioxide (species ‘2’). The whole system is at ambient pressure and temperature. Consider the mixture between two nearby points z and $z + dz$ in the capillary. The two components are moving through each other with local velocities u_1 and u_2 . The differences in velocity cause friction between the two species.

The velocities that we are talking about are the average ‘diffusive’ velocities of the species. These diffusive velocities should not be confused with the thermal velocities of individual molecules: they are *much* lower. Thermal velocities are hundreds of metres per second; the diffusive velocity in a gas might be one centimetre per second. However, the thermal velocities are for the greater part random, and the random part gives neither a contribution to the species velocity, nor to the momentum of the species.

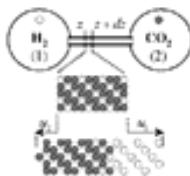


Fig. 3.5 Gases moving through each other

We now consider the momentum balance of hydrogen in the slice between z and $z + dz$ (Figure 3.6) This contains the following terms:

1. a force due to the partial pressure at z : $p_1 A|_z$
2. a force due to the partial pressure at $z + dz$: $-p_1 A|_{z+dz}$
3. the friction force exerted by carbon dioxide on hydrogen.

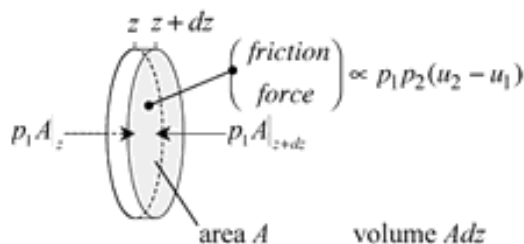


Fig. 3.6 Forces on species (1)

We expect friction between carbon dioxide and hydrogen to be proportional to the amounts of the two gases in the slice and to their difference in velocity. The amounts are proportional to the partial pressures:

$$(\text{friction force}) \propto p_1 p_2 (u_2 - u_1)$$

There will also be friction between hydrogen and the wall. However, except in very narrow pores or at low pressures the interactions between the two gases are much larger¹. Finally the velocity of hydrogen changes a little across the slice, but the resulting terms are also small². So we neglect these terms. In a steady state the three remaining terms must cancel:

$$p_1 A|_z - p_1 A|_{z+dz} \propto p_1 p_2 (u_2 - u_1)$$

Taking the limit for $dz \rightarrow 0$ yields:

¹ We consider this in Chapter 21.

² See exercise 3.1. Velocity effects *are* important in centrifuges (Chapter 12) and in shock waves from detonations.

$$-\frac{dp_1}{dz} \propto p_1 p_2 (u_1 - u_2)$$

These are forces per unit volume. We obtain the force per mole of hydrogen by dividing by its concentration:

$$c_1 = \frac{p_1}{RT}$$

This yields:

$$-\frac{RT}{p_1} \frac{dp_1}{dz} \propto RT p_2 (u_1 - u_2)$$

The left-hand side is the *driving force* on hydrogen:

$$F_1 = -\frac{RT}{p_1} \frac{dp_1}{dz}$$

You will find that this is in Newton per mole of hydrogen. The right-hand side is the *friction force* exerted by carbon dioxide on hydrogen. Using $x_2 \propto p_2$ we rewrite it as:

$$\zeta_{1,2} x_2 (u_1 - u_2)$$

Here $\zeta_{1,2}$ is the *friction coefficient* between species (1) and (2).

3.3 The Driving Force: a Potential Gradient

You can easily check that the driving force on hydrogen is the negative gradient of its chemical potential³:

$$F_1 = -\frac{d\mu_1}{dz}$$

In this form, the formula is not only valid for binary gases but for any fluid not too far from equilibrium at constant temperature and pressure⁴. A few forms of this driving force in fluids are given in Figure 3.7.

The gradient of the chemical potential causes an *internal force*. Internal forces cause motion inside a mixture, but not of the mixture as a whole. The force we saw in the beginning of this chapter – gravity – is an *external force*. It does have an effect on the whole mixture.

³ In our example p and T are constants: their values in the chemical potential disappear in the differentiation

⁴ This is well founded in the theory of Thermodynamics of Irreversible Processes, but we do not cover that in this book.

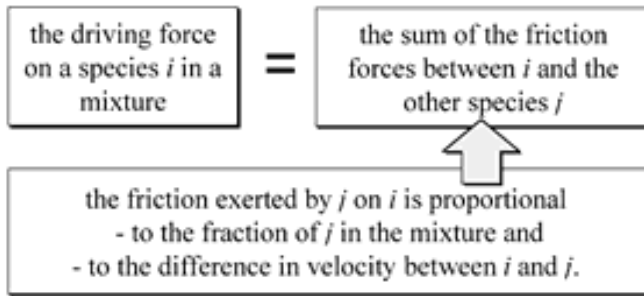


Fig. 3.9 MS-equation in words

3.5 Simplifying the Mathematics

The complete theory of multicomponent diffusion is extensive: it is too large for a short course. This has forced us to cut a corner. Our choice has been to avoid mathematical complexity as far as we can:

1. The book only considers diffusion in one direction: one-dimensional diffusion.
2. It uses a simple engineering model of the flow near interfaces: the 'film' model.
3. You will be doing your exercises using a difference form of the Maxwell-Stefan equation, such as

$$-\frac{\Delta\psi}{\Delta z} = \sum_{j \neq i} \zeta_{i,j} \bar{x}_j (\bar{u}_i - \bar{u}_j)$$

The left side of the equation contains the ratio of the change of the potential across the film to the film thickness. The right side of the equation uses suitably chosen average values of composition and the velocities. We come back to these in Chapter 4. The difference form of the equation contains all the main features of the differential equation. Also its accuracy is adequate for most engineering applications. Using it allows us to cover a broad range of mass transfer problems in a short time (Figure 3.10). Finally: when you have mastered the approximate form, you will be quite far in understanding the behaviour of the complete equations.

We will occasionally step outside the limitations of the difference equation. In Chapter 10 we show how to use the difference equation to allow for more realistic flow models than the film theory. In a number of examples we will also look at complete concentration profiles using the differential equation.

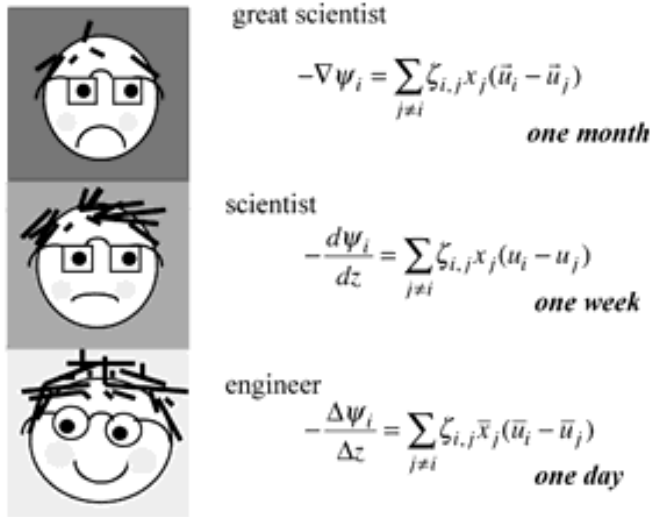


Fig. 3.10 Why we use a difference equation

3.6 The Film Model

Mass transfer through an interface is usually caused by interplay of diffusion and fluid flow. So we need to solve the Maxwell-Stefan equations simultaneously with a flow model.

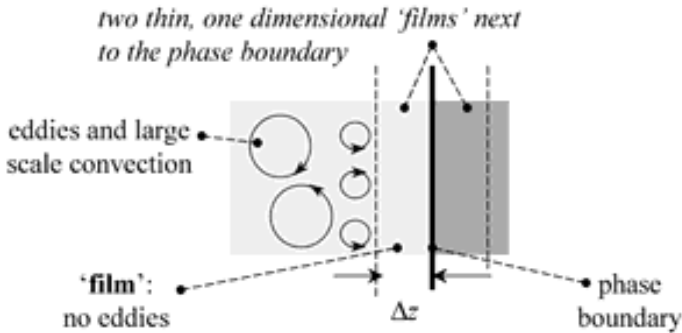


Fig. 3.11 Film theory: a model of flow near an interface

A simple model – very popular with chemical engineers – that has many of the main properties of real systems, is the *film* model⁵ (Figure 3.11). The idea is that bulk fluids are turbulent: that they contain convective currents and eddies of all sizes. These cause rapid mixing of the fluid, so that concentration gradients in the bulk cannot develop. Near phase interfaces the eddies die out, and transport is only by

⁵ To avoid misunderstanding: the film model is *not* a part of the general theory of mass transfer that we are developing here. It is just a convenient starting point, and a useful model for engineering problems. The MS-equations can be combined with *any* flow model.

diffusion. The film theory assumes that the eddies disappear at a defined distance from the interface – at the film thickness.

The film is usually very thin; Figure 3.12 shows a few orders of magnitude. We can of course also use the film model to describe a membrane, and we shall see that it is even (approximately) applicable to diffusion inside solid particles.

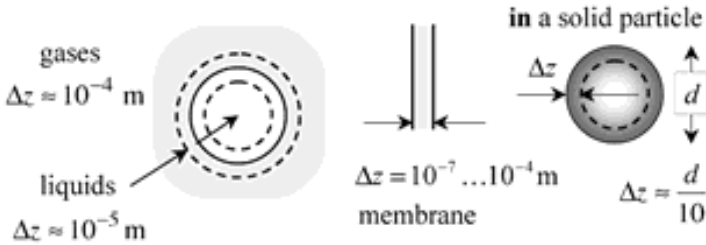


Fig. 3.12 Thickness of films

3.7 Difference Form of the Driving Force

As noted, we will mostly be using a difference form of the Maxwell-Stefan equations. The difference form of the composition driving force is given in Figure 3.13, together with an approximation.

$$F_i = -\frac{\Delta\mu_i}{\Delta z} = -RT \frac{\Delta \ln a_i}{\Delta z} = -\frac{RT}{\bar{a}_i} \frac{\Delta a_i}{\Delta z} \rightarrow -\frac{RT}{x_i} \frac{\Delta x_i}{\Delta z}$$

for a given T and p in ideal solutions

Fig. 3.13 Difference form of the driving force

Figure 3.14 shows how the potential difference varies with the ratio of the activities on the two sides of the film. It also shows that the approximation holds over wide spans of compositions. The approximate difference formula gives better results in the MS-equations than the exact one, so we always use the approximate formula. Apparently there are compensating errors.

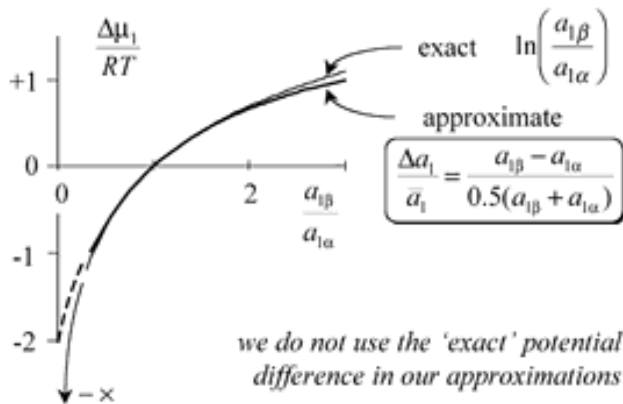


Fig. 3.14 The difference approximation

To become accustomed to the previous formula, you might try the exercise in Figure 3.15. You are to calculate the force driving carbon dioxide out of beer (or cola, if you prefer) into bubbles. Also check the dimensions. The problem should only take you a minute or so to solve.

Try it.

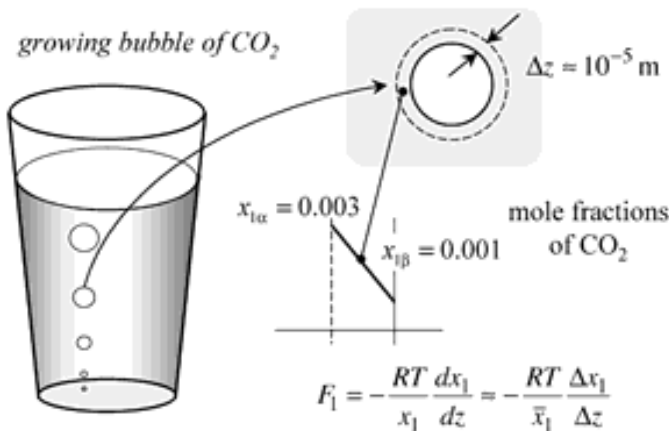


Fig. 3.15 A glass of beer

You should have obtained a value of about two hundred and fifty meganewton per mole or five hundred thousand ton force per kilogram of carbon dioxide. Every kilogram feels the weight of a supertanker! (Figure 3.16). This illustrates the enormous size of molecular forces in mass transfer. Although the forces are large, their effects are not dramatic. This is because the force has to propel huge numbers of molecules; the force per molecule is not extreme.

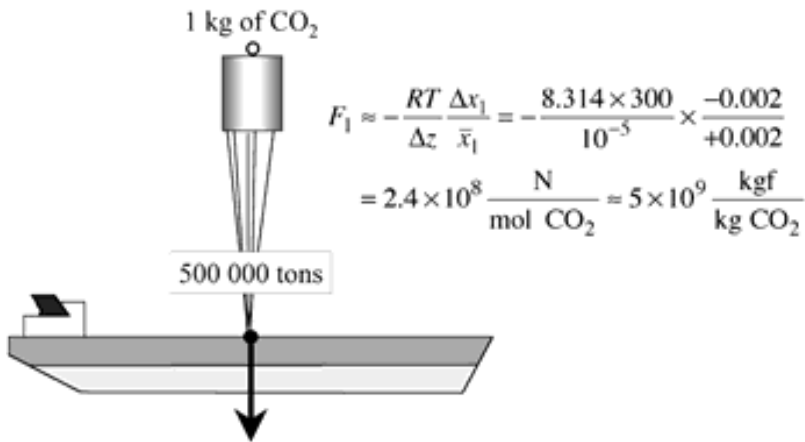


Fig. 3.16 Each kilogram feels the weight of a supertanker

3.8 Summary

In this chapter we have seen the following.

- The concepts of potential, potential gradient, chemical potential, momentum; and the momentum balance.
- We have set up a mass transfer theory based on a momentum balance of each species in a mixture.
- The important terms in the balance are the driving force on the species and friction forces with other species.
- The driving force on a species is its potential gradient.
- An important driving force is the gradient of the chemical potential.
- We use difference equations and the film theory to keep our mathematics simple.
- On a molecular scale, forces due to potential gradients can be extremely large.

You should memorise the approximate form for the potential difference and driving force in Figures 3.13 and 3.14.

3.9 Further Reading

Sherwood, T.K., Pigford, R.L. and Wilke, C.R. (1975) *Mass Transfer*. McGraw-Hill, New York.

A good explanation of the film theory of mass transfer.

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

A rigorous development of the proper driving forces for mass transfer.

3.10 Exercises

3.1 A species in a gas has a molar mass of $M = 0.03 \text{ kg mol}^{-1}$. The gas diffuses through a film with a thickness $\Delta z = 10^{-4} \text{ m}$. The velocity of the gas changes from $u_\alpha = 1 \text{ cm s}^{-1}$ to $u_\beta = 2 \text{ cm s}^{-1}$. There are driving forces and friction forces on the species. The driving force during transport through a film has a value of 10^7 N mol^{-1} . The momentum balance for the species reads:

$$F_{oni}^{driving} + F_{oni}^{friction} = \frac{\Delta(M_i u_i)}{\Delta t}$$

How does the change in momentum compare with the driving force?

3.2 Chemical potential gradients yield forces which are of the order of magnitude of 10^8 N mol^{-1} (see for example the glass of beer in Figures 3.15 and 3.16). You will find similar values in different situations, independent of particle size. This is quite different from the behaviour of particles under influence of gravity (Figure 3.1) which is proportional to the mass of the species. Estimate for which particle size, gravity will become more important than the chemical potential gradient. Take the particles to be spheres with a density $\rho = 1000 \text{ kg m}^{-3}$. You will also need the number of particles per mole: $\mathcal{A} = 6.02 \times 10^{23} \text{ mol}^{-1}$.

3.3 Consider a room with central heating. The air at the ceiling will be warmer than that at the floor; the density near the ceiling will be several percent lower than that at the floor. Fick's law tells us that we should expect a diffusion flux from the floor to the ceiling. This prediction is a little surprising: a cold floor producing air and a hot ceiling which annihilates the same amount (?!). What does the equation in Figure 3.13 say about the driving force? You may assume that there are no differences in the mole fractions of oxygen and nitrogen between the floor and the ceiling.

3.4 The correct form of the driving force for diffusion can be derived from the theory of Irreversible Thermodynamics. We have not followed that approach in this book. It is however instructive to follow the fundamental derivations. Study Chapter 2 of Taylor and Krishna (1993) and satisfy yourself that the relations used in this book are well founded.