4 Mass transfer in food and bioprocesses

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Introduction

As well as the movement of heat, many processing operations involve mass transfer; this can be the extraction of a product, such as apple juice from apples, or the supply of a material such as the oxygen required by a bacterial fermentation. The principles of mass transfer are similar to those of heat transfer; however, the process is more complicated. This is for a number of reasons, not least because the range of species which may be transferred is much larger. The concept of equilibrium is also more difficult in mass transfer than in heat transfer; whilst for two bodies to be in thermal equilibrium they have to be the same temperature, two phases may be in equilibrium in mass transfer terms even if the concentration of the species transferring is different in both. Before the processes of mass transfer can be described, therefore, it is necessary to discuss the idea of equilibrium between phases, expressed by such ideas as the partition coefficient or the equilibrium constant.

The previous chapter has shown that heat transfer in static (conduction) and in moving systems (convection) can be very different. The same applies to mass transfer. In a static system, such as the movement of moisture through to the surface of a solid, the governing process is diffusion; when the fluid is moving, the data are best expressed using mass transfer coefficients. This chapter introduces the concepts of mass transfer with reference to a number of specific examples, such as the problem of getting enough air into a fermentation to ensure that the bacteria will grow at the optimal rate.

One of the key ideas of process engineering, that the rate of a process which occurs in several steps is controlled by the rate of the slowest step, was introduced in the previous chapter. Since mass transfer is usually a slower process than heat transfer, this idea is even more important. In studying any process, it is vital to identify the limiting condition; in drying, for example, the rate of internal diffusion within a solid will usually be much slower than the rate of mass transfer from the surface to the surrounding air. This limits the possibility of enhancing mass transfer by increasing the air velocity over a body, and thus the mass transfer coefficient. In addition,

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many 'reaction' processes are in practice controlled by the rate of supply of reactants or the rate of removal of products from the reaction zone. The ideas developed in this chapter are thus directly useful in the design of processes and equipment.

Mass transfer is concerned with the net movement of molecules in response to a driving force. Operations depending on mass transfer are of great importance in the food industry in, most obviously, recovery and extraction processes, such as oil extraction from seeds, sugar from cane and beet, or the extraction of flavours and colours. However, there are many other operations where mass transfer plays a key role such as aeration, drying (where mass and heat transfer are intimately linked), and in biological processes with immobilized cells or enzymes. In most of these processes fast transfer is a requirement; in others, such as in the use of packaging, it is important to eliminate transfer as far as possible.

In many situations of importance there are significant analogies and interrelationships between the transfer of mass and the transfer of heat and momentum. In particular we shall see many connections between the material in this chapter and that in Chapter 3 of this book on heat transfer processes.

4.1 Why does transfer occur?

Just as a ball rolls downhill when released or heat is transferred when temperatures are not uniform, so mass transfer also occurs when a system is not at equilibrium. If an oilseed is immersed in a solvent in which the oil is very soluble, oil will tend to move into solution in the solvent. If a packaging material is at all permeable gases on either side will tend – however slowly – to equilibrate. In other situations solvents move across semipermeable membranes under osmotic driving forces. Bulk flows will also transport molecules from one region to another. As we shall see, there are many mechanisms for transfer, and we must take care in defining the equilibrium conditions and the frame of reference for transfer. Order can be imposed on the study of mass transfer, however, by recognizing that in many situations the component flux (that is, the flowrate/unit area) is proportional to:

- the driving force, that is, the distance from equilibrium, and
- the reciprocal of the resistance to movement (which depends on the solute and the medium, such as the packaging film).

4.2 Mechanisms

In the real world molecules are never at rest; even in an otherwise totally stationary medium their random motion gives rise to **diffusion**. Diffusion is

usually a rather slow process, and not surprisingly it is slower with large molecules and as the surrounding medium becomes more viscous or solid. If we waited for diffusion to mix the contents of a cake mix we would wait for an awfully long time. This process is analogous to that of conduction in heat transfer.

Fortunately for life on earth, mass transfer also occurs by **convection**: that is, by bulk motion. Sometimes this arises naturally when there is a low-density region (perhaps because it is hotter) underneath one of higher density; in other situations convection is imposed, as in a mixing device (see Chapter 10 for a more detailed discussion), or as a result of mixing and movement due to turbulent eddies in the fluid.

Before discussing these mechanisms in a little more detail we first consider what we mean by equilibrium.

4.3 Equilibrium

4.3.1 The equilibrium state

In an environment at rest in which there is only one physical phase, such as the liquid contents of a bottle of lemonade, and in the absence of any imposed potential gradients or driving forces, the equilibrium state is one of uniform concentration. Local variations in concentration will, even when the bottle isn't shaken, tend to disappear. If there is an imposed potential – if the bottle is swung in a high-speed centrifuge for example, or there is an imposed electrical field – the equilibrium state is no longer necessarily uniform.

In the simplest cases of transfer within a single phase, therefore, the driving force to restore equilibrium will usually be simply related to the local concentration gradients.

However, most realistic situations involve two or more distinct phases in contact. The lemonade bottle initially contains a (small) gas phase and this phase and its components are also in equilibrium with the liquid. Thus the carbon dioxide in the gas is equilibrated with the dissolved species. Indeed, all the species in the recipe will be in equilibrium across the two phases; at equilibrium their chemical potentials are equal and, it is important to note, this no longer implies that the concentrations and relative proportions of the species in the two phases are the same. Indeed we capitalize on this fact in extraction processes such as solvent extraction.

A convenient way of handling equilibrium processes is to define a **partition** or **equilibrium coefficient**. This relates the equilibrium concentrations (usually in molar units) of a given species or solute in the two phases:

$$K = \frac{x}{y} \tag{4.1}$$

where x, y are the mole fractions in phases 1, 2.

It will be seen that K is a measure of the enrichment of the species, as a value other than 1 implies that the concentration in one phase is greater than that in the other.

In the context of separation processes, where the differential extraction of different species is sought, the **selectivity** is important. This is defined as the ratio of the enrichments of two species. With two solutes A and B for example, with concentrations x_A, etc. the selectivity is

$$S_{A/B} = \frac{\left[x_A / y_A\right]}{\left[x_B / y_B\right]} = K_A / K_B \tag{4.2}$$

Thus, for example, a K-value of 100 implies a 100-fold higher concentration of the particular species in one phase over the other; an S-value of 1 implies no differential enrichment of one species over the other.

While the K-values can be handled as if they were purely empirical constants, they can be related to more fundamental thermodynamic measures, as at equilibrium the chemical potentials of the various species in the different phases are equal. We shall look at some examples of the use of partition coefficients in subsequent sections.

4.3.2 The equilibrium stage

If the contact or processing time is sufficiently long for mass transfer to occur, or agitation sufficiently rapid, the system will approach **equilibrium**. The idea of an operation that has essentially reached equilibrium is an important one, and is particularly useful in analysing separation processes such as distillation, solvent extraction and evaporators. In Chapter 3, on heat transfer, we saw some ways of estimating whether transfer was fast or slow in relation to the processing time – that is, whether equilibrium is approached or not – and we shall develop similar ideas in relation to mass transfer in section 4.5. We shall be concerned there to estimate (roughly) a characteristic time (really a relaxation time or time constant) for mass transfer. Equilibrium will be approached if the characteristic time for mass transfer is short in comparison to the processing time. However, if mass transfer is relatively slow – that is, has a long characteristic time compared with other processes – equilibrium will not be approached and the process is likely to be controlled by the rate of transfer. First, let us see how the idea of an equilibrium stage can be developed and used.

Consider first a single equilibrium stage, such as a solid/liquid or liquid/liquid contactor. The stage either operates batchwise (with quantities F and S of feed and solvent) or continuously with feed rate F and pure solvent feed S. The concentrations of the species of interest are also indicated in Fig. 4.1.

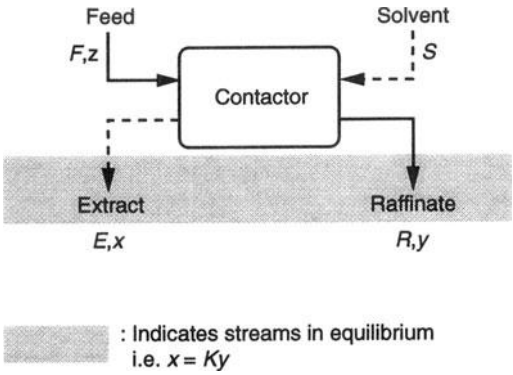


Fig. 4.1 The equilibrium stage.

If we assume that the feed and solvent phases are immiscible and mutually insoluble then

$$F = R$$

and

$$S = E$$

(These relationships are strictly true only when the extent of mass transfer is small or the concentrations are defined on a solute-free basis.)

A mass balance on solute at steady state gives

$$Fz = Ex + Ry \tag{4.3}$$

Now the equilibrium assumption implies that the phases **leaving** the stage have equilibrated, so that equation (4.1) applies to streams E and R and

$$x = Ky$$

and from these two

$$y = \frac{z}{1 + EK/F} \tag{4.4}$$

and

$$x = \frac{Kz}{1 + EK/F} \tag{4.5}$$

Lower values of y (that is, more complete extraction) can be achieved by high solvent/feed ratios and a high K-value. For a given partition coefficient, more complete extraction can be achieved by using higher solvent/feed ('treat') ratios; unfortunately this will also give lower concentrations of the solute in the extract phase, so there is a trade-off between efficient recovery and concentration.

EXAMPLE 4.1

An aqueous stream contains 10 wt% (on a solute-free basis) of a component that can be recovered by solvent extraction. The partition coefficient K = 2, and it is proposed to use a solvent/feed ratio of 2 in a single-stage extraction. Calculate the recovery and concentrations of the component in the extract and waste streams.

As $z = 0.1$, substitution for K and E/F into equations (4.4) and (4.5) gives $y = 0.02$ and $x = 0.04$. 80% of the solute is recovered, but it is more dilute in the extract than in the feed. Doubling K or E/F would lead to an improved recovery, as $y = 0.0111$. If this was achieved by doubling E/F, the extract concentration x would be 0.0222 (which is lower than in the first calculation); if K was doubled, $x = 0.0444$. In practice, of course, it is usually easier to change E/F than the partition coefficient.

4.3.3 Multistage processes

In practice, with a single stage it is difficult in general to achieve high extractions; an obvious extension to circumvent this is to add further stages to recover more solute (Fig. 4.2). In the first scheme, (a), the extract stream from stage 2 will presumably be rather dilute; alternatively it can itself be used as the solvent feed to stage 1, as shown in Fig. 4.2(b). In practice, this is commonly done; many stagewise extraction processes have similar, or more complicated, structures.

The equilibrium stages need not necessarily be identified with separate pieces of equipment: a distillation or solvent extraction column with a set of plates inside is essentially a multistage countercurrent process. Surprisingly, perhaps, multistage equilibrium systems, for which the steady-state mathematical models are simply sets of algebraic equations, can often also be used as fair mathematical models for column-based separations, such as chromatographs, where the 'stage' is identified with a defined length of column.

EXAMPLE 4.2

Consider the two-stage process shown in Fig. 4.2(b), where in view of the equilibrium assumption $x_1 = Ky_1$ *and* $x_2 = Ky_2$ *(assuming that the K-values are the same in the two stages). We assume the same values of z, E/F and K as in Example 4.1. Calculate the unknown concentrations and the extraction yield.*

For the two-stage unit we can set up a mass balance over each unit, giving

$$Fz - Fy_1 = Ex_1 - Ex_2$$

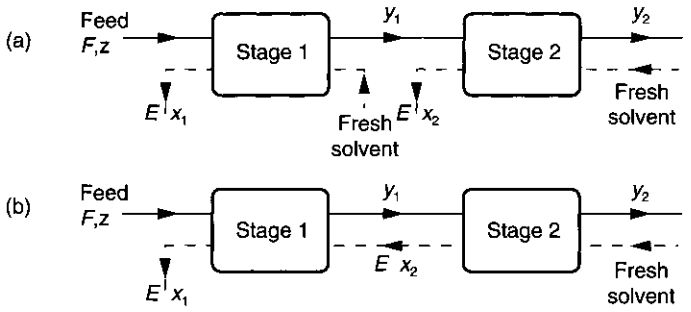


Fig. 4.2 Two multistage flowsheets.

and

$$Fy_1 - Fy_2 = Ex_2$$

where because of the assumption that equilibrium is achieved in both stages

$$x_1 = Ky_1$$

and

$$x_2 = Ky_2$$

There are thus four linear equations for the four unknowns. Solving by repeated substitution gives

$$y_1 = 0.0238 \qquad y_2 = 0.00476$$
$$x_1 = 0.0476 \qquad x_2 = 0.00952$$

95% of the solute is now recovered, as a result of the addition of the extra stage. Further stages would give increased recovery.

For a single-component system an n-stage process would be described by n material balance equations and n equilibrium relationships. The method illustrated above for a single species and constant K-values can be readily extended to multicomponent systems, ones where the K-values are not constant, and ones where the feed enters at an intermediate stage. There are many numerical and graphical techniques (of which the most famous is probably the McCabe Thiele method (e.g. King, 1984; Coulson and Richardson, Vol 2, 1977) for the solution of these problems.

4.4 Diffusion

As noted above, theories of mass transfer must account for two phenomena: diffusion and convection. We first consider **molecular diffusion**: that is,

transfer in the absence of convection. The earliest classical experiment on diffusional exchange was carried out on the transfer between two reservoirs connected by a tube, the reservoirs initially having different concentrations of the component. These experiments showed clearly that the rate of mass transfer between the reservoirs was proportional to the cross-sectional area of the tube and to the concentration difference. In fact the result holds only for equimolar counterdiffusion (that is, where the flow of molecules in one direction is exactly balanced by a compensating flow of another species in the opposite direction); strictly, the finding is true for the flow relative to the net velocity. This result was subsequently embodied in **Fick's law**, which states that the flux j (that is, the flowrate per unit area, or the species velocity) is directly proportional to the local concentration gradient. Thus, as diffusion occurs down the gradient:

$$j = -\mathcal{D}\frac{\mathrm{d}c}{\mathrm{d}z} \tag{4.6}$$

The constant of proportionality $\mathcal{D}$ is the **molecular diffusion coefficent**, which depends on the molecule and its environment. Note that in this equation the flux is measured in units such as $\mathrm{mol\,m^{-2}\,s^{-1}}$, and the diffusion coefficient will be in $\mathrm{m^2\,s^{-1}}$. Fick's law has Fourier's law (equation (3.1)) as its analogue in heat conduction, and we can draw on this in finding the solution to many common problems.

Typical orders of magnitude of the diffusion coefficient are as follows

Gases	10^{-5}
Liquids	10^{-9}
Solids	10^{-12}–10^{-14}

4.4.1 The effective diffusion coefficient

While the diffusion coefficient of, say, sucrose in water is around $4.5 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ (in fact its value depends on the concentration), its measured value in extraction from beet would be smaller than this, even if the cell walls were well and truly disrupted. This is one example of the way in which the **effective diffusion coefficient** might differ from the molecular coefficient; in a porous medium the measured coefficient will be significantly smaller than the molecular diffusion coefficient because of tortuosity effects (the more tortuous the region the more devious the route between two points) and because of the hindering effects of the surface of the pores on the molecule's random oscillations. There are many situations in food and biotechnology processing where the effective diffusion coefficient is the key parameter. Situations where movement is governed by Fick's law include processes such as oil extraction from seeds, the movement of salt in cheese, and the movement of solutes in immobilized pellets in biological reactors.

4.4.2 *Transport across a film: 1*

Let us see how Fick's law can be used to describe the steady diffusional flow across a film of defined thickness L; the concentration of the species is kept constant on either side of the film as shown in Fig. 4.3.

If the flow is steady (that is, doesn't vary with time), then the flux at any distance z into the film must be constant. Thus from equation (4.6) we can write

$$j = \text{constant with distance} = a = -\mathcal{D}\frac{dc}{dz}$$

and the concentration must therefore vary linearly with z across the film.

The form of the linear variation can be seen intuitively or more formally by integrating the flux equation; using the two boundary conditions, this gives

$$c = c_1 - \frac{(c_1 - c_2)z}{L} \tag{4.7}$$

Note that the concentration profile is independent of the diffusion coefficient: but a moment's thought will surely show that this is as it ought to be. The flux, however, does depend on $\mathcal{D}$ as it is given by the differential of equation (4.7):

$$j = \frac{\mathcal{D}}{L}(c_1 - c_2) \tag{4.8}$$

The value of $\mathcal{D}$ to use is its value in the film. This result is precisely analogous to the steady-state heat conduction problem in section 3.1.1; equation (4.8) is mathematically identical to equation (3.2) for the heat flux:

$$q = h(T_1 - T_2)$$

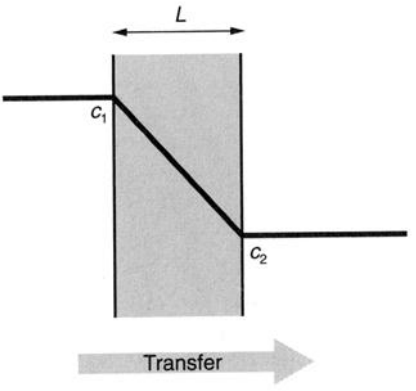


Fig. 4.3 Mass transfer across a film.

and, by analogy with Chapter 3, we can define a mass transfer coefficient $k = \mathcal{D}/L$ and write

$$j = k(c_1 - c_2) \tag{4.9}$$

Note that the mass transfer coefficient has the dimensions of velocity: $m\,s^{-1}$.

We can also introduce another important dimensionless group, analogous to the Nusselt number in heat transfer, which we define as $kd/\mathcal{D}$, where d is a characteristic dimension (here the film thickness, L). In this problem the dimensionless group, called the **Sherwood number**, Sh, is therefore

$$Sh = \frac{kL}{\mathcal{D}}$$

and from equation (4.9) we see that $Sh = 1$ for this problem (just as $Nu = 1$ for the corresponding heat conduction problem). (Note, the requirement that j is constant with distance leads to $dj/dz = 0$ and thus to $\mathcal{D}d^2c/dz^2 = 0$, which is known as **Fick's second law**.)

You might also consider how in a realistic situation the concentrations c_1 and c_2 could be maintained constant.

4.4.3 Steady diffusion from a sphere

Another result of theoretical and practical importance, which can also be deduced by using the analogy with heat conduction, is that for steady diffusion into or out of a sphere in an infinite stagnant medium. (This might, for example, describe the supply of a nutrient to a microorganism, or the slow leaching of sugar from a spherical piece of beet.)

Following the treatment of conductive heat transfer through a thick-walled hollow sphere (section 3.1.2), the total rate of mass transfer past any radius r (Fig. 4.4) is

$$J = 4\pi r^2 j \tag{4.10}$$

where Fick's law is:

$$j = -\mathcal{D}\frac{dc}{dr} \tag{4.6}$$

Now, as J must be independent of r for there to be no accumulation of mass (that is, steady state) then (cf. equation (3.5)):

$$j = \frac{J}{4\pi r^2} = -\mathcal{D}\frac{dc}{dr} \tag{4.11}$$

which can be integrated as in Chapter 3 to give an equation for the total rate of mass transfer between the spherical surfaces at r_1 and r_2:

$$J = \frac{4\pi\mathcal{D}(c_1 - c_2)}{(1/r_1 - 1/r_2)} \tag{4.12}$$

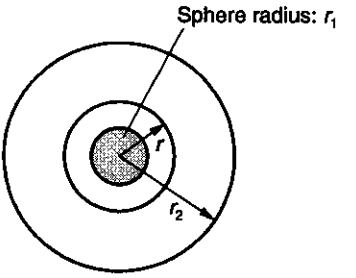


Fig. 4.4 Transfer from a sphere.

For the particular case of mass transfer from a sphere of radius r_1 into an infinite environment, i.e. $r_2 \to \infty$, we obtain

$$\frac{J}{4\pi r_1} = \mathcal{D}(c_1 - c_2)$$

or

$$\frac{J}{4\pi r_1^2} = \frac{\mathcal{D}(c_1 - c_2)}{r_1}$$

That is,

$$j = k(c_1 - c_2) \tag{4.13}$$

where k $(= \mathcal{D}/r_1)$ is the **mass transfer coefficient**, and c_1, c_2 are the concentrations at the sphere boundary and infinity respectively. (Of course, the same expression holds for transfer in the reverse direction.) In defining the Sherwood number for this situation it is, as with the Nusselt number, usual to use the sphere diameter $(= 2r_1)$ as the characteristic length dimension, so that in this case

$$Sh = \frac{kD}{\mathcal{D}} = 2 \tag{4.14}$$

EXAMPLE 4.3

Calculate the maximum rate of uptake of glucose to a spherical bacterium of diameter (a) 1 μm (= 10^{-6} m) and (b) 100 μm (which is unrealistically large in practice) in a stagnant medium containing 100 kg m^{-3} glucose. Take the molecular diffusion coefficient of glucose in aqueous solution to be 6×10^{-10} m^2 s^{-1}.

In this situation we have $Sh = 2$ so that the mass transfer coefficient is

$$k = 1.2\ 10^{-3}\,\mathrm{m\,s^{-1}},\ D = 1\,\mu\mathrm{m}$$
$$k = 1.2\ 10^{-5}\,\mathrm{m\,s^{-1}},\ D = 100\,\mu\mathrm{m}$$

Now the rate of mass transfer of glucose is

$$J = \pi D^2 k(100 - c)$$

where c is the glucose concentration at the bacterium surface; the maximum transfer rate to the organism will occur when the glucose is instantaneously consumed so that $c = 0$, and is

$$\begin{aligned} J &= \pi D^2 k 100 \\ &= 1.2\pi 10^{-13}\,\mathrm{kg\,s^{-1}},\ D = 1\,\mu\mathrm{m} \\ &= 1.2\pi 10^{-11}\,\mathrm{kg\,s^{-1}},\ D = 100\,\mu\mathrm{m} \end{aligned}$$

Note how the mass transfer coefficient varies with D^{-1}, and the absolute rate of transfer varies directly with diameter. (You may like to carry this calculation a little further so as to estimate the maximum doubling time for the bacterium, assuming a yield coefficient of 1. Because the mass of the organism is proportional to D^3, and the rate of nutrient uptake varies with D the growth rate falls dramatically with increasing diameter. We can conclude that while a small bacterium can happily achieve reasonable growth rates when nutrient is supplied by molecular diffusion only, the same would not be true of an elephant (Haldane, 1985).

4.4.4 Transport across a film: 2

The example in section 4.4.2 is not one that is easily realized in practice. As a more realistic example, consider what happens when the transported species is soluble in the film, as a gas might be in plastic packaging; specifically, let us assume that the solubility of the species in the packaging film, c_{film}, is related to its composition in the gas adjacent to the film, c_{gas}, (with which it is in equilibrium) by

$$c_{\mathrm{film}} = K c_{\mathrm{gas}} \tag{4.15}$$

where the partition coefficient $K \ll 1$; see Fig. 4.5.

Consider now the steady transport of the component across the packaging film from the interior, where its concentration is c_1, to the outside environment, where it can be assumed that its concentration is effectively zero. Then the previous result (equation (4.8)) leads to

$$j = \frac{\mathcal{D}}{L} K c_1 \tag{4.16}$$

The mass transfer coefficient k written in terms of the overall driving force ($= c_1$) is $K\mathcal{D}/L$.

Thus we arrive at the result that the rates of diffusional loss across the film, or transfer into the packaged material (as the boundary conditions and

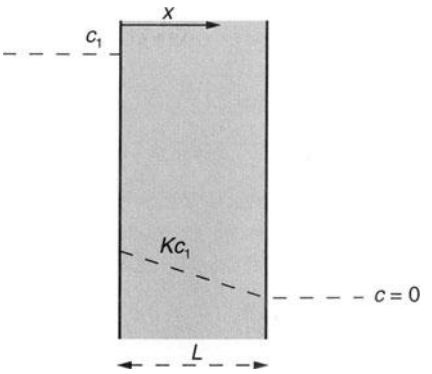


Fig. 4.5 Mass transfer across a film: 2.

direction of movement can readily be reversed), are proportional to the effective diffusion coefficent of the species in the film and to its solubility in the film, while being inversely proportional to the film thickness.

4.5 Transient behaviour

The steady-state assumption gives considerable insight into transfer, but it is extremely restrictive. If oxygen, say, was diffusing across the packaging film the concentration in the pack would change with time, implying that one of the boundary conditions was not constant. So, too, the extraction of sugar from beet or coffee components from the bean imply a depletion of the extracted component with time. Many processes are time-varying.

We can make some progress towards understanding this situation by extending the simple one-dimensional film model above. Because the local concentration changes with time we can no longer assume constant flux. Instead, consider a material balance on the diffusing species across a very thin element dz of the film (Fig. 4.6).

Flux across plane z – flux across plane $z + dz$ = accumulation in dz. That is:

$$-\mathcal{D}\left.\frac{\partial c}{\partial z}\right|_z + \mathcal{D}\left.\frac{\partial c}{\partial z}\right|_{z+dz} = \frac{\partial c}{\partial t} \times dz$$

Using

$$c(z+dz) = c(z) + \frac{dc}{dz} \times dz + \ldots$$

leads to

$$\mathcal{D}\frac{\partial^2 c}{\partial z^2} = \frac{\partial c}{\partial t} \tag{4.17}$$

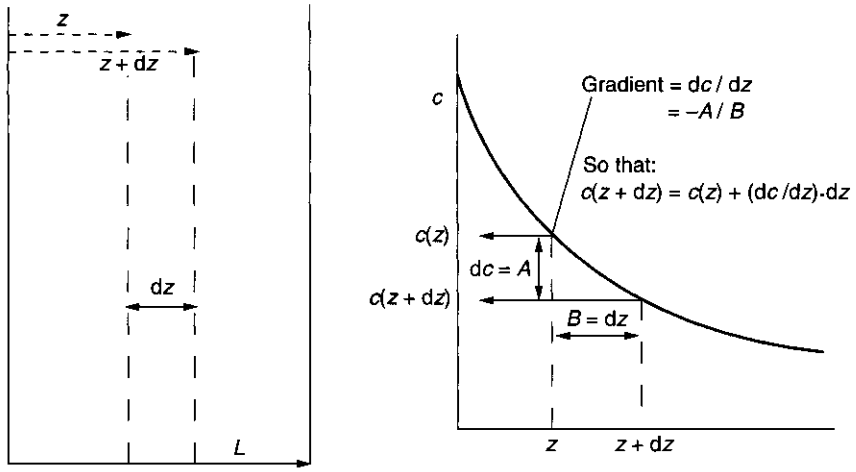


Fig. 4.6 Concentration profile for mass balance.

which is precisely analogous to the equation for unsteady one-dimensional heat transfer, equation (3.9); $\mathcal{D}$ in equation (4.17) corresponds to the thermal diffusivity α in the heat transfer equation. Thus many of the results obtained for transient heat transfer can readily be adapted to the corresponding mass transfer problem. For example, the results presented in Fig. 3.7 for the variation in the temperature distribution within a slab can be translated directly to the analogous mass transfer problem of a slab with initial uniform concentration c_0 immersed in a well-stirred environment such that thereafter the surface concentration is maintained at c_s, by substituting c_0 and c_s for T_0 and T_s respectively. Instead of being $4\alpha t/l^2$ the dimensionless parameter (compare equations (3.9) and (4.17)) is now $4\mathcal{D}t/l^2$. As before, when $4\mathcal{D}t/l^2 = 2$ (that is, an immersion time $t = l^2/2\mathcal{D}$), the concentration profile is uniform: transfer is essentially complete. In other words, significant mass transfer occurs while the processing time $\ll l^2/2\mathcal{D}$, so that the key concentrations will be changing during this transient period. However, for processing times $> l^2/2\mathcal{D}$ one can fairly assume that the system has come to equilibrium and that transfer is essentially complete.

For example, for a sugar beet cassette slice 1 cm thick, the time for complete transfer of the sugar will be of order 2.5×10^5 s – that is, 70 h – assuming an effective diffusivity in the beet of 2×10^{-10} m^2 s^{-1}.

In the same way, Fig. 3.8 can be transformed to show the transient concentration profiles inside a sphere of radius r_s that is exchanging mass with a well-mixed external environment held at some concentration c_s. To do this we replace T_0 by the initial concentration in the sphere, c_0, and T_s by c_s; the characteristic dimensionless group is now Dt/r_s^2, and the characteristic time for complete transfer is $r_s^2/2\mathcal{D}$.

These characteristic times ($= l^2/2\mathcal{D}$) for a plate of thickness l and a sphere of radius l respectively) give a fair measure of the time to reach equilibrium – the **transient period** – and are very useful indicators. For example, if a process lasts longer than the characteristic time, it can be considered to act as an equilibrium stage (see above). A transfer process will be to all intents and purposes steady over a time interval that is small in comparison with the characteristic time. For example, gas diffusion across a packaging film is so slow that over a period of an hour or so the change in concentration on either side of the film will be so small that the flux is given by equation (4.16) rather than the solution to equation (4.17).

4.6 Flowing systems

4.6.1 Bulk convection and diffusion

As noted in the introduction to this chapter, few situations involving mass transfer are stagnant. Just as we stir the cup of tea to speed up the rate of dissolution and transfer, so many industrial processes involve fluids in motion, which *inter alia* enhance the rate of transfer: the liquid surrounding the cassettes of sugar beet or the coffee bean from which species are being extracted (by diffusion!) is invariably moving. From the discussion in Chapter 3 of convective heat transfer we would expect analogous behaviour in the moving fluid insofar as mass transfer is concerned. And it is true that we can often usefully visualize mass transfer as occurring through the movement of packets of fluid. Although there are important limits to the quantitative analogies that we can draw between the transfer of heat and mass, perhaps the single most useful point is that we can deal with both processes in terms of a transfer coefficient.

4.6.2 Flowing systems: film theory

As noted above, many real situations involve the coupled effects of convective motion – that is, where molecules are swept along by a moving fluid – and diffusion. Turbulence and complex geometries make many of these situations rather difficult to analyse from first principles; however, it is possible to handle many complex problems in ways analogous to those used to deal with convective heat transfer. In particular, the simplest model for mass transfer is built around the film theory as developed in Chapter 2. In this theory it is assumed that all the resistance to mass transfer lies within a (more or less) thin boundary layer in the region between the bulk flow and its boundary: that is, it is assumed that all the concentration changes occur over this region. This is analogous to the assumption made in the treatment of heat transfer in Chapter 2 that transfer across the film was by pure

conduction. As with heat transfer we expect the film thickness L to vary with the operating conditions. The film model thus assumes a concentration profile (for transfer from the bulk to the solid boundary) of the form shown in Fig. 4.7.

The concentration profile is given by the theory developed earlier for transfer across a film (section 4.4.2):

$$c = c_1 - \frac{(c_1 - c_2)z}{L} \tag{4.7}$$

and the flux is given by

$$j = \frac{\mathcal{D}}{L}(c_1 - c_2) \tag{4.8}$$

which, as we saw, can be written

$$j = k(c_1 - c_2) \tag{4.9}$$

where k $(= \mathcal{D}/L)$ is the **mass transfer coefficient**.

We would expect the film thickness to depend on a variety of factors including the bulk flow velocity (or more likely the Reynolds number) and the physical properties of the fluid and the transported species. Typical calculated values for the film thickness in transfer to or from a bulk fluid to a sphere or gas bubble are around 10^{-4}m for a gas and 10^{-5}m for a liquid.

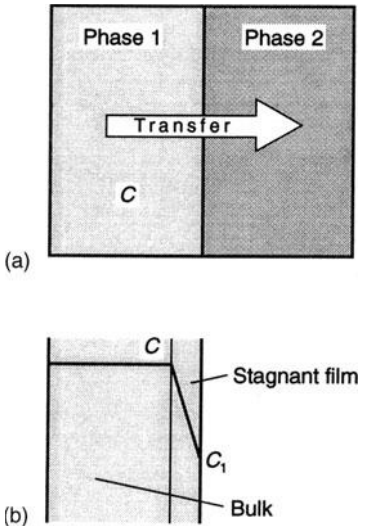


Fig. 4.7 The film theory. The interfacial region in each fluid phase (e.g. phase 1) is treated as a hypothetical stagnant film. Mass transfer occurs across this film by diffusion; there is no resistance to mass transfer in the remaining bulk region, so the concentration there is constant, as shown schematically in (b).

Values of the mass transfer coefficient k range very widely: from 10^{-2} to $1\,m\,s^{-1}$ in gases and from 10^{-5} to $10^{-3}\,m\,s^{-1}$ in liquids. The transfer coefficient in a porous medium could be up to a factor of ten smaller still (cf. the discussion earlier about effective and molecular diffusion coefficients). The stagnant diffusion situation sets a lower bound on the coefficient.

It is important to realize that the film theory depends on a drastically simplified picture, and that there are more realistic and complicated theories and models available. According to the film theory (equations (4.8) and (4.9)) the mass transfer coefficient should be proportional to the diffusion coefficient; because of the range and magnitude of the diffusion coefficients encountered in practice it is not easy to test this theory, but the evidence available suggests that it is not true and that it is more likely that k varies with $D^{2/3}$, as predicted by other more realistic models.

4.6.3 Dimensionless groups

In a typical situation we might expect the mass transfer coefficient k for forced convection in a given fluid to depend on the following five quantities (cf. section 3.2.1):

L = a characteristic length dimension, e.g. a pipe or sphere diameter (m)
v_m = a characteristic mean velocity ($m\,s^{-1}$)
$\mathcal{D}$ = the molecular diffusivity ($m^2\,s^{-1}$)
ρ = the density of the bulk fluid ($kg\,m^{-3}$)
μ = fluid viscosity ($N\,s\,m^{-2}$)

In addition, in processes driven by natural convection or density differences we should also include:

g = gravitational acceleration ($m\,s^{-2}$)
$\Delta\rho$ = the density difference between the phases ($kg\,m^{-3}$)

Note that five independent quantities are needed to describe forced convection. Dimensionless analysis of the convective transfer situation leads to

$$Sh = f(Re, Sc)$$

where Sh is the Sherwood number = $kL/\mathcal{D}$; Re is the Reynold number = $\rho vl/\mu$; Sc is the Schmidt number = $\mu/\rho\mathcal{D} = \nu/\mathcal{D}$.

We have already met the Sherwood number and commented on its similarity to the Nusselt number. The **Schmidt number** (cf. the Prandtl number) involves the ratio of the kinematic viscosity to the diffusivity of mass. Like the Prandtl number its value is around unity for most gases, but higher and more variable (typically 10^2–10^3) for liquids. (For example, $Sc \approx$ 560 and 2250 for dissolved oxygen and sucrose in water respectively.)

When a flow is developing – as in laminar flow along a pipe – the mass transfer coefficient might also depend on a second length dimension such as

the distance along the pipe, x. In this case, the correlation will also include a dependence on x/L.

The treatment of natural convection adds an additional dimensionless group, the **Grashof number**:

$$Gr = \frac{\rho \Delta \rho g L^3}{\mu^2}$$

4.6.4 *Some results and correlations*

Not surprisingly, many of the correlations developed for the simpler situations in mass transfer bear a striking resemblence to those for heat transfer.

Flow in circular pipes. Application of the film model (section 3.2.2) to mass transfer between a flowing fluid and a pipe wall leads directly, for turbulent flow, to

$$Sh = 0.04Re^{3/4} \tag{4.18}$$

The j-factor method (section 3.2.4), also for turbulent flows, assumes that the factors j_D and j_H for mass and heat transfer are equal and, in particular, equal to $c_f/2$, where c_f is the friction factor. Thus, while j_H is defined by equation (3.17) (= $St\ Pr^{2/3}$), here, for dilute systems, the analogous mass transfer equivalent, j_D, is given by

$$j_D = \left(\frac{k}{v_m}\right) Sc^{2/3}$$

(where k/v_m is a modified Stanton number). Thus

$$j_D = \left(\frac{k}{v_m}\right) Sc^{2/3} = \frac{c_f}{2} \tag{4.19}$$

Setting $j_D = j_H$ and using the Dittus–Boelter equation for heat transfer (see section 3.2.5) gives its equivalent for mass transfer:

$$Sh = 0.023Re^{0.8}Sc^{0.33} \tag{4.20}$$

The same observations about the reliability and accuracy of these correlations can be made as were noted in the earlier chapter on heat transfer.

For laminar flow in a circular pipe a typical correlation has the form

$$Sh = 1.67\left[\left(\frac{d}{x}\right) ReSc\right]^{1/3} \tag{4.21}$$

which, for large $x/d \rightarrow kx/\mathcal{D} = 3.65$. The term in x/d allows for the development of the flow field along the pipe towards the fully developed parabolic velocity profile (see Chapter 2). This is very similar to equation (3.19).

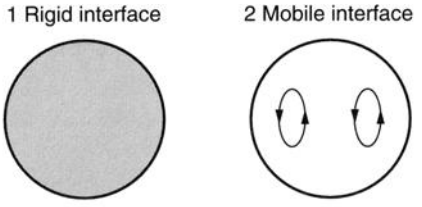
Note that in laminar flow the mass transfer coefficient increases with $Re^{1/3}$, while in turbulent flow the dependence is much stronger, the mass transfer coefficient varying with $Re^{0.8}$. The equation corresponding to (4.21) for laminar flow over a flat plate is

$$\frac{kx}{\mathcal{D}} = 0.332\left(\frac{xv\rho}{\mu}\right)^{0.5}\left(\frac{\mu}{\rho\mathcal{D}}\right)^{0.333} \tag{4.22}$$

In equations (4.21) and (4.22) the mass transfer coefficient is an average over the pipe length x; it should be used in conjunction with a logarithmic mean driving force.

Spheres, pellets and bubbles. Many situations of industrial importance involve transfer to or from solid, liquid or gaseous entities with a surrounding phase. Often, we can approximate these 'objects' by regular geometrical shapes such as spheres or cylinders (the assumption will be a fair one for peas, but less good for potatoes, which should not be seen as a modeller's argument for identical food products).

We must distinguish between transfer inside and outside the object. For example, the extraction of coffee from ground beans in a packed bed involves at least two distinct mass transfer steps: first, transport of the extracted solutes through the bean to the surface; second, transport away from the bean and into the bulk, moving fluid. Usually, these processes will be dominated by different mechanisms and will occur at very different rates (Fig. 4.8). Movement within a porous or semiporous body, as in many solid/liquid extractions, or in adsorption processes, is normally dominated by (slow) diffusion; transfer away from the solid into the bulk liquid will



	Mechanisms	
	1	2
Internal	Diffusion	Diffusion and convection
External	Diffusion and convection	Depends on conditions

Fig. 4.8 Mass transfer from a sphere.

typically involve convective transfer. If the 'object' is a gas bubble or liquid droplet, internal transfer will involve convection, if the contents are in motion. Proteins or surfactants adsorbed on the fluid/fluid interface may add an additional barrier to transfer.

The transfer rate will also depend on the relative proximity of other objects, as these can seriously modify the flow and concentration fields. In other words, the rate of mass transfer from a single bubble of diameter d will not be the same as that from the same-sized bubble rising in a swarm; transfer from a sphere in an infinite fluid is different from transfer from the same sphere in a packed bed.

A few examples of some typical correlations for transfer from solid, liquid and gaseous spheres are given below. In these correlations the characteristic length is the appropriate sphere diameter d.

External transfer coefficient

Rigid interface

Single particles:

$$\text{Low } Re, \qquad Sh = 2 \text{ as } Re \to 0 \tag{4.14}$$

$$\text{More generally,} \quad Sh = 2 + bRe^{0.5}Sc^{0.33} \tag{4.23}$$

For larger particles at low Re:

$$k = 0.3\left(g\Delta\rho\mathcal{D}^2/\nu\rho\right)^{1/3} \tag{4.24}$$

Packed bed of particles:

$$j_D = 1.17\ Re^{-0.415} \tag{4.25}$$

where Re is defined in terms of the particle diameter (or the diameter of the equivalent sphere) and the superficial velocity in the bed.

Mobile interface

$$k = 0.4\left[1 + \left(\frac{\rho_i}{\rho}\right)^{0.5}\right]^{-0.5}\left(\frac{g^2\Delta\rho^2\mathcal{D}^3}{\nu\rho^2}\right)^{1/6} \tag{4.26}$$

Internal transfer coefficient

Rigid sphere. Transfer is governed by the unsteady mass transfer equation (4.17). An approximate solution to the problem gives for short transfer times, i.e. early in the transfer process:

$$Sh = 10 \tag{4.27}$$

Mobile interface. Equation (4.26) also holds for this case. In this equation ρ and ν are properties of the external phase; the value of $\mathcal{D}$ depends on the phase considered: that is, when calculating the external coefficient, $\mathcal{D}$ should correspond to diffusion of the solute in the external phase. When the internal coefficient is being computed, the appropriate value of $\mathcal{D}$ is that for the solute in the internal phase.

EXAMPLE 4.4

50 kg of sugar crystals have been left in the bottom of a cylindrical vessel, and it is decided to dissolve them by recirculating a large volume (5 m^3) of water through the bed of crystals. The superficial velocity of the liquid through the bed is 0.5 $m\,s^{-1}$. Assume that the crystals have an initial uniform equivalent diameter of 1 mm. The rate of mass transfer per unit area of crystal surface can be assumed to be given by

$$k_L(660 - c)$$

where c is the instantaneous concentration of sugar in solution and k_L is the liquid-side transfer coefficient.

How long will it take to dissolve the crystals?

Assume:

$$\rho(\text{crystals}) = 1200\,kg\,m^{-3}$$
$$\rho = 1000\,kg\,m^{-3}$$
$$\mu = 1\,mN\,s\,m^{-2}$$
$$\mathcal{D} = 5 \times 10^{-10}\,m^2\,s^{-1}$$

Hence Re = 500 and Sc = 2000, based on the initial crystal size.

From equations (4.19) and (4.25),

$$j_D = kSc^{2/3}/v_m = 1.17Re^{-0.415} = 0.089$$

and

$$k = 0.00028\,m\,s^{-1}$$

Now consider a single crystal, diameter D_c; then at any moment

$$\frac{1200\,d}{dt}(\pi D_c^3/6) = -k_L \pi D_c^2 (660 - c)$$

Now the sugar solution is always very dilute, so we can assume $c << 660$, and thus

$$\frac{d(D_c)}{dt} = -3.3k_L$$

Integrating:

$$D_c(t) = D_c(0) - 3.3k_L t$$

and the time for complete dissolution is $t = 0.3D_c(0)/k_L$, where $D_c(0)$ is the initial particle diameter. Hence $t = 1.07$ s. You should consider whether basing the calculation of the mass transfer coefficient on the initial conditions leads to an under- or overestimate of the dissolution time.

4.6.5 Bulk flow and diffusion: concentration polarization

In some situations the opposing effects of bulk flow and diffusion give rise to a phenomenon known as **concentration polarization**. As an example of this problem we discuss a simple model of a very important operation: the cross-flow ultrafilter. In this device (Fig. 4.9), which is frequently used for concentration or selective separation of macromolecules, process fluid is passed over a filtration membrane; as the pressure is higher in the feed side, there is a flow of permeate through the membrane, so that the feed-side solution (or retentate) leaving the membrane system will have a higher concentration of species unable to pass through the membrane.

Now consider what happens to species – such as a protein – unable to pass through the membrane. We suppose that the species concentration in the bulk stream is c_b; suppose also that the flowrate across the membrane is high in comparison to the permeate flow, so that the bulk concentration remains effectively constant in the membrane module. Recalling the basic fluid mechanics and heat transfer discussed above in Chapters 2 and 3, we assume that the stream flowing across the membrane comprises a well-mixed turbulent core and a thin boundary layer (Fig. 4.10). We assume that the concentration changes occur across the thin film. The flowrate of permeate is Q and the flux J of permeate is therefore Q/A, where A is the membrane area; suppose that none of the protein species is transported across the membrane.

If we consider the membrane as a porous body, then the permeate flux through it may reasonably be expected to follow Darcy's law (section 2.3.3):

$$J = \frac{\Delta P}{W_m} \tag{4.28}$$

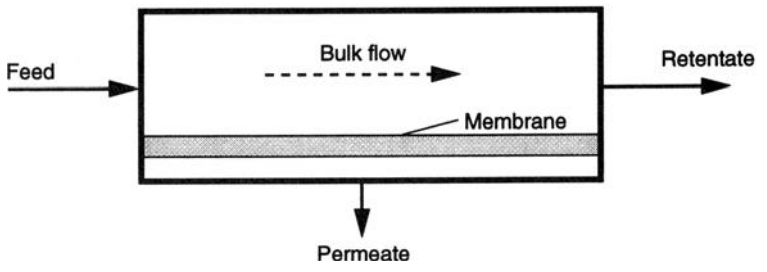


Fig. 4.9 Cross-flow filtration.

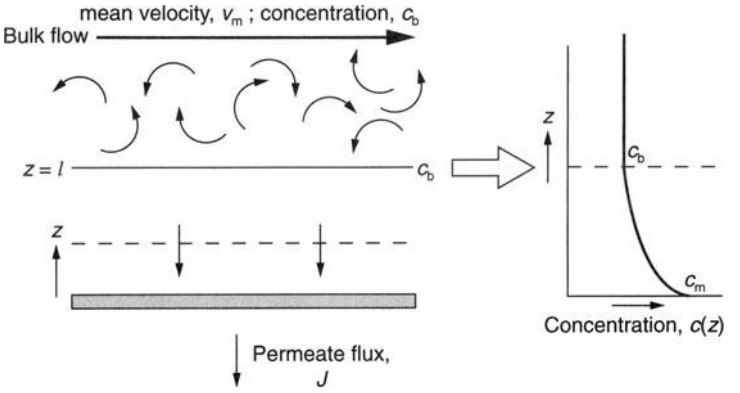


Fig. 4.10 Flows and concentration profile near the membrane.

where ΔP is the pressure drop and W_m is the hydraulic resistance of the membrane. As the discussion in Chapter 2 shows, this parameter depends on the membrane pore size distribution and voidage fraction, as well as on the viscosity of the permeate, equation (2.50).

The permeate, flowing at right angles to the bulk flow, transports dissolved species within it towards the membrane. If the protein concentration is c at some point in the boundary layer the bulk flux of the protein towards the membrane because of the permeate flow will thus be Jc. However, the protein cannot pass through the membrane and will tend to accumulate in the boundary film; because the concentration therefore increases towards the membrane surface, protein, following Fick's law, will tend to diffuse back towards the bulk. Thus if a steady state is established and a steady concentration profile is established within the boundary layer the fact that there is no net transfer towards the membrane implies that the bulk flux and the back, diffusional flux ($= -\mathcal{D}\mathrm{d}c/\mathrm{d}z$, by Fick's law, equation (4.6)) must be equal:

$$Jc(z) = -\frac{\mathcal{D}\mathrm{d}c}{\mathrm{d}z} \tag{4.29}$$

Integrating, and using the boundary conditions that $c = c_b$ at the edge of the boundary layer, $z = l$ and $= c_m$, say, at the membrane surface, $z = 0$ gives

$$J = \left(\frac{\mathcal{D}}{l}\right)\ln\left(\frac{c_m}{c_b}\right) \tag{4.30}$$

or

$$\frac{c_m}{c_b} = \exp\left(\frac{Jl}{\mathcal{D}}\right) \tag{4.31}$$

which relates the concentration at the surface to the permeate flux (Fig. 4.11).

Note that the higher the diffusion coefficient $\mathcal{D}$ and the thinner the boundary layer thickness l, the smaller is c_m for a given J. This results from the balance between the sweeping effect of the permeate flux J and the back-diffusional flow, which tends to reduce the concentration at the membrane. We see that the concentration necessarily increases towards the membrane surface: a phenomenon called concentration polarization. We shall also see below that it can have significant consequences for the performance of a cross-flow membrane.

In practice it would be extremely difficult to measure the boundary layer thickness (if indeed it really exists other than in the model-maker's mind), and it is common to lump the the two terms $\mathcal{D}$ and l into one – a mass transfer coefficient $k = \mathcal{D}/l$ – to give

$$J = k \ln\left(\frac{c_m}{c_b}\right) \tag{4.32}$$

Note that here the mean driving force over the boundary layer is the log-mean concentration difference.

Now consider one of the predicted consequences of concentration polarization. As we have seen, the theory predicts an inevitable increase in solute concentration towards the membrane. For a typical solute, such as a protein, there will be an upper limit (set by its solubility) to c_m. We write c_s to denote this saturation concentration; we further assume that the protein precipitates as a gel at this concentration, so that a gel layer forms at the membrane surface whenever $c_m = c_s$. From equation (4.30) we see therefore that there must be an upper limit to the permeate flux given by

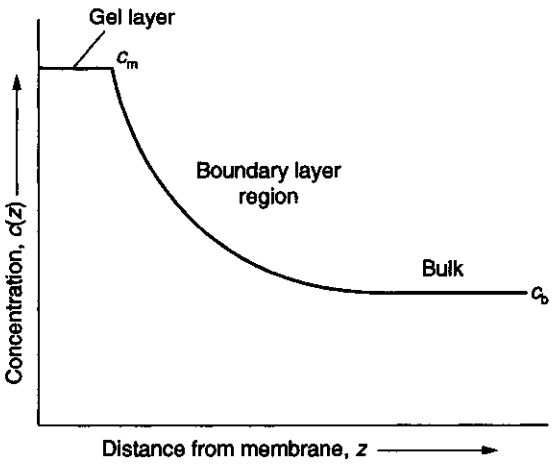


Fig. 4.11 Concentration profile near the membrane.

$$J = k \ln\left(\frac{c_s}{c_b}\right) = \text{constant} \tag{4.33}$$

This may seem incompatible with the fluid mechanics, equation (4.28). However, one theory explains how the two phenomena can be reconciled by accepting that the protein layer itself offers resistance to the passage of permeate, so that instead of equation (4.28) we have

$$J = \frac{\Delta P}{W_m + W_g} \tag{4.34}$$

where W_g is the additional resistance due to the gel layer, whose value (directly depending on the protein gel thickness) is such that equations (4.33) and (4.34) are satisfied simultaneously. If the pressure drop is increased – as the operator would be likely to do in order to increase the flux – there will be a brief increase in flux followed by a new steady state as the the protein gel layer builds up further resistance (Fig. 4.12).

The phenomenon whereby the permeate flux becomes independent of the applied pressure drop is an important and frustrating feature of polarized membranes.

4.7 Interphase transfer

4.7.1 Overall resistances and coefficients

As we have seen, many mass transfer operations involve more than one transfer step. First, we consider how a process involving a series of transfer

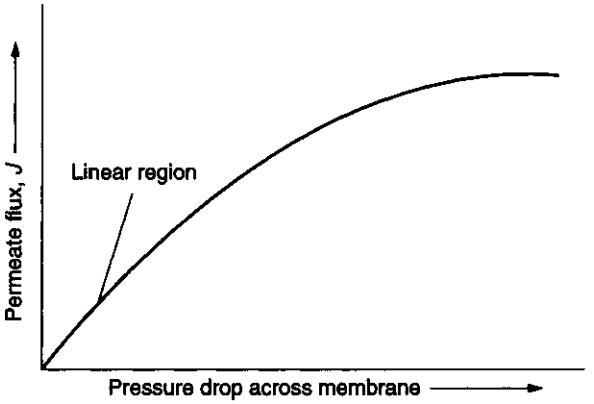


Fig. 4.12 Typical flux–pressure-drop curve.

steps can be reduced to a simpler single-stage process. Then we discuss the general, related problem of identifying the rate-limiting step. The first problem is parallel to the classic heat transfer problem of producing an overall heat transfer coefficient to describe a process involving more than one identifiable resistance to transfer (for example, in a heat exchanger, conductive transfer through the tube wall, through a fouling layer, and the convective transfer within the process fluid). In dealing with such heat transfer problems and some – but by no means all – mass transfer problems it can be helpful to consider an electrical analogy involving resistances in series. For example, the two-stage process in Fig. 4.13 illustrates a simple circuit, where the current flow I is driven by potential (voltage) differences $V_1 - V_2$ and $V_2 - V_3$ across resistances R_1 and R_2. The current flow is given by

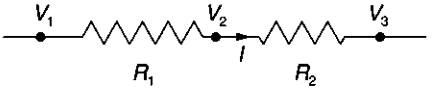
$$I = \frac{1}{R_1}\left(V_1 - V_2\right) \tag{4.35a}$$

$$I = \frac{1}{R_2}\left(V_2 - V_3\right) \tag{4.35b}$$

As indicated in Fig. 4.13, we could represent heat or mass transfer processes in the same way. Thus the mass flux j across the transfer resistances would be given by

$$j = \frac{1}{R_1}\left(c_1 - c_2\right) = k_1\left(c_1 - c_2\right) \tag{4.36a}$$

$$j = \frac{1}{R_2}\left(c_2 - c_3\right) = k_2\left(c_2 - c_3\right) \tag{4.36b}$$



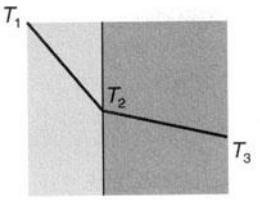
V_1, V_2, V_3 : voltage
R_1, R_2 : resistance
I : current

$$I = \frac{V_1 - V_2}{R_1} = \frac{V_2 - V_3}{R_2}$$

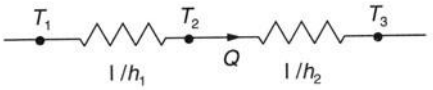
$$I = \frac{(V_1 - V_3)}{(R_1 + R_2)}$$

(a)

Fig. 4.13 Resistances in series: (a) electrical resistances; (b) heat transfer; (c) mass transfer.

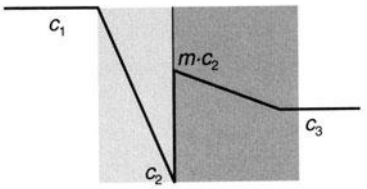


T_1, T_2, T_3 : temperature
$h_1, h_2,$: (film) heat transfer coefficients
Q : heat flux (= rate of heat transfer / area)
U : overall heat transfer coefficient

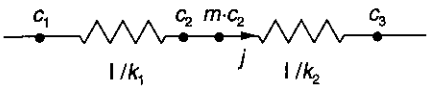


$$Q = h_1 (T_1 - T_2) = h_2 (T_2 - T_3)$$

(b)
$$Q = \frac{(T_1 - T_3)}{[1/h_1 + 1/h_2]} = U (T_1 - T_3)$$



k_1, k_2 : (film) heat transfer coefficients
j : heat flux (= rate of heat transfer / area)
K_L : overall mass transfer coefficient



$$j = k_1 (c_1 - c_2) = k_2 (m \cdot c_2 - c_3)$$

(c)
$$j = \frac{(c_1 - c_3/m)}{[1/k_1 + 1/m \cdot k_2]} = K_L (c_1 - c_3/m)$$

Fig. 4.13 *Continued.*

where k_1 and k_2 are the mass transfer coefficients (that is, reciprocal resistances) for the two stages.

The current flow indicated in Fig. 4.13a is readily found in terms of the overall voltage drop $V_1 - V_3$ by multiplying equations (4.35a) and (4.35b) by R_1 and R_2 respectively and adding the two equations:

$$I(R_1 + R_2) = V_1 - V_3$$

or

$$I = \frac{1}{R_1 + R_2}(V_1 - V_3) = \frac{1}{R}(V_1 - V_3) \tag{4.37}$$

where the overall resistance $R = (R_1 + R_2)$.

Carrying out the same operations for the hypothetical mass transfer process:

$$j\left(\frac{1}{k_1} + \frac{1}{k_2}\right) = c_1 - c_3$$

or

$$j = \left(\frac{1}{k_1} + \frac{1}{k_2}\right)^{-1}(c_1 - c_3) = K_L(c_1 - c_3) \tag{4.38}$$

where the overall mass transfer coefficient K_L is defined by

$$\frac{1}{K_L} = \frac{1}{k_1} + \frac{1}{k_2} \tag{4.39}$$

Note in particular that just as $R \to R_1$ when R_2 is small, so does $K \to k_1$ when k_2 is large (that is, the mass transfer resistance associated with step 2 is small), and $K_L \to k_2$ when k_1 is large.

The result corresponding to equation (4.39) for the overall heat transfer coefficient U in terms of the individual coefficients h_1 and h_2 is

$$\frac{1}{U} = \frac{1}{h_1} + \frac{1}{h_2} \tag{4.40}$$

While the procedure adopted above is correct in principle, it is not so easily applied to mass transfer problems because these often involve changes of phase (between water and a solvent, for example) between the different resistances. Because of the phase changes, solubility differences (see section 4.4.4 above) therefore imply concentration changes even at equilibrium in the region of the phase interface. We discuss that problem, and its solution summarized in Fig. 4.13c, in the following section.

4.7.2 Interphase transfer: the two-film theory

This theory, developed by Whitman, considers a solute being transferred across the interface between two separate adjacent phases. These could be

two immiscible liquids, a liquid and a gas (see section 4.8 below), or a gas and a membrane (see above). In each case it is assumed that the resistance to transfer in each phase lies in a film parallel to the plane interface. The concentration profile of the solute in the phases is shown in Fig. 4.14; because the solute does not have the same solubility in the two phases the interfacial concentrations are different. The diffusivity of the solute may also be different in the two phases, as may the film thicknesses L_1 and L_2.

The fluxes (that is, transfer rate per unit area of interface) in each phase are given by

$$j_1 = k_1(c_1 - c_{1i}) \tag{4.41}$$

and

$$j_2 = k_2(c_{2i} - c_2) \tag{4.42}$$

respectively. As in the previous section we wish to derive an expression for the flux in terms of the overall driving force (determined by c_1 and c_2).

At steady state the fluxes in the two phases must be equal. In order to relate the interfacial concentrations we make another crucial assumption, that the concentrations at the interface are at equilibrium, so that

$$c_{2i} = mc_{1i} \tag{4.43}$$

where m is the partition (solubility) coefficient between the two phases.

Thus, as in the previous section, we can write for the flux j, which is the same in the two phases

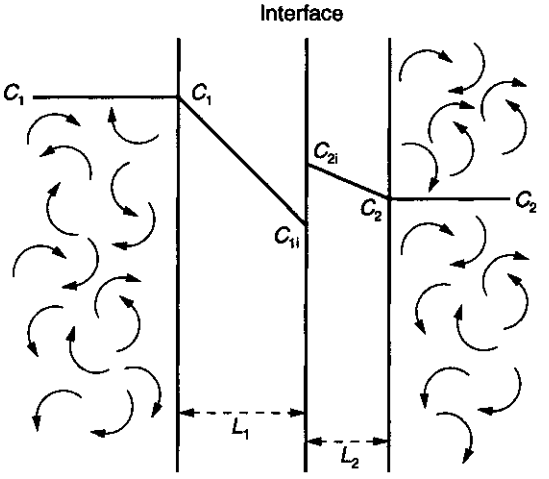


Fig. 4.14 The two-film theory.

$$\frac{j}{k_1} = c_1 - c_{1i} \tag{4.44}$$

and

$$\frac{j}{k_2} = mc_{1i} - c_2 \tag{4.45}$$

or

$$\frac{j}{mk_2} = c_{1i} - \frac{c_2}{m} \tag{4.46}$$

Adding equations (4.44) and (4.46) gives

$$j = K_1\left(c_1 - \frac{c_2}{m}\right) \tag{4.47}$$

where the overall transfer coefficient K_1 is given by

$$\frac{1}{K_1} = \frac{1}{k_1} + \frac{1}{mk_2} \tag{4.48}$$

Note the difference between this equation and equation (4.39): in particular note that the solubility m appears in the expression for the overall coefficient. Also, note that when $k_1 << mk_2$, $K_1 \rightarrow k_1$; when $k_1 >> mk_2$, $K_1 \rightarrow mk_2$.

It is also important to note that the overall driving force is **not** $(c_1 - c_2)$ but $(c_1 - c_2/m)$. The reason for this is that the solubilities in the two phases are different and are therefore strictly incommensurate (that is, writing $c_1 - c_2$ is like writing 'apples minus oranges'). We can write the driving force as $(c_1 - c_1^*)$, where c_1^* $(= c_2/m)$ is the concentration in phase 1 that **would** exist if it were in equilibrium with c_2.

It will also be seen that equation (4.45) correctly represents what happens when equilibrium between the two phases is achieved. Under these conditions there is no net flux: the driving force is zero as then $c_2 = mc_1$, or $c_1 = c_1^*$.

Thus the overall form of the two-film representation is

$$j = K_1\left(c_1 - c_1^*\right) \tag{4.49}$$

where K_1 is given by equation (4.48) and the individual transfer coefficients are given by $k_1 = \mathcal{D}_1/L_1$ and $k_2 = \mathcal{D}_2/L_2$ respectively.

(It is also possible to derive the flux equation in terms of a driving force based on the concentration in the second phase: c_2 and mc_1 or c_2^*. Depending on which procedure we follow we call the appropriate overall transfer coefficient K_1 or K_2.)

EXAMPLE 4.5

Consider the solvent extraction of rape seed oil from a single seed, assumed diameter 1 cm, into a large pool of stagnant solvent.

Assume the following data:
Voidage fraction of seed = 0.5
Effective diffusion coefficient of oil in the seed, $\mathcal{D}_e = 2.5 \times 10^{-10}\,m^2\,s^{-1}$
Diffusion coefficient of the oil in the solvent, $\mathcal{D} = 10^{-9}\,m^2\,s^{-1}$
Partition coefficient between solvent and seed liquid, m = *20*
Mass transfer coefficients:
Assume the internal coefficient is given by $\mathrm{Sh} = k_1 d/\mathcal{D}_e = 10$ *(equation (4.27))*
The external coefficient is given by $\mathrm{Sh} = k_2 d/\mathcal{D} = 2$ *(equation (4.14))*

(1) Calculate the overall mass transfer coefficient.
(2) Calculate the rate of transfer of oil from a seed with initial oil content $10\,g\,l^{-1}$*. How much oil would be extracted in (a) 1 h, (b) 10 h?*

First we calculate the internal and external transfer coefficients k_1 and k_2. The expression quoted for the internal coefficient is a useful approximation for the early stages of non-steady diffusion through a sphere (see section 4.4.3).

Internal coefficient
From $k_1 d/\mathcal{D}_e = 10$ we find that $k_1 = 2.5 \times 10^{-7}\,m\,s^{-1}$.
External coefficient
From $k_2 d/\mathcal{D} = 2$ we find $k_2 = 2 \times 10^{-7}\,m\,s^{-1}$ and $mk_2 = 4 \times 10^{-6}\,m\,s^{-1}$.

Thus from equation (4.48), the overall coefficient K_1 is

$$K_1 = \left(\frac{1}{k_1} + \frac{1}{mk_2}\right)^{-1} = \left(\frac{10^7}{2.5} + \frac{10^6}{4}\right)^{-1} = 2.35 \times 10^{-7}\,m\,s^{-1}$$

The rate of mass transfer at any moment is given by

$$J = (\text{Surface area of seed}) \times j$$

where the flux j is given by equation (4.47); thus

$$J = 2.35 \times 10^{-7} \pi 10^{-4} \left(c_1 - \frac{c_2}{m}\right)$$

The initial rate of transfer of oil from the seed is thus (per seed)

$$= 7.4 \times 10^{-10}\,kg\,s^{-1}$$

If we assume that the reservoir of solvent is large, so that its change in concentration is negligible, the rate of change in oil content c_1 of the seed is given by

$$0.5\left(\frac{10^{-2}}{6}\right)\frac{dc_1}{dt} = -2.35\times10^{-7}c_1$$

That is,

$$\frac{dc_1}{dt} = -2.82\times10^{-4}c_1$$

Integrating, with initial condition $c_1 = 10\,kg\,m^{-3}$ at $t = 0$:

$$c_1 = 10\exp(-2.82\times10^{-4}t)$$

Thus in 1 h and 10 h the oil concentration in the seed will have fallen to $3.6\,kg\,m^{-3}$ and $0.0004\,kg\,m^{-3}$ respectively.

4.7.3 Limiting resistances

From both a practical and theoretical point of view it is interesting to know which, if any, of the mass transfer resistances is dominant or limiting. In Example 4.5 we can see that the transfer coefficient for the diffusion in the seed (k_1) is 16 times smaller than the external contribution (mk_2), so that the overall coefficient K is actually not very different from k_1 (2.35×10^{-7} as opposed to $2.5 \times 10^{-7}\,m\,s^{-1}$). From a practical point of view this means that if we wish to increase the rate of transfer we should focus on the internal diffusional process rather than external transfer. For example, reducing the seed diameter by grinding would give a significant improvement in the rate of transfer, whereas agitating the solvent surrounding the seed would have only a minor effect. It also implies (cf. Chapter 3) that the concentration gradients inside the seed are much greater than those outside (Fig. 4.15).

In this situation we say that internal transfer controls or is limiting. Conversely, if $mk_2 << k_1$, K_1 is approximately equal to mk_2, in which case external transfer is limiting.

4.8 Aeration

There are many very important practical operations involving transfer of a solute from a gaseous phase to a liquid, or vice versa. In particular, oxygen transfer from an injected air jet or stream of bubbles is a key operation in fermentation processes. We can develop expressions for the rate of oxygen transfer using the same procedure as in the sections above.

We assume that there are only two significant resistances to mass transfer: on the gas side, within the bubble or jet; in the liquid between the bubble–liquid interface and the liquid bulk. Again, we work in terms of the transfer rate per unit area of interface, which for simplicity is represented as a plane in Fig. 4.16 showing the oxygen concentration profiles. As is usual,

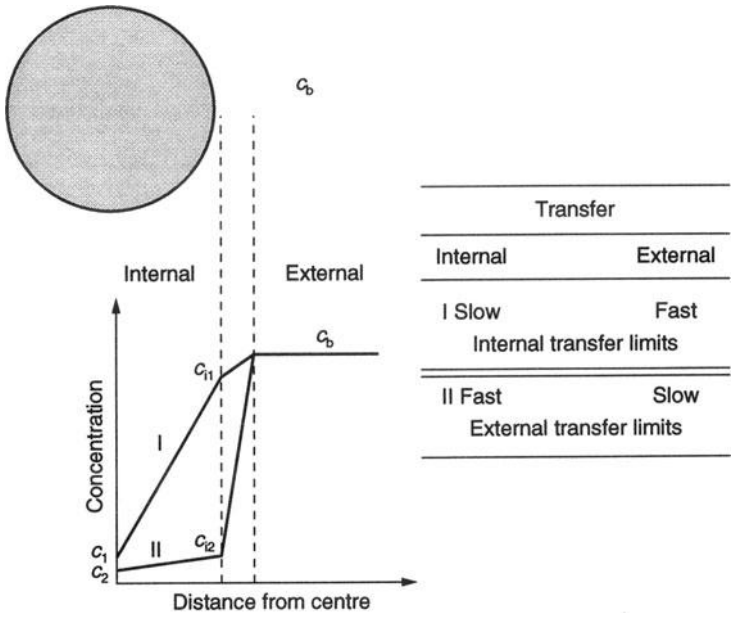


Fig. 4.15 The limiting resistance and concentration gradients. The diagram illustrates transfer from the bulk to a sphere. In Case I the resistance to internal transfer is high, so that there is a large concentration gradient inside the sphere. In Case II the main resistance to transfer is outside the sphere in the bulk, so the concentration gradient outside the sphere is high.

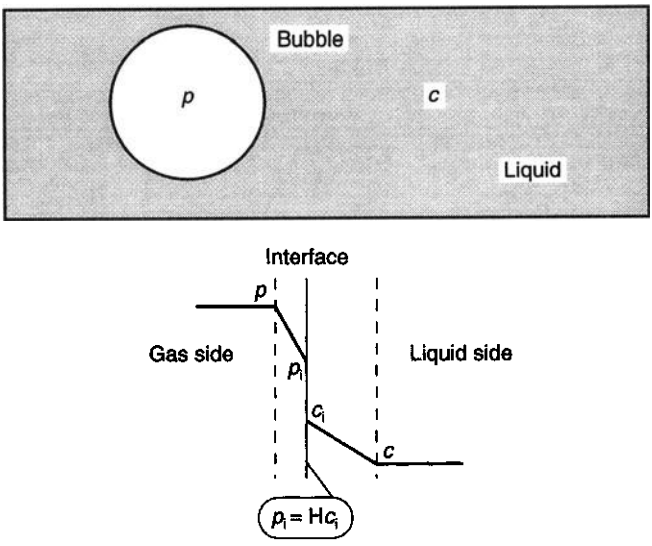


Fig. 4.16 Mass transfer from a bubble to a liquid.

partial pressure p is used as the measure of concentration in the gas phase. The dissolved oxygen concentration is denoted c.

Thus, as in section 4.7.2, the oxygen fluxes in the two phases are written:

$$j_1 = k_G(p - p_i) \tag{4.50}$$

and

$$j_2 = k_L(c_i - c) \tag{4.51}$$

where k_G and k_L are the gas-side and liquid-side film mass transfer coefficients.

The solubility or partition law for a gas such as oxygen in aqueous solution can be represented by **Henry's law** (cf. equation (4.43)):

$$p_i = Hc_i \tag{4.52}$$

where H is **Henry's constant**. At this stage we should note that oxygen is only sparingly soluble in aqueous solution; at atmospheric temperature and pressure its solubility in equilibrium with air (that is, with a partial pressure of 0.21 atm) is around $10\,mg\,l^{-1}$, so that for oxygen H is around $0.021\,atm\,l\,mg^{-1}$. The value of H for a more soluble gas such as carbon dioxide is much smaller.

Assuming equilibrium at the bubble–liquid interface, that is,

$$p_i = Hc_i \tag{4.53}$$

and following the same algebraic procedure as in section 4.7.2, in particular substituting p_i/H for c_i in equation (4.51), the steady flux of oxygen can thus be written in terms of an overall mass transfer and concentration driving force as

$$j = K_L(c^* - c) \tag{4.54}$$

where the overall mass transfer coefficient is given by

$$K_L = \left(\frac{1}{k_L} + \frac{1}{Hk_G}\right)^{-1} \tag{4.55}$$

and $c^* = p/H$; that is, the concentration which **would** exist in the liquid if it were in equilibrium with the oxygen in the air bubbles. Typically, therefore, c^* is around $10\,mg\,l^{-1}$. If the liquid phase is saturated then, of course, there is no net transfer. (If the liquid were sparged with, say, pure nitrogen so that the partial pressure of oxygen in the gas phase $p = 0$, equation (4.54) would describe the de-oxygenation of the liquid.)

Alternatively, instead of substituting for c_i in equation (4.51), we could substitute p_i by Hc_i in equation (4.50), to arrive at an equation for the flux with partial pressure as the driving force:

$$j = K_G(p - p^*) \tag{4.56}$$

where $p^* = Hc$ and

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{H}{k_L} \tag{4.57}$$

A little algebraic manipulation shows that these two methods of representation are formally identical, although the first, in terms of the liquid-side properties (that is, with concentration as the driving force) is more convenient and common.

The reason for this in the particular case of oxygen transfer to aqueous solutions is that typically k_L is approximately 10^{-5}–$10^{-4}\,m\,s^{-1}$, while k_G is approximately $9 \times 10^{-4}\,mol\,cm^{-2}\,s^{-1}\,atm^{-1}$ (!) and, in this set of units, H is approximately $8 \times 10^5\,atm\,cm^3\,mol^{-1}$, so that Hk_G is approximately $7\,m\,s^{-1}$.

Thus we see that $k_G H >> k_L$: transfer is controlled by the liquid-side behaviour and to a very good degree of accuracy $K_L = k_L$. It must be emphasized that the same approximation may not be true with a more soluble gas such as carbon dioxide.

For oxygen transfer, therefore, we can write

$$j = k_L(c^* - c) \tag{4.58}$$

where k_L is the liquid-side film coefficient.

In a fermenter or aeration vessel of volume V the total interfacial area for transfer is aV, where a is the specific interfacial area; the oxygen transfer rate per unit volume of vessel is

$$Q = k_L a(c^* - c) \tag{4.59}$$

Both k_L and a depend on a range of factors, such as the physical properties of the liquid, the sparging and mixing conditions, and rather than correlate each parameter separately it is usual to use $k_L a$ as if it were a single parameter. Values of $k_L a$ for stirred sparged vessels range from 10^{-5} to $10^{-2}\,s^{-1}$, but acceptable values are at the top end of this range. There are many correlations available for $k_L a$ in terms of geometrical and operating parameters such as air flowrate and specific power input to the vessel. A typical correlation for a stirred vessel (see Chapter 10) with coalescing bubbles is $k_L a = 2.6 \times 10^{-2}(P/V)^{0.4} U^{0.5}\,(s^{-1})$; like many other correlations this is restricted to a specific range of vessel sizes and water-like liquids, is not properly dimensionless, and so must be used with caution.

EXAMPLE 4.6

A liquid food contains 20 mg l^{-1} of a volatile sparingly soluble compound responsible for an off-flavour. It is proposed to reduce the level of the

flavour to an acceptable level of 0.01 mg l^{-1} by sparging a well-mixed tank of the liquid with a large excess of air. Under these conditions, k_La = *0.005 s^{-1}. It can be assumed that the liquid is saturated with oxygen. How long will it take to reduce the off-flavour to the desired value?*

The rate of transfer of the flavour compound to the gas phase is, per unit volume:

$$r = k_L a(c - c^*)$$

where c is the dissolved concentration and c^* its equilibrium concentration = p/H, where p is the partial pressure in the gas phase and H is Henry's constant.

If a large excess of air is used, $p \sim 0$ and $c^* \sim 0$.

Thus a mass balance on the compound in the liquid phase gives:

$$\frac{dc}{dt} = -k_L ac$$

that is,

$$c = c(0)\exp(-k_L at)$$

where $c(0)$ is the initial concentration (= 20 mg l^{-1}). Substituting for c, $c(0)$ and k_La gives t = 1520 s, that is 25 min.

4.9 Mass transfer limitations

We now consider the situation where mass transfer and reaction occur in series: such as when a substrate like oxygen or glucose is transported to a microorganism, oxygen diffuses across a packaging layer to be taken up by a foodstuff in a spoiling reaction, or substrate is transferred to an enzyme immobilized in a porous matrix.

There are two ways of viewing the possible consequences of the interaction between transport and reaction. The reaction may speed up transfer by removing the transported species as it arrives, thus effectively increasing the driving force (Fig. 4.17): this is what was assumed in the example of glucose transfer to a microorganism (section 4.4.3). Alternatively, the transport process may not be able to deliver the reagent at anything like the rate at which it could potentially be reacted, so that the rate of reaction is controlled by the transfer process itself. In the following section we consider one important example to illustrate the phenomenon.

4.9.1 Oxygen transfer in a fermenter

We consider here the important question of oxygen transfer and oxygen limitation in a continuous fermenter (see Chapter 8 for the background to

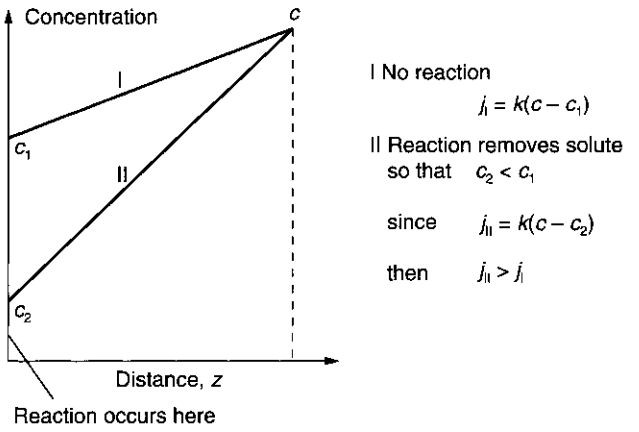


Fig. 4.17 Enhanced mass transfer by mass reaction at boundary.

this problem). Consider unit volume of fermenter. At steady state the rate of oxygen transport from the air to the liquid (= Q) must exactly balance the rate of consumption or demand (R) by the growing organisms, which have concentration x kg m^{-3} in the fermenter. Assuming that the organism growth follows Monod kinetics (equation (8.13)) and that (dissolved) oxygen with concentration c is the growth limiting substrate, the cell growth rate per unit volume of fermenter is thus

$$r_x = \frac{\mu_{max} c x}{K_0 + c} \tag{4.60}$$

where K_0 is the Monod constant for oxygen. Further, assuming a constant yield coefficient Y_0 for cell growth in oxygen, the oxygen consumption rate necessary to sustain cell growth at r_x must be

$$R = \frac{r_x}{Y_0} = \frac{\mu_{max} c x}{Y_0 (K_0 + c)} \tag{4.61}$$

Thus, using equations (4.58) and (4.60) and the fact that at steady state $Q = R$:

$$k_L a (c^* - c) = \frac{\mu_{max} x c}{Y_0 (K_0 + c)} \tag{4.62}$$

The oxygen concentration c in the fermenter is the solution to equation (4.62) for given $k_L a$, c^* and growth kinetic parameters. If the solution to equation (4.62) has c close to c^* and $>K_0$, the rate of growth can be high, as under these conditions the specific growth rate μ tends to μ_{max}. However, if the solution to the equation is close to $c = 0$, microbial growth will be seriously slowed because of the limited rate of oxygen transfer. The solution

to equation (4.62) is represented graphically in Fig. 4.18. The intersections (a, b, etc.) between the straight lines representing oxygen supply, Q, and the curves for the consumption rate, R, are the solution points, and $c(1)$, $c(2)$ etc. the corresponding oxygen concentrations.

Four situations are represented on the figure:

	Oxygen supply	Oxygen demand	*Da*	Oxygen concentration
a	Q_2 low	R_1 high	High	Low
b	Q_2 low	R_2 low	Quite high	Moderate/low
c	Q_1 high	R_1 high	Moderate	Moderate
d	Q_1 high	R_2 low	Low	High

An approximate idea of the importance or otherwise of transfer limitations can be obtained by comparing the maximum possible values of Q and R. The maximum value of Q, the oxygen transfer rate, occurs when the driving force is also maximum, i.e. $c \rightarrow 0$, and is

$$Q_{max} = k_L a c^* \tag{4.63}$$

The maximum demand or consumption rate of oxygen to sustain cell growth occurs when they are growing logarithmically, i.e. at μ_{max}, when $c >> K_0$:

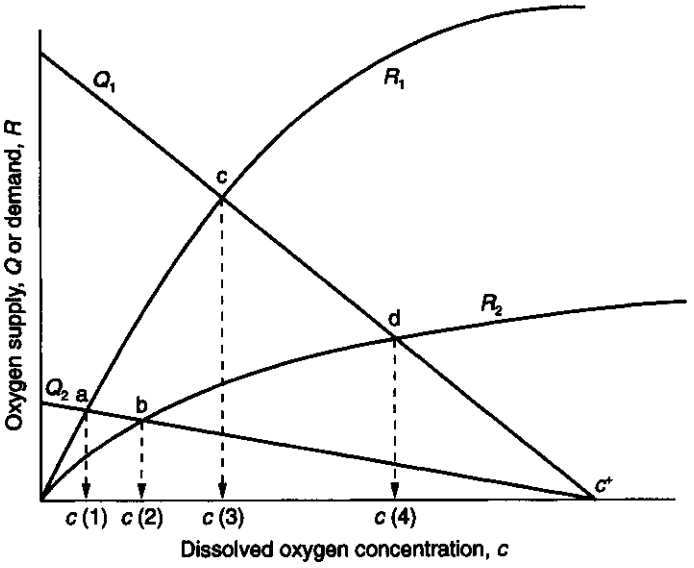


Fig. 4.18 The oxygen balance.

$$R_{max} = \frac{\mu_{max} x}{Y_0} \tag{4.64}$$

If the ratio $R_{max}/Q_{max} << 1$, there are unlikely to be problems due to oxygen transfer; however, if $R_{max}/Q_{max} >> 1$, then oxygen transfer limitations are indicated. The ratio R_{max}/Q_{max} ($= \mu_{max} x/k_L a c^* Y_0$) is called the **Damköhler number**, *Da*, for which qualitative values are given in the table above.

To demonstrate this, equation (4.62) can be written

$$\left(1 - \frac{c}{c^*}\right) = \frac{Da\left(c/c^*\right)}{\left(K_0/c^*\right) + \left(c/c^*\right)} \tag{4.65}$$

or

$$1 - f = \frac{Da\, f}{K + f}$$

Typically, $K(= K_0/c^*) \sim 0.1$; substituting this value and rearranging:

$$f^2 + \left(Da - 0.9\right) f - 0.1 = 0 \tag{4.66}$$

For large *Da*, the solution to equation (4.66) is $f = c/c^* \approx 0$, so that the cell growth rate μ (equation (4.60)) is small. For small *Da*, the solution to equation (4.66) is $f \approx 1$, so that $\mu \approx \mu_{max}$.

EXAMPLE 4.7

Microbial cells are to be grown in continuous culture such that the specific growth rate $\mu = 0.15 h^{-1}$. *The maximum specific growth rate for the organism is* $0.2 h^{-1}$. *What cell concentration would be achieved with* $k_L a = 0.0005 s^{-1}$, *if cell growth followed Monod kinetics under oxygen limitation with* $K_0 = 0.1$, *and the yield coefficient* $Y_0 = 1$ *kg cell/kg oxygen consumed? Assume all other nutrients are in large excess and that* $c^* = 10 mg l^{-1}$.

At steady state:

$$k_L a\left(c^* - c\right) = \frac{\mu_{max} x c}{Y_0\left(K_0 + c\right)} \tag{4.67}$$

so that

$$x = \frac{k_L a Y_0 \left(c^* - c\right)\left(K_0 + c\right)}{\mu_{max} c}$$

Also

$$\mu = \frac{\mu_{max} c}{\left(K_0 + c\right)} \qquad \text{or} \qquad c = \frac{K_0 \mu}{\left(\mu_{max} - \mu\right)}$$

Hence $c = 0.3\,\text{mg l}^{-1}$; then substituting for the known parameters, $x = 116.4\,\text{kg m}^{-3}$. Under these conditions $Da >> 1$.

Note that a lower value for $k_L a$ would lead to lower c and thus to a lower cell concentration at the same specific growth rate.

A final example illustrates the application of the same reasoning to another biological situation.

EXAMPLE 4.8

A biosensor for the in-line measurement of glucose concentrations consists of an ultra-thin film of enzyme immobilized onto a flat surface. The electrical output from the biosensor is directly proportional to the rate of enzymatic reaction of glucose on the sensor surface, which is given by

$$r = \frac{ke_0 c}{K_m + c}$$

In this equation r *is the rate of reaction per unit area of biosensor surface;* c *is the glucose concentration – assumed uniform – at the enzyme film;* e_0 *is the enzyme concentration.*

Under the process conditions where the biosensor is used the rate of mass transfer of glucose to the surface is given by $k_L(c_b - c)$, *where* c_b *is the bulk glucose concentration, which it is hoped to measure.*

The parameters have the following values:

$$ke_0 = 5 \times 10^{-4}\,\text{kg glucose m}^{-2}\text{s}^{-1}$$
$$K_m = 0.01\,\text{kg m}^{-3}$$
$$k_L = 2.5 \times 10^{-4}\,\text{m s}^{-1}$$

(a) What is the Damköhler number appropriate to this situation?
(b) The biosensor is claimed to measure glucose concentrations from $50\,\text{kg m}^{-3}$ *down to* $0.1\,\text{kg m}^{-3}$, *and it is claimed that high accuracy can be obtained. Is this true? What would be the observed glucose concentration (i.e.* c*) under these conditions?*

At steady state, per unit area of biosensor, the flux of glucose towards the sensor surface = rate of reaction on the surface; that is,

$$k_L(c_b - c) = \frac{ke_0 c}{K_m + c} \tag{4.68}$$

Hence Da = max reaction rate/max transfer rate = $ke_0/k_L c_b$

Thus when $c_b = 50\,\text{kg m}^{-3}$, $Da = 1/25$: there should be no serious transfer limitations. However, when $c_b = 0.1\,\text{kg m}^{-3}$, $Da = 20$: thus expect serious limitations, i.e. $c < c_b$.

The concentration c at the sensor is calculated as follows. Rearranging the glucose balance equation (4.68) and substituting for $k_L a$ etc. gives

$$c^2 + (2.01 - c_b)c - 0.01c_b = 0$$

with solution $c = 47.99\,\text{kg m}^{-3}$, when $c_b = 50\,\text{kg m}^{-3}$
$c = 0.0052\,\text{kg m}^{-3}$, when $c_b = 0.1\,\text{kg m}^{-3}$

We conclude that the accuracy of the biosensor is fair in the first case (at higher bulk concentrations), but very poor at lower bulk concentrations where there are very severe transfer limitations, resulting in serious underestimation of the measured concentration.

These examples illustrate how the physics of a process – in this case, the rate of mass transfer of a key nutrient – can determine the apparent kinetic and growth behaviour. The result can be generalized to many other important situations: in particular, ones involving immobilized enzymes and cells, where diffusional limitations on the rate of transfer can seriously constrain behaviour.

Conclusions

This discussion of some of the elements of mass transfer is no more than an introduction to a vast and hugely important subject. Here, we have only dealt with rather simple processes where concentration differences are the main driving force; we have dealt essentially with single rather than multicomponent transfer processes (and it should not be assumed that the effects of other solute transfers are merely additive); we have not touched on the very important situations, such as drying and the like, where heat and mass transfer are coupled. Some suggestions for further reading and study are given below.

The processes of heat and mass transfer will have been seen to have much in common, despite the additional complications inherent in mass transfer operations. There is much in common between the processes of thermal diffusion (i.e. conduction) and mass diffusion, and the basic equations (Fourier's and Fick's laws respectively) are mathematically identical, so that solutions to many conductive heat transfer problems can be used, with the appropriate change of variable, for the equivalent mass transfer problem. Although these problems can generally be formulated in terms of an equivalent heat or mass transfer coefficient rather than a diffusion coefficient, this normally has little advantage for solving transient problems since it results in a time-varying transfer coefficient.

As soon as interphase transfer is considered (such as in solvent extraction

or solute extraction from solids or oxygen transfer between air bubbles and a solution) the problems become more complex. Convective transfer (in which the Schmidt number plays a similar role to the Prandtl number in heat transfer) is also an important mechanism in mass transfer – convection is invariably much faster than pure diffusion. You should understand the principles of and analogies, in so far as they exist, between the two processes. However, important differences between heat and mass transfer emerge. In both cases, the driving force for transfer is the deviation from equilibrium. In heat transfer, equilibrium always corresponds to equal temperatures in the two phases. In mass transfer problems, equilibrium does not imply equal concentrations in the phases, since solubilities are not the same. A consequence is that whereas in heat transfer problems the overall transfer process can always be defined in terms of an overall heat transfer coefficient and an overall temperature difference, the equivalent mass transfer rate is proportional to an overall transfer coefficient multiplied by an effective driving force. Moreover, whilst the overall heat transfer coefficient is obtained by summing the individual resistances, the resistance terms in the overall mass transfer coefficient include a solubility multiplier. You should, after reading this chapter, know the basic principles behind formulating overall mass transfer processes, and understand the meaning of a rate limiting process in this type of situation, and understand what it means to say that a combined process involving mass transfer and a reaction may be mass transfer limited. The other side of the same coin is that a reaction (which effectively increases the concentration driving force by removing a reagent) can enhance the rate of mass transfer. Most importantly, you should understand the implications of finding that transfer in one phase or another is rate-limiting, since this is the clue to improving the overall rate.

It is also noteworthy that some transfer processes are very fast in relation to the residence time in the equipment. In this ideal situation, overall process yields are determined only by the equilibrium conditions. This situation forms the basis of equilibrium stage analyses, which are a convenient and powerful means of designing or assessing many transfer operations.

Further reading

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