Diffusion in Dilute Solutions

In this chapter, we consider the basic law that underlies diffusion and its application to several simple examples. The examples that will be given are restricted to dilute solutions. Results for concentrated solutions are deferred until Chapter 3.

This focus on the special case of dilute solutions may seem strange. Surely, it would seem more sensible to treat the general case of all solutions and then see mathematically what the dilute-solution limit is like. Most books use this approach. Indeed, because concentrated solutions are complex, these books often describe heat transfer or fluid mechanics first and then teach diffusion by analogy. The complexity of concentrated diffusion then becomes a mathematical cancer grafted onto equations of energy and momentum.

I have rejected this approach for two reasons. First, the most common diffusion problems do take place in dilute solutions. For example, diffusion in living tissue almost always involves the transport of small amounts of solutes like salts, antibodies, enzymes, or steroids. Thus many who are interested in diffusion need not worry about the complexities of concentrated solutions; they can work effectively and contentedly with the simpler concepts in this chapter.

Second and more important, diffusion in dilute solutions is easier to understand in physical terms. A diffusion flux is the rate per unit area at which mass moves. A concentration profile is simply the variation of the concentration versus time and position. These ideas are much more easily grasped than concepts like momentum flux, which is the momentum per area per time. This seems particularly true for those whose backgrounds are not in engineering, those who need to know about diffusion but not about other transport phenomena.

This emphasis on dilute solutions is found in the historical development of the basic laws involved, as described in Section 2.1. Sections 2.2 and 2.3 of this chapter focus on two simple cases of diffusion: steady-state diffusion across a thin film and unsteady-state diffusion into an infinite slab. This focus is a logical choice because these two cases are so common. For example, diffusion across thin films is basic to membrane transport, and diffusion in slabs is important in the strength of welds and in the decay of teeth. These two cases are the two extremes in nature, and they bracket the behavior observed experimentally. In Section 2.4 and Section 2.5, these ideas are extended to other examples that demonstrate mathematical ideas useful for other situations.

2.1 Pioneers in Diffusion

2.1.1 Thomas Graham

Our modern ideas on diffusion are largely due to two men, Thomas Graham and Adolf Fick. Graham was the elder. Born on December 20, 1805, Graham was the

son of a successful manufacturer. At 13 years of age he entered the University of Glasgow with the intention of becoming a minister, and there his interest in science was stimulated by Thomas Thomson.

Graham's research on the diffusion of gases, largely conducted during the years 1828 to 1833, depended strongly on the apparatus shown in Fig. 2.1-1 (Graham, 1829; Graham, 1833). This apparatus, a "diffusion tube," consists of a straight glass tube, one end of which is closed with a dense stucco plug. The tube is filled with hydrogen, and the end is sealed with water, as shown. Hydrogen diffuses through the plug and out of the tube, while air diffuses back through the plug and into the tube.

Because the diffusion of hydrogen is faster than the diffusion of air, the water level in this tube will rise during the process. Graham saw that this change in water level would lead to a pressure gradient that in turn would alter the diffusion. To avoid this pressure gradient, he continually lowered the tube so that the water level stayed constant. His experimental results then consisted of a volume-change characteristic of each gas originally held in the tube. Because this volume change was characteristic of diffusion, "the diffusion or spontaneous intermixture of two gases in contact is effected by an interchange of position of infinitely minute volumes, being, in the case of each gas, inversely proportional to the square root of the density of the gas" (Graham, 1833, p. 222). Graham's original experiment was unusual because the diffusion took place at constant pressure, not at constant volume (Mason, 1970).

Graham also performed important experiments on liquid diffusion using the equipment shown in Fig. 2.1-2 (Graham, 1850); in these experiments, he worked with dilute solutions. In one series of experiments, he connected two bottles that contained solutions at different concentrations; he waited several days and then separated the bottles and analyzed their contents. In another series of experiments, he placed a small bottle containing a solution of known concentration in a larger jar containing only water. After waiting several days, he removed the bottle and analyzed its contents.

Graham's results were simple and definitive. He showed that diffusion in liquids was at least several thousand times slower than diffusion in gases. He recognized that the diffusion process got still slower as the experiment progressed, that "diffusion must
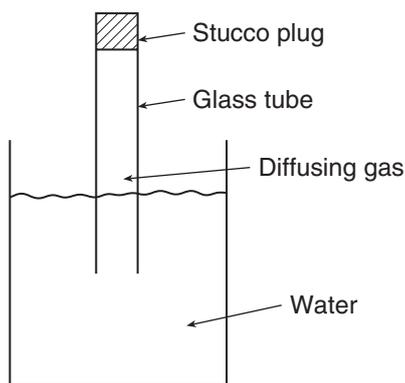

Fig. 2.1-1. Graham's diffusion tube for gases. This apparatus was used in the best early study of diffusion. As a gas like hydrogen diffuses out through the plug, the tube is lowered to ensure that there will be no pressure difference.
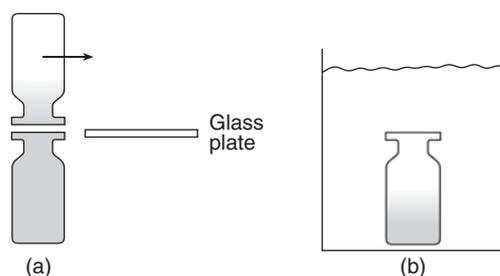
Fig. 2.1-2. Graham's diffusion apparatus for liquids. The equipment in (a) is the ancestor of free diffusion experiments; that in (b) is a forerunner of the capillary method.

Table 2.1-1 *Graham's results for liquid diffusion*

Weight percent of sodium chloride	Relative flux
1	1.00
2	1.99
3	3.01
4	4.00

Source: Data from Graham (1850).

necessarily follow a diminishing progression." Most important, he concluded from the results in Table 2.1-1 that "the quantities diffused appear to be closely in proportion . . . to the quantity of salt in the diffusion solution" (Graham, 1850, p. 6). In other words, the flux caused by diffusion is proportional to the concentration difference of the salt.

2.1.2 Adolf Fick

The next major advance in the theory of diffusion came from the work of Adolf Eugen Fick. Fick was born on September 3, 1829, the youngest of five children. His father, a civil engineer, was a superintendent of buildings. During his secondary schooling, Fick was delighted by mathematics, especially the work of Poisson. He intended to make mathematics his career. However, an older brother, a professor of anatomy at the University of Marburg, persuaded him to switch to medicine.

In the spring of 1847, Fick went to Marburg, where he was occasionally tutored by Carl Ludwig. Ludwig strongly believed that medicine, and indeed life itself, must have a basis in mathematics, physics, and chemistry. This attitude must have been especially appealing to Fick, who saw the chance to combine his real love, mathematics, with his chosen profession, medicine.

In the fall of 1849, Fick's education continued in Berlin, where he did a considerable amount of clinical work. In 1851 he returned to Marburg, where he received his degree. His thesis dealt with the visual errors caused by astigmatism, again illustrating his determination to combine science and medicine (Fick, 1852). In the fall of 1851, Carl Ludwig became professor of anatomy in Zurich, and in the spring of 1852 he brought Fick along as a prosector. Ludwig moved to Vienna in 1855, but Fick remained in Zurich until 1868.

Paradoxically, the majority of Fick's scientific accomplishments do not depend on diffusion studies at all, but on his more general investigations of physiology (Fick, 1903). He did outstanding work in mechanics (particularly as applied to the functioning of muscles), in hydrodynamics and hemorheology, and in the visual and thermal functioning of the human body. He was an intriguing man. However, in this discussion we are interested only in his development of the fundamental laws of diffusion.

In his first diffusion paper, Fick (1855a) codified Graham's experiments through an impressive combination of qualitative theories, casual analogies, and quantitative experiments. His paper, which is refreshingly straightforward, deserves reading today. Fick's introduction of his basic idea is almost casual: "[T]he diffusion of the dissolved material ... is left completely to the influence of the molecular forces basic to the same law ... for the spreading of warmth in a conductor and which has already been applied with such great success to the spreading of electricity" (Fick, 1855a, p. 65). In other words, diffusion can be described on the same mathematical basis as Fourier's law for heat conduction or Ohm's law for electrical conduction. This analogy remains a useful pedagogical tool.

Fick seemed initially nervous about his hypothesis. He buttressed it with a variety of arguments based on kinetic theory. Although these arguments are now dated, they show physical insights that would be exceptional in medicine today. For example, Fick recognized that diffusion is a dynamic molecular process. He understood the difference between a true equilibrium and a steady state, possibly as a result of his studies with muscles (Fick, 1856). Later, Fick became more confident as he realized his hypothesis was consistent with Graham's results (Fick, 1855b).

Using this basic hypothesis, Fick quickly developed the laws of diffusion by means of analogies with Fourier's work (Fourier, 1822). He defined a total one-dimensional flux J_1 as

$$J_1 = Aj_1 = -AD\frac{\partial c_1}{\partial z} \tag{2.1-1}$$

where A is the area across which diffusion occurs, j_1 is the flux per unit area, c_1 is concentration, and z is distance. This is the first suggestion of what is now known as Fick's law. The quantity D, which Fick called "the constant depending of the nature of the substances," is, of course, the diffusion coefficient. Fick also paralleled Fourier's development to determine the more general conservation equation

$$\frac{\partial c_1}{\partial t} = D\left(\frac{\partial^2 c_1}{\partial z^2} + \frac{1}{A}\frac{\partial A}{\partial z}\frac{\partial c_1}{\partial z}\right) \tag{2.1-2}$$

When the area A is a constant, this becomes the basic equation for one-dimensional unsteady-state diffusion, sometimes called Fick's second law.

Fick next had to prove his hypothesis that diffusion and thermal conduction can be described by the same equations. He was by no means immediately successful. First, he tried to integrate Eq. 2.1-2 for constant area, but he became discouraged by the numerical effort required. Second, he tried to measure the second derivative experimentally. Like many others, he found that second derivatives are difficult to measure: "the second difference increases exceptionally the effect of [experimental] errors."
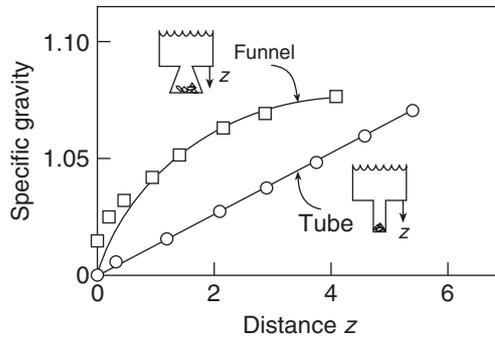
Fig. 2.1-3. Fick's experimental results. The crystals in the bottom of each apparatus saturate the adjacent solution, so that a fixed concentration gradient is established along the narrow, lower part of the apparatus. Fick's calculation of the curve for the funnel was his best proof of Fick's law.

His third effort was more successful. He used a glass cylinder containing crystalline sodium chloride in the bottom and a large volume of water in the top, shown as the lower apparatus in Fig. 2.1-3. By periodically changing the water in the top volume, he was able to establish a steady-state concentration gradient in the cylindrical cell. He found that this gradient was linear, as shown in Fig. 2.1-3. Because this result can be predicted either from Eq. 2.1-1 or from Eq. 2.1-2, this was a triumph.

But this success was by no means complete. After all, Graham's data for liquids anticipated Eq. 2.1-1. To try to strengthen the analogy with thermal conduction, Fick used the upper apparatus shown in Fig. 2.1-3. In this apparatus, he established the steady-state concentration profile in the same manner as before. He measured this profile and then tried to predict these results using Eq. 2.1-2, in which the funnel area A available for diffusion varied with the distance z. When Fick compared his calculations with his experimental results, he found good agreement. These results were the initial verification of Fick's law.

2.1.3 Forms of Fick's Law

Useful forms of Fick's law in dilute solutions are shown in Table 2.1-2. Each equation closely parallels that suggested by Fick, that is, Eq. 2.1-1. Each involves the same phenomenological diffusion coefficient. Each will be combined with mass balances to analyze the problems central to the rest of this chapter.

One must remember that these flux equations imply no convection in the same direction as the one-dimensional diffusion. They are thus special cases of the general equations given in Table 3.2-1. This lack of convection often indicates a dilute solution. In fact, the assumption of a dilute solution is more restrictive than necessary, for there are many concentrated solutions for which these simple equations can be used without inaccuracy. Nonetheless, for the novice, I suggest thinking of diffusion in a dilute solution.

2.2 Steady Diffusion Across a Thin Film

In the previous section we detailed the development of Fick's law, the basic relation for diffusion. Armed with this law, we can now attack the simplest example: steady

Table 2.1-2 *Fick's law for diffusion without convection*

For one-dimensional diffusion in Cartesian coordinates	$-j_1 = D\dfrac{dc_1}{dz}$
For radial diffusion in cylindrical coordinates	$-j_1 = D\dfrac{dc_1}{dr}$
For radial diffusion in spherical coordinates	$-j_1 = D\dfrac{dc_1}{dr}$

Note: More general equations are given in Table 3.2-1.

diffusion across a thin film. In this attack, we want to find both the diffusion flux and the concentration profile. In other words, we want to determine how much solute moves across the film and how the solute concentration changes within the film.

This problem is very important. It is one extreme of diffusion behavior, a counterpoint to diffusion in an infinite slab. Every reader, whether casual or diligent, should try to master this problem now. Many may be superficial because film diffusion is so simple mathematically. Please do not dismiss this important problem; it is mathematically straightforward but physically subtle. Think about it carefully.

2.2.1 The Physical Situation

Steady diffusion across a thin film is illustrated schematically in Fig. 2.2-1. On each side of the film is a well-mixed solution of one solute, species 1. Both these solutions are dilute. The solute diffuses from the fixed higher concentration, located at $z \leqslant 0$ on the left-hand side of the film, into the fixed, less concentrated solution, located at $z \geqslant l$ on the right-hand side.

We want to find the solute concentration profile and the flux across this film. To do this, we first write a mass balance on a thin layer Δz, located at some arbitrary position z within the thin film. The mass balance in this layer is

$$\begin{pmatrix} \text{solute} \\ \text{accumulation} \end{pmatrix} = \begin{pmatrix} \text{rate of diffusion} \\ \text{into the layer at } z \end{pmatrix} - \begin{pmatrix} \text{rate of diffusion} \\ \text{out of the layer} \\ \text{at } z + \Delta z \end{pmatrix}$$
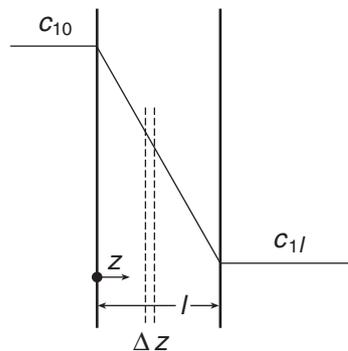

Fig. 2.2-1. Diffusion across a thin film. This is the simplest diffusion problem, basic to perhaps 80% of what follows. Note that the concentration profile is independent of the diffusion coefficient.

Because the process is in steady state, the accumulation is zero. The diffusion rate is the diffusion flux times the film's area A. Thus

$$0 = A\left(j_1|_z - j_1|_{z+\Delta z}\right) \tag{2.2-1}$$

Dividing this equation by the film's volume, $A\Delta z$, and rearranging,

$$0 = -\left(\frac{j_1|_{z+\Delta z} - j_1|_z}{(z+\Delta z) - z}\right) \tag{2.2-2}$$

When Δz becomes very small, this equation becomes the definition of the derivative

$$0 = -\frac{d}{dz}j_1 \tag{2.2-3}$$

Combining this equation with Fick's law,

$$-j_1 = D\frac{dc_1}{dz} \tag{2.2-4}$$

we find, for a constant diffusion coefficient D,

$$0 = D\frac{d^2c_1}{dz^2} \tag{2.2-5}$$

This differential equation is subject to two boundary conditions:

$$z = 0, \quad c_1 = c_{10} \tag{2.2-6}$$

$$z = l, \quad c_1 = c_{1l} \tag{2.2-7}$$

Again, because this system is in steady state, the concentrations c_{10} and c_{1l} are independent of time. Physically, this means that the volumes of the adjacent solutions must be much greater than the volume of the film.

2.2.2 Mathematical Results

The desired concentration profile and flux are now easily found. First, we integrate Eq. 2.2-5 twice to find

$$c_1 = a + bz \tag{2.2-8}$$

The constants a and b can be found from Eqs. 2.2-6 and 2.2-7, so the concentration profile is

$$c_1 = c_{10} + (c_{1l} - c_{10})\frac{z}{l} \tag{2.2-9}$$

This linear variation was, of course, anticipated by the sketch in Fig. 2.2-1. The flux is found by differentiating this profile:

$$j_1 = -D\frac{dc_1}{dz} = \frac{D}{l}(c_{10} - c_{1l}) \tag{2.2-10}$$

Because the system is in steady state, the flux is a constant.

As mentioned earlier, this case is easy mathematically. Although it is very important, it is often underemphasized because it seems trivial. Before you conclude this, try some of the examples that follow to make sure you understand what is happening.

Example 2.2-1: Membrane diffusion   Derive the concentration profile and the flux for a single solute diffusing across a thin membrane. As in the preceding case of a film, the membrane separates two well-stirred solutions. Unlike the film, the membrane is chemically different from these solutions.

    Solution   As before, we first write a mass balance on a thin layer Δz:

$$0 = A\left(j_1|_z - j_1|_{z+\Delta z}\right)$$

This leads to a differential equation identical with Eq. 2.2-5:

$$0 = D\frac{d^2 c_1}{dz^2}$$

However, this new mass balance is subject to somewhat different boundary conditions:

$$z = 0, \quad c_1 = HC_{10}$$

$$z = l, \quad c_1 = HC_{1l}$$

where H is a partition coefficient, the concentration in the membrane divided by that in the adjacent solution. This partition coefficient is an equilibrium property, so its use implies that equilibrium exists across the membrane surface. In many cases, it can be about equal to the relative solubility within the film compared with that outside. For a film containing pores, H may just be the void fraction of the film.

    The concentration profile that results from these relations is

$$c_1 = HC_{10} + H(C_{1l} - C_{10})\frac{z}{l}$$

which is analogous to Eq. 2.2-9. This result looks harmless enough. However, it suggests concentration profiles likes those in Fig. 2.2-2, which contain sudden discontinuities at the interface. If the solute is more soluble in the membrane than in the surrounding
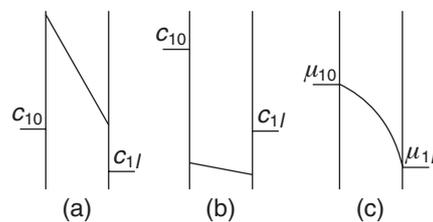

Fig. 2.2-2. Concentration profiles across thin membranes. In (a), the solute is more soluble in the membrane than in the adjacent solutions; in (b), it is less so. Both cases correspond to a chemical potential gradient like that in (c).

solutions, then the concentration increases. If the solute is less soluble in the membrane, then its concentration drops. Either case produces enigmas. For example, at the left-hand side of the membrane in Fig. 2.2-2(a), solute diffuses from the solution at C_{10} into the membrane at *higher* concentration.

This apparent quandary is resolved when we think carefully about the solute's diffusion. Diffusion often can occur from a region of low concentration into a region of high concentration; indeed, this is the basis of many liquid–liquid extractions. Thus the jumps in concentration in Fig. 2.2-2 are not as bizarre as they might appear; rather, they are graphical accidents that result from using the same scale to represent concentrations inside and outside membrane.

This type of diffusion can also be described in terms of the solute's energy or, more exactly, in terms of its chemical potential. The solute's chemical potential does not change across the membrane's interface, because equilibrium exists there. Moreover, this potential, which drops smoothly with concentration, as shown in Fig. 2.2-2(c), is the driving force responsible for the diffusion. The exact role of this driving force is discussed more completely in Sections 6.3 and 7.2.

The flux across a thin membrane can be found by combining the foregoing concentration profile with Fick's law:

$$j_1 = \frac{[DH]}{l}(C_{10} - C_{1l})$$

This is parallel to Eq. 2.2-10. The quantity in square brackets in this equation is called the permeability, and it is often reported experimentally. The quantity ($[DH]/l$) is called the permeance. The partition coefficient H is often found to vary more widely than the diffusion coefficient D, so differences in diffusion tend to be less important than the differences in solubility.

Example 2.2-2: Membrane diffusion with fast reaction Imagine that while a solute is diffusing steadily across a thin membrane, it can rapidly and reversibly react with other immobile solutes fixed within the membrane. Find how this fast reaction affects the solute's flux.

Solution The answer is surprising: The reaction has no effect. This is an excellent example because it requires careful thinking. Again, we begin by writing a mass balance on a layer Δz located within the membrane:

$$\begin{pmatrix} \text{solute} \\ \text{accumulation} \end{pmatrix} = \begin{pmatrix} \text{solute diffusion in} \\ \text{minus that out} \end{pmatrix} + \begin{pmatrix} \text{amount produced} \\ \text{by chemical reaction} \end{pmatrix}$$

Because the system is in steady state, this leads to

$$0 = A\left(j_1|_z - j_1|_{z+\Delta z}\right) - r_1 A \Delta z$$

or

$$0 = -\frac{d}{dz}j_1 - r_1$$

where r_1 is the rate of disappearance of the mobile species 1 in the membrane. A similar mass balance for the immobile product 2 gives

$$0 = -\frac{d}{dz}j_2 + r_1$$

But because the product is immobile, j_2 is zero, and hence r_1 is zero. As a result, the mass balance for species 1 is identical with Eq. 2.2-3, leaving the flux and concentration profile unchanged.

This result is easier to appreciate in physical terms. After the diffusion reaches a steady state, the local concentration is everywhere in equilibrium with the appropriate amount of the fast reaction's product. Because these local concentrations do not change with time, the amounts of the product do not change either. Diffusion continues unaltered.

This case in which a chemical reaction does not affect diffusion is unusual. For almost any other situation, the reaction can engender dramatically different mass transfer. If the reaction is irreversible, the flux can be increased many orders of magnitude, as shown in Section 17.1. If the diffusion is not steady, the apparent diffusion coefficient can be much greater than expected, as discussed in Example 2.3-2. However, in the case described in this example, the chemical reaction does not affect diffusion.

Example 2.2-3: Concentration-dependent diffusion   The diffusion coefficient is remarkably constant. It varies much less with temperature than the viscosity or the rate of a chemical reaction. It varies surprisingly little with solute: for example, most diffusion coefficients of solutes dissolved in water fall within a factor of ten.

Diffusion coefficients also rarely vary with solute concentration, although there are some exceptions. For example, a small solute like water may show a concentration-dependent diffusion when diffusing into a polymer. To explore this, assume that

$$D = \frac{D_0 c_1}{c_{10}}$$

Then calculate the concentration profile and the flux across a thin film.

   Solution   Finding the concentration profile is a complete parallel to the simpler case of constant diffusion coefficient discussed at the start of this section. We again begin with a steady-state mass balance on a differential volume $A\Delta z$:

$$0 = A(j_1|_z - j_1|_{z+\Delta z})$$

Dividing by this volume, taking the limit as Δz goes to zero and combining with Fick's law gives

$$0 = \frac{dj_1}{dz} = -\frac{d}{dz}\left(-\frac{D_0 c_1}{c_{10}}\frac{dc_1}{dz}\right)$$

This parallels Equation 2.2-5, but with a concentration-dependent D. This mass balance is subject to the boundary conditions

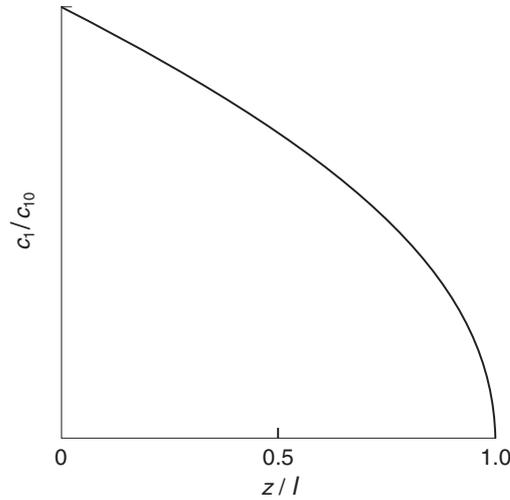$$z = 0, \quad c_1 = c_{10}$$

$$z = l, \quad c_1 = 0$$

Fig. 2.2-3. Concentration-dependent diffusion across a thin film. While the steady-state flux is constant, the concentration gradient changes with position.

These are a special case of Eqs. 2.2-6 and 2.2-7. Integration gives the concentration profile

$$c_1 = c_{10}\left(1 - \frac{z}{l}\right)^{1/2}$$

This profile can be combined with Fick's law to give the flux

$$j_1 = -D\frac{dc_1}{dz} = -\frac{D_0 c_1}{c_{10}}\frac{dc_1}{dz} = \frac{D_0 c_{10}}{2l}$$

The flux is half that of the case of a constant diffusion coefficient D_0.

The meaning of this result is clearer if we consider the concentration profile shown in Fig. 2.2-3. The profile is nonlinear; indeed, its slope at $z = l$ is infinite. However, at that boundary, the diffusion coefficient is zero because the concentation is zero. The product of this infinite gradient and a zero coefficient is the constant flux, with an apparent diffusion coefficient equal to $(D_0/2)$. This unexceptional average value illustrates why Fick's law works so well.

Example 2.2-4: Diaphragm-cell diffusion   One easy way to measure diffusion coefficients is the diaphragm cell shown in Fig. 2.2-4. These cells consist of two well-stirred volumes separated by a thin porous barrier or diaphragm. In the more accurate experiments, the diaphragm is often a sintered glass frit; in many successful experiments, it is just a piece of filter paper (see Section 5.5). To measure a diffusion coefficient with this cell, we fill the lower compartment with a solution of known concentration and the upper compartment with solvent. After a known time, we sample both upper and lower compartments and measure their concentrations.

Find an equation that uses the known time and the measured concentrations to calculate the diffusion coefficient.
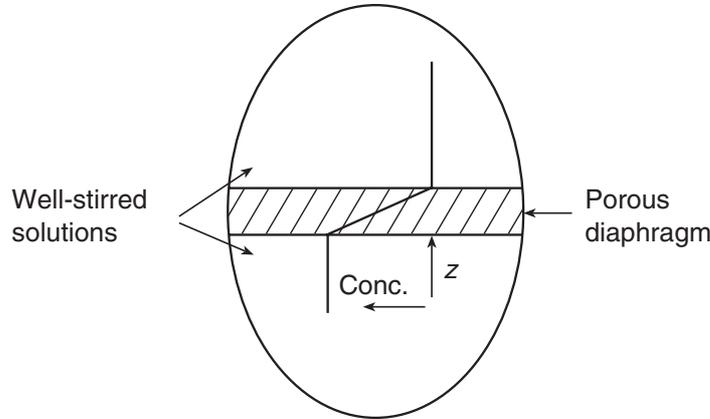
Fig. 2.2-4. A diaphragm cell for measuring diffusion coefficients. Because the diaphragm has a much smaller volume than the adjacent solutions, the concentration profile within the diaphragm has essentially the linear, steady-state value.

Solution   An exact solution to this problem is elaborate and unnecessary. The useful approximate solution depends on the assumption that the flux across the diaphragm quickly reaches its steady-state value. This steady-state flux is approached even though the concentrations in the upper and lower compartments are changing with time. The approximations introduced by this assumption will be considered later.

In this pseudosteady state, the flux across the diaphragm is that given for membrane diffusion:

$$j_1 = \left[\frac{DH}{l}\right](C_{1,\text{lower}} - C_{1,\text{upper}})$$

Here, the quantity H includes the fraction of the diaphragm's area that is available for diffusion. We next write an overall mass balance on the adjacent compartments:

$$V_{\text{lower}}\frac{dC_{1,\text{lower}}}{dt} = -Aj_1$$

$$V_{\text{upper}}\frac{dC_{1,\text{upper}}}{dt} = +Aj_1$$

where A is the diaphragm's area. If these mass balances are divided by V_{lower} and V_{upper}, respectively, and the equations are subtracted, one can combine the result with the flux equation to obtain

$$\frac{d}{dt}(C_{1,\text{lower}} - C_{1,\text{upper}}) = D\beta(C_{1,\text{upper}} - C_{1,\text{lower}})$$

in which

$$\beta = \frac{AH}{l}\left(\frac{1}{V_{\text{lower}}} + \frac{1}{V_{\text{upper}}}\right)$$

is a geometrical constant characteristic of the particular diaphragm cell being used. This differential equation is subject to the obvious initial condition

$$t = 0, \quad C_{1,\text{lower}} - C_{1,\text{upper}} = C^0_{1,\text{lower}} - C^0_{1,\text{upper}}$$

If the upper compartment is initially filled with solvent, then its initial solute concentration will be zero.

Integrating the differential equation subject to this condition gives the desired result:

$$\frac{C_{1,\text{lower}} - C_{1,\text{upper}}}{C^0_{1,\text{lower}} - C^0_{1,\text{upper}}} = e^{-\beta D t}$$

or

$$D = \frac{1}{\beta t} \ln \left(\frac{C^0_{1,\text{lower}} - C^0_{1,\text{upper}}}{C_{1,\text{lower}} - C_{1,\text{upper}}} \right)$$

We can measure the time t and the various concentrations directly. We can also determine the geometric factor β by calibration of the cell with a species whose diffusion coefficient is known. Then we can determine the diffusion coefficients of unknown solutes.

There are two major ways in which this analysis can be questioned. First, the diffusion coefficient used here is an effective value altered by the tortuosity in the diaphragm. Theoreticians occasionally assert that different solutes will have different tortuosities, so that the diffusion coefficients measured will apply only to that particular diaphragm cell and will not be generally usable. Experimentalists have cheerfully ignored these assertions by writing

$$D = \frac{1}{\beta' t} \ln \left(\frac{C^0_{1,\text{lower}} - C^0_{1,\text{upper}}}{C_{1,\text{lower}} - C_{1,\text{upper}}} \right)$$

where β' is a new calibration constant that includes any tortuosity. So far, the experimentalists have gotten away with this: Diffusion coefficients measured with the diaphragm cell do agree with those measured by other methods.

The second major question about this analysis comes from the combination of the steady-state flux equation with an unsteady-state mass balance. You may find this combination to be one of those areas where superficial inspection is reassuring, but where careful reflection is disquieting. I have been tempted to skip over this point, but have decided that I had better not. Here goes:

The adjacent compartments are much larger than the diaphragm itself because they contain much more material. Their concentrations change slowly, ponderously, as a result of the transfer of a lot of solute. In contrast, the diaphragm itself contains relatively little material. Changes in its concentration profile occur quickly. Thus, even if this profile is initially very different from steady state, it will approach a steady state before the concentrations in the adjacent compartments can change much. As a result, the profile across the diaphragm will always be close to its steady value, even though the compartment concentrations are time dependent.

These ideas can be placed on a more quantitative basis by comparing the relaxation time of the diaphragm, l^2/D, with that of the compartments, $1/(D\beta)$. The analysis used here will be accurate when (Mills, Woolf, and Watts, 1968)

$$1 \gg \frac{l^2/D_{\text{eff}}}{1/(\beta D_{\text{eff}})} = V_{\substack{\text{diaphragm} \\ \text{voids}}} \left(\frac{1}{V_{\text{lower}}} + \frac{1}{V_{\text{upper}}} \right)$$

This type of "pseudosteady-state approximation" is common and underlies most mass transfer coefficients discussed later in this book.

The examples in this section show that diffusion across thin films can be difficult to understand. The difficulty does not derive from mathematical complexity; the calculation is easy and essentially unchanged. The simplicity of the mathematics is the reason why diffusion across thin films tends to be discussed superficially in mathematically oriented books. The difficulty in thin-film diffusion comes from adapting the same mathematics to widely varying situations with different chemical and physical effects. This is what is difficult to understand about thin-film diffusion. It is an understanding that you must gain before you can do creative work on harder mass transfer problems. Remember: this case is the base for perhaps 80 percent of the diffusion problems in this book.

2.3 Unsteady Diffusion in a Semi-infinite Slab

We now turn to a discussion of diffusion in a semi-infinite slab, which is basic to perhaps 10 percent of the problems in diffusion. We consider a volume of solution that starts at an interface and extends a long way. Such a solution can be a gas, liquid, or solid. We want to find how the concentration varies in this solution as a result of a concentration change at its interface. In mathematical terms, we want to find the concentration and flux as a function of position and time.

This type of mass transfer is sometimes called free diffusion simply because this is briefer than "unsteady diffusion in a semi-infinite slab." At first glance, this situation may seem rare because no solution can extend an infinite distance. The previous thin-film example made more sense because we can think of many more thin films than semi-infinite slabs. Thus we might conclude that this semi-infinite case is not common. That conclusion would be a serious error.

The important case of a semi-infinite slab is common because any diffusion problem will behave as if the slab is infinitely thick at short enough times. For example, imagine that one of the thin membranes discussed in the previous section separates two identical solutions, so that it initially contains a solute at constant concentration. Everything is quiescent, at equilibrium. Suddenly the concentration on the left-hand interface of the membrane is raised, as shown in Fig. 2.3-1. Just after this sudden increase, the concentration near this left interface rises rapidly on its way to a new steady state. In these first few seconds, the concentration at the right interface remains unaltered, ignorant of the turmoil on the left. The left might as well be infinitely far away; the membrane, for these first few seconds, might as well be infinitely thick. Of course, at larger times, the system will slither into the steady-state limit in Fig. 2.3-1(c). But in those first seconds, the membrane does behave like a semi-infinite slab.

This example points to an important corollary, which states that cases involving an infinite slab and a thin membrane will bracket the observed behavior. At short times,
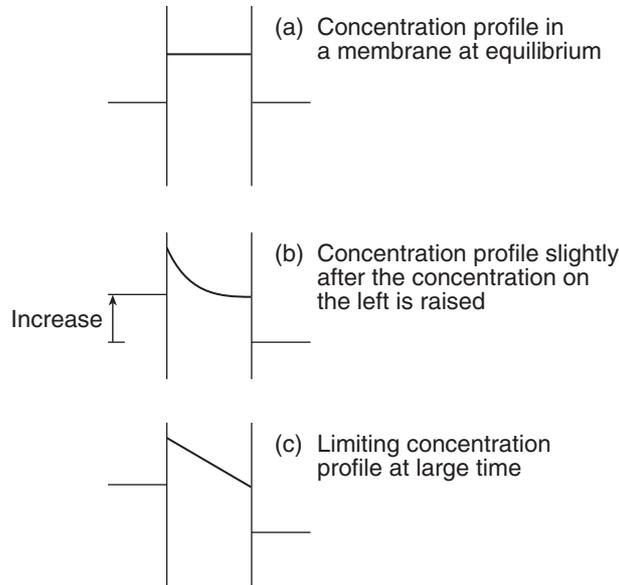
Fig. 2.3-1. Unsteady- versus steady-state diffusion. At small times, diffusion will occur only near the left-hand side of the membrane. As a result, at these small times, the diffusion will be the same as if the membrane was infinitely thick. At large times, the results become those in the thin film.

diffusion will proceed as if the slab is infinite; at long times, it will occur as if the slab is thin. By focussing on these limits, we can bracket the possible physical responses to different diffusion problems.

2.3.1 The Physical Situation

The diffusion in a semi-infinite slab is schematically sketched in Fig. 2.3-2. The slab initially contains a uniform concentration of solute $c_{1\infty}$. At some time, chosen as time zero, the concentration at the interface is suddenly and abruptly increased, although the solute is always present at high dilution. The increase produces the time-dependent concentration profile that develops as solute penetrates into the slab.

We want to find the concentration profile and the flux in this situation, and so again we need a mass balance written on the thin layer of volume $A\Delta z$:

$$\begin{pmatrix} \text{solute accumulation} \\ \text{in volume } A\Delta z \end{pmatrix} = \begin{pmatrix} \text{rate of diffusion} \\ \text{into the layer at } z \end{pmatrix} - \begin{pmatrix} \text{rate of diffusion} \\ \text{out of the layer} \\ \text{at } z + \Delta z \end{pmatrix} \quad (2.3\text{-}1)$$

In mathematical terms, this is

$$\frac{\partial}{\partial t}(A\Delta z c_1) = A\left(j_1|_z - j_1|_{z+\Delta z}\right) \quad (2.3\text{-}2)$$
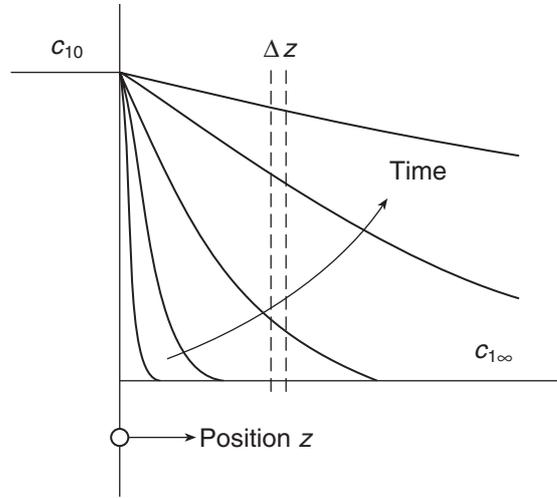
Fig. 2.3-2. Free diffusion. In this case, the concentration at the left is suddenly increased to a higher constant value. Diffusion occurs in the region to the right. This case and that in Fig. 2.2-1 are basic to most diffusion problems.

We divide by $A\Delta z$ to find

$$\frac{\partial c_1}{\partial t} = -\left(\frac{j_1|_{z+\Delta z} - j_1|_z}{(z + \Delta z) - z}\right) \tag{2.3-3}$$

We then let Δz go to zero and use the definition of the derivative

$$\frac{\partial c_1}{\partial t} = -\frac{\partial j_1}{\partial z} \tag{2.3-4}$$

Combining this equation with Fick's law and assuming that the diffusion coefficient is independent of concentration, we get

$$\frac{\partial c_1}{\partial t} = D \frac{\partial^2 c_1}{\partial z^2} \tag{2.3-5}$$

This equation is sometimes called Fick's second law, or "the diffusion equation." In this case, it is subject to the following conditions:

$$t = 0, \quad \text{all } z, \qquad c_1 = c_{1\infty} \tag{2.3-6}$$

$$t > 0, \quad z = 0, \quad c_1 = c_{10} \tag{2.3-7}$$

$$z = \infty, \quad c_1 = c_{1\infty} \tag{2.3-8}$$

Note that both $c_{1\infty}$ and c_{10} are taken as constants. The concentration $c_{1\infty}$ is constant because it is so far from the interface as to be unaffected by events there; the concentration c_{10} is kept constant by adding material at the interface.

2.3.2 Mathematical Solution

The solution of this problem is easiest using the method of "combination of variables." This method is easy to follow, but it must have been difficult to invent. Fourier, Graham, and Fick failed in the attempt; it required Boltzmann's tortured imagination (Boltzmann, 1894).

The trick to solving this problem is to define a new variable

$$\zeta = \frac{z}{\sqrt{4Dt}} \tag{2.3-9}$$

The differential equation can then be written as

$$\frac{dc_1}{d\zeta}\left(\frac{\partial \zeta}{\partial t}\right) = D\frac{d^2c_1}{d\zeta^2}\left(\frac{\partial \zeta}{\partial z}\right)^2 \tag{2.3-10}$$

or

$$\frac{d^2c_1}{d\zeta^2} + 2\zeta\frac{dc_1}{d\zeta} = 0 \tag{2.3-11}$$

In other words, the partial differential equation has been almost magically transformed into an ordinary differential equation. The magic also works for the boundary conditions: from Eq. 2.3-7,

$$\zeta = 0, \quad c_1 = c_{10} \tag{2.3-12}$$

and from Eqs. 2.3-6 and 2.3-8,

$$\zeta = \infty, \quad c_1 = c_{1\infty} \tag{2.3-13}$$

With the method of combination of variables, the transformation of the initial and boundary conditions is often more critical than the transformation of the differential equation.

The solution is now straightforward. One integration of Eq. 2.3-11 gives

$$\frac{dc_1}{d\xi} = ae^{-\xi^2} \tag{2.3-14}$$

where a is an integration constant. A second integration and use of the boundary conditions give

$$\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} = \text{erf}\,\zeta \tag{2.3-15}$$

where

$$\text{erf}\,\zeta = \frac{2}{\sqrt{\pi}}\int_0^{\zeta} e^{-s^2}\,ds \tag{2.3-16}$$

is the error function of ζ. This is the desired concentration profile giving the variation of concentration with position and time.

In many practical problems, the flux in the slab is of greater interest than the concentration profile itself. This flux can again be found by combining Fick's law with Eq. 2.3-15:

$$j_1 = -D\frac{\partial c_1}{\partial z} = \sqrt{D/\pi t}\, e^{-z^2/4Dt}(c_{10} - c_{1\infty}) \tag{2.3-17}$$

One particularly useful limit is the flux across the interface at $z = 0$:

$$j_1|_{z=0} = \sqrt{D/\pi t}(c_{10} - c_{1\infty}) \tag{2.3-18}$$

This flux is the value at the particular time t and not that averaged over time. This distinction will be important in Section 9.2.

At this point, I have the same pedagogical problem I had in the previous section: I must convince you that the apparently simple results in Eqs. 2.3-15 and 2.3-18 are valuable. These results are exceeded in importance only by Eqs. 2.2-9 and 2.2-10. Fortunately, the mathematics may be difficult enough to spark thought and reflection; if not, the examples that follow should do so.

Example 2.3-1: Diffusion across an interface   The picture of the process in Fig. 2.3-2 implies that the concentration at $z = 0$ is continuous. This would be true, for example, if when $z \geqslant 0$ there was a highly swollen gel, and when $z < 0$ there was a stirred solution.

A much more common case occurs when there is a gas–liquid interface at $z = 0$. Ordinarily, the gas at $z < 0$ will be well mixed, but the liquid will not. How will this interface affect the results given earlier?

Solution   Basically, it will have no effect. The only change will be a new boundary condition, replacing Eq. 2.3-7:

$$z = 0, \quad c_1 = cx_1 = c\frac{p_{10}}{H}$$

where c_1 is the concentration of solute in the liquid, x_1 is its mole fraction, p_{10} is its partial pressure in the gas phase, H is the Henry's law constant, and c is the total molar concentration in the liquid.

The difficulties caused by a gas–liquid interface are another result of the plethora of units in which concentration can be expressed. These difficulties require concern about units, but they do not demand new mathematical weapons. The changes required for a liquid–liquid interface can be similarly subtle.

Example 2.3-2: Free diffusion with fast chemical reaction   In many problems, the diffusing solutes react rapidly and reversibly with surrounding material. The surrounding material is stationary and cannot diffuse. For example, in the dyeing of wool, some dyes can react quickly and reversibly with the wool as dye diffuses into the fiber. How does such a rapid chemical reaction change the concentration profile and the flux?

Solution   In this case, the chemical reaction can radically change the process by reducing the apparent diffusion coefficient and increasing the interfacial flux of solute. These radical changes stand in stark contrast to the steady-state result, where the chemical reaction produces no effect.

To solve this example, we first recognize that the solute is effectively present in two forms: (1) free solute that can diffuse and (2) reacted solute fixed at the point of reaction. If this reaction is reversible and faster than diffusion,

$$c_2 = Kc_1$$

where c_2 is the concentration of the solute that has already reacted, c_1 is the concentration of the unreacted solute that can diffuse, and K is the equilibrium constant of the reaction. If the reaction is minor, K will be small; as the reaction becomes irreversible, K will become very large.

With these definitions, we now write a mass balance for each solute form. These mass balances should have the form

$$\begin{pmatrix} \text{accumulation} \\ \text{in } A\Delta z \end{pmatrix} = \begin{pmatrix} \text{diffusion in} \\ \text{minus that out} \end{pmatrix} + \begin{pmatrix} \text{amount produced by} \\ \text{reaction in } A\Delta z \end{pmatrix}$$

For the diffusing solute, this is

$$\frac{\partial}{\partial t}[A\Delta z c_1] = A(j_1|_z - j_1|_{z+\Delta z}) - r_1 A\Delta z$$

where r_1 is the rate of disappearance per volume of species 1, the diffusing solute. By arguments analogous to Eqs. 2.2-2 to 2.2-5, this becomes

$$\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} - r_1$$

The term on the left-hand side is the accumulation; the first term on the right is the diffusion in minus the diffusion out; the term r_1 is the effect of chemical reaction.

When we write a similar mass balance on the second species, we find

$$\frac{\partial}{\partial t}[A\Delta z c_2] = -r_1 A\Delta z$$

or

$$\frac{\partial c_2}{\partial t} = r_1$$

We do not get a diffusion term because the reacted solute cannot diffuse. We get a reaction term that has a different sign but the same magnitude, because any solute that disappears as species 1 reappears as species 2.

To solve these questions, we first add them to eliminate the reaction term:

$$\frac{\partial}{\partial t}(c_1 + c_2) = D\frac{\partial^2 c_1}{\partial z^2}$$

We now use the fact that the chemical reaction is at equilibrium:

$$\frac{\partial}{\partial t}(c_1 + Kc_1) = D\frac{\partial^2 c_1}{\partial z^2}$$

$$\frac{\partial c_1}{\partial t} = \frac{D}{1 + K}\frac{\partial^2 c_1}{\partial z^2}$$

This result is subject to the same initial and boundary conditions as before in Eqs. 2.3-6, 2.3-7, and 2.3-8. As a result, the only difference between this example and the earlier problem is that $D/(1 + K)$ replaces D.

This is intriguing. The chemical reaction has left the mathematical form of the answer unchanged, but it has altered the apparent diffusion coefficient. The concentration profile now is

$$\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} = \text{erf}\frac{z}{\sqrt{4[D/(1 + K)]t}}$$

and the interfacial flux is

$$j_1|_{z=0} = \sqrt{D(1 + K)/\pi t}(c_{10} - c_{1\infty})$$

The flux has been increased by the chemical reaction.

These effects of chemical reaction can easily be several orders of magnitude. As will be detailed in Chapter 5, diffusion coefficients tend to fall in fairly narrow ranges. Those coefficients for gases are around 0.1 cm^2/sec; those in ordinary liquids cluster about 10^{-5} cm^2/sec. Deviations from these values of more than an order of magnitude are unusual. However, differences in the equilibrium constant K of a million or more occur frequently. Thus a fast chemical reaction can tremendously influence the unsteady diffusion process.

Example 2.3-3: Determining diffusion coefficients from free diffusion experiments   Diffusion in an infinite slab is the geometry used for the most accurate measurements of diffusion coefficients. These most accurate measurements determine the concentration profile by interferometry. One relatively simple method, the Rayleigh interferometer, uses a rectangular cell in which there is an initial step function in refractive index. The decay of this refractive index profile is followed by collimated light through the cell to give interference fringes. These fringes record the refractive index versus camera position and time.

Find equations that allow this information to be used to calculate diffusion coefficients.

Solution   The concentration profiles established in the diffusion cell closely approach the profiles calculated earlier for a semi-infinite slab. The cell now effectively contains two semi-infinite slabs joined together at $z = 0$. The concentration profile is unaltered from Eq. 2.3-15:

$$\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} = \text{erf}\frac{z}{\sqrt{4Dt}}$$

where $c_{10}[= (c_{1\infty} + c_{1-\infty})/2]$ is the average concentration between the two ends of the cell. How accurate this equation is depends on how exactly the initial change in concentration can be realized; in practice, this change can be within 10 seconds of a true step function.

We must convert the concentration and cell position into the experimental measured refractive index and camera position. The refractive index n is linearly proportional to the concentration:

$$n = n_{solvent} + bc_1$$

where $n_{solvent}$ is the refractive index of the solvent and b is a constant determined from experiment. Each position in the camera Z is proportional to a position in the diffusion cell:

$$Z = az$$

where a is the magnification of the apparatus. It is experimentally convenient not to measure the position of one fringe but rather to measure the intensity minima between the many fringes. These minima occur when

$$\frac{n - n_0}{n_\infty - n_0} = \frac{j}{J/2}$$

where n_∞ and n_0 are the refractive indices at $z = \infty$ and $z = 0$, respectively; J is the total number of interference fringes, and j is an integer called the fringe number. This number is most conveniently defined as zero at $z = 0$, the center of the cell. Combining these equations,

$$\frac{j}{J/2} = \mathrm{erf}\, \frac{Z_j}{a\sqrt{4Dt}}$$

where Z_j is the intensity minimum associated with the jth fringe. Because a and t are experimentally accessible, measurements of Z_j (j, J) can be used to find the diffusion coefficient D. While the accuracy of interferometric experiments like this remains unrivaled, the use of these methods has declined because they are tedious.

2.4 Three Other Examples

The two previous sections describe diffusion across thin films and in semi-infinite slabs. In this section, we turn to discussing mathematical variations of diffusion problems. This mathematical emphasis changes both the pace and the tone of this book. Up to now, we have consistently stressed the physical origins of the problems, constantly harping on natural effects like changing liquid to gas. Now we shift to the more common text book composition, a sequence of equations sometimes as jarring as a twelve-tone concerto.

In these examples, we have three principal goals:

(1) We want to show how the differential equations describing diffusion are derived.
(2) We want to examine the effects of spherical and cylindrical geometries.
(3) We want to supply a mathematical primer for solving these different diffusion equations.

In all three examples, we continue to assume dilute solutions. The three problems examined next are physically important and will be referred to again in this book. However, they are introduced largely to achieve mathematical goals.

2.4.1 Decay of a Pulse (Laplace Transforms)

As a first example, we consider the diffusion away from a sharp pulse of solute. This example is the third truly important problem for diffusion. It complements the cases of a thin film and the semi-infinite slab to form the basis of perhaps 95 percent of all the diffusion problems which are encountered. The initially sharp concentration gradient relaxes by diffusion in the z direction into the smooth curves shown in Fig. 2.4-1. We want to calculate the shape of these curves. This calculation illustrates the development of a differential equation and its solution using Laplace transforms.

As usual, our first step is to make a mass balance on the differential volume $A\Delta z$ as shown:

$$\begin{pmatrix} \text{solute} \\ \text{accumulation} \\ \text{in } A\Delta z \end{pmatrix} = \begin{pmatrix} \text{solute} \\ \text{diffusion into} \\ \text{this volume} \end{pmatrix} - \begin{pmatrix} \text{solute} \\ \text{diffusion out of} \\ \text{this volume} \end{pmatrix} \qquad (2.4\text{-}1)$$

In mathematical terms, this is

$$\frac{\partial}{\partial t}[A\Delta z c_1] = Aj_1|_z - Aj_1|_{z+\Delta z} \qquad (2.4\text{-}2)$$

Dividing by the volume and taking the limit as Δz goes to zero gives

$$\frac{\partial c_1}{\partial t} = -\frac{\partial j_1}{\partial z} \qquad (2.4\text{-}3)$$

Combining this relation with Fick's law of diffusion,

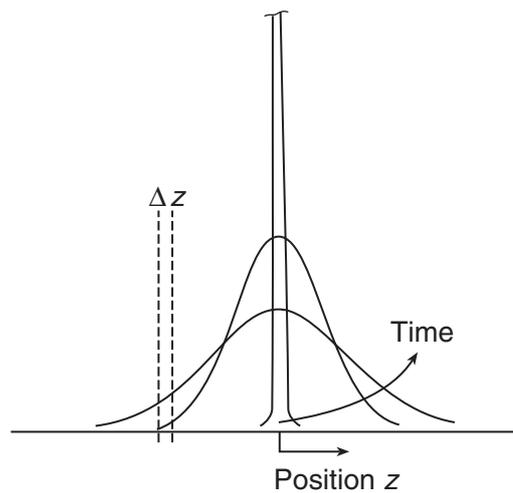$$\frac{\partial c_1}{\partial t} = D\frac{\partial^2 c_1}{\partial z^2} \qquad (2.4\text{-}4)$$

Fig. 2.4-1. Diffusion of a pulse. The concentrated solute originally located at $z = 0$ diffuses as the Gaussian profile shown. This is the third of the three most important cases, along with those in Figs. 2.2-1 and 2.3-2.

This is the same differential equation basic to diffusion in a semi-infinite slab and considered in the previous section. The boundary conditions on this equation are different as follows. First, far from the pulse, the solute concentration is zero:

$$t > 0, \quad z = \infty, \quad c_1 = 0 \tag{2.4-5}$$

Second, because diffusion occurs at the same speed in both directions, the pulse is symmetric:

$$t > 0, \quad z = 0, \quad \frac{\partial c_1}{\partial z} = 0 \tag{2.4-6}$$

This is equivalent to saying that at $z = 0$, the flux has the same magnitude in the positive and negative directions.

The initial condition for the pulse is more interesting in that all the solute is initially located at $z = 0$:

$$t = 0, \quad c_1 = \frac{M}{A} \delta(z) \tag{2.4-7}$$

where A is the cross-sectional area over which diffusion is occurring, M is the total amount of solute in the system, and $\delta(z)$ is the Dirac function. This can be shown to be a reasonable condition by a mass balance:

$$\int_{-\infty}^{\infty} c_1 A \mathrm{d}z = \int_{-\infty}^{\infty} \frac{M}{A} \delta(z) A \mathrm{d}z = M \tag{2.4-8}$$

In this integration, we should remember that $\delta(z)$ has dimensions of $(\text{length})^{-1}$.

To solve this problem, we first take the Laplace transform of Eq. 2.4-4 with respect to time:

$$s\bar{c}_1 - c_1(t = 0) = D\frac{\mathrm{d}^2\bar{c}_1}{\mathrm{d}z^2} \tag{2.4-9}$$

where $\bar{c}_1$ is the transformed concentration. The boundary conditions are

$$z = 0, \quad \frac{\mathrm{d}\bar{c}_1}{\mathrm{d}z} = -\frac{M/A}{2D} \tag{2.4-10}$$

$$z = \infty, \quad \bar{c}_1 = 0 \tag{2.4-11}$$

The first of these reflects the properties of the Dirac function, but the second is routine. Equation 2.4-9 can then easily by integrated to give

$$\bar{c}_1 = a\mathrm{e}^{\left(\sqrt{s/D}\,z\right)} + b\mathrm{e}^{\left(-\sqrt{s/D}\,z\right)} \tag{2.4-12}$$

where a and b are integration constants. Clearly, a is zero by Eq. 2.4-11. Using Eq. 2.4-10, we find b and hence $\bar{c}_1$:

$$\bar{c}_1 = \frac{M/A}{2D} \sqrt{D/s} \exp\left(-\sqrt{s/D}\,z\right) \tag{2.4-13}$$

The inverse Laplace transform of this function gives

$$\bar{c}_1 = \frac{M/A}{\sqrt{4\pi Dt}}e^{-z^2/4Dt} \tag{2.4-14}$$

which is a Gaussian curve. You may wish to integrate the concentration over the entire system to check that the total solute present is M.

This solution can be used to solve many unsteady diffusion problems that have unusual initial conditions. More important, it is often used to correlate the dispersion of pollutants, especially in the air, as discussed in Chapter 4.

2.4.2 Steady Dissolution of a Sphere (Spherical Coordinates)

Our second example, which is easier mathematically, is the steady dissolution of a spherical particle, as shown in Fig. 2.4-2. The sphere is of a sparingly soluble material, so that the sphere's size does not change much. However, this material quickly dissolves in the surrounding solvent, so that the solute's concentration at the sphere's surface is saturated. Because the sphere is immersed in a large fluid volume, the concentration far from the sphere is zero.

The goal is to find both the dissolution rate and the concentration profile around the sphere. Again, the first step is a mass balance. In contrast with the previous examples, this mass balance is most conveniently made in spherical coordinates originating from the center of the sphere. Then we can make a mass balance on a spherical shell of thickness Δr located at some arbitrary distance r from the sphere. This spherical shell is like the rubber of a balloon of surface area $4\pi r^2$ and thickness Δr.

A mass balance on this shell has the same general form as those used earlier:

$$\begin{pmatrix} \text{solute accumulation} \\ \text{within the shell} \end{pmatrix} = \begin{pmatrix} \text{diffusion} \\ \text{into the shell} \end{pmatrix} - \begin{pmatrix} \text{diffusion} \\ \text{out of the shell} \end{pmatrix} \tag{2.4-15}$$
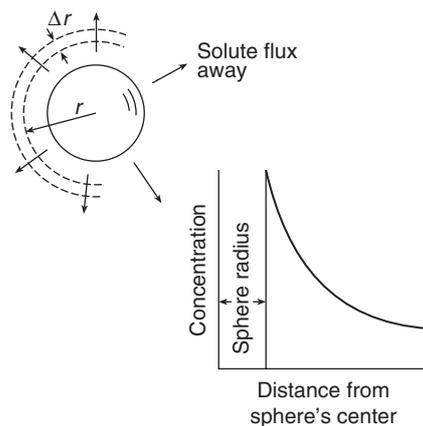

Fig. 2.4-2. Steady dissolution of a sphere. This problem represents an extension of diffusion theory to a spherically symmetric situation. In actual physical situations, this dissolution can be complicated by free convection caused by diffusion.

In mathematical terms, this is

$$\frac{\partial}{\partial t}\left(4\pi r^2 \Delta r c_1\right) = 0 = \left(4\pi r^2 j_1\right)_r - \left(4\pi r^2 j_1\right)_{r+\Delta r} \tag{2.4-16}$$

The accumulation on the left-hand side of this mass balance is zero because diffusion is steady, not varying with time. Novices frequently make a serious error at this point by canceling the r^2 out of both terms on the right-hand side. This is wrong. The term $r^2 j_1$ is evaluated at r in the first term; that is, it is $r^2(j_1|_r)$. The term is evaluated at $(r + \Delta r)$ in the second term; so it equals $(r + \Delta r)^2(j_1|_{r+\Delta r})$.

If we divide both sides of this equation by the spherical shell's volume and take the limit as $\Delta r \rightarrow 0$, we find

$$0 = -\frac{1}{r^2}\frac{d}{dr}\left(r^2 j_1\right) \tag{2.4-17}$$

Combining this with Fick's law and assuming that the diffusion coefficient is constant,

$$0 = \frac{D}{r^2}\frac{d}{dr}\left(r^2 \frac{dc_1}{dr}\right) \tag{2.4-18}$$

This basic differential equation is subject to two boundary conditions:

$$r = R_0, \quad c_1 = c_1(\text{sat}) \tag{2.4-19}$$

$$r = \infty, \quad c_1 = 0 \tag{2.4-20}$$

where R_0 is the sphere radius. If the sphere were dissolving in a partially saturated solution, this second condition would be changed, but the basic mathematical structure would remain unaltered. One integration of Eq. 2.4-18 yields

$$\frac{dc_1}{dr} = \frac{a}{r^2} \tag{2.4-21}$$

where a is an integration constant. A second integration gives

$$c_1 = b - \frac{a}{r} \tag{2.4-22}$$

Use of the two boundary conditions gives the concentration profile

$$c_1 = c_1(\text{sat})\frac{R_0}{r} \tag{2.4-23}$$

The dissolution flux can then be found from Fick's law:

$$j_1 = -D\frac{dc_1}{dr} = \frac{DR_0}{r^2}c_1(\text{sat}) \tag{2.4-24}$$

which, at the sphere's surface, is

$$j_1 = \frac{D}{R_0}c_1(\text{sat}) \tag{2.4-25}$$

This example is a mainstay of the analysis of diffusion. It is a good mathematical introduction of spherical coordinates, and it gives a result which is much like that for steady diffusion across a thin film. After all, Eq. 2.4-25 is the complete parallel of Eq. 2.2-10, but with the sphere radius R_0 replacing the film thickness l. Thus most teachers repeat this example as gospel.

Unfortunately, this result is only rarely supported by experiment. The reason is that the dissolution of the sphere almost always causes a density difference in the surrounding solution, which in turn causes flow by free convection. This flow accelerates the dissolution rate. For example, for dissolution in water, a density difference of 10^{-6} g/cm^3, almost too small to measure, causes a 400 percent increase in the dissolution expected from Eqs. 2.4-25. Students should beware: don't trust your teacher on this point.

2.4.3 Unsteady Diffusion into Cylinders (Cylindrical Coordinates and Separation of Variables)

The final example, probably the hardest of the three, concerns the diffusion of a solute into the cylinder shown in Fig. 2.4-3. The cylinder initially contains no solute. At
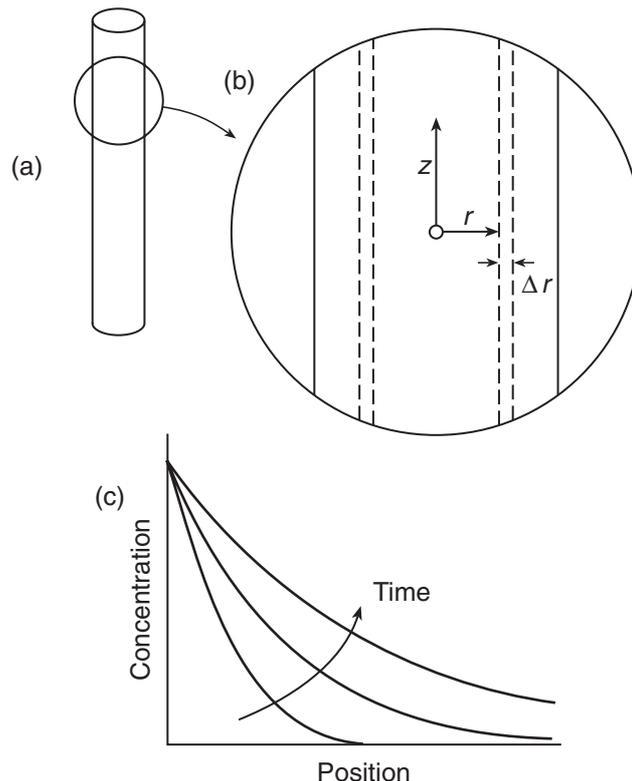

Fig. 2.4-3. Waterproofing a fence post. This problem is modeled as diffusion in an infinite cylinder, and so represents an extension to a cylindrically symmetric situation. In reality, the ends of the post must be considered, especially because diffusion with the grain is faster than across the grain.

time zero, it is suddenly immersed in a well-stirred solution that is of such enormous volume that its solute concentration is constant. The solute diffuses into the cylinder symmetrically. Problems like this are important in the chemical treatment of wood.

We want to find the solute's concentration in this cylinder as a function of time and location. As in the previous examples, the first step is a mass balance; in contrast, this mass balance is made on a cylindrical shell located at r, of area $2\pi Lr$, and of volume $2\pi Lr\Delta r$, where L is the cylinder's length. The basic balance

$$\begin{pmatrix} \text{solute accumulation} \\ \text{in this cylindrical shell} \end{pmatrix} = \begin{pmatrix} \text{solute diffusion} \\ \text{into the shell} \end{pmatrix} - \begin{pmatrix} \text{solute diffusion} \\ \text{out of the shell} \end{pmatrix} \quad (2.4\text{-}26)$$

becomes in mathematical terms

$$\frac{\partial}{\partial t}(2\pi r L \Delta r c_1) = (2\pi r L j_1)_r - (2\pi r L j_1)_{r+\Delta r} \quad (2.4\text{-}27)$$

We can now divide by the shell's volume and take the limit as Δr becomes small:

$$\frac{\partial}{\partial t} c_1 = -\frac{1}{r}\frac{\partial}{\partial r}(r j_1) \quad (2.4\text{-}28)$$

Combining this expression with Fick's law gives the desired mass balance

$$\frac{\partial c_1}{\partial t} = \frac{D}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_1}{\partial r}\right) \quad (2.4\text{-}29)$$

which is subject to the following conditions:

$$t \leq 0, \quad \text{all } r, \quad c_1 = 0 \quad (2.4\text{-}30)$$

$$t > 0, \quad r = R_0, \quad c_1 = c_1(\text{surface}) \quad (2.4\text{-}31)$$

$$r = 0, \quad \frac{\partial c_1}{\partial r} = 0 \quad (2.4\text{-}32)$$

In these equations, $c_1(\text{surface})$ is the concentration at the cylinder's surface and R_0 is the cylinder's radius. The first of the boundary conditions results from the large volume of surrounding solution, and the second reflects the symmetry of the concentration profiles.

Problems like this are often algebraically simplified if they are written in terms of dimensionless variables. This is standard practice in many advanced textbooks. I often find this procedure confusing, because for me it produces only a small gain in algebra at the expense of a large loss in physical insight. Nonetheless, we shall follow this procedure here to illustrate the simplification possible. We first define three new variables:

$$\text{dimensionless concentration}: \theta = 1 - \frac{c_1}{c_1(\text{surface})} \quad (2.4\text{-}33)$$

$$\text{dimensionless position}: \xi = \frac{r}{R_0} \quad (2.4\text{-}34)$$

$$\text{dimensionless time}: \tau = \frac{Dt}{R_0^2} \quad (2.4\text{-}35)$$

The differential equation and boundary conditions now become

$$\frac{\partial \theta}{\partial \tau} = \frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi\frac{\partial \theta}{\partial \xi}\right) \tag{2.4-36}$$

subject to

$$\tau = 0, \quad \text{all } \xi, \quad \theta = 1 \tag{2.4-37}$$

$$\tau > 0, \quad \xi = 1, \quad \theta = 0 \tag{2.4-38}$$

$$\xi = 0, \ \frac{\partial \theta}{\partial \xi} = 0 \tag{2.4-39}$$

For the novice, this manipulation can be more troublesome than it looks.

To solve these equations, we first assume that the solution is the product of two functions, one of time and one of radius:

$$\theta(\tau, \xi) = g(\tau)\, f(\xi) \tag{2.4-40}$$

When Eqs. 2.4-36 and 2.4-40 are combined, the resulting tangle of terms can be separated by division with $g(\tau)f(\xi)$:

$$f(\xi)\frac{\mathrm{d}g(\tau)}{\mathrm{d}\tau} = \frac{g(\tau)}{\xi}\frac{\mathrm{d}}{\mathrm{d}\xi}\xi\frac{\mathrm{d}f(\xi)}{d\xi}$$

$$\frac{1}{g(\tau)}\frac{\mathrm{d}g(\tau)}{\mathrm{d}\tau} = \frac{1}{\xi f(\xi)}\frac{\mathrm{d}}{\mathrm{d}\xi}\xi\frac{\mathrm{d}f(\xi)}{\mathrm{d}\xi} \tag{2.4-41}$$

Now, if one fixes ξ and changes τ, $f(\xi)$ remains constant but $g(\tau)$ varies. As a result,

$$\frac{1}{g(\tau)}\frac{\mathrm{d}g(\tau)}{\mathrm{d}\tau} = -\alpha^2 \tag{2.4-42}$$

where α is a constant. Similarly, if we hold τ constant and let ξ change, we realize

$$\frac{1}{\xi f(\xi)}\frac{\mathrm{d}}{\mathrm{d}\xi}\xi\frac{\mathrm{d}f(\xi)}{\mathrm{d}\xi} = -\alpha^2 \tag{2.4-43}$$

Thus the partial differential Eq. 2.4-36 has been converted into two ordinary differential Eqs. 2.4-42 and 2.4-43.

The solution of the time-dependent part of this result is easy:

$$g(\tau) = a'\mathrm{e}^{-\alpha^2\tau} \tag{2.4-44}$$

where a' is an integration constant. The solution for $f(\xi)$ is more complicated, but straightforward:

$$f(\xi) = aJ_0(\alpha\xi) + bY_0(\alpha\xi) \tag{2.4-45}$$

where J_0 and Y_0 are Bessel functions and a and b are two more constants. From Eq. 2.4-39 we see that $b = 0$. From Eq. 2.4-38, we see that

$$0 = aJ_0(\alpha) \tag{2.4-46}$$

Because a cannot be zero, we recognize that there must be an entire family of solutions for which

$$J_0(\alpha_n) = 0 \tag{2.4-47}$$

The most general solution must be the sum of all solutions of this form found for different integral values of n:

$$\theta(\tau, \xi) = \sum_{n=1}^{\infty} (aa'_n)J_0(\alpha_n\xi)e^{-\alpha_n^2\tau} \tag{2.4-48}$$

We now use the initial condition Eq. 2.4-37 to find the remaining integration constant $(aa')_n$:

$$1 = \sum_{n=1}^{\infty} (aa')_n J_0(\alpha_n\xi) \tag{2.4-49}$$

We multiply both sides of this equation by $\xi J_0(\alpha_n\xi)$ and integrate from $\xi = 0$ to $\xi = 1$ to find (aa'). The total result is then

$$\theta = \sum_{n=1}^{\infty} \left[\frac{2}{\alpha_n J_1(\alpha_n)} \right] J_0(\alpha_n\xi)e^{-\alpha_n\tau} \tag{2.4-50}$$

or, in terms of our original variables,

$$\frac{c_1}{c_1(\text{surface})} = 1 - 2\sum_{n=1}^{\infty} \frac{e^{-D\alpha_n^2 t/R_0^2} J_0(\alpha_n r/R_0)}{\alpha_n J_1(\alpha_n r/R_0)} \tag{2.4-51}$$

This is the desired result, though the α_n must still be found from Eq. 2.4-47.

This problem clearly involves a lot of work. The serious reader should certainly work one more problem of this type to get a feel for the idea of separation of variables and for the practice of evaluating integration constants. Even the serious reader probably will embrace the ways of avoiding this work described in the next chapter.

2.5 Convection and Dilute Diffusion

In many practical problems, both diffusion and convective flow occur. In some cases, especially in fast mass transfer in concentrated solutions, the diffusion itself causes the convection. This type of mass transfer, a subject of Chapter 3, requires more complicated physical and mathematical analyses.

There is another group of important problems in which diffusion and convection can be more easily handled. These problems arise when diffusion and convection occur normal to each other. In other words, diffusion occurs in one direction, and convective

flow occurs in a perpendicular direction. Three of these problems are examined in this section. The first, steady diffusion across a thin flowing film, parallels Section 2.2; the second, diffusion into a liquid film, is a less obvious analogue to Section 2.3. These two examples tend to bracket the observed experimental behavior, and they are basic to theories relating diffusion and mass transfer coefficients (see Chapter 9).

2.5.1 Steady Diffusion Across a Falling Film

The first of the problems of concern here, sketched in Fig. 2.5-1, involves steady-state diffusion across a thin, moving liquid film. The concentrations on both sides of this film are fixed by electrochemical reactions, but the film itself is moving steadily. I have chosen this example not because it occurs often but because it is simple. I ask that readers oriented toward the practical will wait with later examples for results of greater applicability.

To solve this problem, we make three key assumptions:

(1) The liquid solution is dilute. This assumption is the axiom for this entire chapter.
(2) The liquid is the only resistance to mass transfer. This implies that the electrode reactions are fast.
(3) Mass transport is by diffusion in the z direction and by convection in the x direction. Transport by the other mechanisms is negligible.

It is the last of these assumptions that is most critical. It implies that convection is negligible in the z direction. In fact, diffusion in the z direction automatically generates convection in this direction, but this convection is small in a dilute solution. The last assumption also suggests that there is no diffusion in the x direction. There is such diffusion, but it is assumed much slower and hence much less important in the x direction than convection.
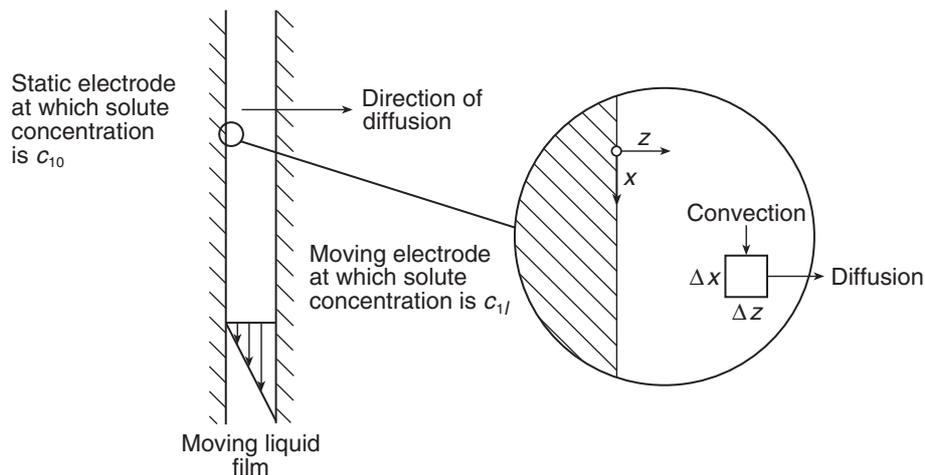

Fig. 2.5-1. Steady diffusion in a moving film. This case is mathematically the same as diffusion across a stagnant film, shown in Fig. 2.2-1. It is basic to the film theory of mass transfer described in Section 9.1.

This problem can be solved by writing a mass balance on the differential volume $W\Delta x\Delta z$, where W is the width of the liquid film, normal to the plane of the paper:

$$\begin{pmatrix} \text{solute accumulation} \\ \text{in } W\Delta x\Delta z \end{pmatrix} = \begin{pmatrix} \text{solute diffusing in at } z \text{ minus} \\ \text{solute diffusing out at } z + \Delta z \end{pmatrix}$$

$$+ \begin{pmatrix} \text{solute flowing in at } x \text{ minus} \\ \text{solute flowing out at } x + \Delta x \end{pmatrix} \quad (2.5\text{-}1)$$

or, in mathematical terms,

$$\frac{\partial}{\partial t}(c_1 W\Delta x\Delta z) = [(j_1 W\Delta x)_z - (j_1 W\Delta x)_{z+\Delta z}]$$
$$+ [(c_1 v_x W\Delta z)_x - (c_1 v_x W\Delta z)_{x+\Delta x}] \quad (2.5\text{-}2)$$

The term on the left-hand side is zero because of the steady state. The second term in square brackets on the right-hand side is also zero, because neither c_1 nor v_x changes with x. The concentration c_1 does not change with x because the film is long, and there is nothing that will cause the concentration to change in the x direction. The velocity v_x certainly varies with how far we are across the film (i.e., with z), but it does not vary with how far we are along the film (i.e., with x).

After dividing by $W\Delta x\Delta z$ and taking the limit as this volume goes to zero, the mass balance in Eq. 2.5-2 becomes

$$0 = -\frac{dj_1}{dz} \quad (2.5\text{-}3)$$

This can be combined with Fick's law to give

$$0 = D\frac{d^2 c_1}{dz^2} \quad (2.5\text{-}4)$$

This equation is subject to the boundary conditions

$$z = 0, \quad c_1 = c_{10} \quad (2.5\text{-}5)$$

$$z = l, \quad c_1 = c_{1l} \quad (2.5\text{-}6)$$

When these results are combined with Fick's law, we have exactly the same problem as that in Section 2.2. The answers are

$$c_1 = c_{10} + (c_{1l} - c_{10})\frac{z}{l} \quad (2.5\text{-}7)$$

$$j_1 = \frac{D}{l}(c_{10} - c_{1l}) \quad (2.5\text{-}8)$$

The flow has no effect. Indeed, the answer is the same as if the fluid was not flowing.

This answer is typical of many problems involving diffusion and flow. When the solutions are dilute, the diffusion and convection often are perpendicular to each other and the solution is straightforward. You may almost feel gypped; you girded yourself for

a difficult problem and found an easy one. Rest assured that more difficult problems follow.

2.5.2 Unsteady Diffusion into a Falling Film

The second problem of interest is illustrated schematically in Fig. 2.5-2. A thin liquid film flows slowly and without ripples down a flat surface. One side of this film wets the surface; the other side is in contact with a gas, which is sparingly soluble in the liquid. We want to find out how much gas dissolves in the liquid.

To solve this problem, we again go through the increasingly familiar litany: we write a mass balance as a differential equation, combine this with Fick's law, and then integrate this to find the desired result. We do this subject to four key assumptions:

(1)   The solution are always dilute.
(2)   Mass transport is by z diffusion and x convection.
(3)   The gas is pure.
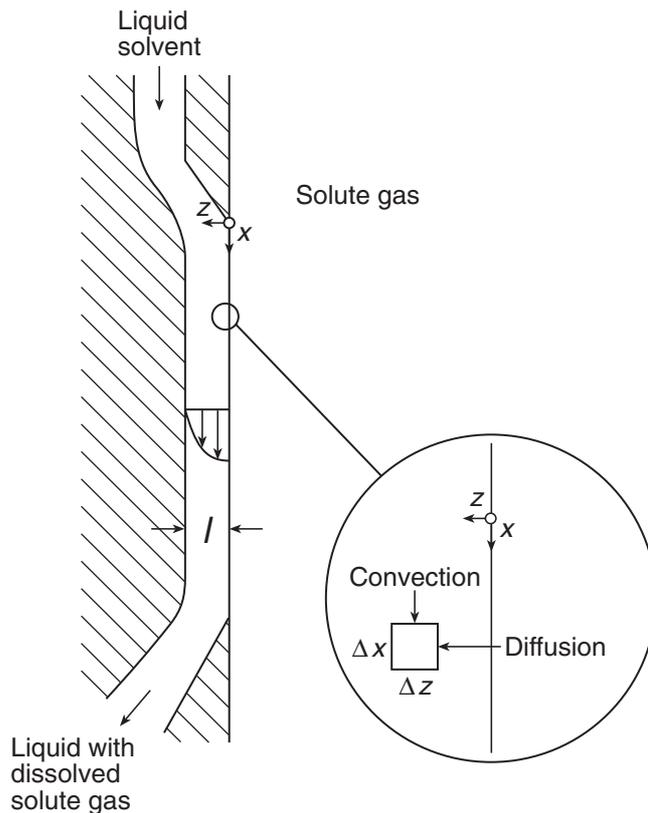(4)   The contact between gas and liquid is short.

Fig. 2.5-2. Unsteady-state diffusion into a falling film. This analysis turns out to be mathematically equivalent to free diffusion (see Fig. 2.3-2). It is basic to the penetration theory of mass transfer described in Section 11.2.

The first two assumptions are identical with those given in the earlier example. The third means that there is no resistance to diffusion in the gas phase, only in the liquid. The final assumption simplifies the analysis.

We now make a mass balance on the differential volume ($W\Delta x\Delta z$), shown in the inset in Fig. 2.5-2:

$$\begin{pmatrix} \text{mass accumulation} \\ \text{within } W\Delta x\Delta z \end{pmatrix} = \begin{pmatrix} \text{mass diffusing in at } z \text{ minus} \\ \text{mass diffusing out at } z + \Delta z \end{pmatrix}$$

$$+ \begin{pmatrix} \text{mass flowing in at } x \text{ minus} \\ \text{mass flowing out at } x + \Delta x \end{pmatrix} \tag{2.5-9}$$

where W is the width, taken perpendicular to the paper. This result is parallel to those found in earlier sections:

$$\left[\frac{\partial}{\partial t}(c_1 W\Delta x\Delta z)\right] = [(W\Delta x j_1)_z - (W\Delta j_1)_{z+\Delta z}]$$

$$+ [(W\Delta z c_1 v_x)_x - (W\Delta z c_1 v_x)_{x+\Delta x}] \tag{2.5-10}$$

When the system is at steady state, the accumulation is zero. Therefore, the left-hand side of the equation is zero. No other terms are zero, because j_1 and c_1 vary with both z and x. If we divide by the volume $W\Delta x\Delta z$ and take the limit as this volume goes to zero, we find

$$0 = -\frac{\partial j_1}{\partial z} - \frac{\partial}{\partial x}c_1 v_x \tag{2.5-11}$$

We now make two further manipulations. First, we combine this with Fick's law. Second, we set v_x equal to its maximum value, a constant. This second change reflects the assumption of short contact times. At such times, the solute barely has a chance to cross the interface, and it diffuses only slightly into the fluid. In this interfacial region, the fluid velocity reaches the maximum suggested in Fig. 2.5-2, so the use of a constant value is probably not a serious assumption. Thus the mass balance is

$$\frac{\partial c_1}{\partial(x/v_{\max})} = D\frac{\partial^2 c_1}{\partial z^2} \tag{2.5-12}$$

The left-hand side of this equation represents the solute flow out minus that in; the right-hand side is the diffusion in minus that out.

This mass balance is subject to the following conditions:

$$x = 0, \quad \text{all } z, \quad c_1 = 0 \tag{2.5-13}$$

$$x > 0, \quad z = 0, \quad c_1 = c_1(\text{sat}) \tag{2.5-14}$$

$$z = l, \quad c_1 = 0 \tag{2.5-15}$$

where $c_1(\text{sat})$ is the concentration of dissolved gas in equilibrium with the gas itself, and l is the thickness of the falling film in Fig. 2.5-2. The last of these three boundary conditions is replaced with

$$x > 0, \quad z = \infty, \quad c_1 = 0 \tag{2.5-16}$$

This again reflects the assumption that the film is exposed only a very short time. As a result, the solute can diffuse only a short way into the film. Its diffusion is then unaffected by the exact location of the other wall, which, from the standpoint of diffusion, might as well be infinitely far away.

This problem is described by the same differential equation and boundary conditions as diffusion in a semi-infinite slab. The sole difference is that the quantity x/v_{max} replaces the time t. Because the mathematics is the same, the solution is the same. The concentration profile is

$$\frac{c_1}{c_1(\text{sat})} = 1 - \text{erf}\frac{z}{\sqrt{4Dx/v_{max}}} \tag{2.5-17}$$

and the flux at the interface is

$$j_1|_{z=0} = \sqrt{Dv_{max}/\pi x}c_1(\text{sat}) \tag{2.5-18}$$

These are the answers to this problem.

These answers appear abruptly because we can adopt the mathematical results of Section 2.3. Those studying this material for the first time often find this abruptness jarring. Stop and think about this problem. It is an important problem, basic to the penetration theory of mass transfer discussed in Section 9.2. To supply a forum for further discussion, we shall now consider this problem from another viewpoint.

The alternative viewpoint involves changing the differential volume on which we make the mass balance. In the foregoing problem, we chose a volume fixed in space, a volume through which liquid was flowing. This volume accumulated no solute, so its use led to a steady-state differential equation. Alternatively, we can choose a differential volume floating along with the fluid at a speed v_{max}. The use of this volume leads to an unsteady-state differential equation like Eq. 2.3-5. Which viewpoint is correct?

The answer is that both are correct; both eventually lead to the same answer. The fixed-coordinate method used earlier is often dignified as "Eulerian," and the moving-coordinate picture is described as "Lagrangian." The difference between them can be illustrated by the situation of watching fish swimming upstream in a fast-flowing river. If we watch the fish from a bridge, we may see only slow movement, but if we watch the fish from a freely floating canoe, we realize that the fish are moving rapidly.

2.5.3 Free Convection Caused by Diffusion

A third, much more difficult, example of convection and diffusion occurs in the apparatus shown schematically in Fig. 2.5-3. The apparatus consists of two well-stirred reservoirs. The upper reservoir contains a dense solution, but the lower one is filled with less dense solvent. Because solution and solvent are miscible, solute diffuses from the upper reservoir into the lower one.

We want to know if the difference in densities between solution and solvent will cause flow. From our experience, we expect that flow will occur if the tube diameter is large. After all, gin tends to rise to the surface of a summer's gin-and-tonic without completely mixing, and vinegar falls below oil in salad dressing. Intuitively, we expect that such flows will cease if the tube diameter becomes small. More speculatively, we might guess
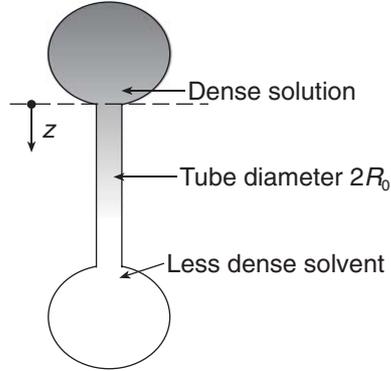
Fig. 2.5-3. Free convection in a vertical tube. A dense solution will not flow when the tube diameter is small. Diffusion damps the tendency to flow.

that whether or not flow occurs depends inversely on viscosity; high viscosity means less chance to flow.

To analyze this problem more completely, we write a mass balance on the solute, an overall mass balance on all species present, and a momentum balance to describe the flow. We then imagine small perturbations in the concentration or in the flow. If our balances indicate that these small perturbations get smaller with time, then the system is stable. If these perturbations grow with time, then the system is unstable, and free convection will occur.

We first write these balances for the unperturbed system in which no free convection exists. These are

$$0 = D\nabla^2 \bar{c}_1 - \bar{\boldsymbol{v}} \cdot \nabla \bar{c}_1 \qquad (2.5\text{-}19)$$

$$0 = -\nabla \cdot \bar{\boldsymbol{v}} \qquad (2.5\text{-}20)$$

$$0 = -\nabla p + \bar{\rho}\boldsymbol{g} \qquad (2.5\text{-}21)$$

where p is the pressure, ρ is the density, and $\mathbf{g}$ is the acceleration due to gravity; the overbars refer to the unperturbed system. The solution of these equations for the situation shown in Fig. 2.5-3 is that expected:

$$\frac{\bar{c}_1 - c_{10}}{c_{1l} - c_{10}} = \frac{\bar{\rho} - \rho_0}{\rho_l - \rho_0} = \frac{z}{l} \qquad (2.5\text{-}22)$$

$$\bar{\boldsymbol{v}} = 0 \qquad (2.5\text{-}23)$$

$$\bar{p} = p_0 + \int_0^z \bar{\rho}\boldsymbol{g}\mathrm{d}z \qquad (2.5\text{-}24)$$

Although we do not need the details of these solutions in the following, I find them reassuring.

The corresponding equations for an incompressible but perturbed system are

$$\frac{\partial c_1}{\partial t} = D\mathbf{V}^2 c_1 - \mathbf{v} \cdot \mathbf{V}c_1 \tag{2.5-25}$$

$$0 = -\mathbf{V} \cdot \mathbf{v} \tag{2.5-26}$$

$$\rho \frac{\partial \mathbf{v}}{\partial t} = \mu \mathbf{V}^2 \mathbf{v} - \mathbf{V}p + \rho \mathbf{g} \tag{2.5-27}$$

where μ is the viscosity. We now rewrite these relations in terms of the perturbations themselves. For example, for the mass balance, we define

$$c_1 = c_1 + c_1' \tag{2.5-28}$$

$$\mathbf{v} = \mathbf{v}' \tag{2.5-29}$$

where the primes signify perturbations from stable values of Eqs. 2.5-22 through 2.5-24. Remember that the stable value of the velocity is zero. We then insert these definitions in Eq. 2.5-25, subtract Eq. 2.5-19, and neglect terms involving the squares of perturbations:

$$\frac{\partial c_1'}{\partial t} = D\mathbf{V}^2 c_1' - v_z' \frac{d\bar{c}_1}{dz} \tag{2.5-30}$$

Equation 2.5-30 is subject to the boundary condition that the tube walls are solid:

$$r = R_0, \quad \frac{\partial c_1'}{\partial r} = 0 \tag{2.5-31}$$

Similar arguments lead to a modified momentum balance:

$$\left(\mu \mathbf{V}^2 - \bar{\rho} \frac{\partial}{\partial t} \right) \mathbf{v}' = -\mathbf{V}p' + \rho'\mathbf{g} = -\mathbf{V}p' + \mathbf{g}\beta c_1' \tag{2.5-32}$$

in which the primed quantities are again perturbations and $\beta (= \partial\rho/\partial c_1)$ describes the density increase caused by the solute. Equation 2.5-32 is subject to the condition

$$r = R_0, \quad v_z' = 0 \tag{2.5-33}$$

This says that there is no vertical flow at the wall.

Equations 2.5-30 and 2.5-32 must now be solved simultaneously. A simple solution requires two chief assumptions. The first is that the time derivatives in these equations can be neglected; this is equivalent to the assertion that marginal stability can exist. The second assumption is that the perturbations have their largest effects normal to the z direction; this implies that any convection cells that occur will be long. I find these assumptions reasonable, but hardly obvious. Because they are justified by experiment, they are tributes to the genius of G. I. Taylor (1954), who had the gall to present the answers to this problem without derivation.

Taylor found that for the perturbations to grow, the Rayleigh number Ra must be

$$Ra = \left(\frac{gR_0^4}{\mu D} \right) \frac{\partial \rho}{dz} > 67.94 \tag{2.5-34}$$

This value corresponds to the case in which solution is falling down one side of the tube and solvent is rising through the other side.

This critical value of the Rayleigh number provides the limit for the stability in the vertical tube. When the density difference is small enough so that the Rayleigh number is less than 67.94, free convection will not occur. When the density difference is so large that the Rayleigh number exceeds 67.94, then free convection does occur. This result also supports our intuitive speculations at the beginning of this section. The chances for free convection decrease sharply as the tube diameter decreases. They also decrease as the viscosity or the diffusion coefficient increases. In every case, the change of a given variable required to spark free convection can be predicted from this critical Rayleigh number.

2.6 A Final Perspective

This chapter is very important, a keystone of this book. It introduces Fick's law for dilute solutions and shows how this law can be combined with mass balances to calculate concentrations and fluxes. The mass balances are made on thin shells. When these shells are very thin, the mass balances become the differential equations necessary to solve the various problems. Thus the bricks from which this chapter is built are largely mathematical: shell balances, differential equations, and integrations in different coordinate systems.

However, we must also see a different and broader blueprint based on physics, not mathematics. This blueprint includes the two limiting cases of diffusion across a thin film and diffusion in a semi-infinite slab. Most diffusion problems fall between these two limits. The first, the thin film, is a steady-state problem, mathematically easy and sometimes physically subtle. The second, the unsteady-state problem of the thick slab, is harder to calculate mathematically and is the limit at short times.

In many cases, we can use a simple criterion to decide which of the two central limits is more closely approached. This criterion hinges on the magnitude of the Fourier number

$$\frac{(\text{length})^2}{\left(\dfrac{\text{diffusion}}{\text{coefficient}}\right)(\text{time})}$$

This variable is the argument of the error function of the semi-infinite slab, it determines the standard deviation of the decaying pulse, and it is central to the time dependence of diffusion into the cylinder. In other words, it is a key to all the foregoing unsteady-state problems. Indeed, it can be easily isolated by dimensional analysis.

This variable can be used to estimate which limiting case is more relevant. If it is much larger than unity, we can assume a semi-infinite slab. If it is much less than unity, we should expect a steady state or an equilibrium. If it is approximately unity, we may be forced to make a fancier analysis. For example, imagine that we are testing a membrane for an industrial separation. The membrane is 0.01 centimeters thick, and the diffusion coefficient in it is 10^{-7} cm^2/sec. If our experiments take only 10 seconds, we have an unsteady-state problem like the semi-infinite slab; if they take three hours, we approach a steady-state situation.

In unsteady-state problems, this same variable may also be used to estimate how far or how long mass transfer has occurred. Basically, the process is significantly advanced

when this variable equals unity. For example, imagine that we want to guess how far gasoline has evaporated into the stagnant air in a glass-fiber filter. The evaporation has been going on about 10 minutes, and the diffusion coefficient is about 0.1 cm^2/sec. Thus

$$\frac{(\text{length})^2}{(0.1\,\text{cm}^2/\text{sec})(600\text{ sec})} = 1; \text{ length} = 8\,\text{cm}$$

Alternatively, suppose we find that hydrogen has penetrated about 0.1 centimeter into nickel. Because the diffusion coefficient in this case is about 10^{-8} cm^2/sec, we can estimate how long this process has been going on:

$$\frac{(10^{-1}\text{cm}^2)}{(10^{-8}\,\text{cm}^2/\text{sec})(\text{time})} = 1; \text{ time} = 10\,\text{d}$$

This sort of heuristic argument is often successful.

A second important perspective between these two limiting cases results from comparing their interfacial fluxes given in Eqs. 2.2-10 and 2.3-18:

$$j_1 = \frac{D}{l}\Delta c_1 \quad \text{(thin film)}$$

$$j_1 = \sqrt{D/\pi t}\Delta c_1 \text{ (thick slab)}$$

Although the quantities D/l and $(D/\pi t)^{1/2}$ vary differently with diffusion coefficients, they both have dimensions of velocity; in fact, in the life sciences, they sometimes are called "the velocity of diffusion." In later chapters, we shall discover that these quantities are equivalent to the mass transfer coefficients used at the beginning of this book.

Questions for Discussion

1. If the concentration difference for diffusion across a thin film is doubled, what happens to the flux?
2. If it is doubled for diffusion into a semi-infinite slab, what happens to the flux?
3. If the diffusion coefficient across a thin film is doubled, what happens to the flux?
4. If it is doubled for diffusion into a semi-infinite slab, what happens to the flux?
5. What is the average flux into a semi-infinite slab over a time t_1?
6. What are some different ways in which an effective diffusion coefficient in a porous medium could be defined?
7. Explain Fig. 2.2-2 to someone without scientific training.
8. Explain why the funnel data in Fig. 2.1-3 curve downwards.
9. Imagine that you have a thin film separating two identical well-stirred solutions. At time zero, the solute concentration in one solution is doubled. Sketch the concentration profiles in the film vs. position and time.
10. Estimate the flux in the previous question at a very short time.
11. Estimate it at a very long time.
12. How would the width of a spreading pulse change if the diffusion coefficient doubled?

13. Would the steady flux across a thin film increase if there was fast reaction producing a mobile product?

14. Imagine you have two films clamped together. The diffusion coefficient in one film is constant, but that in the other depends on concentration. If you reverse the concentration difference, the flux will reverse. Will its magnitude change?

Problems

1. Water evaporating from a pond does so as if it were diffusing across an air film 0.15 cm thick. The diffusion coefficient of water in 20 °C air is about 0.25 cm^2/sec. If the air out of the film is fifty percent saturated, how fast will the water level drop in a day? *Answer:* 1.24 cm/d.

2. In 1765, Benjamin Franklin made a variety of experiments on the spreading of oils on the pond in Clapham Common, London. Franklin estimated the thickness of the oil layers to be about 25 Å. Many more recent scientists have tried to use similar layers of fatty acids and alcohols to retard evaporation from ponds and reservoirs in arid regions. The monolayers used today usually are characterized by a resistance around 2 sec/cm. Assuming that they are the thickness of Franklin's layer and that they can dissolve up to 1.8% water, estimate the diffusion coefficient across the monolayers. *Answer:* $7 \cdot 10^{-6}$ cm^2/sec.

3. The diffusion coefficient of NO_2 into stagnant water can be measured with the apparatus shown below. Although the water is initially pure, the mercury drop moves to show that 0.82 cm^3 of NO_2 is absorbed in 3 minutes. The gas–liquid interface has an area of 36.3 cm^2, the pressure is 0.93 atm, the temperature is 16 °C, and the Henry's law constant is 37,000 cm^3 atm/mol. What is the desired diffusion coefficient? (J. Kopinsky) *Answer:* $5 \cdot 10^{-6}$ cm^2/sec.
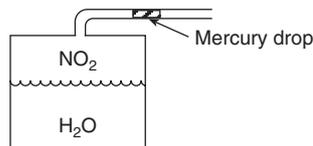
4. About 85.6 cm^2 of a flexible polymer film 0.051 cm thick is made into a bag, filled with distilled water, and hung in an oven at 35 °C and 75% relative humidity. The bag is weighed, giving the following data:

| Time (d)	Bag weight (g)
0	14.0153
1	13.9855
4	13.9104
7	13.8156
8	13.7710
12	13.6492
14	13.5830
16	13.5256

What is the permeability (DH) of the polymer film? (R. Contravas) *Answer:* $2.2 \cdot 10^5$ cm^2/sec.

5. Diaphragm cells are frequently calibrated by allowing 1-M potassium chloride to diffuse into pure water. The average diffusion coefficient in this case is $1.859 \cdot 10^{-5}$ cm^2/sec. Your cell has compartment volumes of 42.3 cm^3 and 40.8 cm^3; the diaphragm is a glass frit 2.51 cm in diameter, 0.16 cm thick, and of porosity 0.34. In one calibration experiment, the concentration difference at 36 hr 6 min is 49.2% of that originally present. (a) What is the cell's calibration constant? *Answer:* 0.294 cm^{-2}. (b) What is the effective length of the diaphragm's pores? *Answer:* 0.28 cm. (c) The current pores are about $2 \cdot 10^{-4}$ cm in diameter. What is the effect of increasing the pore diameter ten times at constant porosity?

6. Diffusion coefficients in gases can be measured by injecting a solute gas into a solvent gas in laminar plug flow and measuring the concentration with a thermistor placed downstream. The concentration downstream is given by

$$c_1 = \frac{Q}{4\pi Dz} e^{-r^2 v/2Dz}$$

where Q is the solute injection rate, z is the distance downstream, r is the distance away from the z axis, and v is the gas flow. One series of measurements involves the diffusion of helium in nitrogen at 25 °C and 1 atm. In one particular measurement, the maximum concentration of helium is 0.48 wt% when z is 1.031 cm and Q is 0.045 cm^3/sec. What is the diffusion coefficient? (H. Beesley) *Answer:* 0.11 cm^2/sec.

7. Low-carbon steel can be hardened for improved wear resistance by carburizing. Steel is carburized by exposing it to a gas, liquid, or solid that provides a high carbon concentration at the surface. The figure below [D. S. Clark and W. R. Varney, *Physical Metallurgy for Engineers*. Princeton, N.J.: Van Nostrand (1962)] shows carbon content versus depth in steel carburized at 930 °C. Estimate D from this graph, assuming diffusion without reaction between carbon and iron. (H. Beesley) *Answer:* $5.3 \cdot 10^{-7}$ cm^2/sec.
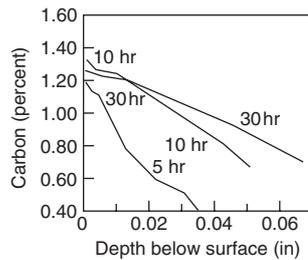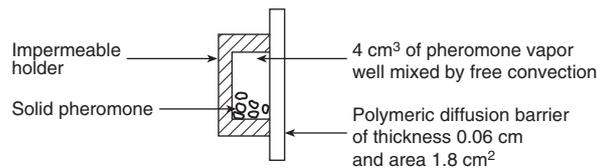

8. The twin-bulb method of measuring diffusion is shown below. The bulbs, which are stirred and of equal volume, initially contain binary gas mixtures of different compositions. At time zero, the valve is opened; at time t, the valve is closed, and the bulk contents are analyzed. Explain how this information can be used to calculate the diffusion coefficient in this binary gas mixture.
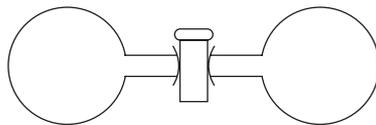
9. Find the steady-state flux out of a pipe with a porous wall. The pipe has an inner radius R_i and an outer radius R_o. The solute has a fixed, finite concentration c_{1i} inside of the pipe, but is essentially at zero concentration outside. As a result, solute diffuses through the wall with a diffusion coefficient D. When you have found the result, compare it with the results for steady-state diffusion across a thin slab and away from a dissolving sphere. *Answer:* $Dc_{1i}[R_o \ln(R_o/R_i)]^{-1}$.

10. Controlled release is important in agriculture, especially for insect control. One common example involves the pheromones, sex attractants released by insects. If you mix this attractant with an insecticide, you can wipe out all of one sex of a particular insect pest. A device for releasing one pheromone is shown schematically below. This pheromone does not subline instantaneously, but at a rate of

$$r_0 = 6 \cdot 10^{-17}[1 - (1.10 \cdot 10^7 \text{cm}^3/\text{mol})c_1] \text{ mol/sec}$$

where c_1 is the concentration in the vapor. The permeability of this material through the polymer (DH) is $1.92 \cdot 10^{-12}$ cm^2/sec. The concentration of pheromone outside of the device is essentially zero. (a) What is the concentration (moles per cubic centimeter) of pheromone in the vapor? (b) How fast is the pheromone released by this device?

Impermeable holder

Solid pheromone

4 cm³ of pheromone vapor well mixed by free convection

Polymeric diffusion barrier of thickness 0.06 cm and area 1.8 cm²

11. Antique glass objects can be dated by measuring the amount of hydration near the object's surface. This amount can be measured using ^{15}N nuclear magnetic resonance [W. A. Lanford, *Science,* **196,** 975 (1977)]. Derive equations for the total amount of hydration, assuming that water reacts rapidly and reversibly with the glass to produce an immobile hydrate. Discuss how this amount can provide a measure of the age of the object.

12. One type of packaging film with thickness "*l*" has an immobile sacrificial reagent at initial concentration c_{20} within the wall of the package. A solute at concentration c_{10} outside of the film, like water, oxygen, or radioactive cesium, diffuses into the film, reacting irreversibly with the sacrificial reagent as it goes. The product may be mobile or immobile; since the reaction is irreversible, it does not matter. This reaction shows the solute's penetration across the film. (a) Write mass balances for the solute and the immobile reagent. (b) Write possible initial and boundary conditions for these equations. (c) If the reaction were infinitely fast, how would your equations change?

13. Researchers in microelectronics have found that a slight scratch on the surface of gallium arsenide causes a zinc dopant to diffuse into the arsenide. Apparently, this occurs because the scratch increases crystal defects and hence the local diffusion coefficient. When these devices are later baked at 850 °C, the small pulse may spread, for its diffusion coefficient at this high temperature is about 10^{-11} cm^2/sec. If it spreads enough to increase the zinc concentration to 10 percent of the maximum at

$4 \cdot 10^{-4}$ cm away from the scratch, the device is ruined. How long can we bake the device? (S. Balloge) *Answer:* 30 min.

14. Adolf Fick made the experiments required to determine the diffusion coefficient using the equipment shown in Fig. 2.1-3. In these devices, he assumed that the salt concentration reached saturation in the bottom and that it was always essentially zero in the large solvent bath. As a result, the concentration profiles eventually reached steady state. Calculate these profiles.

15. Consider a layer of bacteria contained between two semipermeable membranes that allow the passage of a chemical solute S, but do not allow the passage of bacteria. The movement of the bacteria B is described with a flux equation roughly parallel to a diffusion equation:

$$j_{\mathrm{B}} = -D_0 \frac{\mathrm{d}}{\mathrm{d}z}[\mathrm{B}] + \chi[\mathrm{B}] \frac{\mathrm{d}}{\mathrm{d}z}[\mathrm{S}]$$

where D_0 and χ are constant transport coefficients. In other words, the bacterial flux is affected by [S], although the bacteria neither produce or consume S. If the concentrations of S are maintained at $[\mathrm{S}]_0$ and 0 at the upper and lower surfaces of the bacterial suspension, (a) determine $[\mathrm{S}](z)$, and (b) determine $[\mathrm{B}](z)$.

16. Extraction of sucrose from food materials is often correlated in terms of diffusion coefficients. The diffusion coefficients can be calculated assuming short times and an infinite slab:

$$D = \left(\frac{\pi}{4t}\right)\left(\frac{M}{c_{10}}\right)^2$$

where M is the total extracted per area and c_{10} is the sucrose concentration at saturation. However, the diffusion coefficients found are not constant, as shown below (H. G. Schwartzberg and R. Y. Chao, *Food Technology,* Feb. 1982, p. 73). The reason the diffusion coefficient is not constant is not because of the failure of the approximation of an infinite slab; it reflects the fact that beets and cane are not homogeneous. Instead, they have a network of cells connected by vascular channels. Diffusion across the cell wall is slow, and it dominates behavior in thin slices; diffusion through vascular channels is much faster and supplements the flux for thick slices. Develop equations
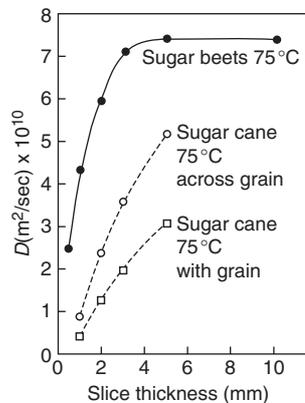
that justify these qualitative arguments. These equations will contain the diffusion coefficient across cell walls D_w, the diffusion coefficient in channels D_c, and the fraction of channels ε.

Further Reading

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