

2.3 Unsteady Diffusion in a Semiinfinite Slab

We now turn to a discussion of diffusion in a semiinfinite slab. We consider a volume of solution that starts at an interface and extends a very 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 functions of position and time.

This type of mass transfer is often called free diffusion (Gosting, 1956) simply because this is briefer than "unsteady diffusion in a semiinfinite 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 semiinfinite slabs. Thus we might conclude that this semiinfinite case is not common. That conclusion would be a serious error.

The important case of an 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 semiinfinite 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, diffusion will proceed as if the slab is infinite; at long times, it will occur as if the slab is thin. By focusing on these limits, we can bracket the possible physical responses to different diffusion problems.

2.3.1 The Physical Situation

The diffusion in a semiinfinite 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 $A\Delta z$:

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

In mathematical terms, this is

$$\frac{\partial}{\partial t}(A\Delta z c_1) = A(j_1|_z - j_1|_{z+\Delta z}) \quad (2.3-2)$$

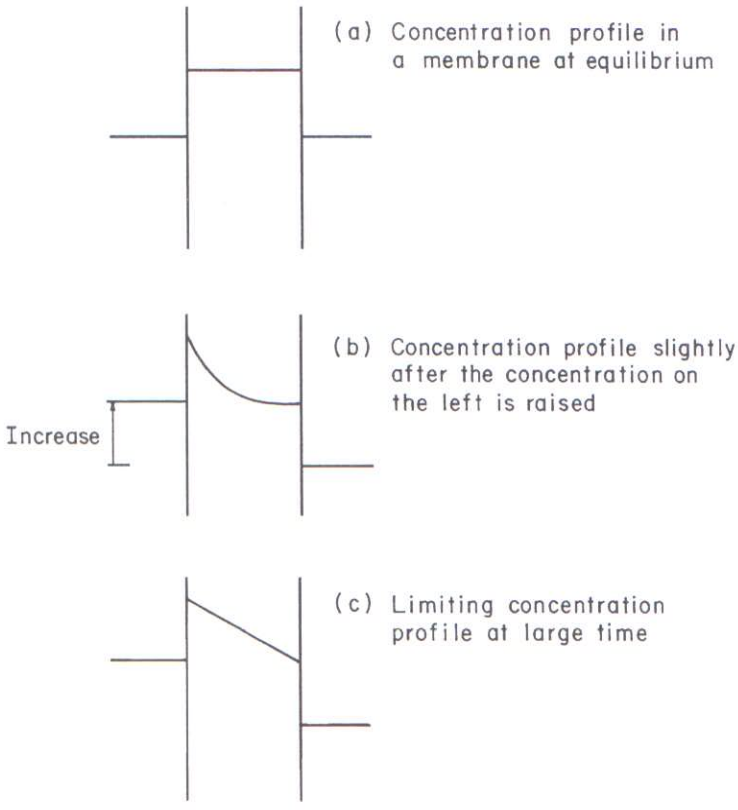


Fig. 2.3-1. Unsteady- versus steady-state diffusion. At small times, diffusion will occur only near the left-hand side of the membrane. As a result, at these small times, the diffusion will be the same as if the membrane was infinitely thick. At large times, the results become those in the thin film.

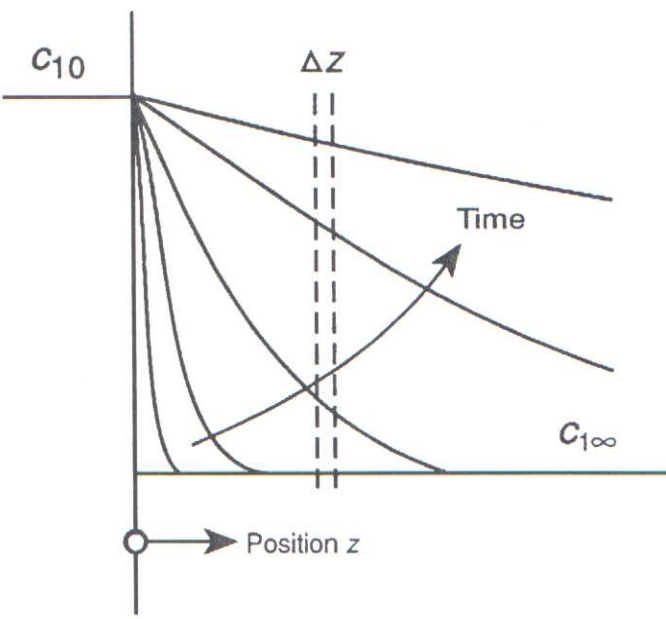


Fig. 2.3-2. Free diffusion. In this case, the concentration at the left is suddenly increased to a higher constant value. Diffusion occurs in the region to the right. This case and that in Fig. 2.2-1 are basic to most diffusion problems.

We divide by $A\Delta z$ to find

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

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

$$\frac{\partial c_1}{\partial t} = - \frac{\partial j_1}{\partial z} \quad (2.3-4)$$

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

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

This equation is sometimes called Fick's second law, and it is often referred to as one example of a "diffusion equation." In this case, it is subject to the following conditions:

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

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

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

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 Boltzman's tortured imagination (Boltzman, 1894).

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

$$\zeta = \frac{z}{\sqrt{4Dt}} \quad (2.3-9)$$

The differential equation can then be written as

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

or

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

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,

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

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

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

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

$$\frac{dc_1}{d\zeta} = ae^{-\zeta^2} \quad (2.3-14)$$

where a is an integration constant. A second integration and use of the boundary condition gives

$$\frac{c_1 - c_{10}}{c_{1\infty} - c_{10}} = \text{erf } \zeta \quad (2.3-15)$$

where

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

which 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:

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

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

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

This flux is the value at the particular time t and not that averaged over time. This distinction will be important in Chapter 13.

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 $z \geq 0$ there was a swollen gel, and when $z < 0$ there was a highly dilute solution.

However, 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:

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