

where c, ρ have their usual meaning for the fluid. Correspondingly for diffusion we have

$$V \partial C / \partial t = D \partial C / \partial x, \quad x = 0.$$

In addition, θ_s will be the temperature just within the surface but the two concentrations may be related by some isotherm equation. Care is needed with algebraic signs as in the previous section.

(f) The conservation principle applied at the interface between two media of different properties leads immediately to boundary conditions

$$\theta_1 = \theta_2, \quad K_1 \partial \theta_1 / \partial x = K_2 \partial \theta_2 / \partial x$$

in heat flow and

$$C_1 = PC_2 + Q, \quad D_1 \partial C_1 / \partial x = D_2 \partial C_2 / \partial x,$$

in diffusion, where the suffices 1 and 2 denote the two media and P and Q are constant.

(g) If heat is produced in a medium, e.g. as a result of an exothermic reaction, at a rate A per unit volume, this must be added to the right side of eqn. (1.20), which can be written

$$c\rho \frac{\partial \theta}{\partial t} = K \frac{\partial^2 \theta}{\partial x^2} + A.$$

The diffusion equation (1.4) must be similarly modified if the diffusing substance is created or removed as diffusion proceeds. We identify A as the rate of creation per unit volume and put $c\rho = 1$, $K = D$ as usual.

(h) Problems in heat flow may involve moving boundaries on which phase changes occur, accompanied by the absorption or liberation of latent heat. In the first case, the relevant feature is that latent heat is removed instantaneously from the heat-conduction process, in which it takes no further part. The diffusion counterpart is the immobilizing of diffusing molecules on fixed sites or in holes. The velocity of the transformation boundary at $X(t)$ is related to the difference between the rate of heat arriving and leaving it by conduction by a condition

$$-K_1 \partial \theta_1 / \partial x + K_2 \partial \theta_2 / \partial x = L\rho dX/dt,$$

where L is the latent heat per unit mass and ρ the density, assuming no volume changes accompany the transformation. The condition in a diffusion problem follows by writing $\theta = C$, $D = K$, $\rho = 1$ as usual, and L becomes the capacity of the immobilizing sites in unit volume for trapped diffusing molecules.

Useful collections of mathematical solutions of the diffusion equations are to be found in books by Barrer (1951), Jost (1952), and Jacobs (1967). Jacob's solutions are of particular interest to biologists and biophysicists.

2

METHODS OF SOLUTION WHEN THE DIFFUSION COEFFICIENT IS CONSTANT

2.1. Types of solution

GENERAL solutions of the diffusion equation can be obtained for a variety of initial and boundary conditions provided the diffusion coefficient is constant. Such a solution usually has one of two standard forms. Either it is comprised of a series of error functions or related integrals, in which case it is most suitable for numerical evaluation at small times, i.e. in the early stages of diffusion, or it is in the form of a trigonometrical series which converges most satisfactorily for large values of time. When diffusion occurs in a cylinder the trigonometrical series is replaced by a series of Bessel functions. Of the three methods of solution described in this chapter, the first two illustrate the physical significance of the two standard types of solution. The third, employing the Laplace transform, is essentially an operator method by which both types of solution may be obtained. It is the most powerful of the three, particularly for more complicated problems. The methods are presented here as simply as possible. The fuller treatments necessary to make the discussion mathematically rigorous are to be found in works on heat conduction, e.g. Carslaw and Jaeger (1959).

2.2. Method of reflection and superposition

2.2.1. Plane source

It is easy to see by differentiation that

$$C = \frac{A}{t^{1/2}} \exp(-x^2/4Dt), \quad (2.1)$$

where A is an arbitrary constant, is a solution of

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (2.2)$$

which is the equation for diffusion in one dimension when D is constant. The expression (2.1) is symmetrical with respect to $x = 0$, tends to zero as x approaches infinity positively or negatively for $t > 0$, and for $t = 0$ it vanishes everywhere except at $x = 0$, where it becomes infinite. The total amount of substance M diffusing in a cylinder of infinite length and unit

cross-section is given by

$$M = \int_{-\infty}^{\infty} C dx, \quad (2.3)$$

and if the concentration distribution is that of expression (2.1) we see, on writing

$$x^2/4Dt = \xi^2, \quad dx = 2(Dt)^{1/2} d\xi, \quad (2.4)$$

that

$$M = 2AD^{1/2} \int_{-\infty}^{\infty} \exp(-\xi^2) d\xi = 2A(\pi D)^{1/2}. \quad (2.5)$$

Expression (2.5) shows that the amount of substance diffusing remains constant and equal to the amount originally deposited in the plane $x = 0$. Thus, on substituting for A from (2.5) in eqn (2.1), we obtain

$$C = \frac{M}{2(\pi Dt)^{1/2}} \exp(-x^2/4Dt), \quad (2.6)$$

and this is therefore the solution which describes the spreading by diffusion of an amount of substance M deposited at time $t = 0$ in the plane $x = 0$. Fig. 2.1 shows typical distributions at three successive times.

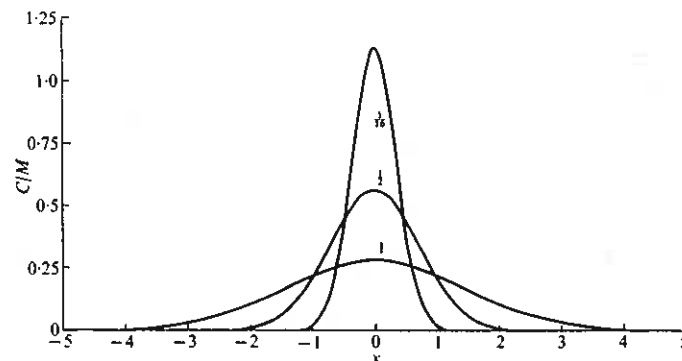


FIG. 2.1. Concentration-distance curves for an instantaneous plane source. Numbers on curves are values of Dt .

2.2.2. Reflection at a boundary

Expression (2.6) can be used to build up solutions of other problems in linear flow by introducing the concept of reflection at a boundary. Thus, in

the problem just considered, half the diffusing substance moves in the direction of positive x and the other half along negative x . If, however, we have a semi-infinite cylinder extending over the region $x > 0$ and with an impermeable boundary at $x = 0$, all the diffusion occurs in the direction of positive x . We can consider the solution for negative x to be reflected in the plane $x = 0$ and superposed on the original distribution in the region $x > 0$. Since the original solution was symmetrical about $x = 0$ the concentration distribution for the semi-infinite cylinder is given by

$$C = \frac{M}{(\pi Dt)^{1/2}} \exp(-x^2/4Dt). \quad (2.7)$$

This procedure of reflection and superposition is mathematically sound, for reflection at $x = 0$ means the adding of two solutions of the diffusion equation. Since this equation is linear the sum of the two solutions is itself a solution, and we see that (2.7) satisfies the condition that the total amount of diffusing substance remains constant at M . Furthermore, the condition to be satisfied at the impermeable boundary is

$$\partial C / \partial x = 0, \quad x = 0, \quad (2.8)$$

since this is the mathematical condition for zero flow across a boundary. As $\partial C / \partial x$ is zero at $x = 0$ in the original solution (2.6), it is clearly still zero after reflection and superposition.

2.2.3. Extended initial distributions

So far we have considered only cases in which all the diffusing substance is concentrated initially in a plane. More frequently in practice, however, the initial distribution occupies a finite region and we have an initial state such as that defined by

$$C = C_0, \quad x < 0, \quad C = 0, \quad x > 0, \quad t = 0. \quad (2.9)$$

This is the initial distribution, for example, when a long column of clear water rests on a long column of solution, or when two long metal bars are placed in contact end to end. The solution to such a problem is readily deduced by considering the extended distribution to be composed of an infinite number of line sources and by superposing the corresponding infinite number of elementary solutions. With reference to Fig. 2.2, consider the diffusing substance in an element of width $\delta\xi$ to be a line source of strength $C_0 \delta\xi$. Then, from (2.6) the concentration at point P , distance ξ from the element, at time t is

$$\frac{C_0 \delta\xi}{2(\pi Dt)^{1/2}} \exp(-\xi^2/4Dt),$$

and the complete solution due to the initial distribution (2.9) is given by

summing over successive elements $\delta\xi$, i.e. by

$$C(x, t) = \frac{C_0}{2(\pi Dt)^{1/2}} \int_x^\infty \exp(-\xi^2/4Dt) d\xi = \frac{C_0}{\pi^{1/2}} \int_{x/2\sqrt{Dt}}^\infty \exp(-\eta^2) d\eta, \quad (2.10)$$

where $\eta = \xi/2\sqrt{Dt}$.

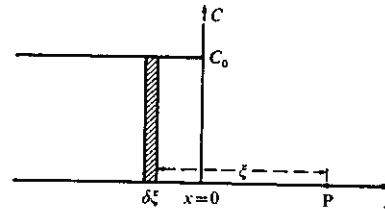


FIG. 2.2. Extended initial distribution.

A standard mathematical function, of which extensive tables are available, is the error function, usually written as $\text{erf } z$, where

$$\text{erf } z = \frac{2}{\pi^{1/2}} \int_0^z \exp(-\eta^2) d\eta. \quad (2.11)$$

This function has the properties

$$\text{erf}(-z) = -\text{erf } z, \quad \text{erf}(0) = 0, \quad \text{erf}(\infty) = 1, \quad (2.12)$$

and hence, since

$$\begin{aligned} \frac{2}{\pi^{1/2}} \int_x^\infty \exp(-\eta^2) d\eta &= \frac{2}{\pi^{1/2}} \int_0^\infty \exp(-\eta^2) d\eta - \frac{2}{\pi^{1/2}} \int_0^x \exp(-\eta^2) d\eta \\ &= 1 - \text{erf } z = \text{erfc } z, \end{aligned} \quad (2.13)$$

where erfc is referred to as the error-function complement, the solution (2.10) of the diffusion problem is usually written in the form

$$C(x, t) = \frac{1}{2} C_0 \text{erfc} \frac{x}{2\sqrt{Dt}}. \quad (2.14)$$

Convenient tables of the error function are those of the Works Project Association (1941) and shorter tables are to be found, for example, in Milne-Thomson and Comrie (1944). Table 2.1, taken from Carslaw and Jaeger (1959), is sufficient for many practical purposes. The form of the concentration distribution is shown in Fig. 2.3. It is clear from (2.14) that $C = \frac{1}{2} C_0$ at $x = 0$ for all $t > 0$.

The error function therefore enters into the solution of a diffusion problem as a consequence of summing the effect of a series of line sources, each yielding an exponential type of distribution.

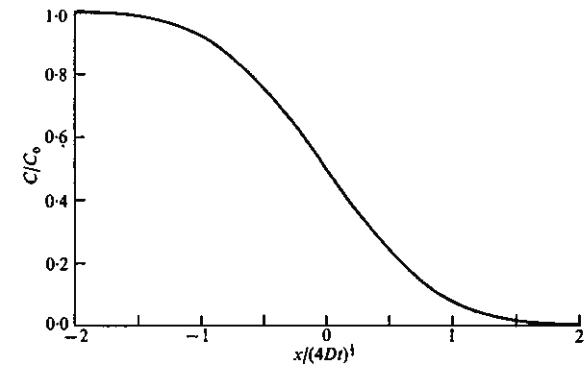


FIG. 2.3. Concentration-distance curve for an extended source of infinite extent.

In the same way, we can study the diffusion of a substance initially confined in the region $-h < x < +h$ as in Fig. 2.4. Here the integration is from $x-h$ to $x+h$ instead of from x to ∞ as in (2.10), leading immediately to the result

$$C = \frac{1}{2} C_0 \left\{ \text{erf} \frac{h-x}{2\sqrt{Dt}} + \text{erf} \frac{h+x}{2\sqrt{Dt}} \right\}. \quad (2.15)$$

The concentration distribution at successive times is shown in Fig. 2.4. It is clear that the system can be cut in half by a plane at $x = 0$ without affecting

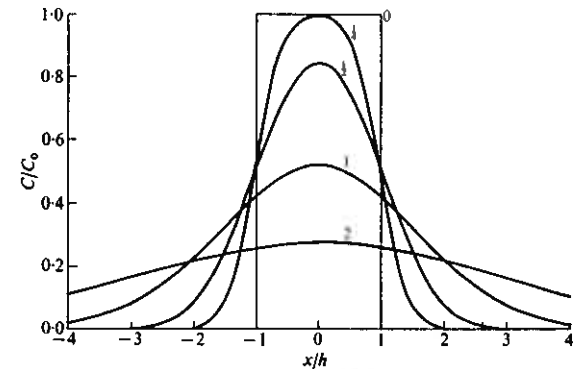


FIG. 2.4. Concentration-distance curves for an extended source of limited extent. Numbers on curves are values of $(Dt/h^2)^{1/2}$.