

THE MATHEMATICS OF DIFFUSION

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PREFACE TO SECOND EDITION

IN preparing this second edition I have tried to incorporate as much new material as possible but to preserve the character of the original volume. The book contains a collection of mathematical solutions of the differential equations of diffusion and methods of obtaining them. They are discussed against a background of some of the experimental and practical situations to which they are relevant. Little mention is made of molecular mechanisms, and I have made only fleeting excursions into the realms of irreversible thermodynamics. These I hope are self-explanatory. A number of general accounts of the subject are already available, but very few mathematical solutions of the equations of non-equilibrium thermodynamics have been obtained for practical systems.

During the last 15–20 years the widespread occurrence of concentration-dependent diffusion has stimulated the development of new analytical and numerical solutions. The time-lag method of measuring diffusion coefficients has also been intensively investigated and extended. Similarly, a lot of attention has been devoted to moving-boundary problems since the first edition was published. These and other matters have now been included by extensive revision of several chapters. Also, the chapter dealing with the numerical solution of the diffusion equations has been completely rewritten and brought up to date. It seems unbelievable now that most of the calculations in the first edition were carried out on desk calculating machines.

Two entirely new chapters have been added. In one are assembled some of the mathematical models of non-Fickian or anomalous diffusion occurring mainly in solvent–polymer systems in the glassy state. The other attempts a systematic review of diffusion in heterogeneous media, both laminates and particulates. A succession of improved solutions are described to the problem of diffusion in a medium in which are embedded discrete particles with different diffusion properties.

I have resisted the temptation to lengthen appreciably the earlier chapters. The enlarged edition of Carslaw and Jaeger's book *Conduction of heat in solids* contains a wealth of solutions of the heat-flow equations for constant heat parameters. Many of them are directly applicable to diffusion problems, though it seems that some non-mathematicians have difficulty in making the necessary conversions. For them I have included a brief 'translator's guide'. A few new solutions have been added, however, some of them in the context in which they arose, that is the measurement of diffusion coefficients.

I should like to express my appreciation to the Vice Chancellor and Council of Brunel University for so readily agreeing to my application for extended leave without which I could not have undertaken the preparation of

to Miss D. Eldridge who, by patient and skilful typing, transformed an almost illegible manuscript into a very clear typescript for the printer. I should also like to thank the following who readily gave permission to use material from various publications: Professor R. M. Barrer, Mr. M. B. Coyle, Dr. P. V. Danckwerts, Dr. L. D. Hall, Dr. P. S. H. Henry, Professor J. C. Jaeger, Dr. G. S. Park, Dr. R. H. Stokes, Dr. C. Wagner, and the publishers of the following journals, *British Journal of Applied Physics*, *Journal of Chemical Physics*, *Journal of Metals*, *Journal of Scientific Instruments*, *Philosophical Magazine*, *Proceedings of the Physical Society*, *Transactions of the Faraday Society*. Finally, it is a pleasure to thank those members of the staff of the Clarendon Press who have been concerned with the production of this book for the kindness and consideration they have shown to me.

Maidenhead
December 1955

J. C.

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THE DIFFUSION EQUATIONS

1.1. The diffusion process

DIFFUSION is the process by which matter is transported from one part of a system to another as a result of random molecular motions. It is usually illustrated by the classical experiment in which a tall cylindrical vessel has its lower part filled with iodine solution, for example, and a column of clear water is poured on top, carefully and slowly, so that no convection currents are set up. At first the coloured part is separated from the clear by a sharp, well-defined boundary. Later it is found that the upper part becomes coloured, the colour getting fainter towards the top, while the lower part becomes correspondingly less intensely coloured. After sufficient time the whole solution appears uniformly coloured. There is evidently therefore a transfer of iodine molecules from the lower to the upper part of the vessel taking place in the absence of convection currents. The iodine is said to have diffused into the water.

If it were possible to watch individual molecules of iodine, and this can be done effectively by replacing them by particles small enough to share the molecular motions but just large enough to be visible under the microscope, it would be found that the motion of each molecule is a random one. In a dilute solution each molecule of iodine behaves independently of the others, which it seldom meets, and each is constantly undergoing collision with solvent molecules, as a result of which collisions it moves sometimes towards a region of higher, sometimes of lower, concentration, having no preferred direction of motion towards one or the other. The motion of a single molecule can be described in terms of the familiar 'random walk' picture, and whilst it is possible to calculate the mean-square distance travelled in a given interval of time it is not possible to say in what direction a given molecule will move in that time.

This picture of random molecular motions, in which no molecule has a preferred direction of motion, has to be reconciled with the fact that a transfer of iodine molecules from the region of higher to that of lower concentration is nevertheless observed. Consider any horizontal section in the solution and two thin, equal, elements of volume one just below and one just above the section. Though it is not possible to say which way any particular iodine molecule will move in a given interval of time, it can be said that on the average a definite fraction of the molecules in the lower element of volume will cross the section from below, and the same fraction of molecules in the

upper element will cross the section from above, in a given time. Thus, simply because there are more iodine molecules in the lower element than in the upper one, there is a net transfer from the lower to the upper side of the section as a result of random molecular motions.

1.2. Basic hypothesis of mathematical theory

Transfer of heat by conduction is also due to random molecular motions, and there is an obvious analogy between the two processes. This was recognized by Fick (1855), who first put diffusion on a quantitative basis by adopting the mathematical equation of heat conduction derived some years earlier by Fourier (1822). The mathematical theory of diffusion in isotropic substances is therefore based on the hypothesis that the rate of transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section, i.e.

$$F = -D \partial C / \partial x, \quad (1.1)$$

where F is the rate of transfer per unit area of section, C the concentration of diffusing substance, x the space coordinate measured normal to the section, and D is called the diffusion coefficient. In some cases, e.g. diffusion in dilute solutions, D can reasonably be taken as constant, while in others, e.g. diffusion in high polymers, it depends very markedly on concentration. If F , the amount of material diffusing, and C , the concentration, are both expressed in terms of the same unit of quantity, e.g. gram or gram molecules, then it is clear from (1.1) that D is independent of this unit and has dimensions (length)² (time)⁻¹, e.g. cm² s⁻¹. The negative sign in eqn (1.1) arises because diffusion occurs in the direction opposite to that of increasing concentration.

It must be emphasized that the statement expressed mathematically by (1.1) is in general consistent only for an isotropic medium, whose structure and diffusion properties in the neighbourhood of any point are the same relative to all directions. Because of this symmetry, the flow of diffusing substance at any point is along the normal to the surface of constant concentration through the point. As will be seen later in § 1.4 (p. 5), this need not be true in an anisotropic medium for which the diffusion properties depend on the direction in which they are measured.

1.3. Differential equation of diffusion

The fundamental differential equation of diffusion in an isotropic medium is derived from eqn (1.1) as follows.

Consider an element of volume in the form of a rectangular parallelepiped whose sides are parallel to the axes of coordinates and are of lengths $2 dx$, $2 dy$, $2 dz$. Let the centre of the element be at $P(x, y, z)$, where the

concentration of diffusing substance is C . Let $ABCD$ and $A'B'C'D'$ be the faces perpendicular to the axis of x as in Fig. 1.1. Then the rate at which diffusing substance enters the element through the face $ABCD$ in the plane $x - dx$ is given by

$$4 dy dz \left(F_x - \frac{\partial F_x}{\partial x} dx \right),$$

where F_x is the rate of transfer through unit area of the corresponding plane through P . Similarly the rate of loss of diffusing substance through the face $A'B'C'D'$ is given by

$$4 dy dz \left(F_x + \frac{\partial F_x}{\partial x} dx \right).$$

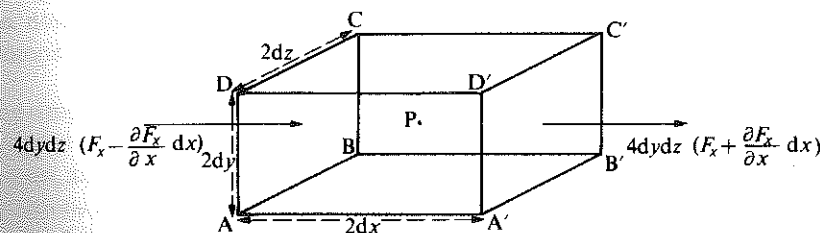


FIG. 1.1. Element of volume.

The contribution to the rate of increase of diffusing substance in the element from these two faces is thus equal to

$$-8 dx dy dz \frac{\partial F_x}{\partial x}.$$

Similarly from the other faces we obtain

$$-8 dx dy dz \frac{\partial F_y}{\partial y} \quad \text{and} \quad -8 dx dy dz \frac{\partial F_z}{\partial z}.$$

But the rate at which the amount of diffusing substance in the element increases is also given by

$$8 dx dy dz \frac{\partial C}{\partial t},$$

and hence we have immediately

$$\frac{\partial C}{\partial t} + \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} = 0. \quad (1.2)$$

If the diffusion coefficient is constant, F_x , F_y , F_z are given by (1.1), and (1.2) becomes

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right), \quad (1.3)$$

reducing simply to

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1.4)$$

if diffusion is one-dimensional i.e. if there is a gradient of concentration only along the x -axis. Expressions (1.1) and (1.4) are usually referred to as Fick's first and second laws of diffusion, since they were first formulated by Fick (1855) by direct analogy with the equations of heat conduction.

In many systems, e.g. the interdiffusion of metals or the diffusion of organic vapours in high-polymer substances, D depends on the concentration of diffusing substance C . In this case, and also when the medium is not homogeneous so that D varies from point to point, eqn (1.2) becomes

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(D \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(D \frac{\partial C}{\partial z} \right), \quad (1.5)$$

where D may be a function of x , y , z , and C .

If D depends on the time during which diffusion has been taking place but not on any of the other variables, i.e.

$$D = f(t),$$

then on introducing a new time-scale T such that

$$dT = f(t) dt,$$

the diffusion equation becomes

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}, \quad (1.6)$$

which is the same as (1.3) for a constant diffusion coefficient equal to unity.

1.3.1. Diffusion in a cylinder and sphere

Other forms of the above equations follow by transformation of co-ordinates, or by considering elements of volume of different shape. Thus by putting

$$x = r \cos \theta,$$

$$y = r \sin \theta,$$

or by considering an element of volume of a cylinder of sides dr , $r d\theta$, dz ,

we obtain the equation for diffusion in a cylinder,

$$\frac{\partial C}{\partial t} = \frac{1}{r} \left\{ \frac{\partial}{\partial r} \left(r D \frac{\partial C}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\frac{D}{r} \frac{\partial C}{\partial \theta} \right) + \frac{\partial}{\partial z} \left(r D \frac{\partial C}{\partial z} \right) \right\}, \quad (1.7)$$

in terms of the cylindrical coordinates r , θ , z . The corresponding equation for a sphere in terms of spherical polar coordinates r , θ , ϕ is obtained by writing

$$x = r \sin \theta \cos \phi,$$

$$y = r \sin \theta \sin \phi,$$

$$z = r \cos \theta,$$

or by considering an element of volume of a sphere of sides dr , $r d\theta$, $r \sin \theta d\phi$. It is

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \left\{ \frac{\partial}{\partial r} \left(D r^2 \frac{\partial C}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(D \sin \theta \frac{\partial C}{\partial \theta} \right) + \frac{D}{\sin^2 \theta} \frac{\partial^2 C}{\partial \phi^2} \right\}. \quad (1.8)$$

The simplified forms of (1.7) and (1.8) for purely radial diffusion, e.g. in a long cylinder where end effects are negligible or in a spherically symmetrical system, are given in Chapters 5 and 6, where some solutions of the differential equations are to be found. All these diffusion equations can be expressed in terms of the nomenclature of vector analysis as

$$\frac{\partial C}{\partial t} = \text{div} (D \text{ grad } C).$$

1.4. Anisotropic media

Anisotropic media have different diffusion properties in different directions. Some common examples are crystals, textile fibres, and polymer films in which the molecules have a preferential direction of orientation. For such media it is not always true, as was stated in § 1.2 (p. 2) for isotropic media, that the direction of flow of diffusing substance at any point is normal to the surface of constant concentration through the point. This means that (1.1) must be replaced in general by the assumptions

$$\left. \begin{aligned} -F_x &= D_{11} \frac{\partial C}{\partial x} + D_{12} \frac{\partial C}{\partial y} + D_{13} \frac{\partial C}{\partial z} \\ -F_y &= D_{21} \frac{\partial C}{\partial x} + D_{22} \frac{\partial C}{\partial y} + D_{23} \frac{\partial C}{\partial z} \\ -F_z &= D_{31} \frac{\partial C}{\partial x} + D_{32} \frac{\partial C}{\partial y} + D_{33} \frac{\partial C}{\partial z} \end{aligned} \right\}, \quad (1.9)$$

so that F_x , for example, depends not only on $\partial C/\partial x$ but also on $\partial C/\partial y$ and $\partial C/\partial z$. The D s have the significance that $D_{13} \partial C/\partial z$, for example, is the contribution to the rate of transfer in the x -direction due to the component of concentration gradient in the z -direction. Substituting from (1.9) for the F s in (1.2) we obtain

$$\begin{aligned} \frac{\partial C}{\partial t} = & D_{11} \frac{\partial^2 C}{\partial x^2} + D_{22} \frac{\partial^2 C}{\partial y^2} + D_{33} \frac{\partial^2 C}{\partial z^2} + (D_{23} + D_{32}) \frac{\partial^2 C}{\partial y \partial z} \\ & + (D_{31} + D_{13}) \frac{\partial^2 C}{\partial z \partial x} + (D_{12} + D_{21}) \frac{\partial^2 C}{\partial x \partial y}, \end{aligned} \quad (1.10)$$

if the D s are taken as constant. The extension to non-constant D s is obvious from (1.5). A transformation to rectangular coordinates ξ, η, ζ can be found which reduces (1.10) to

$$\frac{\partial C}{\partial t} = D_1 \frac{\partial^2 C}{\partial \xi^2} + D_2 \frac{\partial^2 C}{\partial \eta^2} + D_3 \frac{\partial^2 C}{\partial \zeta^2}. \quad (1.11)$$

This is the same transformation as that by which the ellipsoid

$$\begin{aligned} D_{11}x^2 + D_{22}y^2 + D_{33}z^2 + (D_{23} + D_{32})yz + (D_{31} + D_{13})zx \\ + (D_{12} + D_{21})xy = \text{constant} \end{aligned} \quad (1.12)$$

is reduced to

$$D_1 \xi^2 + D_2 \eta^2 + D_3 \zeta^2 = \text{constant}. \quad (1.13)$$

The new axes may be called the principal axes of diffusion and D_1, D_2, D_3 the principal diffusion coefficients. If we make the further transformation

$$\xi_1 = \xi \sqrt{(D/D_1)}, \quad \eta_1 = \eta \sqrt{(D/D_2)}, \quad \zeta_1 = \zeta \sqrt{(D/D_3)}, \quad (1.14)$$

where D may be chosen arbitrarily, (1.11) becomes

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial \xi_1^2} + \frac{\partial^2 C}{\partial \eta_1^2} + \frac{\partial^2 C}{\partial \zeta_1^2} \right). \quad (1.15)$$

This has the same form as eqn (1.3) for isotropic media, and hence certain problems in anisotropic media can be reduced to corresponding problems in isotropic media. Whether or not this can be done in a given case depends on the boundary conditions. Thus it is possible when the medium is infinite, or when it is bounded by planes perpendicular to the principal axes of diffusion so that the boundary conditions are of the familiar form $C = \text{constant}$, $\xi = 0$, $\xi = l$, $t > 0$, for example, and similarly for η and ζ . The problem of diffusion into an anisotropic cylinder which has its axis along ξ and is bounded by planes perpendicular to ξ reduces to the corresponding problem in an isotropic cylinder provided $D_2 = D_3$.

Certain properties deduced by Carslaw and Jaeger (1959, p. 46) indicate the physical significance of the ellipsoid and also of the principal axes of diffusion. Thus it can be shown that the square of the radius vector of the ellipsoid in any direction is inversely proportional to the diffusion coefficient normal to the surfaces of constant concentration at points where their normals are in that direction. Hence the diffusion coefficient D_n at right angles to surfaces whose normals have direction cosines l, m, n relative to the principal axes of diffusion is given by

$$D_n = l^2 D_1 + m^2 D_2 + n^2 D_3. \quad (1.16)$$

Carslaw and Jaeger further show that if there is symmetry about the planes $\xi = 0$ and $\eta = 0$, then the general relationships (1.9) for the F s reduce to

$$-F_\xi = D_1 \partial C / \partial \xi, \quad -F_\eta = D_2 \partial C / \partial \eta, \quad -F_\zeta = D_3 \partial C / \partial \zeta. \quad (1.17)$$

This simplification also occurs for other types of crystallographic symmetry. It means that the flow through a surface perpendicular to a principal axis of diffusion is proportional simply to the concentration gradient normal to the surface as is the case for isotropic media.

1.4.1. Significance of measurements in anisotropic media

Since in the majority of experiments designed to measure a diffusion coefficient the flow is arranged to be one-dimensional, it is worth while to see how such measurements are affected by anisotropy. If the diffusion is one-dimensional in the sense that a concentration gradient exists only along the direction of x , it is clear from (1.10), since both C and $\partial C/\partial x$ are everywhere independent of y and z , that the diffusion is governed by the simple equation

$$\frac{\partial C}{\partial t} = D_{11} \frac{\partial^2 C}{\partial x^2}, \quad (1.18)$$

and D_{11} is the diffusion coefficient measured. If the direction of diffusion is chosen to be that of a principal axis, then D_{11} is equal to one or other of the principal diffusion coefficients D_1, D_2 , or D_3 . Otherwise the coefficient $D_{11} = D_n$, related to D_1, D_2, D_3 , by (1.16) is measured. This would be measured, for example, by an observation of the rate of flow through a plane sheet of a crystal cut so that its normal has direction cosines (l, m, n) relative to the principal axes of diffusion of the crystal. Similar remarks apply to a high polymer sheet in which there is both uniplanar and undirectional orientation, i.e., the molecules are arranged with their long axes lying mainly parallel to the plane of the sheet and all parallel to one direction in that plane. The principal axes of diffusion of such a sheet will be normal to the plane sheet, and along and perpendicular to the preferred direction of orientation in that plane. Even if a concentration gradient exists in one direction only,

it is clear from (1.9) and (1.15) that the diffusion flow is not along this direction unless it coincides with a principal axis of diffusion.

1.4.2. Conversion of heat flow to diffusion solutions

Carslaw and Jaeger (1959) and other books contain a wealth of solutions of the heat-conduction equation. There is general awareness among scientists and engineers that the phenomena of heat flow and diffusion are basically the same. Nevertheless, many non-mathematicians experience difficulty in making the changes of notation needed to transcribe from one set of solutions to the other. In this section we examine in detail the correspondence between the physical parameters, the variables, and the equations and boundary conditions which occur in heat-flow and diffusion problems. We take the one-dimensional case with constant properties as an illustration.

(i) *The equations.* Diffusion theory is based on Fick's two equations (1.1) and (1.4), where C is the concentration of diffusant expressed, say, in mass per unit volume, and D is the diffusion coefficient. The two corresponding equations in heat flow are

$$F = -K \partial\theta/\partial x, \quad (1.19)$$

$$\frac{\partial\theta}{\partial t} = \left(\frac{K}{c\rho}\right) \frac{\partial^2\theta}{\partial x^2}, \quad (1.20)$$

where θ is temperature, K is the heat conductivity, ρ is density, and c specific heat, so that ρc is the heat capacity per unit volume. The space coordinate is x and t is time. In (1.19), F is the amount of heat flowing in the direction of x increasing per unit time through unit area of a section which is normal to the direction of x .

(ii) *Variables and parameters.* In order that the two sets of equations should correspond we may identify concentration C with temperature θ , and take $D = K$ in (1.1) and (1.19) and $D = K/(c\rho)$ in (1.4) and (1.20). The two together mean $c\rho = 1$. This is a consequence of our having identified C with θ . The 'diffusing substance' in heat flow is heat not temperature. The factor $c\rho$ is needed to convert temperature to the amount of heat per unit volume; but concentration is, by definition, the amount of diffusing substance per unit volume and so no conversion factor is needed, i.e. $c\rho = 1$. It is usual to write $K/(c\rho) = k$, the heat diffusivity. All three of K , k , $c\rho$ appear in heat-flow equations, and to convert to diffusion terms we take

$$D = K = k \quad \text{and} \quad c\rho = 1. \quad (1.21)$$

(iii) *Boundary conditions.* (a) Prescribed surface temperature corresponds to prescribed concentration just within the surface, say of a plane sheet. If the surface is in contact with a vapour at pressure p , there is some relation

between p and C such as $C = Sp$, where S is the solubility. There is no analogue to S in heat flow.

(b) Prescribed heat flux corresponds to flux of diffusant and we have

$$-K \partial\theta/\partial x = F(t), \quad \text{in heat}, \quad (1.22a)$$

$$-D \partial C/\partial x = F(t), \quad \text{in diffusion}, \quad (1.22b)$$

where F is in general a known function of time but may be constant.

(c) A heat-insulated surface corresponds to an impermeable surface and is the special case of (1.22a, b) with $F = 0$, i.e.

$$\partial C/\partial x = \partial\theta/\partial x = 0.$$

(d) What is referred to as a 'radiation boundary condition' in heat flow usually means that the heat flux across unit area of the surface is proportional to the difference between the surface temperature θ_s and the temperature θ_0 of the outside medium, i.e. is given by $H(\theta_s - \theta_0)$. But the rate of heat loss from unit area of a surface is $-K \partial\theta/\partial n$ in the direction of the normal \mathbf{n} , measured away from the surface, so that the boundary condition is

$$K \partial\theta/\partial n + H(\theta_s - \theta_0) = 0,$$

i.e.

$$\partial\theta/\partial n + h(\theta_s - \theta_0) = 0,$$

where $h = H/K$. Sometimes this is referred to as Newton's law of cooling. It corresponds to surface evaporation in diffusion, and we have

$$\partial C/\partial n + \alpha(C_s - C_0) = 0$$

where $\alpha = h = H/D$.

If the surface is perpendicular to the x -direction, as an example, $\partial C/\partial n = \partial C/\partial x$ if n is along the direction of x increasing but $\partial C/\partial n = -\partial C/\partial x$ if along x decreasing. Thus for a slab between $x = 0$ and $x = 1$ we have

$$\partial c/\partial x + \alpha(C_s - C_0) = 0, \quad x = 1,$$

but

$$-\partial c/\partial x + \alpha(C_s - C_0) = 0, \quad x = 0.$$

(e) A perfect conductor of heat is always at a uniform temperature and so is equivalent in this respect to a well-stirred fluid. Thus, a boundary condition describing thermal contact with a perfect conductor also describes diffusion of solute from a well-stirred solution or vapour. Conservation of heat from a well-stirred fluid of fixed volume V and uniform temperature θ_s , a function of time, gives as a boundary condition on the surface $x = 0$ of a medium, $x > 0$, in contact with the fluid

$$c\rho V \partial\theta_s/\partial t = K \partial\theta/\partial x, \quad x = 0,$$

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

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

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.

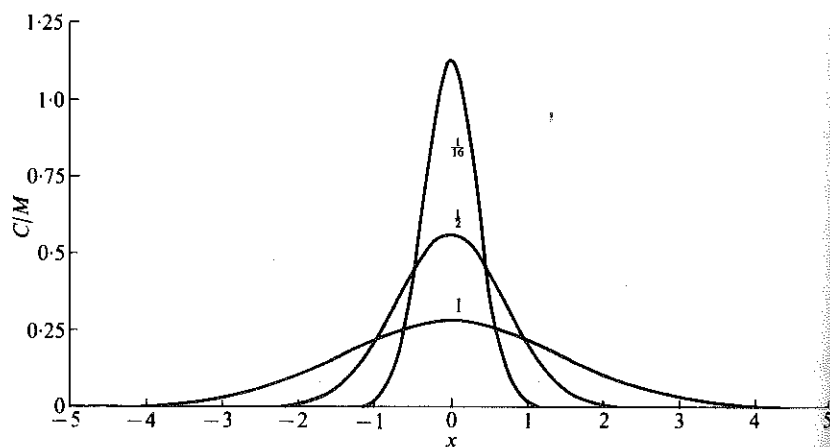


FIG. 2.1. Concentration-distance curves for an instantaneous plane source. Numbers on curves are values of Dt .

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

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

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

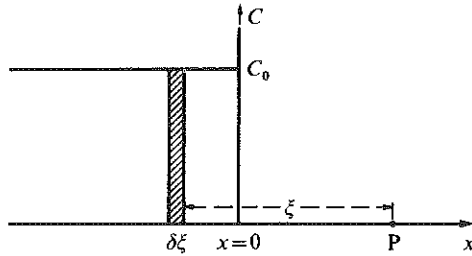


FIG. 2.2. Extended initial distribution.

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

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

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

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

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.

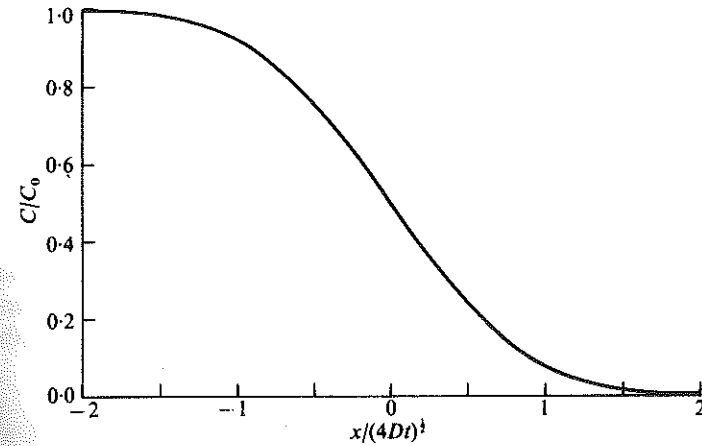


FIG. 2.3. Concentration-distance curve for an extended source of infinite extent.

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

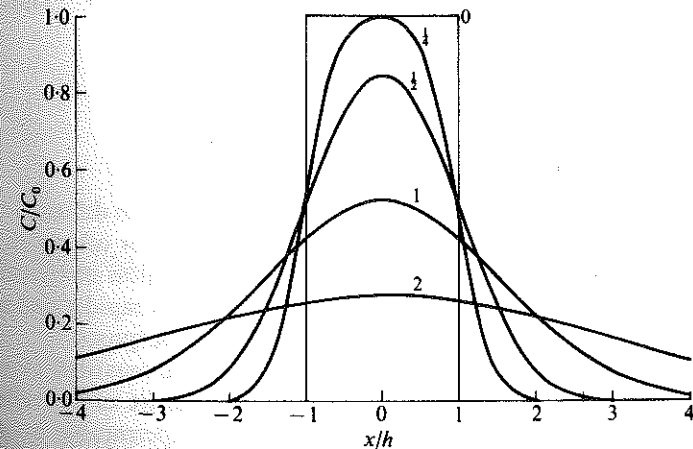


FIG. 2.4. Concentration-distance curves for an extended source of limited extent. Numbers on curves are values of $(Dt/h^2)^{\frac{1}{2}}$.

the distribution, which is symmetrical about $x = 0$. Therefore expression (2.15) also gives the distribution in a semi-infinite system. Such a system is realized in practice in the classical experiment in which a cylinder contains a layer of solution having on top of it an infinitely-long column of water, initially clear. In practice, this means that concentration changes do not reach the top of the column during the time of the experiment.

2.2.4. Finite systems

If the column of water, referred to above, is of finite length l , the condition that the concentration tends to zero as x approaches infinity is to be replaced by the condition that there is no flow of diffusing substance through the top surface, i.e.

$$\partial C / \partial x = 0, \quad x = l. \quad (2.16)$$

We have seen that this condition is satisfied if the concentration curve is considered to be reflected at the boundary and the reflected curve superposed on the original one. In the finite system we are considering now, the curve reflected at $x = l$ is reflected again at $x = 0$, and then at $x = l$, and so on, the result of each successive reflection being superposed on the original curve (2.15). Since the original solution is the sum of two error functions, the complete expression for the concentration in the finite system is an infinite series of error functions or error-function complements so that

$$\begin{aligned} C &= \frac{1}{2}C_0 \left\{ \operatorname{erfc} \frac{x-h}{2\sqrt{Dt}} - \operatorname{erfc} \frac{x+h}{2\sqrt{Dt}} + \operatorname{erfc} \frac{2l-h-x}{2\sqrt{Dt}} \right. \\ &\quad - \operatorname{erfc} \frac{2l+h-x}{2\sqrt{Dt}} + \operatorname{erfc} \frac{2l-h+x}{2\sqrt{Dt}} - \operatorname{erfc} \frac{2l+h+x}{2\sqrt{Dt}} \\ &\quad \left. + \operatorname{erfc} \frac{4l-h-x}{2\sqrt{Dt}} - \operatorname{erfc} \frac{4l-x+h}{2\sqrt{Dt}} + \dots \right\} \\ &= \frac{1}{2}C_0 \sum_{n=-\infty}^{\infty} \left\{ \operatorname{erf} \frac{h+2nl-x}{2\sqrt{Dt}} + \operatorname{erf} \frac{h-2nl+x}{2\sqrt{Dt}} \right\}. \end{aligned} \quad (2.17)$$

A solution of this kind can be obtained for most problems in diffusion by use of the Laplace transform, to be discussed in § 2.4 (p. 19), or otherwise. Such solutions are most useful for calculating the concentration distribution in the early stages of diffusion, for then the series converges rapidly and two or three terms give sufficient accuracy for most practical purposes.

In all cases the successive terms in the series can be regarded as arising from successive reflections at the boundaries. The nature of the reflection depends on the condition to be satisfied. For the impermeable boundary already considered a simple reflection ensures that $\partial C / \partial x = 0$ as required. Another boundary condition which occurs frequently is of the type $C = 0$,

in which case it is necessary to change the sign of the concentration when it is reflected at the boundary. A further example of the use of this method is given by Jost (1952). For more complicated problems, however, the reflection and superposition method soon becomes unwieldy and results are more readily obtained by other methods.

2.3. Method of separation of variables

A standard method of obtaining a solution of a partial differential equation is to assume that the variables are separable. Thus we may attempt to find a solution of (2.2) by putting

$$C = X(x)T(t), \quad (2.18)$$

where X and T are functions of x and t respectively. Substitution in (2.2) yields

$$X \frac{dT}{dt} = DT \frac{d^2 X}{dx^2},$$

which may be rewritten

$$\frac{1}{T} \frac{dT}{dt} = \frac{D}{X} \frac{d^2 X}{dx^2}, \quad (2.19)$$

so that we have on the left-hand side an expression depending on t only, while the right-hand side depends on x only. Both sides therefore must be equal to the same constant which, for the sake of the subsequent algebra, is conveniently taken as $-\lambda^2 D$. We have, therefore, two ordinary differential equations

$$\frac{1}{T} \frac{dT}{dt} = -\lambda^2 D, \quad (2.20)$$

and

$$\frac{1}{X} \frac{d^2 X}{dx^2} = -\lambda^2, \quad (2.21)$$

of which solutions are

$$T = e^{-\lambda^2 Dt}, \quad (2.22)$$

and

$$X = A \sin \lambda x + B \cos \lambda x, \quad (2.23)$$

leading to a solution of (2.2) of the form

$$C = (A \sin \lambda x + B \cos \lambda x) \exp(-\lambda^2 Dt), \quad (2.24)$$

where A and B are constants of integration. Since (2.2) is a linear equation, the most general solution is obtained by summing solutions of type (2.24), so that we have

$$C = \sum_{m=1}^{\infty} (A_m \sin \lambda_m x + B_m \cos \lambda_m x) \exp(-\lambda_m^2 D t), \quad (2.25)$$

where A_m , B_m , and λ_m are determined by the initial and boundary conditions for any particular problem. Thus if we are interested in diffusion out of a plane sheet of thickness l , through which the diffusing substance is initially uniformly distributed and the surfaces of which are kept at zero concentration, the conditions are

$$C = C_0, \quad 0 < x < l, \quad t = 0 \quad (2.26)$$

$$C = 0, \quad x = 0, \quad x = l, \quad t > 0. \quad (2.27)$$

The boundary conditions (2.27) demand that

$$B_m = 0, \quad \lambda_m = m\pi/l, \quad (2.28)$$

and hence the initial condition (2.26) becomes

$$C_0 = \sum_{m=1}^{\infty} A_m \sin(m\pi x/l), \quad 0 < x < l. \quad (2.29)$$

By multiplying both sides of (2.29) by $\sin(p\pi x/l)$ and integrating from 0 to l using the relationships

$$\int_0^l \sin \frac{p\pi x}{l} \sin \frac{m\pi x}{l} dx = \begin{cases} 0, & m \neq p, \\ \frac{1}{2}l, & m = p, \end{cases} \quad (2.30)$$

we find that terms for which m is even vanish, and

$$A_m = 4C_0/m\pi, \quad m = 1, 3, 5, \dots$$

The final solution is therefore

$$C = \frac{4C_0}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \exp\{-D(2n+1)^2\pi^2 t/l^2\} \sin \frac{(2n+1)\pi x}{l}, \quad (2.31)$$

where $2n+1$ has been substituted for m for convenience so that n takes values $0, 1, 2, \dots$. This trigonometrical-series type of solution converges satisfactorily for moderate and large times, and it is then used for numerical evaluation in preference to the error-function type of solution discussed earlier in § 2.2.4 (p. 16).

In (2.29) the initial distribution is expressed as a sum of sine functions. This reveals the physical significance of the trigonometrical series in (2.31), each term of which corresponds to a term in the Fourier series (2.29) by which the initial distribution can be represented.

2.4. Method of the Laplace transform

The Laplace transformation is a mathematical device which is useful for the solution of various problems in mathematical physics. Application of the Laplace transform to the diffusion equation removes the time variable, leaving an ordinary differential equation the solution of which yields the transform of the concentration as a function of the space variables x, y, z . This is then interpreted, according to certain rules, to give an expression for the concentration in terms of x, y, z and time, satisfying the initial and boundary condition. Historically the method may be regarded as derived from the operational methods introduced by Heaviside. Full accounts of the Laplace transform and its application have been given by Carslaw and Jaeger (1941), Churchill (1944), and others. Shorter accounts by Jaeger (1949) and Tranter (1951) are also available. Here we shall deal only with its application to the diffusion equation, the aim being to describe rather than to justify the procedure.

The solution of many problems in diffusion by this method calls for no mathematics beyond ordinary calculus. No attempt is made here to explain its application to the more difficult problems for which the theory of functions of a complex variable must be used, though solutions to problems of this kind are quoted in later chapters. The fuller accounts should be consulted for the derivation of such solutions.

2.4.1. Definition of the Laplace transform

Suppose $f(t)$ to be a known function of t for positive values of t . Then the Laplace transform $\bar{f}(p)$ of $f(t)$ is defined as

$$\bar{f}(p) = \int_0^{\infty} e^{-pt} f(t) dt, \quad (2.32)$$

where p is a number sufficiently large to make the integral (2.32) converge. It may be a complex number whose real part is sufficiently large, but in the present discussion it suffices to think of it simply as a real positive number. For example, if $f(t) = e^{at}$, p must exceed a . Unless it is necessary to emphasize that \bar{f} is a function of p , just as f is a function of t , we shall usually denote the Laplace transform of f by \bar{f} .

Laplace transforms of common functions are readily constructed by carrying out the integration in (2.32) as in the following examples:

$$f(t) = 1, \quad \bar{f}(p) = \int_0^{\infty} e^{-pt} dt = 1/p, \quad (2.33)$$

$$f(t) = e^{at}, \quad \bar{f}(p) = \int_0^{\infty} e^{-pt} e^{at} dt = \int_0^{\infty} e^{-(p-a)t} dt = \frac{1}{p-a}, \quad (2.34)$$

$$f(t) = \sin \omega t, \quad \bar{f}(p) = \int_0^{\infty} e^{-pt} \sin \omega t dt = \frac{\omega}{p^2 + \omega^2}. \quad (2.35)$$

Extensive tables or dictionaries of Laplace transforms are available, some in the works referred to above. A short table of transforms occurring frequently in diffusion problems is reproduced from Carslaw and Jaeger's book (1959) in Table 2.2.

2.4.2. Semi-infinite medium

As an example of the application of the Laplace transform, consider the problem of diffusion in a semi-infinite medium, $x > 0$, when the boundary is kept at a constant concentration C_0 , the initial concentration being zero throughout the medium. We need a solution of

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (2.36)$$

satisfying the boundary condition

$$C = C_0, \quad x = 0, \quad t > 0, \quad (2.37)$$

and the initial condition

$$C = 0, \quad x > 0, \quad t = 0. \quad (2.38)$$

On multiplying both sides of (2.36) by e^{-pt} and integrating with respect to t from 0 to ∞ we obtain

$$\int_0^\infty e^{-pt} \frac{\partial^2 C}{\partial x^2} dt - \frac{1}{D} \int_0^\infty e^{-pt} \frac{\partial C}{\partial t} dt = 0. \quad (2.39)$$

If we assume that the orders of differentiation and integration can be interchanged, and this can be justified for the functions in which we are interested, then

$$\int_0^\infty e^{-pt} \frac{\partial^2 C}{\partial x^2} dt = \frac{\partial^2}{\partial x^2} \int_0^\infty C e^{-pt} dt = \frac{\partial^2 \bar{C}}{\partial x^2}. \quad (2.40)$$

Also, integrating by parts, we have

$$\int_0^\infty e^{-pt} \frac{\partial C}{\partial t} dt = [C e^{-pt}]_0^\infty + p \int_0^\infty C e^{-pt} dt = p \bar{C}, \quad (2.41)$$

since the term in the square bracket vanishes at $t = 0$ by virtue of the initial condition (2.38) and at $t = \infty$ through the exponential factor. Thus (2.36) reduces to

$$D \frac{\partial^2 \bar{C}}{\partial x^2} = p \bar{C}. \quad (2.42)$$

By treating the boundary condition (2.37) in the same way we obtain

$$\bar{C} = \int_0^\infty C_0 e^{-pt} dt = \frac{C_0}{p}, \quad x = 0. \quad (2.43)$$

Thus the Laplace transform reduces the partial differential equation (2.36) to the ordinary differential equation (2.42). The solution of (2.42) satisfying (2.43), and for which \bar{C} remains finite as x approaches infinity is

$$\bar{C} = \frac{C_0}{p} e^{-qx}, \quad (2.44)$$

where $q^2 = p/D$. Reference to Table 2.2, item 8, shows that the function whose transform is given by (2.44) is

$$C = C_0 \operatorname{erfc} \frac{x}{2\sqrt{(Dt)}}, \quad (2.45)$$

where, as before,

$$\operatorname{erfc} z = 1 - \operatorname{erf} z. \quad (2.46)$$

It is easy to verify that (2.45) satisfies (2.36), (2.37), and (2.38) and that it is therefore the required solution of the diffusion problem.

2.4.3. Plane sheet

In the problem just considered the transform solution could be interpreted immediately by reference to the table of transforms. Consider now, as an example of a slightly more difficult problem in which this is not so, a plane sheet of thickness $2l$, whose surface are maintained at constant concentration C_0 , and with zero concentration of diffusing substance throughout the sheet initially. Let the sheet occupy the region $-l \leq x \leq l$, so that there is symmetry about $x = 0$ and the boundary conditions may be written

$$C = C_0, \quad x = l, \quad t \geq 0, \quad (2.47)$$

$$\partial C / \partial x = 0, \quad x = 0, \quad t \geq 0. \quad (2.48)$$

Eqn (2.48) expresses the condition that there is no diffusion across the central plane of the sheet. It is often more convenient to use this condition and to consider only half the sheet, $0 \leq x \leq l$, instead of using the condition $C = C_0, x = -l$.

The equations for the Laplace transform \bar{C} are

$$\frac{d^2 \bar{C}}{dx^2} - q^2 \bar{C} = 0, \quad 0 < x < l, \quad (2.49)$$

with

$$d\bar{C}/dx = 0, \quad x = 0, \quad (2.50)$$

and

$$\bar{C} = C_0/p, \quad x = l, \quad (2.51)$$

where $q^2 = p/D$ as before. The solution of these is

$$\bar{C} = \frac{C_0 \cosh qx}{p \cosh ql}. \quad (2.52)$$

There are two methods of dealing with this transform solution, leading to the two standard types of solution we have already met. We shall first obtain a solution useful for small values of the time.

(i) *Expansion in negative exponentials.* We express the hyperbolic function in (2.52) in terms of negative exponentials and expand in a series by the binomial theorem. Thus we obtain from (2.52),

$$\begin{aligned} \bar{C} &= \frac{C_0(e^{qx} + e^{-qx})}{p e^{ql}(1 + e^{-2ql})} = \frac{C_0}{p} \{e^{-q(l-x)} + e^{-q(l+x)}\} \sum_{n=0}^{\infty} (-1)^n e^{-2nql} \\ &= \frac{C_0}{p} \sum_{n=0}^{\infty} (-1)^n e^{-q((2n+1)l-x)} + \frac{C_0}{p} \sum_{n=0}^{\infty} (-1)^n e^{-q((2n+1)l+x)}. \end{aligned} \quad (2.53)$$

Thus, using item 8 of the table of transforms (Table 2.2), we obtain

$$C = C_0 \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \frac{(2n+1)l-x}{2\sqrt{Dt}} + C_0 \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \frac{(2n+1)l+x}{2\sqrt{Dt}}. \quad (2.54)$$

This is a series of error functions such as we obtained by the method of reflection and superposition. Successive terms are in fact the concentration at depths $l-x$, $l+x$, $3l-x$, $3l+x$, ... in the semi-infinite medium. The series converges quite rapidly for all except large values of Dt/l^2 . For example, we have for the concentration at the centre of the sheet ($x = 0$) when $Dt/l^2 = 1$

$$C/C_0 = 0.9590 - 0.0678 + 0.0008 = 0.8920, \quad (2.55)$$

and when $Dt/l^2 = 0.25$

$$C/C_0 = 0.3146 - 0.0001 = 0.3145. \quad (2.56)$$

(ii) *Expression in partial fractions.* It can be shown that if a transform has the form

$$\bar{y} = \frac{f(p)}{g(p)}, \quad (2.57)$$

where $f(p)$ and $g(p)$ are polynomials in p which have no common factor, the degree of $f(p)$ being lower than that of $g(p)$, and if

$$g(p) = (p-a_1)(p-a_2) \dots (p-a_n), \quad (2.58)$$

where a_1, a_2, \dots, a_n are constants which may be real or complex but must all

be different, then the function $y(t)$ whose transform is $\bar{y}(p)$ is given by

$$y(t) = \sum_{r=1}^n \frac{f(a_r)}{g'(a_r)} e^{a_r t}. \quad (2.59)$$

Here $g'(a_r)$ denotes the value of $dg(p)/dp$ when $p = a_r$. A proof of this by Jaeger (1949) is reproduced in the Appendix to this chapter. It is derived by expressing (2.57) in partial fractions. Since the hyperbolic functions $\cosh z$ and $\sinh z$ can be represented by the following infinite products (see, e.g. Carslaw (1909, p. 275))

$$\cosh z = \left(1 + \frac{4z^2}{\pi^2}\right) \left(1 + \frac{4z^2}{3^2\pi^2}\right) \left(1 + \frac{4z^2}{5^2\pi^2}\right) \dots, \quad (2.60)$$

$$\sinh z = z \left(1 + \frac{z^2}{\pi^2}\right) \left(1 + \frac{z^2}{2^2\pi^2}\right) \left(1 + \frac{z^2}{3^2\pi^2}\right) \dots, \quad (2.61)$$

a quotient of these functions such as in (2.52) may still be regarded as being of the type (2.57) except that now $f(p)$ and $g(p)$ have an infinite number of factors. The a_1, a_2, \dots are the zeros of $g(p)$, i.e. solutions of the equation, $g(p) = 0$, and if these are all different it is plausible to assume that (2.59) still holds with $n = \infty$. The justification of this assumption involves the theory of functions of a complex variable in order to carry out a contour integration and is to be found in the fuller accounts of the subject. There is, in fact, a rigorous mathematical argument by which the use of (2.59) with $n = \infty$, can be justified in diffusion problems in a finite region only. It must not be applied to (2.44), for example, for the semi-infinite region. The above refers to a_1, a_2, \dots all different. The extension of (2.59) to cases in which $g(p)$ has repeated zeros, e.g. one of its factors is square, is given in the Appendix. Its application to an infinite number of factors is still justifiable.

We may now consider the application of (2.59) to (2.52). First the zeros of the denominator must be found. Clearly, $p = 0$ is a zero, and the other zeros are given by the values of q for which $\cosh ql = 0$, i.e.

$$q = \pm \frac{(2n+1)\pi i}{2l}, \quad n = 0, 1, 2, \dots \quad (2.62)$$

and hence

$$p = -\frac{D(2n+1)^2\pi^2}{4l^2}, \quad n = 0, 1, 2, \dots \quad (2.63)$$

To apply (2.59) to (2.52) we need

$$g'(p) = \frac{d}{dp}(p \cosh ql) = \cosh ql + \frac{1}{2}ql \sinh ql. \quad (2.64)$$

For the zero $p = 0$, $g'(p) = 1$. For the other zeros, given by (2.62) and (2.63) with boundary conditions $\cosh ql = 0$, and

$$\sinh ql = \sinh \frac{(2n+1)\pi i}{2} = i \sin \frac{(2n+1)\pi}{2} = i(-1)^n, \quad (2.65)$$

so that for these zeros, by substituting in (2.64) we obtain

$$g'(p) = \frac{(2n+1)\pi(-1)^{n+1}}{4}.$$

Hence finally by inserting the zeros into (2.59) we obtain

$$C = C_0 - \frac{4C_0}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\{-D(2n+1)^2\pi^2 t/4l^2\} \cos \frac{(2n+1)\pi x}{2l}. \quad (2.67)$$

This is the trigonometrical-series type of solution obtained previously by the method of separation of the variables. The series converges rapidly for large values of t . Thus for the concentration at the centre of the sheet ($x = 0$) when $Dt/l^2 = 1$,

$$C/C_0 = 1 - 0.1080 = 0.8920, \quad (2.68)$$

and when $Dt/l^2 = 0.25$

$$C/C_0 = 1 - 0.6872 + 0.0017 = 0.3145. \quad (2.69)$$

2.5. Solutions in two and three dimensions

2.5.1. Solutions expressed as the product of the solutions of simpler problems

Consider the equation of diffusion

$$\frac{\partial^2 c}{\partial x_1^2} + \frac{\partial^2 c}{\partial x_2^2} + \frac{\partial^2 c}{\partial x_3^2} = \frac{1}{D} \frac{\partial c}{\partial t}, \quad (2.70)$$

in the rectangular parallelepiped

$$a_1 < x_1 < b_1, \quad a_2 < x_2 < b_2, \quad a_3 < x_3 < b_3.$$

For certain types of initial and boundary conditions, the solution of (2.70) is the product of the solutions of the three one-variable problems, and thus can be written down immediately if these are known. The following proof is given by Carslaw and Jaeger (1959, p. 33).

Suppose $c_r(x_r, t)$, $r = 1, 2, 3$, is the solution of

$$\frac{\partial^2 c_r}{\partial x_r^2} = \frac{1}{D} \frac{\partial c_r}{\partial t}, \quad a_r < x_r < b_r,$$

$$\alpha_r \frac{\partial c_r}{\partial x_r} - \beta_r c_r = 0, \quad x_r = a_r, \quad t > 0, \quad (2.73)$$

$$\alpha_r \frac{\partial c_r}{\partial x_r} + \beta_r c_r = 0, \quad x_r = b_r, \quad t > 0, \quad (2.74)$$

where the α_r and β_r are constants, either of which may be zero (so that the cases of zero surface concentration and no flow of heat at the surface are included) and with initial conditions

$$c_r(x_r, t) = C_r(x_r), \quad t = 0, \quad a_r < x_r < b_r. \quad (2.75)$$

Then the solution of (2.70) in the region defined by (2.71) with

$$c = C_1(x_1)C_2(x_2)C_3(x_3), \quad t = 0, \quad (2.76)$$

and with boundary conditions

$$\alpha_r \frac{\partial c}{\partial x_r} - \beta_r c = 0, \quad x_r = a_r, \quad t > 0, \quad r = 1, 2, 3, \quad (2.77)$$

$$\alpha_r \frac{\partial c}{\partial x_r} + \beta_r c = 0, \quad x_r = b_r, \quad t > 0, \quad r = 1, 2, 3, \quad (2.78)$$

$$c = c_1(x_1, t)c_2(x_2, t)c_3(x_3, t). \quad (2.79)$$

For substituting (2.79) in (2.70) gives

$$c_2 c_3 \frac{\partial^2 c_1}{\partial x_1^2} + c_3 c_1 \frac{\partial^2 c_2}{\partial x_2^2} + c_1 c_2 \frac{\partial^2 c_3}{\partial x_3^2} - \frac{1}{D} \left(c_2 c_3 \frac{\partial c_1}{\partial t} + c_3 c_1 \frac{\partial c_2}{\partial t} + c_1 c_2 \frac{\partial c_3}{\partial t} \right) = 0, \quad (2.80)$$

using (2.72). Clearly the initial and boundary conditions (2.76), (2.77), and (2.78) are satisfied.

An essential condition is (2.76), namely that the initial condition must be expressible as a product of the initial conditions for the one-variable problems taken separately. Carslaw and Jaeger (1959) give solutions for a rectangular corner, rectangles, parallelepipeds, cylinders and some examples of isotherms are shown graphically.

2.5.2. A general relationship

Goldenberg (1963) derived a much more general relationship between the transient solutions of two-dimensional problems for an infinite cylinder of arbitrary cross-section, and the transient solutions of the corresponding three-dimensional problems in finite cylinders. The boundary conditions

on the end faces of the cylinder may be of the type describing constant concentration, constant flux, or evaporation, and heat may be generated at rate independent of time and the axial coordinate.

An example of Goldenberg's relationships is afforded by the homogeneous slab, bounded by the planes $z = 0$ and $z = l$, with heat produced in the cylindrical region R of arbitrary cross-section for time $t > 0$, at the constant rate A per unit time per unit volume.

The slab is initially at zero temperature with its faces maintained at zero temperature for $t > 0$. The corresponding two-dimensional problem obtained when the thickness l of the slab is infinite and the solution independent of z . Goldenberg (1963) shows that the solution $V(x, y, z)$ for the finite slab is related to $f(x, y, t)$ for the infinite slab by the expression

$$V = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{\sin \{(2n+1)\pi z/l\}}{2n+1} \left\{ e^{-\delta t} f + \delta \int_0^t e^{-\delta t} f dt \right\}, \quad (2.8)$$

where $\delta = D\pi^2(2n+1)^2/l^2$ and D is the diffusion coefficient.

The same relationship is valid for a hollow cylinder of arbitrary cross-section and for the region external to a cylinder of arbitrary cross-section. Similar relationships hold in other situations discussed by Goldenberg.

2.6. Other solutions

Langford (1967) obtained new solutions of the one-dimensional heat equation for temperature and heat flux both prescribed at the same fixed boundary. They take the form of series of polynomial and quasi-polynomial solutions for plane sheets, cylinders, and spheres. They include as special cases some of the old or classical solutions. They also have applications to phase change problems with boundaries moving at a constant velocity.

APPENDIX TO CHAPTER 2

To deduce the function $y(t)$ whose Laplace transform $\bar{y}(p)$ is given by

$$\bar{y}(p) = \frac{f(p)}{g(p)},$$

we first put $\bar{y}(p)$ into partial fractions in the usual way by assuming

$$\frac{f(p)}{g(p)} = \sum_{r=1}^n \frac{A_r}{p-a_r} = \frac{A_1}{p-a_1} + \frac{A_2}{p-a_2} + \frac{A_3}{p-a_3} + \dots + \frac{A_n}{p-a_n}.$$

Then

$$f(p) \equiv \sum_{r=1}^n A_r (p-a_1) \dots (p-a_{r-1})(p-a_{r+1}) \dots (p-a_n),$$

and putting $p = a_r$ in this gives

$$f(a_r) = A_r (a_r - a_1) \dots (a_r - a_{r-1})(a_r - a_{r+1}) \dots (a_r - a_n) \quad (r = 1, 2, \dots, n). \quad (4)$$

Substituting for A_r from (4) in (2) gives

$$\bar{y}(p) = \sum_{r=1}^n \frac{1}{p-a_r} \frac{f(a_r)}{(a_r - a_1) \dots (a_r - a_{r-1})(a_r - a_{r+1}) \dots (a_r - a_n)}. \quad (5)$$

Now since

$$g(p) = (p-a_1)(p-a_2) \dots (p-a_n), \quad (6)$$

we have, on differentiating by the ordinary rule for differentiation of a product,

$$g'(p) = \sum_{r=1}^n (p-a_1) \dots (p-a_{r-1})(p-a_{r+1}) \dots (p-a_n). \quad (7)$$

Putting $p = a_r$ in this, gives

$$g'(a_r) = (a_r - a_1) \dots (a_r - a_{r-1})(a_r - a_{r+1}) \dots (a_r - a_n), \quad (8)$$

and using (8) in (5) gives a further form for $\bar{y}(p)$ namely

$$\bar{y}(p) = \sum_{r=1}^n \frac{f(a_r)}{(p-a_r)g'(a_r)}. \quad (9)$$

On applying item 3 of Table 2.2 to successive terms of (9) we obtain immediately

$$y(t) = \sum_{r=1}^n \frac{f(a_r)}{g'(a_r)} e^{a_r t}. \quad (10)$$

This result applies only to the case in which $g(p)$ has no repeated zeros, but it can readily be generalized for the case of repeated factors. Thus (10) implies that to each linear factor $p - a_r$ of the denominator of $\bar{y}(p)$ there corresponds a term

$$\frac{f(a_r)}{g'(a_r)} e^{a_r t} \quad (11)$$

in the solution. The generalization is that, to each squared factor $(p-b)^2$ of the denominator of $\bar{y}(p)$ there corresponds a term

$$\left[\frac{(p-b)^2 f(p)}{g(p)} \right]_{p=b} t e^{bt} + \left[\frac{d}{dp} \left\{ \frac{(p-b)^2 f(p)}{g(p)} \right\} \right]_{p=b} e^{bt} \quad (12)$$

in the solution. To each multiple factor $(p-c)^m$ of the denominator of $\bar{y}(p)$ there corresponds a term

$$\sum_{s=0}^{m-1} \left[\frac{d^s}{dp^s} \left\{ \frac{(p-c)^m f(p)}{g(p)} \right\} \right]_{p=c} \frac{t^{m-s-1}}{s!(m-s-1)!} e^{ct} \quad (13)$$

in the solution.

3

INFINITE AND SEMI-INFINITE MEDIA

3.1. Introduction

IN this and the following three chapters solutions of the diffusion equation are presented for different initial and boundary conditions. In nearly all cases the diffusion coefficient is taken as constant. In many cases the solutions are readily evaluated numerically with the help of tables of standard mathematical functions. Where this is not so, and where numerical evaluation is tedious, as many graphical and tabulated solutions as space permits are given.

3.2. Instantaneous sources

Under this heading are included all problems in which an amount of diffusing substance is deposited within a certain restricted region at time $t = 0$ and left to diffuse throughout the surrounding medium. For example it may be located initially at a point, or in a plane, or within a sphere, where we have an instantaneous point, plane, or spherical source as the case may be.

The solution for an instantaneous plane source in an infinite medium has already been given in Chapter 2, eqn (2.6). The corresponding solution for an instantaneous point source on an infinite plane surface is obtained in the same way by recognizing that

$$C = \frac{A}{t} \exp \{-(x^2 + y^2)/4Dt\}$$

is a solution of

$$\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} = \frac{1}{D} \frac{\partial C}{\partial t},$$

which is the equation for diffusion in two dimensions when the diffusion coefficient is constant. The arbitrary constant A is expressed in terms of the total amount of substance diffusing, by performing the integration

$$M = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C \, dx \, dy = 4\pi DA,$$

the concentration C being expressed in this problem as the amount of diffusing substance per unit area of surface. The concentration at a distance

r from a point source on an infinite plane surface is thus given by

$$C = \frac{M}{4\pi Dt} \exp(-r^2/4Dt). \quad (3.4)$$

The corresponding expression for a point source in an infinite volume is

$$C = \frac{M}{8(\pi Dt)^{3/2}} \exp(-r^2/4Dt). \quad (3.5)$$

By integrating the appropriate solution for a point source with respect to the relevant space variables, solutions may be obtained for line, surface, and volume sources. Thus for surface diffusion in the x, y plane due to a line source along the y -axis we have

$$C = \int_{-\infty}^{\infty} \frac{M}{4\pi Dt} \exp \{-(x^2 + y^2)/4Dt\} \, dy = \frac{M}{2(\pi Dt)^{1/2}} \exp(-x^2/4Dt), \quad (3.6)$$

where now M is the amount of diffusing substance deposited initially per unit length of the line source. This is the same as expression (2.6) of Chapter 2 for a plane source of strength M per unit area in an infinite volume. The corresponding result for a line source of strength M per unit length in an infinite volume, obtained by integrating (3.5), is

$$C = \frac{M}{4\pi Dt} \exp(-r^2/4Dt), \quad (3.7)$$

which is the same expression as (3.4) for a point source on an infinite plane surface, though M has a different significance in the two cases. Results for a variety of sources are derived by Carslaw and Jaeger (1959, p. 255). The spherical and cylindrical sources are likely to be of practical interest. If the diffusing substance is initially distributed uniformly through a sphere of radius a , the concentration C at radius r , and time t is given by

$$C = \frac{1}{2} C_0 \left\{ \operatorname{erf} \frac{a-r}{2\sqrt{Dt}} + \operatorname{erf} \frac{a+r}{2\sqrt{Dt}} \right\} - \frac{C_0}{r} \sqrt{\frac{Dt}{\pi}} \left[\exp \{-(a-r)^2/4Dt\} - \exp \{-(a+r)^2/4Dt\} \right], \quad (3.8)$$

where C_0 is the uniform concentration in the sphere initially. Expression (3.8) may easily be written in terms of the total amount of diffusing substance M , since

$$M = \frac{4}{3}\pi a^3 C_0. \quad (3.9)$$

The corresponding result for a cylinder of radius a may be written in the form

$$C = \frac{C_0}{2Dt} \exp(-r^2/4Dt) \int_0^a \exp(-r'^2/4Dt) I_0 \left(\frac{rr'}{2Dt} \right) r' \, dr', \quad (3.10)$$

where I_0 is the modified Bessel function of the first kind of order zero. Tables of I_0 are available. The integral in (3.10) has to be evaluated numerically except on the axis $r = 0$, where (3.10) becomes

$$C = C_0 \{1 - \exp(-a^2/4Dt)\}.$$

These expressions may be applied, for example, to the diffusion of a sphere or cylinder of solute into a large volume of solvent. Curves showing the concentration distribution at successive times are given in Figs. 3.1 and 3.2.

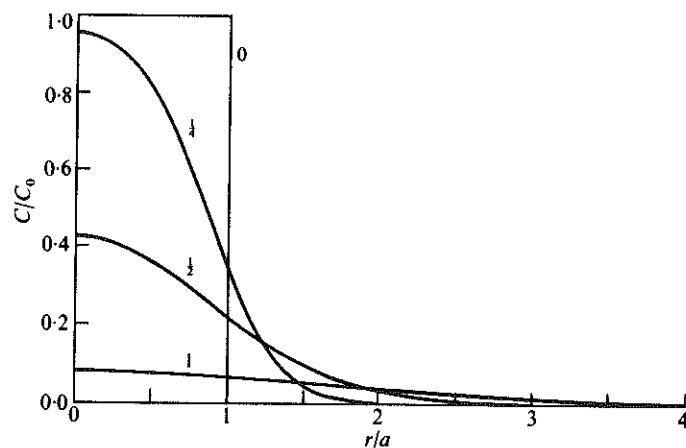


FIG. 3.1. Concentration distributions for a spherical source. Numbers on curves are values of $(Dt/a^2)^{1/2}$.

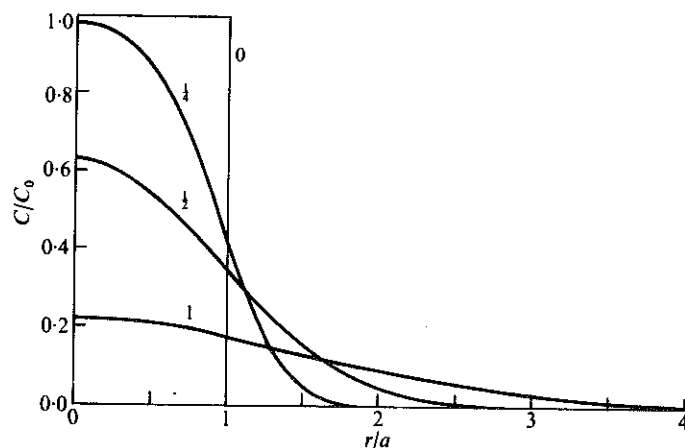


FIG. 3.2. Concentration distributions for a cylindrical source. Numbers on curves are values of $(Dt/a^2)^{1/2}$.

The expression (3.10) and the curves of Fig. 3.2 also apply to a circular disc source, of radius a , on an infinite plane surface, if C_0 denotes the uniform concentration of the diffusing substance over the region $0 < r < a$ initially. An alternative solution given by Rideal and Tadayon (1954) is

$$C = aC_0 \int_0^\infty J_1(ua)J_0(ur) \exp(-Dtu^2) du, \quad (3.10a)$$

where J_0 and J_1 are Bessel functions of the first kind and of order zero and one respectively. Tables of J_0 and J_1 are available. Rideal and Tadayon also give an expression for the total amount of diffusing substance Q remaining on the disc after time t , which is

$$Q = 2\pi a^2 C_0 \int_0^\infty \frac{J_1^2(ua)}{u} \exp(-Dtu^2) du. \quad (3.10b)$$

For small values of t , (3.10b) becomes

$$Q = \pi a^2 C_0 \left\{ 1 - \frac{2}{a} \left(\frac{Dt}{\pi} \right)^{1/2} \right\}, \quad (3.10c)$$

and when t is large we have

$$Q = \pi a^4 C_0 / (4Dt). \quad (3.10d)$$

Cases of an extended source in an infinite medium, where the diffusing substance initially occupies the semi-infinite region $x < 0$ or is confined to the region $-h < x < h$, have been considered (see eqns (2.14) and (2.15) in Chapter 2). The solution to the corresponding problem in which the region $-h < x < h$ is at zero concentration and $|x| > h$ at a uniform concentration C_0 initially is

$$C = \frac{1}{2} C_0 \left\{ \operatorname{erfc} \frac{h-x}{2\sqrt{Dt}} + \operatorname{erfc} \frac{h+x}{2\sqrt{Dt}} \right\}. \quad (3.12)$$

Knight and Philip (1973) have obtained an exact explicit solution for $D = a(1 - b^{-1}C)^{-2}$ with a and b positive constants and for an instantaneous distributed source at concentration b and the initial concentration uniform but arbitrary away from the source. The analysis holds for infinite and semi-infinite media, and physical applications are discussed.

3.2.1. Continuous sources

A solution for a continuous source, from which diffusing substance is liberated continuously at a certain rate, is deduced from the solution for the corresponding instantaneous source by integrating with respect to time t . Thus if diffusing substance is liberated continuously from a point in an infinite volume at the rate ϕ per second, the concentration at a point distant r

from the source at time t is obtained by integrating (3.5) and is

$$C = \frac{1}{8(\pi D)^{\frac{1}{2}}} \int_0^t \phi(t') \exp \left\{ -r^2/4D(t-t') \right\} \frac{dt'}{(t-t')^{\frac{1}{2}}}. \quad (3.5)$$

If ϕ is constant and equal to q , then

$$C = \frac{q}{4\pi Dr} \operatorname{erfc} \frac{r}{2\sqrt{(Dt)}}. \quad (3.5)$$

Solutions for other continuous sources are obtained similarly and examples are given by Carslaw and Jaeger (1959, p. 261).

3.3. Semi-infinite media

The solution for a plane source deposited initially at the surface, $x = 0$, of a semi-infinite medium was given in Chapter 2, eqn (2.7), and that for the initial distribution $C = C_0$, $0 < x < h$, $C = 0$, $x > h$, was seen to be given by eqn (2.15) for x positive.

The problem of the semi-infinite medium whose surface is maintained at a constant concentration C_0 , and throughout which the concentration is initially zero, was handled by the method of the Laplace transform in Chapter 2, p. 21 (see eqn (2.45)). Other results of practical importance which may be obtained in the same way are given below.

(i) The concentration is C_0 throughout, initially, and the surface is maintained at a constant concentration C_1 .

$$\frac{C - C_1}{C_0 - C_1} = \operatorname{erf} \frac{x}{2\sqrt{(Dt)}}. \quad (3.11)$$

The special case of zero surface concentration is immediately obvious. The rate of loss of diffusing substance from the semi-infinite medium when the surface concentration is zero, is given by

$$\left(D \frac{\partial C}{\partial x} \right)_{x=0} = \frac{DC_0}{\sqrt{(\pi Dt)}}, \quad (3.12)$$

so that the total amount M_t of diffusing substance which has left the medium at time t is given by integrating (3.12) with respect to t and is

$$M_t = 2C_0 \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}}. \quad (3.13)$$

The same expression with C_0 replaced by C_1 gives the total amount taken up by the medium in time t if the initial concentration C_0 is zero. If the initial concentration is zero throughout the semi-infinite medium, and the surface concentration varies with time, solutions are still obtainable by the Laplace

transform. Cases of practical interest are given below. Here M_t is used throughout to denote the total amount of diffusing substance which has entered the medium at time t .

(ii) $C_{x=0} = kt$, where k is a constant.

$$\begin{aligned} C &= kt \left[\left(1 + \frac{x^2}{2Dt} \right) \operatorname{erfc} \frac{x}{2\sqrt{(Dt)}} - \frac{x}{\sqrt{(\pi Dt)}} \exp \left\{ -x^2/4Dt \right\} \right] \\ &= 4kt i^2 \operatorname{erfc} \frac{x}{2\sqrt{(Dt)}}. \end{aligned} \quad (3.16)$$

$$M_t = \frac{4}{3}kt \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}}. \quad (3.17)$$

The function $i^2 \operatorname{erfc}$ is defined and tabulated in Table 2.1, so that values of C may be written down immediately. The effect of an increasing surface concentration is shown in Fig. 3.3.

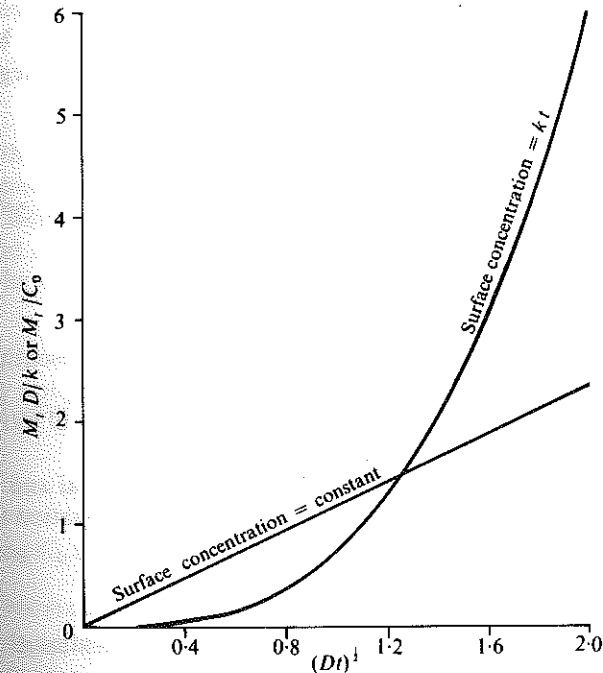


FIG. 3.3. Sorption curves for variable and constant surface concentrations in a semi-infinite medium.

(iii) $C_{x=0} = kt^{\frac{1}{2}}$, where k is a constant.

$$C = kt^{\frac{1}{2}} \left\{ \exp(-x^2/4Dt) - \frac{x\pi^{\frac{1}{2}}}{2\sqrt{(Dt)}} \operatorname{erfc} \frac{x}{2\sqrt{(Dt)}} \right\} \\ = k(\pi t)^{\frac{1}{2}} \operatorname{ierfc} \frac{x}{2\sqrt{(Dt)}}. \quad (3.18)$$

$$M_t = \frac{1}{2}kt(\pi D)^{\frac{1}{2}}. \quad (3.19)$$

The function ierfc is defined and tabulated in Table 2.1. In this case M is directly proportional to t and so the rate of uptake of diffusing substance is constant.

(iv) $C_{x=0} = kt^{\frac{1}{2}n}$, where k is a constant and n is any positive integer, even or odd.

$$C = k\Gamma(\frac{1}{2}n+1)(4t)^{\frac{1}{2}n} \operatorname{i^n erfc} \frac{x}{2\sqrt{(Dt)}}. \quad (3.20)$$

$$M_t = \frac{k}{2^n\sqrt{(Dt)}}(4t)^{\frac{1}{2}n} \frac{\Gamma(\frac{1}{2}n+1)}{\Gamma(\frac{1}{2}n+\frac{3}{2})}. \quad (3.21)$$

The function $\operatorname{i^n erfc}$ is defined and tabulated up to $n = 6$ in Table 2.1. $\Gamma(n)$ is the gamma function defined and tabulated, for example, by Milne-Thomson and Comrie (1944). If n is even, so that $\frac{1}{2}n = N$, an integer, then

$$\Gamma(\frac{1}{2}n+1) = \Gamma(N+1) = N!. \quad (3.22)$$

If n is odd, so that $\frac{1}{2}n = M - \frac{1}{2}$, then

$$\Gamma(\frac{1}{2}n+1) = \Gamma(M+\frac{1}{2}) = 1 \cdot 3 \cdot 5 \dots (2M-3)(2M-1)\pi^{\frac{1}{2}}/2^M. \quad (3.23)$$

Other properties of gamma functions are

$$\Gamma(n+1) = n\Gamma(n); \quad \Gamma(\frac{1}{2}) = \pi^{\frac{1}{2}}. \quad (3.24)$$

A polynomial in $t^{\frac{1}{2}}$ may sometimes be a useful way of representing a given surface concentration empirically. In such a case the complete expression for the concentration at any point is the sum of a number of terms of type (3.20) corresponding to successive terms in the polynomial.

(v) These solutions can be extended to cover other initial and boundary conditions by using the fact that for a linear differential equation the sum of two solutions is itself a solution. For example, if

$$C_{x=0} = C_0 + kt \quad (3.25)$$

and the semi-infinite medium is initially at zero concentration throughout, the solution is given by

$$C = C_0 \operatorname{erfc} \frac{x}{2\sqrt{(Dt)}} + 4kt \operatorname{i^2 erfc} \frac{x}{2\sqrt{(Dt)}}, \quad (3.26)$$

since the first term on the right-hand side of (3.26) is the solution satisfying the conditions

$$\left. \begin{aligned} C &= C_0, & x &= 0 \\ C &= 0, & x &> 0 \end{aligned} \right\}, \quad (3.27)$$

and the second term satisfies

$$\left. \begin{aligned} C &= kt, & x &= 0 \\ C &= 0, & x &> 0 \end{aligned} \right\}. \quad (3.28)$$

In general the solution to the problem of the semi-infinite medium in which the surface concentration is given by $F(t)$ and in which the initial distribution is $f(x)$, is given by

$$C = c_1 + c_2, \quad (3.29)$$

where c_1 is a solution of the diffusion equation which satisfies

$$\left. \begin{aligned} c_1 &= 0, & t &= 0 \\ c_1 &= F(t), & x &= 0 \end{aligned} \right\}, \quad (3.30)$$

and c_2 is another solution satisfying

$$\left. \begin{aligned} c_2 &= f(x), & t &= 0 \\ c_2 &= 0, & x &= 0 \end{aligned} \right\}. \quad (3.31)$$

Clearly, with c_1 and c_2 so defined, the diffusion equation and the initial and boundary conditions are satisfied. Consider, as an example, the problem of desorption from a semi-infinite medium having a uniform initial concentration C_0 , and a surface concentration decreasing according to (3.25), with k negative. The solution is

$$C = C_0 + 4kt \operatorname{i^2 erfc} \frac{x}{2\sqrt{(Dt)}}, \quad (3.32)$$

which is obtained by adding to (3.26) the solution satisfying

$$\left. \begin{aligned} C &= C_0, & x &> 0, & t &= 0 \\ C &= 0, & x &= 0, & t &> 0 \end{aligned} \right\}, \quad (3.33)$$

i.e. by adding $C_0 \operatorname{erf} \{x/2\sqrt{(Dt)}\}$.

3.3.1. Surface evaporation condition

In some cases the boundary condition relates to the rate of transfer of diffusing substance across the surface of the medium. Thus, if a stream of dry air passes over the surface of a solid containing moisture, loss of moisture occurs by surface evaporation. Similarly if the solid is initially dry and the

air contains water vapour, the solid takes up moisture. In each case the rate of exchange of moisture at any instant depends on the relative humidity of the air and the moisture concentration in the surface of the solid. The simplest reasonable assumption is that the rate of exchange is directly proportional to the difference between the actual concentration C_s in the surface at any time and the concentration C_0 which would be in equilibrium with the vapour pressure in the atmosphere remote from the surface. Mathematically this means that the boundary condition at the surface is

$$-D \frac{\partial C}{\partial x} = \alpha(C_0 - C_s), \quad x = 0, \quad (3.34)$$

where α is a constant of proportionality.

If the concentration in a semi-infinite medium is initially C_2 throughout and the surface exchange is determined by (3.34), the solution is

$$\frac{C - C_2}{C_0 - C_2} = \operatorname{erfc} \frac{x}{2\sqrt{(Dt)}} - \exp(hx + h^2 Dt) \operatorname{erfc} \left\{ \frac{x}{2\sqrt{(Dt)}} + h\sqrt{(Dt)} \right\}, \quad (3.35)$$

where $h = \alpha/D$. The special cases of zero concentration in the medium initially ($C_2 = 0$), and evaporation into an atmosphere of zero relative humidity ($C_0 = 0$), are immediately obvious from (3.35). The rate at which the total amount M_t of diffusing substance in the semi-infinite medium per unit cross-sectional area changes is given by

$$\frac{dM_t}{dt} = - \left(D \frac{\partial C}{\partial x} \right)_{x=0} = \alpha(C_0 - C_s), \quad (3.36)$$

and, on substituting for C_s the value obtained from (3.35) by putting $x = 0$, after integration with respect to t we obtain for the total quantity of diffusing substance having crossed unit area of the surface,

$$M_t = \left(\frac{C_0 - C_2}{h} \right) \left\{ \exp(h^2 Dt) \operatorname{erfc} h\sqrt{(Dt)} - 1 + \frac{2}{\pi^{1/2}} h\sqrt{(Dt)} \right\} \quad (3.37)$$

If C_0 is greater than C_2 this amount is taken up by the medium; if C_0 is less than C_2 this amount is lost by evaporation from the surface. The expression (3.35) can be written in terms of any two of the dimensionless parameters

$$\frac{x}{2\sqrt{(Dt)}}, \quad h\sqrt{(Dt)}, \quad \text{or} \quad hx. \quad (3.38)$$

In Fig. 3.4 the ratio $(C - C_2)/(C_0 - C_2)$ is plotted as a function of $x/2\sqrt{(Dt)}$ for various values of $h\sqrt{(Dt)}$. In order to evaluate $hM_t/(C_0 - C_2)$ from (3.37), only one dimensionless parameter $h\sqrt{(Dt)}$ is needed. The relationship is readily evaluated from standard functions and is shown graphically in

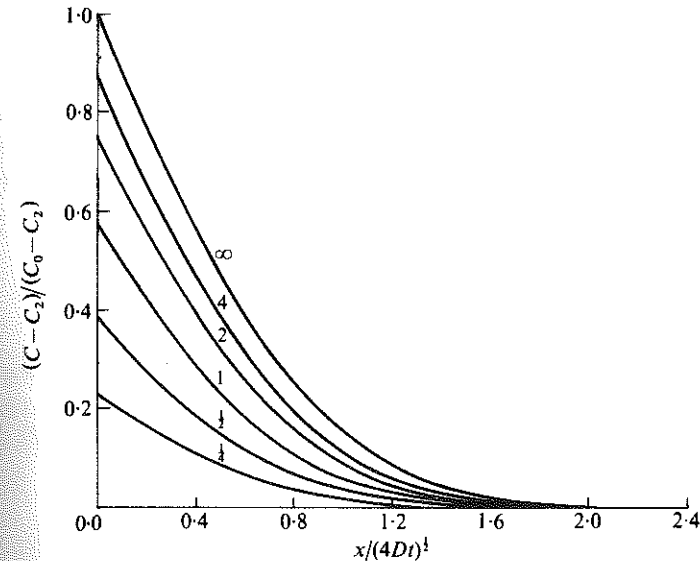


Fig. 3.4. Concentration distribution for a surface evaporation condition in a semi-infinite medium. Numbers on curves are values of $h(Dt)^{1/2}$.

Fig. 3.5. The evaluation for large $h\sqrt{(Dt)}$ is made easier by using the asymptotic formula

$$\exp(z^2) \operatorname{erfc} z = \frac{1}{\pi^{1/2}} \left(\frac{1}{z} - \frac{1}{2z^3} + \frac{1.3}{2^2 \cdot z^5} \dots \right). \quad (3.39)$$

3.3.2. Square-root relationship

Expression (2.45) shows that the solution of the problem of diffusion into a semi-infinite medium having zero initial concentration and the surface of which is maintained constant, involves only the single dimensionless parameter

$$\frac{x}{2\sqrt{(Dt)}}. \quad (3.40)$$

It follows from this that

- (i) the distance of penetration of any given concentration is proportional to the square root of time;
- (ii) the time required for any point to reach a given concentration is proportional to the square of its distance from the surface and varies inversely as the diffusion coefficient;
- (iii) the amount of diffusing substance entering the medium through unit area of its surface varies as the square root of time.

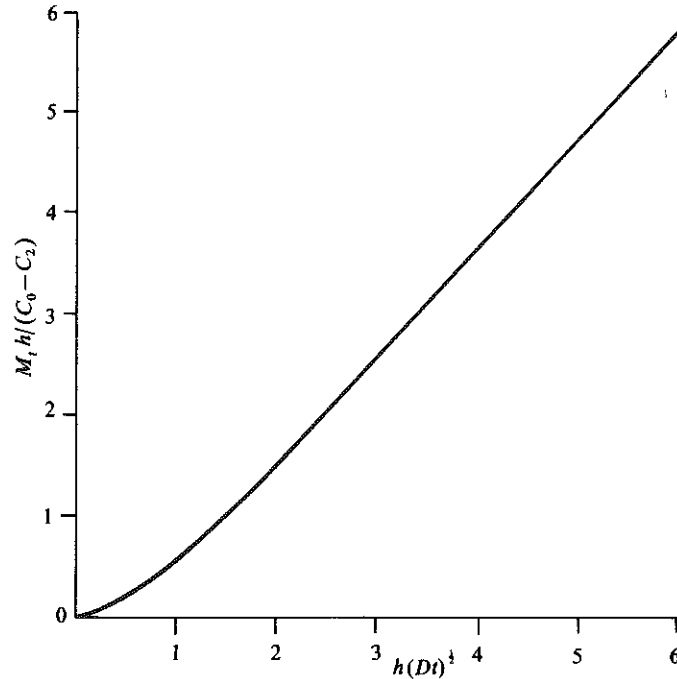


FIG. 3.5. Sorption curve for a surface evaporation condition in a semi-infinite medium.

These fundamental properties hold in general in semi-infinite media, provided the initial concentration is uniform and the surface concentration remains constant. They also hold for point and line sources on infinite surfaces or in infinite media, and also for the case of diffusion in an infinite medium where the diffusing substance is initially confined to the region $x < 0$. Clearly they do not apply to cases where parameters other than $x/2\sqrt{(Dt)}$ are involved, such as the width of an extended source or the rate of change of surface concentration, etc.

3.4. The infinite composite medium

Here we consider diffusion in systems in which two media are present. Suppose the region $x > 0$ is of one substance in which the diffusion coefficient is D_1 , and in the region $x < 0$ the diffusion coefficient is D_2 . In the simplest case, the initial conditions are that the region $x > 0$ is at a uniform concentration C_0 , and in $x < 0$ the concentration is zero initially. If we write c_1 for the concentration in $x > 0$ and c_2 in $x < 0$ the boundary conditions at the interface $x = 0$ may be written

$$c_2/c_1 = k, \quad x = 0, \quad (3.41)$$

$$D_1 \partial c_1 / \partial x = D_2 \partial c_2 / \partial x, \quad x = 0, \quad (3.42)$$

where k is the ratio of the uniform concentration in the region $x < 0$ to that in $x > 0$ when final equilibrium is attained. The condition (3.42) expresses the fact that there is no accumulation of diffusing substance at the boundary. A solution to this problem is easily obtained by combining solutions for the semi-infinite medium so as to satisfy the initial and boundary conditions. We seek solutions of the type

$$c_1 = A_1 + B_1 \operatorname{erf} \frac{x}{2\sqrt{(D_1 t)}}, \quad x > 0, \quad (3.43)$$

$$c_2 = A_2 + B_2 \operatorname{erf} \frac{|x|}{2\sqrt{(D_2 t)}}, \quad x < 0, \quad (3.44)$$

which are known to satisfy the diffusion equations in the two regions. By choosing the constants A_1, B_1, A_2, B_2 to satisfy the initial conditions and (3.41), (3.42) we obtain

$$c_1 = \frac{C_0}{1 + k(D_2/D_1)^{1/2}} \left\{ 1 + k(D_2/D_1)^{1/2} \operatorname{erf} \frac{x}{2\sqrt{(D_1 t)}} \right\}, \quad (3.45)$$

$$c_2 = \frac{kC_0}{1 + k(D_2/D_1)^{1/2}} \operatorname{erfc} \frac{|x|}{2\sqrt{(D_2 t)}}. \quad (3.46)$$

Fig. 3.6 shows a typical concentration distribution for the case where $D_2 = 4D_1$ and $k = \frac{1}{2}$. Graphs for other cases are shown by Jost (1952) and by Barrer (1951). We may note that, as diffusion proceeds, the concentrations at the interface, $x = 0$, remain constant at the values

$$c_1 = \frac{C_0}{1 + k(D_2/D_1)^{1/2}}, \quad c_2 = \frac{kC_0}{1 + k(D_2/D_1)^{1/2}}. \quad (3.47)$$

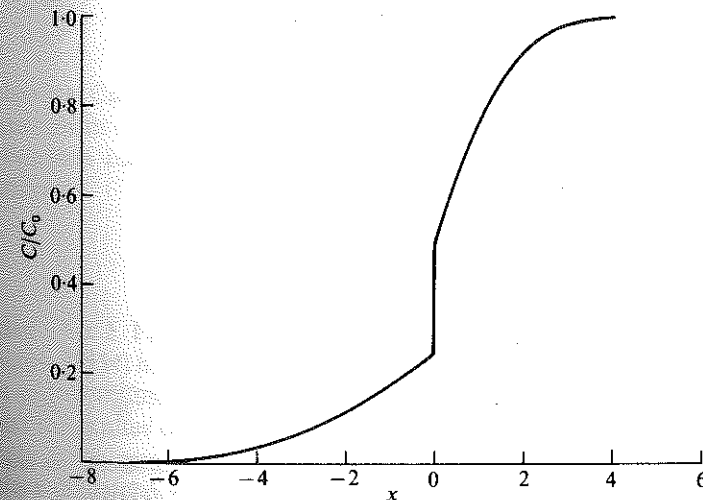


FIG. 3.6. Concentration distribution in a composite medium. $D_1 t = 1$, $D_2 = 4D_1$, $k = \frac{1}{2}$.

DIFFUSION IN A PLANE SHEET

4.1. Introduction

IN this chapter we consider various cases of one-dimensional diffusion in a medium bounded by two parallel planes, e.g. the planes at $x = 0$, $x = l$. These will apply in practice to diffusion into a plane sheet of material so thick that effectively all the diffusing substance enters through the plane faces and a negligible amount through the edges.

4.2. Steady state

Consider the case of diffusion through a plane sheet or membrane of thickness l and diffusion coefficient D , whose surfaces, $x = 0$, $x = l$, are maintained at constant concentrations C_1 , C_2 respectively. After a time, steady state is reached in which the concentration remains constant at all points of the sheet. The diffusion equation in one dimension then reduces to

$$d^2C/dx^2 = 0, \quad (4.1)$$

provided the diffusion coefficient D is constant. On integrating with respect to x we have

$$dC/dx = \text{constant}, \quad (4.2)$$

and by a further integration we have, on introducing the conditions at $x = 0$, $x = l$,

$$\frac{C - C_1}{C_2 - C_1} = \frac{x}{l}. \quad (4.3)$$

Both (4.2) and (4.3) show that the concentration changes linearly from C_1 to C_2 through the sheet. Also, the rate of transfer of diffusing substance is the same across all sections of the membrane and is given by

$$F = -D dC/dx = D(C_1 - C_2)/l. \quad (4.4)$$

If the thickness l and the surface concentrations C_1 , C_2 are known, D can be deduced from an observed value of F by using (4.4). Experimental arrangements for measuring D in this and other ways have been reviewed by Newns (1950).

If the surface $x = 0$ is maintained at a constant concentration C_1 and at $x = l$ there is evaporation into an atmosphere for which the equilibrium

concentration just within the surface is C_2 , so that

$$\partial C/\partial x + h(C - C_2) = 0, \quad x = l,$$

then we find

$$\frac{C - C_1}{C_2 - C_1} = \frac{hx}{1 + hl}, \quad (4.3a)$$

and

$$F = \frac{Dh(C_1 - C_2)}{1 + hl}. \quad (4.4a)$$

If the surface conditions are

$$\partial C/\partial x + h_1(C_1 - C) = 0, \quad x = 0; \quad \partial C/\partial x + h_2(C - C_2) = 0, \quad x = l,$$

then

$$C = \frac{h_1 C_1 \{1 + h_2(l - x)\} + h_2 C_2 (1 + h_1 x)}{h_1 + h_2 + h_1 h_2 l}, \quad (4.3b)$$

and

$$F = \frac{Dh_1 h_2 (C_1 - C_2)}{h_1 + h_2 + h_1 h_2 l}. \quad (4.4b)$$

Corresponding solutions for a funnel-shaped region are easily obtained (Jacobs 1967).

4.2.1. Permeability constant

In some practical systems, the surface concentrations C_1 , C_2 may not be known but only the gas or vapour pressures p_1 , p_2 on the two sides of the membrane. The rate of transfer in the steady state is then sometimes written

$$F = P(p_1 - p_2)/l, \quad (4.5)$$

and the constant P is referred to as the permeability constant. Here P is expressed, for example, as cm^3 gas at some standard temperature and pressure passing per second through 1 cm^2 of the surface of a membrane 1 cm thick when the pressure difference across the membrane is 1 cm of mercury. The permeability constant is a much less fundamental constant than the diffusion coefficient which is expressed in units such as $\text{cm}^2 \text{ s}^{-1}$, particularly as different investigators use different units and even different definitions of P .

If the diffusion coefficient is constant, and if the sorption isotherm is linear, i.e. if there is a linear relationship between the external vapour pressure and the corresponding equilibrium concentration within the

membrane, then eqns (4.4) and (4.5) are equivalent, but not otherwise. The drop in concentration is linear isotherm may be written

$$C = Sp, \quad (4.6)$$

where C is the concentration within the material of the membrane in equilibrium with an external vapour pressure p , and S is the solubility. Since C_1 and C_2 , p_1 and p_2 in (4.4) and (4.5) are connected by (4.6) it follows that, with due regard to units,

$$P = DS. \quad (4.7)$$

4.2.2. Concentration-dependent diffusion coefficient

If the diffusion coefficient varies with concentration it is clear that the simple value of D deduced from a measurement of the steady rate of flow of some kind of mean value over the range of concentration involved. Thus if D is a function of C (4.1) is to be replaced by

$$\frac{d}{dx} \left(D \frac{dC}{dx} \right) = 0, \quad (4.8)$$

and hence the relationship

$$F = -D dC/dx = \text{constant} \quad (4.9)$$

still holds, as of course it must in the steady state. Integrating between C_1 and C_2 , the two surface concentrations, we have

$$F = -\frac{1}{l} \int_{C_1}^{C_2} D dC = D_l (C_1 - C_2)/l, \quad (4.10)$$

where

$$D_l = \frac{1}{C_1 - C_2} \int_{C_1}^{C_2} D dC, \quad (4.11)$$

and this is the mean value deduced from a measurement of F . It follows from (4.9) that if D depends on C the concentration no longer depends linearly on distance through the membrane. Concentration distributions for D depending on C in a number of ways are given in Chapter 9.

4.2.3. Composite membrane

If we have a composite membrane composed of n sheets of thicknesses l_1, l_2, \dots, l_n , and diffusion coefficients D_1, D_2, \dots, D_n , the fall in concentration through the whole membrane is the sum of the falls through the component sheets. Since the rate of transfer F is the same across each section, the total

$$\frac{Fl_1}{D_1} + \frac{Fl_2}{D_2} + \dots + \frac{Fl_n}{D_n} = (R_1 + R_2 + \dots + R_n)F, \quad (4.12)$$

where $R_1 = l_1/D_1$, etc. may be termed formally the resistance to diffusion of each sheet. Thus the resistance to diffusion of the whole membrane is simply the sum of the resistances of the separate layers, assuming that there are no barriers to diffusion between them. This subject is treated more generally in § 12.2(i) (p. 266).

4.3. Non-steady state

All the solutions presented here can be obtained either by the method of separation of the variables or by the Laplace transform as described in § 2.4. Many of the results are quoted by Barrer (1951), Carslaw and Jaeger (1959), Jacobs (1967), Jost (1952) and others. The emphasis here is on numerical evaluation.

4.3.1. Surface concentrations constant. Initial distribution $f(x)$

If

$$C = C_1, \quad x = 0, \quad t \geq 0, \quad (4.13)$$

$$C = C_2, \quad x = l, \quad t \geq 0, \quad (4.14)$$

$$C = f(x), \quad 0 < x < l, \quad t = 0, \quad (4.15)$$

the solution in the form of a trigonometrical series is

$$C = C_1 + (C_2 - C_1) \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi x}{l} \exp(-Dn^2\pi^2 t/l^2) + \frac{2}{l} \sum_{n=1}^{\infty} \sin \frac{n\pi x}{l} \exp(-Dn^2\pi^2 t/l^2) \int_0^l f(x') \sin \frac{n\pi x'}{l} dx'. \quad (4.16)$$

In the cases of most common occurrence $f(x)$ is either zero or constant so that the integral in (4.16) is readily evaluated. Very often the problem is symmetrical about the central plane of the sheet, and the formulae are then most convenient if this is taken as $x = 0$ and the surfaces at $x = \pm l$.

4.3.2. Uniform initial distribution. Surface concentrations equal

This is the case of sorption and desorption by a membrane. If the region $-l < x < l$ is initially at a uniform concentration C_0 , and the surfaces are kept at a constant concentration C_1 , the solution (4.16) becomes

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\{-D(2n+1)^2\pi^2 t/l^2\} \cos \frac{(2n+1)\pi x}{2l}. \quad (4.17)$$

If M_t denotes the total amount of diffusing substance which has entered the

sheet at time t , and M_∞ the corresponding quantity after infinite time, the

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \{ -D(2n+1)^2 \pi^2 t / 4l^2 \}. \quad (4.18)$$

The corresponding solutions useful for small times are

$$\begin{aligned} \frac{C - C_0}{C_1 - C_0} &= \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \frac{(2n+1)l - x}{2\sqrt{(Dt)}} \\ &+ \sum_{n=0}^{\infty} (-1)^n \operatorname{erfc} \frac{(2n+1)l + x}{2\sqrt{(Dt)}}, \end{aligned} \quad (4.19)$$

and

$$\frac{M_t}{M_\infty} = 2 \left(\frac{Dt}{l^2} \right)^{\frac{1}{2}} \left\{ \pi^{-\frac{1}{2}} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{nl}{\sqrt{(Dt)}} \right\}. \quad (4.20)$$

The modifications to these expressions for $C_0 = 0$ or $C_1 = 0$ are obvious.

Jason and Peters (1973) analyse the bimodal diffusion of water in fish muscle by combining two expressions of the type (4.18), one for each mode and each having its own diffusion coefficient.

Eqn (4.18) can be solved graphically for Dt/l^2 and hence D obtained from measured sorption or desorption time curves. An alternative suggested by Talbot and Kitchener (1956) is the approximate formula

$$\theta = -\ln x + \frac{q}{p} + \frac{rq^2}{2p^3}$$

where $\theta = \pi^2 Dt / 4l^2$, $x = \frac{1}{8} \pi^2 M_t / M_\infty$ and $p = 1 + x^8 + x^{24}$, $q = \frac{1}{9} x^8 + \frac{1}{25} x^{24}$ and, $r = 1 + 9x^8 + 25x^{24}$.

The solution is correct to four significant figures when $M_t/M_\infty < \frac{2}{3}$ for desorption. The solution (4.18) also applies to diffusion along a cylindrical rod or tube of length l , with one end and its surface sealed and the other end maintained at a constant concentration.

Talbot and Kitchener also obtained a solution for a slightly tapering tube. If d_1 and d_2 are the diameters of the two ends, the degree of taper is specified by $\mu = (d_2 - d_1)/d_1$, where d_1 is the closed end, and may be positive or negative. For small μ , e.g. around 0.01, we have effectively radial diffusion and a solution is

$$\frac{M_t}{M_\infty} = \frac{6(1+\mu)^2}{3+3\mu+\mu^2} \sum_{n=1}^{\infty} \frac{\alpha_n^2 + \mu^2}{\alpha_n^2(\alpha_n^2 + \mu^2 + \mu)} \exp(-D\alpha_n^2 t / l^2),$$

where the α_n are the roots of $\tan \alpha = -\alpha/\mu$, and, to the first order in μ , $\alpha_n^2 = (n - \frac{1}{2})^2 \pi^2 + 2\mu$. The solution becomes, with this approximation,

$$\frac{M_t}{M_\infty} = \sum_{n=1}^{\infty} \frac{8}{(2n-1)^2 \pi^2} \{ 1 + (k_n - \lambda \theta) \mu \exp(-(2n-1)^2 \theta) \},$$

where $\theta = \pi^2 Dt / 4l^2$, $\lambda = 8/\pi^2$, $k_n = 1 - \frac{3}{2} \lambda / (2n-1)^2$, i.e.

$$\lambda = 0.81057, \quad k_1 = -0.21585, \quad k_2 = 0.86491, \quad k_3 = 0.95137.$$

Thus putting $x = \frac{1}{8} \pi^2 M_t / M_\infty$ as before, θ must satisfy

$$\begin{aligned} x &= \{ 1 + (k_1 - \lambda \theta) \mu \} e^{-\theta} + \frac{1}{9} \{ 1 + (k_2 - \lambda \theta) \mu \} e^{-9\theta} \\ &+ \frac{1}{25} \{ 1 + (k_3 - \lambda \theta) \mu \} e^{-25\theta} + \dots \end{aligned}$$

If the solution (4.18) is applied to the tapered tube to calculate θ , the approximate value, say θ_0 , obtained can be corrected by using

$$\theta = \theta_0 \left\{ 1 - \mu \frac{\lambda(1+q) - s/\theta_0}{p} \right\} = \theta_0(1 - \kappa \mu)$$

where $s = k_1 + \frac{1}{9} k_2 x^8 + \frac{1}{25} k_3 x^{24}$, p and q are defined above, and $\kappa \mu$ is the correction term. Talbot and Kitchener (1956) quote

$$\kappa = 0.807 - 0.60x^8 + (0.212 - 0.25x^8)/\theta_0$$

approximately and discuss in more detail the capillary tube method (Anderson and Saddington 1949) for measuring diffusion coefficients.

It is clear that expressions (4.17), (4.18), (4.19), (4.20) can be written in terms of the dimensionless parameters

$$T = Dt/l^2, \quad X = x/l, \quad (4.21)$$

so that the solutions for all values of D , l , t , and x can be obtained from graphs or tabulated values covering these two parameters. Graphs of $(C - C_0)/(C_1 - C_0)$ are shown for various times in Fig. 4.1. These are reproduced with change of nomenclature from Carslaw and Jaeger's book (1959, p. 101). Tabulated values of $(C - C_0)/(C_1 - C_0)$ and of M_t/M_∞ are given by Henry (1939). Values of M_t/M_∞ have also been tabulated by McKay (1930) and extensive numerical values for the concentration at the centre of the sheet, $x = 0$, are given by Olson and Schulz (1942). The curve labelled zero fractional uptake in Fig. 4.6 shows how M_t/M_∞ varies with the square root of time in a sheet of thickness $2a$ when the concentration at each surface remains constant.

4.3.3. Uniform initial distribution. Surface concentrations different

This is the case of flow through a membrane. If one face $x = 0$ of a membrane is kept at a constant concentration C_1 and the other $x = l$ at C_2 , and the membrane is initially at a uniform concentration C_0 , there is a finite interval of time during which the steady-state condition previously discussed

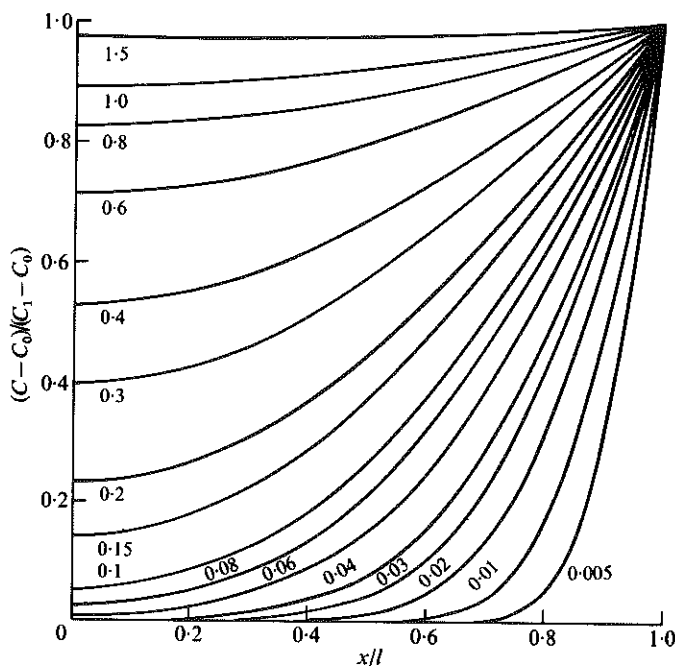


FIG. 4.1. Concentration distributions at various times in the sheet $-l < x < l$ with initial uniform concentration C_0 and surface concentration C_1 . Numbers on curves are values of Dt/l^2 .

in § 4.2 (p. 44) is set up. During this time the concentration changes according to

$$C = C_1 + (C_2 - C_1) \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi x}{l} \exp(-Dn^2\pi^2 t/l^2) + \frac{4C_0}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \sin \frac{(2m+1)\pi x}{l} \exp\{-D(2m+1)^2\pi^2 t/l^2\}. \quad (4.22)$$

As t approaches infinity the terms involving the exponentials vanish and we have simply the linear concentration distribution obtained in § 4.2. Barnes (1934) examined the errors introduced by assuming a linear gradient to exist across the membrane during the whole course of diffusion.

If M_t denotes the total amount of diffusing substance which enters the sheet during time t , and M_{∞} the corresponding amount during infinite time, then

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\{-D(2n+1)^2\pi^2 t/l^2\}. \quad (4.23)$$

In this case $M_{\infty} = l\{\frac{1}{2}(C_1 + C_2) - C_0\}$ and the total content of the membrane

at time t is given by $M_t + lC_0$. The expression (4.23) is similar to (4.18) and is readily evaluated from the curve labelled zero fractional uptake in Fig. 4.6, with the proviso that in (4.23) l signifies the whole thickness of the membrane but in (4.18) it denotes the half-thickness.

The rate at which the gas or other diffusing substance emerges from unit area of the face $x = l$ of the membrane is given by $-D(\partial C/\partial x)_{x=l}$ which is easily deduced from (4.22). By integrating then with respect to t , we obtain the total amount of diffusing substance Q_t which has passed through the membrane in time t .

$$Q_t = D(C_1 - C_2) \frac{t}{l} + \frac{2l}{\pi^2} \sum_{n=1}^{\infty} \frac{C_1 \cos n\pi - C_2}{n^2} \{1 - \exp(-Dn^2\pi^2 t/l^2)\} + \frac{4C_0 l}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \{1 - \exp(-D(2m+1)^2\pi^2 t/l^2)\}. \quad (4.24)$$

In the commonest experimental arrangement both C_0 and C_2 are zero, i.e. the membrane is initially at zero concentration and the concentration at the face through which diffusing substance emerges is maintained effectively at zero concentration. In this case we find

$$\frac{Q_t}{lC_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp(-Dn^2\pi^2 t/l^2), \quad (4.24a)$$

which, as $t \rightarrow \infty$, approaches the line

$$Q_t = \frac{DC_1}{l} \left(t - \frac{l^2}{6D} \right). \quad (4.25)$$

This has an intercept L on the t -axis given by

$$L = l^2/6D \quad (4.26)$$

Following Daynes (1920), Barrer (1951) has used (4.26) as the basis of a method for obtaining the diffusion constant, the permeability constant, and the solubility of a gas by analysing stationary and non-stationary flow through a membrane. Thus from an observation of the intercept, L , D is deduced by (4.26); from the steady-state flow rate the permeability constant P is deduced by using (4.5), and S follows from (4.7). The intercept L is referred to as the 'time lag'.

A graph of Q_t/lC_1 as a function Dt/l^2 is shown for the case $C_0 = C_2 = 0$ in Fig. 4.2. To within the accuracy of plotting the steady state is achieved when $Dt/l^2 = 0.45$ approximately.

An alternative form of solution useful for small times, usually attributed to Holstein (Rogers, Buritz, and Alpert 1954) is easily derived by using Laplace transforms as in § 2.4.3(i). Still keeping $C_0 = C_2 = 0$, we find the rate of

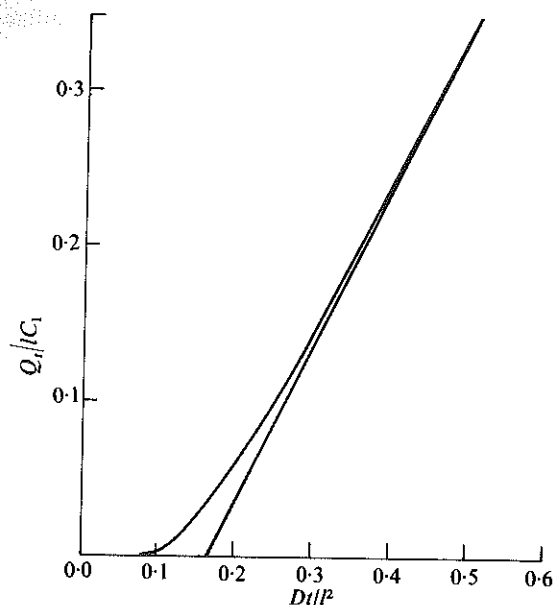


FIG. 4.2. Approach to steady-state flow through a plane sheet.

flow $F(t)$ per unit area of the surface $x = l$ to be

$$F(t) = -\left(\frac{D\partial C}{\partial x}\right)_{x=l} = 2C_1 \sum_1^{\infty} \left(\frac{D}{\pi t}\right)^{\frac{1}{2}} \exp\left\{-(2m+1)^2 l^2/(4Dt)\right\} \quad (4.27)$$

This series converges most rapidly for small t . Rogers *et al.* take only the leading term and obtain essentially

$$\ln(t^{\frac{1}{2}}F) = \ln\left\{2C_1\left(\frac{D}{\pi}\right)^{\frac{1}{2}}\right\} - \frac{l^2}{4Dt}. \quad (4.27a)$$

From the slope and intercept of this line experimental data yield D and C_1 , and hence solubility. They discuss the advantages of their method compared with the use of the time lag given by eqn (4.26).

Other applications of Holstein's solution are discussed in § 10.6 and § 10.6.2 (pp. 216 and 224). Jenkins, Nelson, and Spirer (1970) examined the more general problems of deducing both the diffusion coefficient and the solubility coefficient from experimental data and mathematical solutions when the outflow volume is finite so that the concentration varies with time at the outgoing face. The necessary solution is given by Carslaw and Jaeger (1959). Jenkins *et al.* tabulate some useful calculated data and also consider varying concentrations at the ingoing face. In particular, they examined the assumption, frequently made in time-lag measurements of the Daynes type, that

steady flow is established after a period of about 3 times the time lag. They concluded that the time lag is underestimated by about 4 per cent by making this assumption.

Paul and Dibenedetto (1965) also obtained solutions for finite outflow volumes. Špaček and Kubin (1967) allowed the concentrations on both sides of the membrane to vary with time.

4.3.4. Variable surface concentration

The solution to the general problem of diffusion in the region $0 < x < l$ with the surfaces at concentrations $\phi_1(t)$ and $\phi_2(t)$ and the initial concentration $f(x)$ is given by Carslaw and Jaeger (1959, p. 102). For empirical values of $\phi_1(t)$, $\phi_2(t)$, and $f(x)$, three integrals arise which have to be evaluated graphically or numerically. In certain cases, however, where the surface concentration can be represented by a mathematical expression, the solution can be considerably simplified.

(i) One case of practical interest is that of a sheet in which the concentration is initially zero and each surface of which approaches an equilibrium concentration C_0 , exponentially, i.e.

$$\phi_1(t) = \phi_2(t) = C_0\{1 - \exp(-\beta t)\}. \quad (4.28)$$

This can represent a surface concentration which is changed rapidly but not instantaneously, a situation which usually arises when an instantaneous change is attempted in an experiment. For the sheet whose surfaces are at $\pm l$ the solution is

$$\frac{C}{C_0} = 1 - \exp(-\beta t) \frac{\cos x(\beta/D)^{\frac{1}{2}}}{\cos l(\beta/D)^{\frac{1}{2}}} - \frac{16\beta l^2}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n \exp(-D(2n+1)^2 \pi^2 t/4l^2)}{(2n+1)\{4\beta l^2 - D\pi^2(2n+1)^2\}} \cos \frac{(2n+1)\pi x}{2l}, \quad (4.29)$$

provided β is not equal to any of the values $D(2n+1)^2 \pi^2/4l^2$. The sorption-time curve, i.e. the curve showing the total amount M_t of diffusing substance in the sheet as a function of time t , is obtained by integrating (4.29) with respect to x between the limits $-l$ and $+l$ and is

$$\frac{M_t}{2lC_0} = 1 - \exp(-\beta t)(D/\beta l^2)^{\frac{1}{2}} \tan(\beta l^2/D)^{\frac{1}{2}} - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)^2 \pi^2 Dt/4l^2\}}{(2n+1)^2 [1 - (2n+1)^2 \{D\pi^2/(4\beta l^2)\}]}. \quad (4.30)$$

Fig. 4.3 shows uptake curves for different values of the parameter $\beta l^2/D$ plotted against $(Dt/l^2)^{\frac{1}{2}}$. When $\beta = \infty$, the surface concentration rises instantaneously to C_0 and the curve of Fig. 4.3 has the characteristic initial

referred to as the 'quadratic-profile' solution. The constant k is arbitrary but must not differ from unity by more than $O(hb)$. Least-squares or Chebyshev criteria can again be used but we choose $k = 1$. Crank and Parker (1966) tabulated their approximate solutions and compared them with the full analytical solution which is

$$v = \sum_{s=1}^{\infty} \frac{2h}{h+b(h^2+\alpha_s^2)} \frac{\cos \alpha_s x}{\cos \alpha_s b} \times \left\{ \frac{\sinh \alpha_s y}{\sinh \alpha_s} + 2\pi \exp(-\alpha_s^2 t) \sum_{r=1}^{\infty} \frac{(-1)^r r \exp(-r^2 \pi^2 t)}{r^2 \pi^2 + \alpha_s^2} \sin r \pi y \right\}, \quad (4.81)$$

where α_s , ($s = 1, 2, \dots$) are the positive roots of

$$\alpha \tan \alpha b = h, \quad (4.82)$$

for a range of values of h and b . They concluded that the 'constant-profile' solution which is usually used as an approximation for a thin sheet or rod is in fact, poor for a thin sheet with a high surface evaporation. But it provides a good approximation for a thick sheet with low surface loss. Both the 'quadratic profile' and the 'partial separation of variables' yield much better approximations over all. Concentration profiles across the sheet support these general conclusions.

As $hb \rightarrow 0$, the roots of (4.82) approach

$$b\alpha_1 \sim \sqrt{(hb)}, b\alpha_{n+1} \sim n\pi, n \geq 1.$$

Also the constant terms outside the curly brackets in (4.81) tend towards unity for $s = 1$ and the other terms either stay of the same order of magnitude or decrease, as s increases. It is easy to see that as $hb \rightarrow 0$ the analytical solution (4.81) approaches the approximate solution given by (4.73), (4.74), and (4.79). Crank and Parker show, however, that the approximate methods can readily be extended to cover some non-linear situations.

5

DIFFUSION IN A CYLINDER

5.1. Introduction

We consider a long circular cylinder in which diffusion is everywhere radial. Concentration is then a function of radius r and time t only, and the diffusion equation (1.7) becomes

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D \frac{\partial C}{\partial r} \right). \quad (5.1)$$

5.2. Steady state

If the medium is a hollow cylinder whose inner and outer radii are a and b respectively, and if the diffusion coefficient is constant, the equation describing the steady-state condition is

$$\frac{d}{dr} \left(r \frac{dC}{dr} \right) = 0, \quad a < r < b. \quad (5.2)$$

The general solution of this is

$$C = A + B \ln r, \quad (5.3)$$

where A and B are constants to be determined from the boundary conditions at $r = a$, $r = b$. If the surface $r = a$ is kept at a constant concentration C_1 , and $r = b$ at C_2 , then

$$C = \frac{C_1 \ln(b/r) + C_2 \ln(r/a)}{\ln(b/a)}. \quad (5.4)$$

The quantity of diffusing substance Q_t which diffuses through unit length of the cylinder in time t is given by

$$Q_t = \frac{2\pi D t (C_2 - C_1)}{\ln(b/a)}. \quad (5.5)$$

If Q_t is measured in a concentration-dependent system, the mean value of the diffusion coefficient obtained from (5.5) is $(\int_{C_1}^{C_2} D dC)/(C_2 - C_1)$ as for the plane sheet (see (4.11)). The concentration distribution defined by (5.4) is not linear, as it is for the plane sheet. Typical distributions are shown in Fig. 5.1 for the cases $C_2 = 0$, $b/a = 2, 5, 10$.

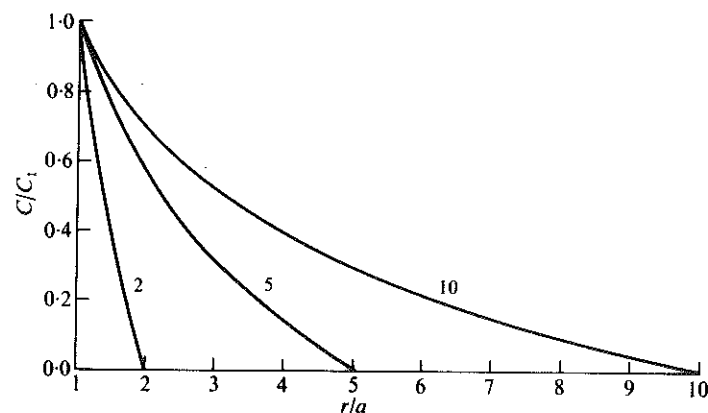


FIG. 5.1. Steady-state concentration distributions through cylinder wall. Numbers on curves are values of b/a .

Another steady-state problem leading to an interesting result is that of the hollow cylinder whose surface $r = a$ is kept at a constant concentration C_1 , and at $r = b$ there is evaporation into an atmosphere for which the equilibrium concentration just within the surface is C_2 . The boundary condition, with the constant of proportionality denoted by h , is

$$\frac{dC}{dr} + h(C - C_2) = 0, \quad r = b, \quad (5.6)$$

and we find

$$C = \frac{C_1 \{1 + hb \ln(b/r)\} + hb C_2 \ln(r/a)}{1 + hb \ln(b/a)}. \quad (5.7)$$

The outward rate of diffusion per unit length of the cylinder is Q_i , where

$$Q_i = 2\pi D(C_1 - C_2) \frac{hb}{1 + hb \ln(b/a)}. \quad (5.8)$$

By differentiating this expression with respect to b , it is easily seen that if $ah > 1$ the rate of diffusion decreases steadily as b increases from a , but if $ah < 1$ the rate first increases and later decreases, passing through a maximum when $b = 1/h$. This is due to the two opposing changes associated with an increase in b . On the one hand, the rate of evaporation is increased because of the increase in area of the surface, $r = b$, as b increases, but on the other hand, the gradient of concentration through the cylinder decreases as b is increased. In certain circumstances, therefore, the rate of diffusion through the wall of a pipe may be increased by making the wall thicker (Porter and Martin 1910). This is illustrated in Fig. 5.2 for $ah = \frac{1}{2}$.

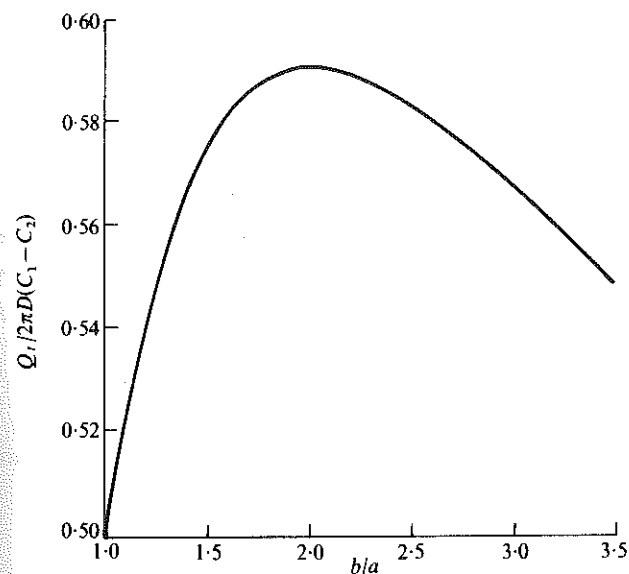


FIG. 5.2. Effect of thickness of cylinder wall on steady-state rate of flow.

If the surface conditions are

$$\partial C / \partial r + h_1(C_1 - C) = 0; \quad \partial C / \partial r + h_2(C - C_2) = 0, \quad (5.6a)$$

we find

$$C = \frac{ah_1 C_1 \{1 + bh_2 \ln(b/r)\} + bh_2 C_2 \{1 + ah_1 \ln(r/a)\}}{ah_1 + bh_2 + abh_1 h_2 \ln(b/a)}, \quad (5.7a)$$

and

$$Q_i = \frac{2\pi Dtabh_1 h_2 (C_2 - C_1)}{ah_1 + bh_2 + abh_1 h_2 \ln(b/a)}. \quad (5.8a)$$

Other problems on diffusion in regions bounded by surfaces of the cylindrical coordinate system and in which the flow is not necessarily radial are treated by Carslaw and Jaeger (1959, p. 214).

5.3. Non-steady state: solid cylinder

Following essentially the method of separating the variables described in § 2.3 (p. 17), we see that

$$C = u \exp(-D\alpha^2 t) \quad (5.9)$$

is a solution of (5.1) for D constant provided u is a function of r only, satisfying

$$\frac{d^2u}{dr^2} + \frac{1}{r} \frac{du}{dr} + \alpha^2 u = 0, \quad (5.10)$$

which is Bessel's equation of order zero. Solutions of (5.10) may be obtained in terms of Bessel functions, suitably chosen so that the initial and boundary conditions are satisfied. Thus if the initial concentration distribution is $f(r)$ and the surface $r = a$ is maintained at zero concentration, a solution of (5.1) is wanted satisfying

$$C = 0, \quad r = a, \quad t \geq 0, \quad (5.11)$$

$$C = f(r), \quad 0 < r < a, \quad t = 0. \quad (5.12)$$

The boundary condition (5.11) is satisfied by

$$C = \sum_{n=1}^{\infty} A_n J_0(\alpha_n r) \exp(-D\alpha_n^2 t), \quad (5.13)$$

provided the α_n s are roots of

$$J_0(a\alpha_n) = 0, \quad (5.14)$$

where $J_0(x)$ is the Bessel function of the first kind of order zero. Roots of (5.14) are tabulated in tables of Bessel functions. For this function C is finite at $r = 0$. The initial condition (5.12) becomes

$$f(r) = \sum_{n=1}^{\infty} A_n J_0(r\alpha_n), \quad (5.15)$$

it being assumed that $f(r)$ can be expanded in a series of Bessel functions of order zero. The A_n s are determined by multiplying both sides of (5.15) by $rJ_0(\alpha_n r)$ and integrating from 0 to a using the results,

$$\int_0^a r J_0(\alpha r) J_0(\beta r) dr = 0, \quad (5.16)$$

when α and β are different roots of (5.14), and

$$\int_0^a r \{J_0(\alpha r)\}^2 dr = \frac{1}{2} a^2 J_1^2(a\alpha_n), \quad (5.17)$$

where $J_1(x)$ is the Bessel function of the first order and α is a root of (5.14). The derivation of the relationships (5.16) and (5.17), and of corresponding expressions which hold when α is a root not of (5.14) but of alternative equations which commonly arise in diffusion problems, is given by Carslaw

and Jaeger (1959, p. 196). Finally the solution satisfying (5.11) and (5.12) is

$$C = \frac{2}{a^2} \sum_{n=1}^{\infty} \exp(-D\alpha_n^2 t) \frac{J_0(r\alpha_n)}{J_1^2(a\alpha_n)} \int_0^a r f(r) J_0(r\alpha_n) dr. \quad (5.18)$$

Alternatively, solutions for both large and small times can be obtained by use of the Laplace transform.

5.3.1. Surface concentration constant: initial distribution $f(r)$

If in the cylinder of radius a the conditions are

$$C = C_0, \quad r = a, \quad t \geq 0, \quad (5.19)$$

$$C = f(r), \quad 0 < r < a, \quad t = 0, \quad (5.20)$$

the solution is

$$C = C_0 \left\{ 1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{1}{\alpha_n} \frac{J_0(r\alpha_n)}{J_1(a\alpha_n)} \exp(-D\alpha_n^2 t) \right\} + \frac{2}{a^2} \sum_{n=1}^{\infty} \exp(-D\alpha_n^2 t) \frac{J_0(r\alpha_n)}{J_1^2(a\alpha_n)} \int_0^a r f(r) J_0(r\alpha_n) dr, \quad (5.21)$$

where the α_n s are the positive roots of (5.14).

If the concentration is initially uniform throughout the cylinder $f(r) = C_1$ and (5.21) reduces to

$$\frac{C - C_1}{C_0 - C_1} = 1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t) J_0(r\alpha_n)}{\alpha_n J_1(a\alpha_n)}. \quad (5.22)$$

If M_t denotes the quantity of diffusing substance which has entered or left the cylinder in time t and M_∞ the corresponding quantity after infinite time, then

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp(-D\alpha_n^2 t). \quad (5.23)$$

The corresponding solution useful for small times is

$$\frac{C - C_1}{C_0 - C_1} = \frac{a^{\frac{1}{2}}}{r^{\frac{1}{2}}} \operatorname{erfc} \frac{a-r}{2\sqrt{(Dt)}} + \frac{(a-r)(Dt)^{\frac{1}{2}}}{4ar^{\frac{1}{2}}} \operatorname{ierfc} \frac{a-r}{2\sqrt{(Dt)}} + \frac{(9a^2 - 7r^2 - 2ar)Dt}{32a^{\frac{3}{2}}r^{\frac{1}{2}}} \operatorname{i}^2 \operatorname{erfc} \frac{a-r}{2\sqrt{(Dt)}} + \dots, \quad (5.24)$$

which holds provided r/a is not small. The case of r/a small is discussed by Carsten and McKerrow (1944). They give a series solution involving modified Bessel functions of order $n \pm \frac{1}{2}$. The necessary functions are tabulated in their paper and numerical calculation is straightforward.

Also for small times we have

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{\frac{1}{2}}} \left(\frac{Dt}{a^2} \right)^{\frac{1}{2}} - \frac{Dt}{a^2} + \frac{1}{3\pi^{\frac{1}{2}}} \left(\frac{Dt}{a^2} \right)^{\frac{3}{2}} + \dots \quad (5.25)$$

Clearly these solutions are not as valuable as the corresponding ones for the plane sheet. In practice the range in t over which they are convenient for evaluation is less than in the plane case.

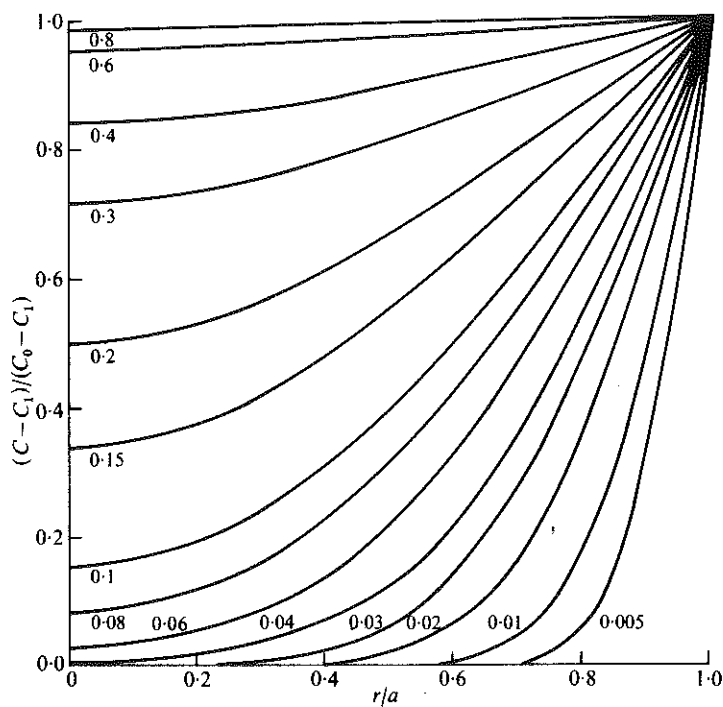


FIG. 5.3. Concentration distributions at various times with initial concentration C_1 and surface concentration C_0 . Numbers on curves are values of Dt/a^2 .

The solutions for the cylinder can be written in terms of the two dimensionless parameters Dt/a^2 and r/a . Curves showing $(C - C_1)/(C_0 - C_1)$ as a function of r/a for different values of Dt/a^2 drawn by Carslaw and Jaeger (1959, p. 200) are reproduced in Fig. 5.3. The curve of Fig. 5.7 for zero fractional uptake shows how M_t/M_∞ depends on Dt/a^2 when the concentration at the surface of the cylinder remains constant.

5.3.2. Variable surface concentration

If the initial concentration in the cylinder is zero and that at the surface is $\phi(t)$, the solution is

$$C = \frac{2D}{a} \sum_{n=1}^{\infty} \exp(-D\alpha_n^2 t) \frac{\alpha_n J_0(r\alpha_n)}{J_1(a\alpha_n)} \int_0^t \exp(D\alpha_n^2 \lambda) \phi(\lambda) d\lambda, \quad (5.26)$$

where the α_n s are the roots of (5.14).

(i) As for the plane sheet, a case of practical interest is when

$$\phi(t) = C_0 \{1 - \exp(-\beta t)\}, \quad (5.27)$$

representing a surface concentration which approaches a steady value C_0 , but not instantaneously. The solution (5.26) then becomes

$$\frac{C}{C_0} = 1 - \frac{J_0\{(\beta r^2/D)^{\frac{1}{2}}\}}{J_0\{(\beta a^2/D)^{\frac{1}{2}}\}} \exp(-\beta t) + \frac{2\beta}{aD} \sum_{n=1}^{\infty} \frac{J_0(r\alpha_n)}{\alpha_n J_1(a\alpha_n)} \frac{\exp(-D\alpha_n^2 t)}{(\alpha_n^2 - \beta/D)}, \quad (5.28)$$

and the sorption-time curve is given by

$$\frac{M_t}{\pi a^2 C_0} = 1 - \frac{2J_1\{(\beta a^2/D)^{\frac{1}{2}}\} \exp(-\beta t)}{(\beta a^2/D)^{\frac{1}{2}} J_0\{(\beta a^2/D)^{\frac{1}{2}}\}} + \frac{4}{a^2} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)}{\alpha_n^2 \{\alpha_n^2/(\beta/D) - 1\}}. \quad (5.29)$$

Fig. 5.4 shows uptake curves for different values of the parameter $\beta a^2/D$.

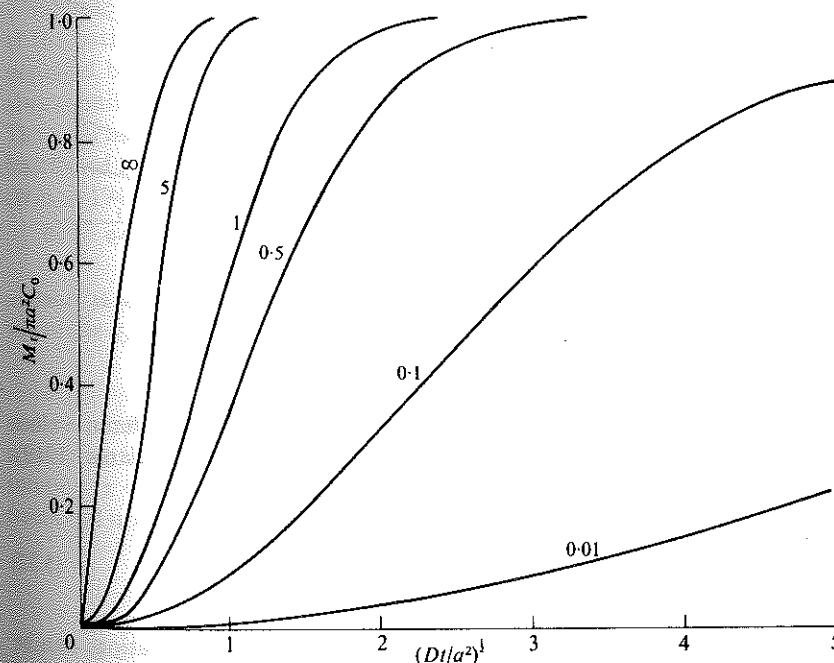


FIG. 5.4. Calculated sorption curves for surface concentration given by $C_0(1 - e^{-\beta t})$. Numbers on curves are values of $\beta a^2/D$.