THE MATHEMATICS OF DIFFUSION

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PREFACE

A MORE precise title for this book would be 'Mathematical solutions of the diffusion equation', for it is with this aspect of the mathematics of diffusion that the book is mainly concerned. It deals with the description of diffusion processes in terms of solutions of the differential equation for diffusion. Little mention is made of the alternative, but less well developed, description in terms of what is commonly called 'the random walk', nor are theories of the mechanism of diffusion in particular systems included.

The mathematical theory of diffusion is founded on that of heat conduction and correspondingly the early part of this book has developed from 'Conduction of heat in solids' by Carslaw and Jaeger. These authors present many solutions of the equation of heat conduction and some of them can be applied to diffusion problems for which the diffusion coefficient is constant. I have selected some of the solutions which seem most likely to be of interest in diffusion and they have been evaluated numerically and presented in graphical form so as to be readily usable. Several problems in which diffusion is complicated by the effects of an immobilizing reaction of some sort are also included. Convenient ways of deriving the mathematical solutions are described.

When we come to systems in which the diffusion coefficient is not constant but variable, and for the most part this means concentration dependent, we find that strictly formal mathematical solutions no longer exist. I have tried to indicate the various methods by which numerical and graphical solutions have been obtained, mostly within the last ten years, and to present, again in graphical form, some solutions for various concentration-dependent diffusion coefficients. As well as being useful in themselves these solutions illustrate the charactoristic features of a concentration-dependent system. Consideration is also given to the closely allied problem of determining the diffusion coefficient and its dependence on concentration from experimental measurements. The diffusion coefficients measured by different types of experiment are shown to be simply related. The final chapter deals with the temperature changes which sometimes accompany diffusion.

In several instances I have thought it better to refer to an casily accessible book or paper rather than to the first published account, which the reader might find difficult to obtain. Ease of reference

PREFACE

usually seemed of primary importance, particularly with regard to mathematical solutions.

I should like to express my thanks to my friend and colleague, Mr. A. C. Newns, who read the typescript and made many valuable comments and suggestions, and also to Mrs. D. D. Whitmore, who did most of the calculations and helped to correct the proofs and compile the index. I am grateful 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. J. C.

Maidenhead December 1955

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I

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

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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 [1], who first put diffusion on a quantitative basis by adopting the mathematical equation of heat conduction derived some years earlier by Fourier [2]. 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.

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

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. grammes or gramme molecules, then it is clear from (1,1) that D is independent of this unit and has dimensions length² time⁻¹, e.g. cm.² sec.⁻¹ The negative sign in equation (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, this need not be true in an anisotropic medium for which the diffusion properties depend on the direction in which they are measured.

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1.3. Differential equation of diffusion

The fundamental differential equation of diffusion in an isotropic medium is derived from equation (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 2dx, 2dy, 2dz. 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



FIG. 1.1. Element of volume.

which diffusing substance enters the element through the face ABCD in the plane x-dx is given by

$$4dydz\left(F_{x}-\frac{\partial F_{x}}{\partial x}\,dx\right),$$

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

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

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

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

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

$$8dxdydz\frac{\partial C}{\partial t}$$
,



and hence we have immediately

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

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

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

 $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2},$ reducing simply to (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 [1] 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, equation (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

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

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

1.31. Diffusion in a cylinder and sphere Other forms of the above equations follow by transformation of coordinates, or by considering elements of volume of different shape. Thus by putting

$$\begin{aligned} x &= r\cos\theta, \\ y &= r\sin\theta, \end{aligned}$$

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,

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

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

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

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

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

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \left\{ \frac{\partial}{\partial r} \left(Dr^2 \frac{\partial C}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(D\sin \theta \frac{\partial C}{\partial \theta} \right) + \frac{D}{\sin^2 \theta} \frac{\partial^2 C}{\partial \phi^2} \right\}.$$
(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 V and VI 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

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

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 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

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$$-F_{x} = D_{11}\frac{\partial C}{\partial x} + D_{12}\frac{\partial C}{\partial y} + D_{13}\frac{\partial C}{\partial z}$$

$$-F_{y} = D_{21}\frac{\partial C}{\partial x} + D_{22}\frac{\partial C}{\partial y} + D_{23}\frac{\partial C}{\partial z}$$
, (1.9)

$$-F_{z} = D_{31}\frac{\partial C}{\partial x} + D_{32}\frac{\partial C}{\partial y} + D_{33}\frac{\partial C}{\partial z}$$

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

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

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

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

This is the same transformation as that by which the ellipsoid

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

is reduced to $D_1\xi^2 + D_2\eta^2 + D_3\zeta^2 = \text{constant.}$ (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

$$\xi_1 = \xi_1 \langle D/D_1 \rangle, \qquad \eta_1 = \eta_1 \langle D/D_2 \rangle, \qquad \zeta_1 = \zeta_1 \langle D/D_3 \rangle, \qquad (1.14)$$

where D may be chosen arbitrarily, (1.11) becomes

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

This has the same form as equation (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 = 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 [3, p. 29] 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, nrelative to the principal axes of diffusion is given by

$$D_n = l^2 D_1 + m^2 D_2 + n^2 D_3. \tag{1.16}$$

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

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

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.

1.41. 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

$$\frac{\partial C}{\partial t} \equiv D_{11} \frac{\partial^2 C}{\partial x^2},\tag{1.18}$$

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

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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 unidirectional 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

THE DIFFUSION EQUATIONS

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.

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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 [1].

2.2. Method of reflection and superposition

2.21. Plane source

It is easy to see by differentiation that

$$C = \frac{A}{t^{i}} e^{-x^{i}/4Dt}, \qquad (2.1)$$

where A is an arbitrary constant, is a solution of

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

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 = 0it 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

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

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

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



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

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 equation (2.1), we obtain

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that

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

DIFFUSION COEFFICIENT IS CONSTANT

2.22. 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

$$C = \frac{M}{(\pi D t)^{\frac{1}{2}}} e^{-x^{\frac{3}{4}Dt}}.$$
 (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

$$\partial C/\partial x = 0, \qquad x = 0,$$
 (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.

2.23. 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

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 $C = C_0$, x < 0, C = 0, x > 0, t = 0. (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 $d\xi$ to be a line source of strength $C_0 d\xi$. Then, from (2.6) the concentration at point P, distance ξ from the element, at time t is



FIG. 2.2. Extended initial distribution.

and the complete solution due to the initial distribution (2.9) is given by summing over successive elements $d\xi$, i.e. by

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

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

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

$$\operatorname{erf} z = \frac{2}{\pi^{\frac{1}{2}}} \int_{0}^{z} e^{-\eta^{*}} d\eta. \qquad (2.11)$$

This function has the properties

 $\operatorname{erf}(-z) = -\operatorname{erf} z, \quad \operatorname{erf}(0) = 0, \quad \operatorname{erf}(\infty) = 1, \quad (2.12)$ and hence, since

$$\int_{z}^{\infty} e^{-\eta^{*}} d\eta = \int_{0}^{\infty} e^{-\eta^{*}} d\eta - \int_{0}^{z} e^{-\eta^{*}} d\eta = 1 - \operatorname{erf} z = \operatorname{erfc} z, \quad (2.13)$$

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

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



§ 2.2] DIFFUSION COEFFICIENT IS CONSTANT

Convenient tables of the error function are those of the Works Project Association [2] and shorter tables are to be found, for example, in Milne-Thomson and Comrie [3]. Table 2.1, taken from Carslaw and Jaeger [1], 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.



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

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.

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

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$$C = \frac{1}{2}C_0 \left\{ \operatorname{erf} \frac{h - x}{2\sqrt{Dt}} + \operatorname{erf} \frac{h + x}{2\sqrt{Dt}} \right\}.$$
(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 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 infinitelylong 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.



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

2.24. 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.

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

We have seen that this condition is satisfied if the concentration curve is considered to be reflected at the land

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

$$C = \frac{1}{2}C_{0} \left\{ \operatorname{erfc} \frac{x-h}{2\sqrt{(Dt)}} - \operatorname{erfc} \frac{x+h}{2\sqrt{(Dt)}} + \operatorname{erfc} \frac{2l-h-x}{2\sqrt{(Dt)}} - \operatorname{erfc} \frac{2l+h-x}{2\sqrt{(Dt)}} + \operatorname{erfc} \frac{2l-h+x}{2\sqrt{(Dt)}} - \operatorname{erfc} \frac{2l+h+x}{2\sqrt{(Dt)}} + \operatorname{erfc} \frac{4l-h-x}{2\sqrt{(Dt)}} - \operatorname{erfc} \frac{4l-x+h}{2\sqrt{(Dt)}} + \ldots \right\}$$
$$= \frac{1}{2}C_{0} \sum_{n=-\infty}^{\infty} \left\{ \operatorname{erf} \frac{h+2nl-x}{2\sqrt{(Dt)}} + \operatorname{erf} \frac{h-2nl+x}{2\sqrt{(Dt)}} \right\}.$$
(2.17)

A solution of this kind can be obtained for most problems in diffusion by use of the Laplace transform, to be discussed below in § 2.4, 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 [4, p. 38]. 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

$$C = \mathbf{Y}(\alpha) \mathcal{D}(0) \tag{2.10}$$

$$\circ = \Delta(x) \Delta(t), \quad (2.18)$$

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

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

which may be rewritten

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

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 must therefore 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

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

and

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

of which solutions are

$$T = e^{-\lambda^2 D l}, \qquad (2.22)$$

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

leading to a solution of (2.2) of the form

$$C = (A \sin \lambda x + B \cos \lambda x)e^{-\lambda^{2}Dt}, \qquad (2.24)$$

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

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

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

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

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

The boundary conditions (2.27) demand that

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

and hence the initial condition (2.26) becomes

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

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

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

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

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

The final solution is therefore

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

where 2n+1 has been substituted for m for convenience so that n takes values 0, 1, 2,.... 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 § 2.24.

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 conditions. 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 Doetsch [5], Carslaw and Jaeger [6], Churchill [7], and others. Shorter accounts by Jaeger [8] and Tranter [9] 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.

2.41. Definition of the Laplace transform

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

$$\tilde{f}(p) = \int_{0}^{\infty} e^{-pt} f(t) \, dt, \qquad (2.32)$$

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 $f(t) = e^{2t}$, p must exceed 2. Unless it is necessary to emphasize that \overline{f} is a function of p, just as f is a function of t, we shall usually denote the Laplace transform of f by \overline{f} .

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

$$f(t) = 1, \qquad \bar{f}(p) = \int_{0}^{\infty} e^{-pt} dt = 1/p,$$
 (2.33)

$$f(t) = e^{at}, \qquad \bar{f}(p) = \int_{0}^{\infty} e^{-pt} e^{at} dt = \int_{0}^{\infty} e^{-(p-a)t} dt = \frac{1}{p-a}, \quad (2.34)$$

$$f(t) = \sin \omega t, \qquad \bar{f}(p) = \int_{0}^{\infty} e^{-pt} \sin \omega t \, dt = \frac{\omega}{p^2 + \omega^2}. \qquad (2.35)$$

Extensive tables or dictionaries of Laplace transforms are available, some in the works referred to above and others by Doetsch [10] and by McLachlan and Humbert [11]. A short table of transforms occurring frequently in diffusion problems is reproduced from Carslaw and Jaeger's book [1] in Table 2.2.

2.42. 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

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

satisfying the boundary condition

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

and the initial condition

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

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

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

$$\int_{0}^{\infty} e^{-pt} \frac{\partial^2 C}{\partial x^2} dt = \frac{\partial^2}{\partial x^2} \int_{0}^{\infty} C e^{-pt} dt = \frac{\partial^2 \bar{C}}{\partial x^2}.$$
 (2.40)

Also, integrating by parts we have

$$\int_{0}^{\infty} e^{-pt} \frac{\partial C}{\partial t} dt = \left[C e^{-pt} \right]_{0}^{\infty} + p \int_{0}^{\infty} C e^{-pt} dt = p \overline{C}, \qquad (2.41)$$

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 $\partial^2 \bar{C} = \bar{C}$

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

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

$$\bar{C} = \int_{0}^{\infty} C_0 e^{-pt} dt = \frac{C_0}{p}, \qquad x = 0.$$
 (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 \overline{C} remains finite as x approaches infinity is

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

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

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

where, as before, $\operatorname{erfc} z = 1 - \operatorname{erf} z.$ (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.

2.43. 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 surfaces are maintained at constant concentration, C_0 , and with zero concentration of diffusing substance throughout the sheet initially. Let the sheet occupy the region $-l \leqslant x \leqslant l$, so that there is symmetry about x = 0 and the boundary conditions may be written

$$C = C_0, \qquad x = l, \qquad t \ge 0, \qquad (2.47)$$

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

Equation (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, $0\leqslant x\leqslant l$, instead of using the condition $C = C_0, x = -l$.

The equations for the Laplace transform $ar{C}$ are

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

with

$$dC/dx = 0, \qquad x = 0,$$
 (2.50)

$$\bar{C} = C_0/p, \qquad x = l, \tag{2.51}$$

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

$$\bar{C} = \frac{C_0 \cosh qx}{p \cosh ql}.$$
(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 functions in (2.52) in terms of negative exponentials and expand in a series by the binomial theorem. Thus we obtain from (2.52),

$$\bar{C} = \frac{C_0(e^{qx} + e^{-qx})}{pe^{ql}(1 + e^{-2ql})} = \frac{C_0}{p} \{e^{-q(l-x)} + e^{-q(l+x)}\} \sum_{n=0}^{\infty} (-1)^n e^{-2nql}$$
$$= \frac{C_0}{n} \sum_{n=0}^{\infty} (-1)^n e^{-q((2n+1)l-x)} + \frac{C_0}{n} \sum_{n=0}^{\infty} (-1)^n e^{-q((2n+1)l+x)} = (-1)^n e^{-q((2n+1)l+x} = (-1)^n e^{-q((2n+1)l+x}) = (-1)^n e^{-$$

$$= \frac{C_0}{p} \sum_{n=0}^{\infty} (-1)^n e^{-q\{(2n+1)l-x\}} + \frac{C_0}{p} \sum_{n=0}^{\infty} (-1)^n e^{-q\{(2n+1)l+x\}}.$$
 (2.53)

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

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

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

and when $Dt/l^2 = 0.25$

$$C/C_0 = 0.3146 - 0.0001 = 0.3145. \tag{2.56}$$

(ii) Expression in partial fractions

It can be shown that if a transform \bar{y} has the form

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

$$g(p) = (p-a_1)(p-a_2)...(p-a_n), \qquad (2.58)$$

where $a_1, a_2, ..., a_n$ 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

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

Here $g'(a_r)$ denotes the value of dg(p)/dp when $p = a_r$. A proof of this by Jaeger [8] 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

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(see, for example, [12], p. 275) $\cosh z = \left(1 + \frac{4z^2}{\pi^2}\right) \left(1 + \frac{4z^2}{3^2 \pi^2}\right) \left(1 + \frac{4z^2}{5^2 \pi^2}\right) \dots,$ (2.60) $\sinh z = z \left(1 + \frac{z^2}{\pi^2}\right) \left(1 + \frac{z^2}{2^2 \pi^2}\right) \left(1 + \frac{z^2}{3^2 \pi^2}\right) \dots,$ (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 $a_1, a_2,...$ 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 $a_1, a_2,...$ 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.

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

and hence

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

To apply (2.59) to (2.52) we need

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

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

$$g'(p) = \frac{(2n+1)\pi(-1)^{n+1}}{4}.$$
 (2.66)

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

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

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

and when $Dt/l^2 = 0.25$

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

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

Consider the equation of diffusion

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

in the rectangular parallelepiped

$$a_1 < x_1 < b_1, \ a_2 < x_2 < b_2, \ a_3 < x_3 < b_3.$$
 (2.71)

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 [1, p. 22].

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

$$\frac{\partial^2 c_r}{\partial x_r^2} = \frac{1}{D} \frac{\partial c_r}{\partial t}, \quad a_r < x_r < b_r, \tag{2.72}$$

with boundary conditions

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

$$lpha_r'rac{\partial c_r}{\partial x_r}+eta_r'c_r=0, \qquad x_r=b_r, \qquad t>0, \qquad (2.74)$$

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

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

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

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

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and with boundary conditions

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$$lpha_{r} rac{\partial c}{\partial x_{r}} - eta_{r} c = 0, \quad x_{r} = a_{r}, \quad t > 0, \quad r = 1, 2, 3, \quad (2.77)$$

 $lpha_{r} rac{\partial c}{\partial x_{r}} - eta_{r} c = 0, \quad x_{r} = b_{r}, \quad t > 0, \quad r = 1, 2, 3, \quad (2.78)$
 $c = c_{1}(x_{1}, t)c_{2}(x_{2}, t)c_{3}(x_{3}, t). \quad (2.79)$

For substituting (2.79) in (2.70) gives

$$c_{2}c_{3}\frac{\partial^{2}c_{1}}{\partial x_{1}^{2}} + c_{3}c_{1}\frac{\partial^{2}c_{2}}{\partial x_{2}^{2}} + c_{1}c_{2}\frac{\partial^{2}c_{3}}{\partial x_{3}^{2}} - \frac{1}{D}\left(c_{2}c_{3}\frac{\partial c_{1}}{\partial t} + c_{3}c_{1}\frac{\partial c_{2}}{\partial t} + c_{1}c_{2}\frac{\partial c_{3}}{\partial t}\right) = 0,$$
(2.80)

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

Similar results hold for combined radial and axial flow in a solid or hollow cylinder, and for other regions such as a rectangular corner [1].

APPENDIX TO CHAPTER II

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

$$\ddot{y}(p) = \frac{f(p)}{g(p)},\tag{1}$$

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

$$\frac{f(p)}{g(p)} = \sum_{r=1}^{n} \frac{A_r}{p-a_r} = \frac{A_1}{p-a_1} + \frac{A_2}{p-a_2} + \frac{A_3}{p-a_3} + \dots + \frac{A_n}{p-a_n}.$$
 (2)

$$f(p) = \sum_{r=1}^{n} A_r(p-a_1)...(p-a_{r-1})(p-a_{r+1})...(p-a_n), \qquad (3)$$

and putting $p = a_r$ in this gives

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

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

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

Now since

$$g(p) = (p-a_1)(p-a_2)...(p-a_n), \tag{6}$$

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

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

Putting $p = a_r$ in this, gives

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

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

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

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

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

(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

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

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

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

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

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

in the solution.

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3.1. Introduction

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In this and the following three chapters solutions of the diffusion equation are presented for different initial and boundary conditions. In 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, when 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 II, equation (2.6). The corresponding solution for an instantaneous point source on an infinite plane surface is obtained in the same way by recognizing that

$$C = \frac{A}{t} e^{-(x^2 + y^2)/4Dt}$$
(3.1)

is a solution of
$$\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} = \frac{1}{D} \frac{\partial C}{\partial t},$$
 (3.2)

which is the equation for diffusion in two dimensions when the diffusion

coefficient is constant. The arbitrary constant A is expressed in terms of M, the total amount of substance diffusing, by performing the integration കര

$$M = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C \, dx dy = 4\pi DA, \qquad (3.3)$$

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

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

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

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

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

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

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 II 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

$$C = \frac{M}{4\pi Dt} e^{-r^2/4Dt},$$
 (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 [1, p. 216]. 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

$$C = \frac{1}{2}C_0 \left\{ \operatorname{erf} \frac{a+r}{2\sqrt{(Dt)}} + \operatorname{erf} \frac{a-r}{2\sqrt{(Dt)}} \right\} - \frac{C_0}{r} \sqrt{\left(\frac{Dt}{\pi}\right)} \left\{ e^{-(a-r)^2/4Dt} - e^{-(a+r)^2/4Dt} \right\},$$
(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 diffusingsubstance, M, since $M = \frac{4}{3}\pi a^3 C_0$.(3.9)

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

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

where I_0 is the modified Bessel function of the first kind of order zero. Tables of I_0 are available [2]. The integral in (3.10) has to be evaluated numerically except on the axis r = 0, where (3.10) becomes

$$C = C_0(1 - e^{-a^3/4Dt}). \tag{3.11}$$

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).

The expression (3.10) and the curves of Fig. 3.2 also apply to a circular disk-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 [3] is

$$C = aC_0 \int_0^{\infty} J_1(ua) J_0(ur) e^{-D(u^2)} du, \qquad (3.10 a)$$

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 [2]. Rideal and Tadayon [3] also give an expression for the total amount of diffusing substance, Q, remaining on the disk after time t, which is

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

For small values of t, (3.10 b) becomes

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

and when t is large we have

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

(3.12)

Cases of an extended source in an infinite medium, where the diffusing substance initially occupies the semi-infinite region x < 0 or is confined

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to the region -h < x < h, have been considered (see equations (2.14) and (2.15) in Chapter II). 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

$$C=rac{1}{2}C_0\Big\{ ext{erfc}rac{h\!-\!x}{2\sqrt{(Dt)}}+ ext{erfc}rac{h\!+\!x}{2\sqrt{(Dt)}}\Big\}.$$



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



Fig. 3.2. Concentration distributions for a cylindrical source. Numbers on curves are values of $(Dt/a^2)^4$.

3.21. 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

$$C = \frac{1}{8(\pi D)^{\frac{1}{2}}} \int_{0}^{t} \phi(t') e^{-r^{2}/4D(t-t')} \frac{dt'}{(t-t')^{\frac{1}{2}}}.$$
 (3.5 a)

If ϕ is constant and equal to q, then

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

Solutions for other continuous sources are obtained similarly and examples are given by Carslaw and Jaeger [1, p. 220].

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 II, equation (2.7), and that for the initial distribution $C = C_0$, 0 < x < h, C = 0, x > h, was seen to be given by equation (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 II, § 2.42 (see equation 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 .

$$\frac{C-C_1}{C_0-C_1} = \operatorname{erf} \frac{x}{2\sqrt{Dt}}.$$
(3.13)

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

$$\left(D\frac{\partial C}{\partial x}\right)_{x=0} = \frac{DC_0}{\sqrt{(\pi Dt)}},\qquad(3.14)$$

so that the total amount M_t of diffusing substance which has left the medium at time t is given by integrating (3.14) with respect to t and is

$$M_t = 2C_0 \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}.$$
 (3.15)

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

$$C = kt \left\{ \left(1 + \frac{x^2}{2Dt} \right) \operatorname{erfc} \frac{x}{2\sqrt{Dt}} - \frac{x}{\sqrt{(\pi Dt)}} e^{-x^2/4Dt} \right\}$$
$$= 4kt \, \mathrm{i}^2 \operatorname{erfc} \frac{x}{2\sqrt{(Dt)}}. \quad (3.16)$$

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

The function i^2 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.

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

$$C = kt^{\frac{1}{2}} \left\{ e^{-x^{\frac{3}{4}Dt}} - \frac{x\pi^{\frac{1}{2}}}{2\sqrt{Dt}} \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \right\}$$
$$= k(\pi t)^{\frac{1}{2}} \operatorname{ierfc} \frac{x}{2\sqrt{Dt}}.$$
(3.18)

$$M_l = \frac{1}{2}kt(\pi D)^{\frac{1}{2}}.$$
 (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.

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

$$M_{i} = \frac{k}{2^{n}} \sqrt{Dt}(4t)^{\frac{1}{2}n} \frac{\Gamma(\frac{1}{2}n+1)}{\Gamma(\frac{1}{2}n+\frac{3}{2})}.$$
(3.20)
(3.21)

The function iⁿerfc is defined and tabulated up to n = 6 in Table 2.1. $\Gamma(n)$ is the gamma function defined and tabulated, for example, in ref. 4, p. 210. If n is even, so that $\frac{1}{2}n = N$, an integer, then

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



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

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(3.22)

If n is odd, so that $\frac{1}{2}n = M - \frac{1}{2}$, then $\Gamma(\frac{1}{2}n+1) = \Gamma(M+\frac{1}{2}) = 1.3.5...(2M-3)(2M-1)\pi^{\frac{1}{2}}/2^{M}.$ (3.23) Other properties of gamma functions are

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

A polynomial in t^{\dagger} 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
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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

$$C_{x=0} = C_0 + kt \tag{3.25}$$

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

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

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

$$\begin{array}{ll} C = C_0, & x = 0 \\ C = 0, & x > 0 \end{array} \right\},$$
 (3.27)

and the second term satisfies

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$$\begin{array}{ll}
C = kt, & x = 0 \\
C = 0, & x > 0
\end{array}$$
(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

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

where c_1 is a solution of the diffusion equation which satisfies

$$c_1 = 0, \qquad t = 0 \\ c_1 = F(t), \qquad x = 0$$
 (3.30)

and c_2 is another solution satisfying

$$\begin{array}{ll} c_2 = f(x), & t = 0 \\ c_2 = 0, & x = 0 \end{array} \right\}.$$
 (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

$$C = C_0 + 4kt \,\mathrm{i}^2 \mathrm{erfe} \,\frac{x}{2\sqrt{(Dt)}},\tag{3.32}$$

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

$$\begin{array}{ll}
C = C_0, & x > 0, & t = 0 \\
C = 0, & x = 0, & t > 0 \end{array}, \quad (3.33)$$

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

3.31. 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

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

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

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

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_0 , of diffusing substance in the semi-infinite medium per unit cross-sectional area changes is given by

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

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,

$$M_{l} = \left(\frac{C_{0} - C_{2}}{h}\right) \left\{ e^{h^{*}Dt} \operatorname{erfc} h_{\sqrt{Dt}} - 1 + \frac{2}{\pi^{*}} h_{\sqrt{Dt}} \right\}.$$
(3.37)

§ 3.3]

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

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



FIG. 3.4. Concentration distribution for a surface evaporation condition in a semiinfinite medium. Numbers on curves are values of $h(Dt)^{\frac{1}{2}}$.

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 $hM_l/(C_0-C_2)$ 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. 3.5. The evaluation for large $h\sqrt{(Dt)}$ is made easier by using the asymptotic formula

$$\exp(z^2)\operatorname{erfe} z = \frac{1}{\pi^4} \left(\frac{1}{z} - \frac{1}{2z^3} + \frac{1}{2^2 \cdot z^5} \cdots \right). \tag{3.39}$$

3.32. 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



medium.

surface of which is maintained constant, involves only the single dimensionless parameter

$$\frac{x}{2\sqrt{(Dt)}}.$$
(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. 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 < 0the boundary conditions at the interface x = 0 may be written

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

$$D_1 \partial c_1 / \partial x = D_2 \partial c_2 / \partial x, \qquad x = 0,$$
 (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

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

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

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$c_{1} = \frac{C_{0}}{1 + k(D_{2}/D_{1})^{\frac{1}{2}}} \left\{ 1 + k(D_{2}/D_{1})^{\frac{1}{2}} \operatorname{erf} \frac{x}{2\sqrt{D_{1}t}} \right\}, \quad (3.45)$ $c_{2} = \frac{kC_{0}}{1 + k(D_{2}/D_{1})^{\frac{1}{2}}} \operatorname{erfe} \frac{|x|}{2\sqrt{D_{2}t}}. \quad (3.46)$

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 [5, p. 26]

and by Barrer [6, p. 10]. We may note that, as diffusion proceeds, the concentrations at the interface, x = 0, remain constant at the values



3.41. Interface resistance

If we have the same problem as in § 3.4 except that there is a contact resistance at x = 0, then (3.41) is to be replaced by

$$D_1 \partial c_1 / \partial x + h(c_2 - c_1) = 0, \qquad x = 0, \qquad (3.48)$$

while (3.42) still holds. The expressions for the concentrations in this case are

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

$$+ e^{h_{1}x + h_{1}^{*}D_{1}t} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{1}t}} + h_{1}\sqrt{D_{1}t}\right) \right) \right], \quad (3.49)$$

$$c_{2} = \frac{C_{0}}{1 + (D_{2}/D_{1})^{\frac{1}{2}}} \left\{ \operatorname{erfc}\frac{|x|}{2\sqrt{D_{2}t}} - e^{h_{2}x + h_{2}^{*}D_{2}t} \operatorname{erfc}\left(\frac{|x|}{2\sqrt{D_{2}t}} + h_{2}\sqrt{D_{2}t}\right) \right\}, \quad (3.50)$$

$$h_{1} = \frac{h}{D_{1}} \{1 + (D_{1}/D_{2})^{\frac{1}{2}}\}, \quad h_{2} = \frac{h}{D_{2}} \{1 + (D_{2}/D_{1})^{\frac{1}{2}}\}. \quad (3.51)$$

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The concentrations on either side of the interface are no longer constant but each approaches the equilibrium value, $\frac{1}{2}C_0$, relatively slowly. This, and the general distribution at successive times, is illustrated in Fig. 3.7 for the case in which $D_1 = D_2$ and $k = \frac{1}{10}D_1$.



F10. 3.7. Concentration distribution in a composite medium with a resistance at the interface. Numbers on curves are values of $D_1 t$. $D_1 = D_3$. $k = \frac{1}{10}D_1$.

3.5. The semi-infinite composite medium

This is the case of a semi-infinite medium which has a skin or surface layer having diffusion properties different from those of the rest of the medium. Thus, suppose in the semi-infinite region $-l < x < \infty$, the diffusion coefficient is D_1 in the region -l < x < 0, and that the concentration is denoted by c_1 there, while the corresponding quantities in x > 0 are D_2 and c_2 . If we assume the conditions at the interface to be

$$c_1 = c_2, \qquad x = 0,$$
 (3.52)

$$D_1 \partial c_1 / \partial x = D_2 \partial c_2 / \partial x, \qquad x = 0, \qquad (3.53)$$

the solution to the problem of zero initial concentration and the surface x = -l maintained at constant concentration C_0 is given by Carslaw and Jaeger [1, p. 263], and is

$$c_{1} = C_{0} \sum_{n=0}^{\infty} \alpha^{n} \left\{ \operatorname{erfc} \frac{(2n+1)l+x}{2\sqrt{D_{1}t}} - \alpha \operatorname{erfc} \frac{(2n+1)l-x}{2\sqrt{D_{1}t}} \right\}, \quad (3.54)$$

$$c_{2} = \frac{2kC_{0}}{k+1} \sum_{n=0}^{\infty} \alpha^{n} \operatorname{erfc} \frac{(2n+1)l+kx}{2\sqrt{D_{1}t}}, \qquad (3.55)$$

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where

$$k = (D_1/D_2)^{\frac{1}{2}}, \quad \alpha = \frac{1-k}{1+k}.$$
 (3.56)

The total quantity entering the medium through unit area of the surface x = -l in time t is M_l , where M_l is given by

$$\frac{M_l}{lC_0} = 2 \left(\frac{D_1 t}{\pi l^2} \right)^{\frac{1}{2}} \left\{ 1 + 2 \sum_{n=1}^{\infty} \alpha^n e^{-n^2 l^2 / D_1 t} \right\} - 4 \sum_{n=1}^{\infty} n \alpha^n \operatorname{erfe} \frac{nl}{\sqrt{D_1 t}}.$$
 (3.57)



FIG. 3.8. Sorption curves for a composite semi-infinite medium. Numbers on curves are values of D_1/D_2 .

Following Carslaw and Jaeger [1, p. 263], for very large times the exponentials in (3.57) may all be replaced by unity. This is true also of the error-function complements in (3.57) and so for large times we have approximately

$$M = (D, t) 1/(-2\alpha) = 4\alpha$$

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[§ 3.5

$$\frac{2n_1}{lC_0} = 2\left(\frac{2r_1}{\pi l^2}\right)^2 \left(1 + \frac{2\alpha}{1 - \alpha}\right) - \frac{4\alpha}{(1 - \alpha)^2},\tag{3.58}$$

provided $\alpha^2 < 1$. Fig. 3.8 shows M_t/lC_0 as a function of $(D_1 t/l^2)^{\frac{1}{2}}$. Whipple [7] has given formulae for the concentration in a semi-infinite region of low diffusion coefficient bisected by a thin well-diffusing slab, at different times after the boundary of the semi-infinite region has been raised suddenly from zero to unit concentration. This is of interest in grain boundary diffusion.

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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 thin 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, a 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 $\frac{d^2C}{dx^2} = 0$ (4.1)

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

provided the diffusion coefficient, D, is constant. On integrating with respect to x we have dC/dx = constant, (4.2)

and by a further integration we have, on introducing the conditions at x = 0, x = l, $C = C_{1} = x$

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

$$F = -D dC/dx = D(C_1 - C_2)/l.$$
(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 [1].

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

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

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

then we find

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

and

If the surface conditions are

$$\frac{\partial C}{\partial x} + h_1(C_1 - C) = 0, \quad x = 0; \qquad \frac{\partial C}{\partial x} + h_2(C - C_2) = 0, \quad x = l,$$

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

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

4.21. 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 $E = B(n-n)^2$

$$F = P(p_1 - p_2)/l, \tag{4.5}$$

and the constant P is referred to as the permeability constant. Here P is expressed, for example, as c.c. 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 cm.²/sec., 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 equations (4.4) and (4.5) are equivalent, but not otherwise. The linear isotherm may be written

$$\mathcal{I} = Sp, \tag{4.6}$$

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 , p_1 and C_2 , p_2 in (4.4) and (4.5) are connected by (4.6) it follows that, with due regard to units,

(4.4 a)

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$$P = DS. \tag{4.7}$$

4.22. 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 is 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

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

and hence the relationship

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

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

$$D_{I} = \frac{1}{C_{1} - C_{2}} \int_{C_{1}}^{C_{1}} D \, dC, \qquad (4.11)$$

where

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 XII.

4.23. Composite membrane

If we have a composite membrane composed of n sheets of thicknesses $l_1, l_2, ..., l_n$, and diffusion coefficients $D_1, D_2, ..., D_n$, 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 drop in concentration is

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

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

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there are no barriers to diffusion between them.

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 [2], Carslaw and Jaeger [3], Jost [4], and others. The emphasis here is on numerical evaluation.

4.31. Surface concentrations constant. Initial distribution f(x) $C = C_1, \qquad x = 0, \qquad t \ge 0,$ If

$$C = C_2, \qquad x = l, \quad t \ge 0, \tag{4.14}$$

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

the solution in the form of a trigonometrical series is

$$C = C_{1} + (C_{2} - C_{1})\frac{x}{l} + \frac{2}{\pi} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n} \sin \frac{n\pi x}{l} e^{-Dn^{2}\pi^{2}l/l^{2}} + \frac{2}{l} \sum_{1}^{\infty} \frac{\sin n\pi x}{l} e^{-D\pi^{2}n^{2}l/l^{2}} \int_{0}^{l} f(x') \sin \frac{n\pi x'}{l} dx'.$$
 (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 $x = \pm l$.

4.32. 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

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

$$\frac{M_l}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-D(2n+1)^2 \pi^3 l/4l^4}.$$
 (4.18)

The corresponding solutions useful for small times are

(4.13)





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

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

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

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



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 .

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 [3, p. 83]. Tabulated values of $(C-C_0)/(C_1-C_0)$ and of M_l/M_{∞} are given by Henry [5]. Values of M_l/M_{∞} have also been tabulated by McKay [6] and extensive numerical values for the concentration at the centre of the sheet, x = 0, are given by Olson and Schulz [7]. The curve labelled zero fractional uptake in Fig. 4.6 shows how M_l/M_{∞} varies with the square root of time in a sheet of thickness 2a when the concentration at each surface remains constant.

[§ 4.3

4.33. 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 in § 4.2 is set up. During this time the concentration changes according to

$$C = C_{1} + (C_{2} - C_{1})\frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n} \sin \frac{n\pi x}{l} e^{-Dn^{2}\pi^{2} l/l^{2}} + \frac{4C_{0}}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \sin \frac{(2m+1)\pi x}{l} e^{-D(2m+1)^{2}\pi^{2} l/l^{2}}.$$
 (4.22)

As t approaches infinity the terms involving the exponentials vanish and we have simply the linear concentration distribution obtained in §4.2. 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

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

In this case $M_{\infty} = l\left(\frac{C_1+C_2}{2}-C_0\right)$ and the total content of the membrane at time *t* is given by M_l+lC_0 . The expression (4.23) is similar to (4.18) and is readily evaluated from the tabulated values in references [5] and [6] or 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 = 0 of the membrane is given by $D(\partial C/\partial x)_{x=0}$, 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, where

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$$Q_{t} = D(C_{2} - C_{1}) \frac{t}{l} + \frac{2l}{\pi^{2}} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}\pi^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}\pi^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{2} \cos n\pi - C_{1}}{n^{2}} (1 - e^{-Dn^{2}/l^{2}}) + \frac{1}{2} \sum_{1}^{\infty} \frac{C_{$$

$$+\frac{4C_0 l}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} (1-e^{-D(2m+1)^2\pi^2/\beta^2}). \quad (4.24)$$

In the commonest experimental arrangement both C_0 and C_1 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 (4.24) reduces to



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

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

$$Q_t = \frac{DC_2}{l} \left(t - \frac{l^2}{6D} \right). \tag{4.26}$$

(4.27)

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

$L := l^2/6D.$

Following Daynes [8], Barrer [2, p. 19] has used (4.27) as the basis of a method of 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 (4.27); from the steady-state flow rate the permeability constant P is deduced by using (4.5), and S follows from (4.7). A graph of Q_l/lC_2 as a function Dt/l^2 is shown for the case $C_0 = C_1 = 0$ in Fig. 4.2. To within the accuracy of plotting the steady state is achieved when $Dt/l^2 = 0.45$ approximately.

4.34. Variable surface concentration

The solution to the general problem of diffusion in the region 0 < x < lwith the surfaces at concentrations $\phi_1(t)$ and $\phi_2(t)$ and the initial concentration f(x) is given by Carslaw and Jaeger [3, p. 86]. 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.

$$\phi_1(t) = \phi_2(t) = C_0(1 - e^{-\beta t}). \tag{4.28}$$

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

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

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_l , 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

$$\frac{M_{t}}{2lC_{0}} = 1 - e^{-\beta t} (D/\beta l^{2})^{\frac{1}{2}} \tan(D/\beta l^{2})^{\frac{1}{2}} - \frac{1}{2} - \frac{1}{2} \left(\frac{1}{2} - \frac{1}{2} \right)^{\frac{1}{2}} \left(\frac{1}{$$

$$-\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-(2n+1)^2 \pi^2 Dl/4l^2}}{(2n+1)^2 [1-(2n+1)^2 \{D\pi^2/(4\beta l^2)\}]}.$$
 (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 linear portion followed by the approach to the equilibrium value, $M_l = 2lC_0$. The uptake curves for finite values of $\beta l^2/D$, for which the surface concentration rises at a finite rate, all show points of inflexion. At first the rate of uptake increases as sorption proceeds but later



F10. 4.3. Calculated sorption curves for surface concentration given by $C_0(1-e^{-\beta t})$. Numbers on curves are values of $\beta l^2/D$.

decreases as the final equilibrium is approached. Curves of this kind are often referred to as sigmoid sorption curves. They may arise in practice because surface equilibrium conditions are not established instantaneously, but they may also result from other causes (see § 12.62below).

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(ii) If the surface concentrations vary linearly with time, i.e.

$$\phi_1(t) = \phi_2(t) = kt, \tag{4.31}$$

the solution is

$$\frac{DC}{kl^2} = \frac{Dt}{l^2} + \frac{1}{2} \left(\frac{x^2}{l^2} - 1 \right) + \frac{16}{\pi^3} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} e^{-D(2n+1)^3 \pi^2 l/4l^2} \cos \frac{(2n+1)\pi x}{2l}.$$
(4.32)



F19. 4.4. Concentration distributions in a plane sheet for surface concentration kt. Numbers on curves are values of Dt/l^2 .



F10. 4.5. Sorption curve for plane sheet with surface concentration kt.

The corresponding expression for M_l is

$$\frac{DM_l}{kl^3} = \frac{2Dt}{l^2} - \frac{2}{3} + \frac{64}{\pi^4} \sum_{n=0}^{\infty} \frac{e^{-D(2n+1)^2 \pi^2 l/4l^2}}{(2n+1)^4}.$$
 (4.33)

Some numerical results are given by Williamson and Adams [9] and Gurney and Lurie [10]. Fig. 4.4 shows DC/kl^2 plotted as a function of x/l for various values of Dt/l^2 . Fig. 4.5 shows DM_l/kl^3 as a function of the single variable Dt/l^2 .

These solutions can be extended to cover modified surface conditions such as $\phi_1(t) = \phi_2(t) = C_0 + kt$, and a non-zero initial concentration by superposing solutions as in § 3.3 (v).

4.35. Diffusion from a stirred solution of limited volume

If a plane sheet is suspended in a volume of solution so large that the amount of solute taken up by the sheet is a negligible fraction of the whole, and the solution is well stirred, then the concentration in the solution remains constant. If, however, there is only a limited volume of solution, the concentration of solute in the solution falls as solute enters the sheet. If the solution is well stirred the concentration in the solution depends only on time, and is determined essentially by the condition that the total amount of solute in the solution and in the sheet remains constant as diffusion proceeds. It is useful from an experimental point of view to have only a limited amount of solution since the rate of uptake of solute by the sheet can be deduced from observations of the uniform concentration in the solution. It is often simpler to do this than to observe directly the amount in the sheet. This has been stressed by Carman and Haul [11], who have written mathematical solutions in forms most appropriate for the measurement of diffusion coefficients by this method.

The general problem can be stated mathematically in terms of a solute diffusing from a well-stirred solution. The modifications necessary for corresponding alternative problems, such as that of a sheet suspended in a vapour, are obvious.

Suppose that an infinite sheet of uniform material of thickness 2*l* is placed in a solution and that the solute is allowed to diffuse into the sheet. The sheet occupies the space $-l \leq x \leq l$, while the solution is of limited extent and occupies the spaces $-l-a \leq x \leq -l, l \leq x \leq l+a$. The concentration of the solute in the solution is always uniform and is initially C_0 , while initially the sheet is free from solute.

We require a solution of the diffusion equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \qquad (4.34)$$

with the initial condition

$$C = 0, \quad -l < x < l, \quad t = 0,$$
 (4.35)

and with a boundary condition expressing the fact that the rate at which solute leaves the solution is always equal to that at which it enters the sheet over the surfaces $x = \pm l$. This condition is

$$a \partial C/\partial t = \mp D \partial C/\partial x, \qquad x = \pm l, \qquad t > 0.$$
 (4.36)

We assume here that the concentration of solute just within the surface of the sheet is the same as that in the solution. This may not be so but there may be a partition factor, K, which is not unity, such that the concentration just within the sheet is K times that in the solution. This can clearly be allowed for by using a modified length of solution, a/K, in place of a in (4.36) and elsewhere.

A solution of this problem by March and Weaver [12], based on the use of an integral equation, was cumbersome for numerical evaluation. More convenient forms of solution have been obtained by Carslaw and Jaeger [3, p. 106], Wilson [13], Berthier [14], while Crank [15] has developed solutions particularly suitable for small values of the time. The solution is most readily obtained by the use of the Laplace transform. In a form expressing the total amount of solute, M_t , in the sheet at time t as a fraction of M_{∞} , the corresponding quantity after infinite time, the solution is

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} e^{-Dq_n^2 t/t^2}, \qquad (4.37)$$

where the q_n 's are the non-zero positive roots of

$$\tan q_n = -\alpha q_n, \tag{4.38}$$

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and $\alpha = a/l$, the ratio of the volumes of solution and sheet, or if there is a partition factor K then $\alpha = a/Kl$. Some roots of (4.38) are given in Table 4.1 for values of α corresponding to several values of final fractional uptake. Roots for other values of α are given by Carslaw and Jaeger [3, p. 378] and by Carman and Haul [11]. It is sometimes convenient to express α in terms of the fraction of total solute finally taken up by the sheet. Thus in the final equilibrium state, since the DIFFUSION IN A PLANE SHEET

total amount of solute in solution and sheet was originally contained in the solution of concentration C_0 , we have

$$\frac{aC_{\infty}}{K} + lC_{\infty} = aC_0, \qquad (4.39) \qquad M$$

where C_{∞} is the uniform concentration in the sheet finally. The content, M_{∞} , of the sheet finally is given by

$$M_{\infty} = 2lC_{\infty} = \frac{2aC_0}{1 + a/(lK)} = \frac{2aC_0}{1 + \alpha}.$$
 (4.40)

The fractional uptake of the sheet finally is therefore given by

$$\frac{M_{\alpha}}{2aC_0} = \frac{1}{1+\alpha}.$$
(4.41)

If, for example, 50 per cent. of the solute initially in the solution is finally in the sheet, $\alpha = 1$. In the particular case of an infinite amount of solute ($\alpha = \infty$) the roots of (4.38) are $q_n = (n + \frac{1}{2})\pi$, and we have

$$\frac{M_l}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} e^{-D(n+\frac{1}{2})^2 \pi^2 l/l^2}, \qquad (4.42)$$

which is expression (4.18) for the case of a constant concentration, C_0 , at the surface of a sheet. The smaller Dt/l^2 is, the more terms in the series in (4.37) are needed for a given accuracy. When more than three or four terms are needed it is better to use an alternative form of solution. For most values of α the simplest expression is

$$\frac{M_i}{M_{\infty}} = (1+\alpha)\{1-e^{T/\alpha^2}\operatorname{erfc}(T/\alpha^2)^{\frac{1}{2}}\},\qquad(4.43)$$

where $T = Dt/l^2$. If very small values of α are required, corresponding to very high fractional uptakes of solute by the sheet, there may be a range of Dt/l^2 in which neither (4.37) nor (4.43) is convenient but where the following is useful:

$$\frac{M_l}{M_{\alpha}} = (1+\alpha) \left\{ 1 - \frac{\alpha}{\pi^{\frac{1}{2}} T^{\frac{1}{2}}} + \frac{\alpha^3}{2\pi^{\frac{1}{2}} T^{\frac{1}{2}}} - \frac{3\alpha^5}{4\pi^{\frac{1}{2}} T^{\frac{1}{2}}} + \dots \right\}.$$
 (4.44)

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 $\frac{1.0}{M_{\infty}}$

0.9

0-8

0.7

0.6

0.5

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This is obtained from (4.43) by substituting the asymptotic expansion for $\exp(T/\alpha^2)$ erfc $(T/\alpha^2)^{\frac{1}{2}}$ when T/α^2 is large.

Fig. 4.6 gives curves showing M_l/M_{∞} against $(Dt/l^2)^{\frac{1}{2}}$ for five values of final fractional uptake. Fig. 4.6 shows that the greater the final fractional uptake of the sheet the faster is the solute removed from the solution. Clearly by comparing the rate of fall of concentration in the solution observed experimentally, with the corresponding calculated

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FIG. 4.6. Uptake by a plane sheet from a stirred solution of limited volume. Numbers on curves show the percentage of total solute finally taken up by the sheet.

a method for measuring self-diffusion using radioactive isotopes. He gives a table of M_l/M_{∞} for values of $1/\alpha$ between 0 and 1.0 at intervals of 0.1. For precision measurements it is advisable to check Berthier's values as in some instances not enough terms of the series solutions have been retained to obtain the accuracy quoted. The concentration within

the sheet is given by the expression

$$C = C_{\infty} \left\{ 1 + \sum_{n=1}^{\infty} \frac{2(1+\alpha)e^{-Dq_n^2 t/l^2}}{1+\alpha+\alpha^2 q_n^2} \frac{\cos(q_n x/l)}{\cos q_n} \right\}.$$
 (4.45)

We have considered diffusion into a plane sheet initially free of solute. There is the complementary problem in which all the solute is initially uniformly distributed through the sheet and subsequently diffuses out into a well-stirred solution. It is easily seen that the mathematical

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solutions presented above for sorption by the sheet also describe desorption, provided M_i is taken to mean the amount of solute leaving the sheet up to time t, and M_x the corresponding amount after infinite time. For the problem of desorption from the sheet we require a solution of (4.34) satisfying (4.36) but with the initial condition (4.35) replaced by

$$C = C_0, \quad -l < x < l, \quad t = 0.$$
 (4.46)

On writing

$$C_1 = C_0 - C, (4.47)$$

(4.46) and the other equations for desorption are identical with (4.34), (4.35), (4.36), with C_1 written for C. Hence the equations and solutions for desorption are identical with those for sorption provided M_t , M_{∞} are suitably interpreted and C_1 , $(C_1)_{\infty}$ replace C, C_{∞} in expression (4.45). The parameter α is equal to a/Kl as before, but its relation to the final uptake of the sheet expressed by (4.40) and (4.41) no longer holds. Instead we have that the fractional uptake of the solution is given by

$$\frac{M_{\infty}}{2lC_0} = \frac{1}{1+1/\alpha}.$$
 (4.48)

Jacger and Clarke [16] have presented solutions of a number of other problems in diffusion from a well-stirred solution in terms of certain fundamental functions. Accurately drawn graphs of these functions, from which solutions of limited accuracy are readily-constructed, are given in their paper.

4.36. Surface evaporation

In § 3.31 the rate of loss of diffusing substance by evaporation from the surface of a sheet was represented by

$$-D \partial C/\partial x = \alpha (C_0 - C_s), \qquad (4.49)$$

where C_s is the actual concentration just within the sheet and C_0 is the concentration required to maintain equilibrium with the surrounding atmosphere. If the sheet, -l < x < l, is initially at a uniform concentration C_2 , and the law of exchange of the type (4.49) holds on both surfaces, the solution is

(4.50)

$$\frac{C-C_2}{C_0-C_2} = 1 - \sum_{n=1}^{\infty} \frac{2L\cos(\beta_n x/l)e^{-\beta_n^2 Dl/l^2}}{(\beta_n^2 + L^2 + L)\cos\beta_n},$$

where the β_n 's are the positive roots of

and
$$\beta \tan \beta = L$$
 (4.51)
 $L = l\alpha/D$, (4.52)

a dimensionless parameter. Roots of (4.51) are given in Table 4.2 for

several values of L. Roots for other values of L are given by Carslaw and Jaeger [3, p. 377]. The total amount of diffusing substance, M_t , entering or leaving the sheet up to time t, depending on whether C_0 is greater or less than C_2 , is expressed as a fraction of M_∞ , the corresponding quantity after infinite time, by



FIG. 4.7. Sorption or desorption curves for the surface condition (4.49). Numbers on curves are values of $L = l_X/D$.

A solution suitable for small values of time may be obtained in the usual way by expanding the expression for the Laplace transform in a series of negative exponentials (Carslaw and Jaeger [3, p. 252]). The terms in the series expression for concentration very soon become cumbersome for numerical evaluation, however. In practice, it is usually sufficient to use only the leading terms corresponding to the interval during which the sheet is effectively semi-infinite, when the concentration is given by expression (3.35), and (3.37) gives the value of M_t for

5 (C)

half the sheet.

Graphs showing M_l/M_{∞} for several values of L are plotted in Fig. 4.7 from numerical values given by Newman [17]. Carslaw and Jaeger [3, p. 102] give corresponding curves as well as others showing how the concentrations at the surfaces and the centre of the sheet vary with time. Newman [17] also gives a table of values from which M_l/M_{∞} can easily be deduced for a parabolic initial distribution instead of a uniform

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initial concentration. All these equations and solutions have a practical application in the drying of porous solids.

Carslaw and Jaeger [3, p. 98] give solutions of more general problems in which there is an initial, non-uniform concentration distribution, or in which the vapour pressure is different on the two surfaces of the sheet, or in which evaporation occurs from one surface only, the other being maintained at a constant concentration. Jaeger and Clarke [16] have also given in graphical form the solutions of a number of problems with an evaporation type of boundary condition.

The more complicated case in which the rate of transfer on the surface is proportional to some power of the surface concentration has been discussed by Jaeger [18].

4.37. Constant flux F_0 at the surfaces

If the sheet, -l < x < l, is initially at a constant concentration C_0 , and diffusing substance enters at a constant rate, F_0 , over unit area of each surface, i.e. $D \partial C / \partial x = F_0$, x = l, (4.54)

then

$$C - C_0 = \frac{F_0 l}{D} \left\{ \frac{Dt}{l^2} + \frac{3x^2 - l^2}{6l^2} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{-Dn^2 \pi^2 l l^2} \cos \frac{n\pi x}{l} \right\}.$$
(4.55)

Obviously the total amount of diffusing substance taken up by unit area of the sheet in time t is $2F_0t$. Concentration-distance curves for various times are shown in Fig. 4.8. An alternative form of solution suitable for small times is given by Macey [19].

4.38. Impermeable surfaces

An impermeable surface is one at which the concentration gradient is zero. This condition holds at the central plane of a sheet provided the initial and boundary conditions are symmetrical about that plane. It follows therefore that the symmetrical solutions already given for

the plane sheet occupying the region -l < x < l apply also to the sheet 0 < x < l when the face x = 0 is impermeable. If, on the other hand, both surfaces x = 0 and x = l are impermeable and the initial distribution is f(x), the solution is

$$C = \frac{1}{l} \int_{0}^{l} f(x') \, dx' + \frac{2}{l} \sum_{n=1}^{\infty} e^{-Dn^2 \pi^2 l l l^2} \cos \frac{n \pi x}{l} \int_{0}^{l} f(x') \cos \frac{n \pi x'}{l} \, dx'.$$
(4.56)

Barrer [2, p. 14] suggests that diffusion from one layer to another as discussed in § 2.24 may be treated by regarding the system as a single



FIG. 4.8. Concentration distributions in a plane sheet for constant flux F_0 at the surface. Numbers on curves are values of Dt/l^2 .

1.2

layer with impermeable boundaries and applying (4.56) where the initial distribution is $f(w) = C = 0 \le w \le h$

$$\begin{cases} f(x) = C_0, & 0 < x < h \\ f(x) = 0, & h < x < l \end{cases}$$
(4.57)

The solution (4.56) becomes

$$C = C_0 \left\{ \frac{h}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi h}{l} e^{-Dn^2 \pi^2 l/l^2} \cos \frac{n\pi x}{l} \right\}.$$
 (4.58)

This solution is complementary to expression (2.17) which is convenient for small times. Numerical values based on (2.17) and (4.58) are available in the well-known tables by Stefan [20] and Kawalki [21], some of which are reproduced by Jost [4, p. 63].

Another special case of (4.56) has been evaluated by Crank and Henry [22] in an investigation of different methods of conditioning a sheet to a required uniform concentration. They consider the problem in which a sheet, initially at zero concentration throughout, has its surfaces maintained at a constant concentration C_0 for a time t_0 , after which they are rendered impermeable. The subsequent change in concentration is described by (4.56) with f(x) given by

$$f(x) = C_0 \left[1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \sin \frac{(2m+1)\pi x}{l} e^{-D(2m+1)^2 \pi^2 l_0 |l^2} \right]. \quad (4.59)$$

In this case the two integrals in (4.56) reduce to

$$\int_{0}^{l} f(x) \, dx = C_0 \, l \bigg[1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} e^{-D(2m+1)^2 \pi^2 l_0 / l^2} \bigg], \qquad (4.60)$$

and

$$\int_{0}^{l} f(x)\cos\frac{2p\pi x}{l} \, dx = \frac{8C_0 l}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{4p^2 - (2m+1)^2} e^{-D(2m+1)^2 \pi^2 l_0 l^2},$$
(4.61)

where 2p is substituted for n since only the terms involving even n are non-zero.

4.39. Composite sheet

Various problems of diffusion into a composite sheet comprised of two layers for which the diffusion coefficients are different have been solved (see, for example, Carslaw and Jaeger [3, pp. 265, 302]). The solutions are similar in form to those presented in this chapter but obviously more complicated. In view of the additional number of parameters involved, no attempt is made to give numerical results here. Jaeger [23] has studied the time-lag involved in establishing the steadystate flow through a composite sheet of several layers.

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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

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

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

The general solution of this is

$$C = A + B \log r, \tag{5.3}$$

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

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

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

$$Q_{t} = \frac{2\pi D t (C_{2} - C_{1})}{\log(b/a)}.$$
(5.5)

If Q_t is measured in a concentration-dependent system, the mean value of the diffusion coefficient obtained from (5.5) is $\left(\int_{C_1}^{C_2} D \, dC\right) / (C_2 - C_1)$ 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. 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

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

and we find
$$C = \frac{C_1\{1+hb\log(b/r)\}+hbC_2\log(r/a)}{1+hb\log(r/a)}$$
. (5.7)



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

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

$$Q_{t} = 2\pi D(C_{1} - C_{2}) \frac{hb}{1 + hb\log(b/a)}.$$
(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 bincreased 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 [1]. This is illustrated in Fig. 5.2 for $ah = \frac{1}{2}$. If the surface conditions are

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

we find
$$C = \frac{ah_1C_1(1+bh_2\log b/r)+bh_2C_2(1+ah_1\log r/a)}{ah_1+bh_2+abh_1h_2\log b/a}$$
, (5.7 a)

$$Q_{t} = \frac{2\pi D t a b h_{1} h_{2} (C_{2} - C_{1})}{a h_{1} + b h_{2} + a b h_{1} h_{2} \log b / a}.$$
 (5.8 a)

and



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

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 [2, p. 187].

5.3. Non-steady state. Solid cylinder

Following essentially the method of separating the variables described in § 2.3, we see that $C = u e^{-D x^2 t}$ (5.9)

is a solution of (5.1) for D constant provided u is a function of r only, satisfying $\frac{d^2u}{dr^2} + \frac{1}{r}\frac{du}{dr} + \alpha^2 u = 0,$ (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

$$C = 0, \qquad r = a, \qquad t \ge 0, \tag{5.11}$$

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

The boundary condition (5.11) is satisfied by ;

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

provided the α_n 's are roots of

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

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 (see for example reference [3], p. 171). For this function C is finite at r = 0. The initial condition (5.12) becomes

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

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,

$$\int_{0}^{a} r J_{0}(\alpha r) J_{0}(\beta r) dr = 0, \qquad (5.16)$$

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

$$\int_{0}^{a} r\{J_{0}(\alpha r)\}^{2} dr = \frac{1}{2}a^{2}J_{1}^{2}(a\alpha_{n}), \qquad (5.17)$$

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,

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is given by Carslaw and Jaeger [2, p. 172]. Finally the solution satisfying (5.11) and (5.12) is

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

Alternatively, solutions for both large and small times can be obtained by use of the Laplace transform. **5.31.** Surface concentration constant. Initial distribution f(r) If in the cylinder of radius *a* the conditions are

$$C = C_0, \qquad r = a, \qquad t \ge 0, \tag{5.19}$$

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

the solution is

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

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

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

$$\frac{M_l}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} e^{-D \alpha_n^2 l}.$$
 (5.23)

The corresponding solution useful for small times is

$$\frac{C-C_{1}}{C_{0}-C_{1}} = \frac{a^{\frac{1}{2}}}{r^{\frac{1}{2}}} \operatorname{erfe} \frac{a-r}{2\sqrt{(Dt)}} + \frac{(a-r)(Dta)^{\frac{1}{2}}}{4ar^{\frac{3}{2}}} \operatorname{ierfe} \frac{a-r}{2\sqrt{(Dt)}} + \frac{(9a^{2}-7r^{2}-2ar)Dt}{32a^{\frac{3}{2}}r^{\frac{1}{2}}} \operatorname{i}^{2}\operatorname{erfe} \frac{a-r}{2\sqrt{(Dt)}} + \dots, \quad (5.24)$$

which holds provided r/a is not small. The case of r/a small is discussed by Carsten and McKerrow [4]. They give a series solution involving modified Bessel functions of order $n \pm \frac{1}{4}$. The necessary functions are

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tabulated in their paper and numerical calculation is straightforward. Also for small times we have

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

The solutions for the cylinder can be written in terms of the two dimensionless parameters Dt/a^2 and r/a. Curves showing $(C-C_1)/(C_0-C_1)$



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 .

as a function of r/a for different values of Dt/a^2 drawn by Carslaw and Jaeger [2, p. 175] are reproduced in Fig. 5.3. The curve of Fig. 5.7 for zero fractional uptake shows how M_l/M_{∞} depends on Dt/a^2 when the concentration at the surface of the cylinder remains constant.

5.32. Variable surface concentration

If the initial concentration in the cylinder is zero and that at the

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surface is $\phi(t)$, the solution is

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

where the α_n 's are the roots of (5.14). (i) As for the plane sheet, a case of practical interest is when

$$\phi(t) = C_0(1 - e^{-\beta t}), \tag{5.27}$$

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

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



Numbers on curves are values of $\beta a^2/D$.

and the sorption-time curve is given by

$$\frac{M_{t}}{\pi a^{2}C_{0}} = 1 - \frac{2J_{1}\{(\beta a^{2}/D)^{\frac{1}{2}}\}e^{-\beta t}}{(\beta a^{2}/D)^{\frac{1}{2}}J_{0}\{(\beta a^{2}/D)^{\frac{1}{2}}\}} + \frac{4}{a^{2}}\sum_{n=1}^{\infty} \frac{e^{-D\alpha_{n}^{2}t}}{\alpha_{n}^{2}\{\alpha_{n}^{2}/(\beta/D)-1\}}.$$
(5.29)

Fig. 5.4 shows uptake curves for different values of the parameter $\beta a^2/D$. (ii) If the surface concentration varies linearly with time, i.e.

$$\phi(t) = kt, \qquad (5.30)$$




the solution is

$$C = k \left(t - \frac{a^2 - r^2}{4D} \right) + \frac{2k}{aD} \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t} \frac{J_0(r\alpha_n)}{\alpha_n^3 J_1(a\alpha_n)}.$$
 (5.31)

In Fig. 5.5, curves showing $DC/(ka^2)$ are drawn against r/a for different values of Dt/a^2 . Numerical values are given by Williamson and Adams [5]. The corresponding expression for M_t is

$$M_{t} = \pi k a^{2} t - \frac{\pi k a^{4}}{8D} + \frac{4\pi k}{D} \sum_{n=1}^{\infty} \frac{e^{-D\alpha_{n}^{2}t}}{\alpha_{n}^{4}}, \qquad (5.32)$$



FIG. 5.6. Sorption curve for cylinder with surface concentration kt,

and $M_t D/(\pi ka^4)$ is plotted against Dt/a^2 in Fig. 5.6. These solutions can be extended by superposition as in § 3.3 (v), to cover modified surface conditions such as $\phi(t) = C_0 + kt$ and a non-zero initial concentration.

5.33. Diffusion from a stirred solution of limited volume

The problem differs only in detail from the corresponding problem considered for the plane sheet in § 4.35 and the results can be written down without explanation.

Suppose that the cylinder occupies the space r < a while the crosssection of the bath of solution in which it is immersed is A (excluding the space occupied by the cylinder). The concentration of solute in the solution is always uniform and is initially C_0 . The cylinder is initially free from solute. The total amount of solute, M_t , in the cylinder after time t is expressed as a fraction of the corresponding amount M_{∞} after infinite time by the relation [6]

[§ 5.3

$$\frac{M_l}{M_x} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1+\alpha)}{4+4\alpha+x^2 q_n^2} e^{-Dq_n^2 l/\alpha^2},$$
 (5.33)

where the q_n 's are the positive, non-zero roots of

$$\alpha q_n J_0(q_n) + 2J_1(q_n) = 0, \qquad (5.34)$$

and $\alpha = A/\pi a^2$, the ratio of the volumes of solution and cylinder. If there is a partition factor, K, between solute in equilibrium in the cylinder and in the solution, $\alpha = A/(\pi a^2 K)$. The parameter α is expressed in terms of the final fractional uptake of solute by the cylinder by the expression M = 1

$$\frac{M_x}{AC_0} = \frac{1}{1 + \alpha}.\tag{5.35}$$

The roots of (5.34) are given in Table 5.1 for several values of α in order to assist the evaluation of (5.33). The convergence of the series in (5.33) becomes inconveniently slow for numerical evaluation when Dt/a^2 is small. An alternative solution suitable for small Dt/a^2 when α is moderate is [7]

$$\frac{M_l}{M_{\infty}} = \frac{1+\alpha}{1+\frac{1}{4}\alpha} [1 - e^{4(1+\frac{1}{4}\alpha)^2 D l/(a^2 \alpha^2)} \operatorname{erfc} \{2(1+\frac{1}{4}\alpha) (Dt_l a^2)^{\frac{1}{2}} / \alpha \}]. \quad (5.36)$$

Carman and Haul [8] have derived an alternative equation which is less easy to use but which is accurate up to considerably higher values of M_t/M_x . Their equation is

$$\frac{M_t}{M_{\infty}} = \frac{\gamma_3}{\gamma_3 + \gamma_4} e^{4\gamma_3^2 Dt/(a^2 \alpha^2)} \operatorname{erfe}\left\{\frac{2\gamma_3}{\alpha} \left(\frac{Dt}{a^2}\right)^{\frac{1}{2}}\right\} + \frac{\gamma_4}{\gamma_3 + \gamma_4} e^{4\gamma_4^2 Dt/(a^2 \alpha^2)} \operatorname{erfe}\left\{-\frac{2\gamma_4}{\alpha} \left(\frac{Dt}{a^2}\right)^{\frac{1}{2}}\right\}, \quad (5.37)$$

where $\gamma_3 = \frac{1}{2} \{ (1+\alpha)^{\frac{1}{2}} + 1 \}, \quad \gamma_4 = \gamma_3 - 1.$ (5.38)

For α very small it is convenient to use the asymptotic expansion for erfc in (5.36) and hence to write

$$\frac{M_t}{M_x} = \frac{1+\alpha}{1+\frac{1}{4}\alpha} \left\{ 1 - \frac{\alpha(Dt/a^2)^{-\frac{1}{2}}}{2\pi^{\frac{1}{2}}(1+\frac{1}{4}\alpha)} + \frac{\alpha^3(Dt/a^2)^{-\frac{1}{2}}}{16\pi^{\frac{1}{2}}(1+\frac{1}{4}\alpha)^3} - \frac{3\alpha^5(Dt/a^2)^{-\frac{1}{2}}}{128\pi^{\frac{1}{2}}(1+\frac{1}{4}\alpha)^5} + \dots \right.$$
(5.39)

If α is very large, the following expression is more convenient,

$$\frac{M_{t}}{M_{x}} = \frac{2}{\alpha} (1+\alpha) \left\{ \frac{2}{\pi^{4}} \left(\frac{Dt}{a^{2}} \right)^{\frac{1}{2}} - \left(\frac{1}{2} + \frac{2}{\alpha} \right) \frac{Dt}{a^{2}} - \frac{4}{3\pi^{4}} \left(\frac{1}{8} - \frac{2}{\alpha} - \frac{4}{\alpha^{2}} \right) \left(\frac{Dt}{a^{2}} \right)^{\frac{3}{2}} + \dots \right\},$$
(5.40)

which for the special case of $\alpha = \infty$, becomes

$$\frac{M_t}{M_{\infty}} = 2\left\{\frac{2}{\pi^{\frac{3}{2}}} \left(\frac{Dt}{a^2}\right)^{\frac{1}{2}} - \frac{1}{2}\frac{Dt}{a^2} - \frac{1}{6\pi^{\frac{1}{2}}} \left(\frac{Dt}{a^2}\right)^{\frac{3}{2}} + \dots\right\}.$$
 (5.41)

The derivation of these solutions for small times is given by Crank [7].

Fig. 5.7 shows curves of M_l/M_{∞} against $(Dt/a^2)^{\frac{1}{2}}$ for five values of the final fractional uptake. Berthier [9] gives a table of M_l/M_{∞} for values of $1/\alpha$ between 0 and 1 at intervals of 0.1. As in the plane case his values are not always reliable to three decimal places.



F1G. 5.7. Uptake by a cylinder from a stirred solution of limited volume. Numbers on curves show percentages of total solute finally taken up by cylinder.

The concentration of solute C within the cylinder is given by

$$C = C_{\infty} \left\{ 1 + \sum_{n=1}^{\infty} \frac{4(\alpha+1)e^{-Dq_n^2 l/a^2}}{(4+4\alpha+\alpha^2 q_n^2)} \frac{J_0(q_n r/a)}{J_0(q_n)} \right\}.$$
 (5.42)

[§ 5.3

As for the plane sheet, § 4.35, the above equations also describe the course of desorption into a well-stirred solution, initially free from solute, from a cylinder in which the concentration is initially uniform and equal to C_0 . The only modifications are that (5.35) is to be replaced by M = 1

$$\frac{M_{\infty}}{\pi a^2 C_0} = \frac{1}{1 + 1/\alpha},$$
 (

(5.43)

and C_1 , $(C_1)_{\infty}$ replace C, C_{∞} in (5.42) where

$$C_1 = C_0 - C, \qquad (C_1)_{\infty} = C_0 - C_{\infty}.$$
 (5.44)

5.34. Surface evaporation

If the cylinder is initially at a uniform concentration C_2 , and there is a surface condition

$$-D \partial C/\partial r = \alpha (C_s - C_0), \qquad (5.45)$$

where C_s is the actual concentration just within the cylinder and C_0 is the concentration required to maintain equilibrium with the surrounding atmosphere, the required solution is

$$\frac{C-C_2}{C_0-C_2} = 1 - \sum_{n=1}^{\infty} \frac{2LJ_0(r\beta_n/a)}{(\beta_n^2 + L^2)J_0(\beta_n)} e^{-\beta_n^2 D l/a^2}.$$
 (5.46)

The β_n 's are the roots of

$$\beta J_1(\beta) - L J_0(\beta) = 0, \qquad (5.47)$$

$$L = a\alpha/D, \tag{5.48}$$

a dimensionless parameter. Roots of (5.47) are given in Table 5.2 for several values of L. The total amount of diffusing substance, M_{l} , entering or leaving the cylinder, depending on whether C_0 is greater or less than C_2 , is expressed as a fraction of M_{∞} , the corresponding quantity after infinite time, by

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{4L^2 e^{-\beta_n^2 D l/a^2}}{\beta_n^2 (\beta_n^2 + L^2)}.$$
(5.49)

The solutions suitable for small values of time, provided r/a is not small, are

$$\frac{C-C_2}{C_0-C_2} = \frac{2h(Dta)^{\frac{1}{2}}}{r^{\frac{1}{2}}}\operatorname{ierfc}\frac{a-r}{2\sqrt{(Dt)}} + \frac{4ha^{\frac{1}{2}}Dt}{r^{\frac{1}{2}}}\left\{\frac{1}{8r} + \frac{3}{8a} - h\right\}i^2\operatorname{erfc}\frac{a-r}{2\sqrt{(Dt)}} + \dots,$$
(5.50)

§ 5.3]

where $h = \alpha/D$, and

$$\frac{M_t}{M_{\infty}} = \frac{2DtL}{a^2} - \frac{8L^2}{3\pi^{\frac{1}{2}}} \left(\frac{Dt}{a^2}\right)^{\frac{3}{2}} - L^2 \left(\frac{Dt}{a^2}\right)^2 \left(\frac{1}{2} - L\right) - \dots$$
(5.51)

Tabulated values of M_t/M_{∞} are given by Newman [10] from which the graphs of Fig. 5.8 are drawn. Newman [10] also gives values of a second function from which M_t/M_{∞} can easily be deduced for a parabolic initial distribution.

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FIG. 5.8. Sorption and desorption curves for the surface condition (5.45). Numbers on curves are values of L = ax/D.

5.35. Constant flux F_0 at the surface

If the cylinder is initially at a uniform concentration C_0 , and there is a constant rate of transfer of diffusing substance F_0 per unit area of the surface, i.e. $-D \partial C/\partial r = F_0$, r = a, (5.52)

then we have

$$C - C_0 = -\frac{F_0 a}{D} \left\{ \frac{2Dt}{a^2} + \frac{r^2}{2a^2} - \frac{1}{4} - 2 \sum_{n=1}^{\infty} e^{-D\alpha_n^2 l/a^2} \frac{J_0(r\alpha_n/a)}{\alpha_n^2 J_0(\alpha_n)} \right\}, \quad (5.53)$$

where the α_n 's are the positive roots of

$$J_1(\alpha) = 0. (5.54)$$

Roots of (5.54) are tabulated in reference [3, p. 171], and the first five roots are to be found in Table 5.2 when L = 0. Obviously the amount of diffusing substance lost by unit length of the cylinder in time t is

 $2\pi a F_0 t$. This is a problem which has been discussed in connexion with the drying of clay by Macey [11], Jaeger [12], and others. A solution useful for small values of time is

$$C - C_0 = -\frac{F_0}{D} \left\{ 2 \left(\frac{Dat}{r} \right)^{\frac{1}{2}} \text{ierfe} \frac{a - r}{2\sqrt{Dt}} + \frac{Dt(a + 3r)}{2a^{\frac{1}{2}}r^{\frac{3}{2}}} i^2 \text{erfe} \frac{a - r}{2\sqrt{Dt}} + \cdots \right\}.$$
(5.55)

Concentration-distance curves, plotted from (5.53) are shown in Fig. 5.9.



intration distributions in a cylinder for constant flux F_0 at the surface. Numbers on curves are values of Dt/a^2 .

5.36. Impermeable surface

If the surface of the cylinder is impermeable and there is an initial concentration distribution f(r) then

$$C = \frac{2}{a^2} \left\{ \int_0^a r'f(r') \, dr' + \sum_{n=1}^\infty e^{-D\alpha_n^2 t} \frac{J_0(r\alpha_n)}{J_0^2(a\alpha_n)} \int_0^a r'f(r') J_0(\alpha_n r') \, dr' \right\},\tag{5.56}$$

where the α_n 's are roots of

$$J_1(a\alpha_n) = 0, \qquad (5.57)$$

which are tabulated in reference [3, p. 171].

5.37. Composite cylinder

Various problems of diffusion into a composite cylinder comprised of two coaxial cylinders having different diffusion coefficients have been solved. (See, for example, Carslaw and Jaeger [2, p. 284].) The extra parameters involved make any attempt at general numerical evaluation too formidable to be attempted here. Some solutions relating to diffusion accompanied by non-linear absorption are discussed in Chapter XII.

5.4. The hollow cylinder

Carslaw and Jaeger [2, p. 180] give the general solution to the problem of the hollow cylinder with the surface r = a maintained at a constant concentration C_1 , and r = b at C_2 , when the initial distribution is f(r), in the region $a \leq r \leq b$. In the special case of a constant initial concentration, $f(r) = C_0$, and when $C_1 = C_2$, the solution is

$$\frac{C-C_0}{C_1-C_0} = 1 - \pi \sum_{n=1}^{\infty} \frac{J_0(a\alpha_n)U_0(r\alpha_n)}{J_0(a\alpha_n) + J_0(b\alpha_n)} e^{-D\alpha_n^2 l},$$
(5.58)

where $U_0(r\alpha_n) = J_0(r\alpha_n)Y_0(b\alpha_n) - J_0(b\alpha_n)Y_0(r\alpha_n), \qquad (5.59)$

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and the α_n 's are the positive roots of

$$U_0(a\alpha_n) = 0. (5.60)$$

Roots of (5.60) are given in Table 5.3 for different values of b/a. This table is reproduced from Carslaw and Jaeger's book [2, p. 379]. In (5.58) and (5.59) J_0 and Y_0 are Bessel functions of the first and second kind respectively, of order zero. They are both tabulated in reference [3].



FIG. 5.10. Uptake curves for hollow cylinder.

The expression for the amount of diffusing substance entering or leaving the region $a \leqslant r \leqslant b$ in time t is given by

$$\frac{M_l}{M_{\alpha}} = 1 - \frac{4}{b^2 - a^2} \sum_{n=1}^{\infty} \frac{J_0(a\alpha_n) - J_0(b\alpha_n)}{\alpha_n^2 \{J_0(a\alpha_n) + J_0(b\alpha_n)\}} e^{-D\alpha_n^2 t}.$$
 (5.61)

In Fig. 5.10, curves of M_l/M_∞ are plotted against $\{Dt/(b-a)^2\}^1$ for different values of b/a.

5.41. Flow through cylinder wall

If the surface r = a is maintained at C_1 , r = b at C_2 , and the region $a \leq r \leq b$ is initially at C_0 , the concentration approaches the steadystate distribution discussed in § 5.2 according to the expression

$$C = \frac{C_1 \log(b/r) + C_2 \log(r/a)}{\log(b/a)} + \pi C_0 \sum_{n=1}^{\infty} \frac{J_0(a\alpha_n) U_0(r\alpha_n) e^{-D\alpha_n^2 t}}{J_0(a\alpha_n) + J_0(b\alpha_n)} - \pi \sum_{n=1}^{\infty} \frac{\{C_2 J_0(a\alpha_n) - C_1 J_0(b\alpha_n)\} J_0(a\alpha_n) U_0(r\alpha_n)}{J_0^2(a\alpha_n) - J_0^2(b\alpha_n)} e^{-D\alpha_n^2 t}, \quad (5.62)$$

where the α_n 's are roots of (5.60). The amount of diffusing substance entering or leaving the cylinder wall in time t is given by M_t , where

$$M_{t} = \frac{1}{2}\pi \frac{(C_{2} - C_{1})(a^{2} - b^{2})}{\log(b/a)} + \pi \{b^{2}(C_{2} - C_{0}) - a^{2}(C_{1} - C_{0})\} + 4\pi \sum_{n=1}^{\infty} \frac{\{(C_{1} - C_{0})J_{0}(b\alpha_{n}) - (C_{2} - C_{0})J_{0}(a\alpha_{n})\}}{\alpha_{n}^{2}\{J_{0}(a\alpha_{n}) + J_{0}(b\alpha_{n})\}} e^{-D\alpha_{n}^{2}t}.$$
 (5.63)

Normally a quantity of greater practical interest is the amount, Q_t , escaping from unit length of the outer surface, r = b. This is readily deduced from (5.62) and is given by obtaining $-2\pi D(r \partial c/\partial r)_{r=b}$ and integrating with respect to time, t. In the most commonly occurring case $C_0 = C_2 = 0$, and we then find

$$\frac{Q_l}{\pi C_1} = \frac{2(Dt - L)}{\log(b/a)} - 4 \sum_{n=1}^{\infty} \frac{J_0(a\alpha_n) J_0(b\alpha_n) e^{-D\alpha_n^3 l}}{\alpha_n^2 \{J_0^2(a\alpha_n) - J_0^2(b\alpha_n)\}}.$$
 (5.64)

For a given b/a the graph of $Q_t/(\pi b^2 C_1)$ against t approaches, at large t, a straight line which makes an intercept L on the t axis given by

(5.65)

 $\frac{a^2 - b^2 + (a^2 + b^2) \log(b/a)}{4 \log(b/a)} \cdot \frac{b^2}{2} \cdot \frac{b^2}$

As Barrer [13, p. 37] suggests, this intercept provides a means of measuring the diffusion coefficient, D, for a material in the form of a hollow cylinder. Fig. 5.11 shows graphs of $Q_t/(\pi b^2 C_1)$, the amount evaporated from unit area of the outer surface r = b, as a function of $Dt/(b-a)^2$ for different values of b/a.



FIG. 5.11. Approach to steady-state flow through wall of cylinder. Numbers on curves are values of b/a.

5.42. A general boundary condition

Jacger [14] has given the solution to the problem of diffusion into a hollow cylinder in which the concentration is initially zero and the boundary conditions on the two surfaces are

$$k_1 \frac{\partial C}{\partial t} + k_2 \frac{\partial C}{\partial r} + k_3 C - k_4, \qquad r = a, \qquad (5.66)$$

$$k_1 + k_2 + k_3 C = k_4, \qquad r = b.$$
 (5.67)

These conditions include as special cases:

(i) Constant concentrations, C_1 on r = a and C_2 on r = b, when $k_1 = k_2 = k'_1 = k'_2 = 0$; $k_4/k_3 = C_1$, $k'_4/k'_3 = C_2$. (ii) Evaporation conditions on the surfaces

$$-D \partial C/\partial r = \gamma_1(C_1 - C), \qquad r = a, \qquad (5.68)$$

$$-D \partial C/\partial r = \gamma_2(C - C_2), \qquad r = b, \qquad (5.69)$$

when $k_1 = k'_1 = 0$, $k_2 = k'_2 = D$, $k_3 = -\gamma_1$, $k_4 = -\gamma_1 C_1$, $k'_3 = \gamma_2$, $k'_4 = \gamma_2 C_2$. This includes the obvious modification for an impermeable surface.

(iii) Diffusion proceeding from a well-stirred solution occurring in the region $0 \le r \le a$, the concentration at r = a being always the same as that throughout the solution; the surface r = b impermeable. At r = a the condition is

 $\pi a^2 \partial C / \partial t = 2\pi a D \partial C / \partial r, \qquad r = a,$

that is

$$\frac{\partial C}{\partial t} - \frac{2D}{a} \frac{\partial C}{\partial r} = 0, \qquad r = a, \qquad (5.70)$$

and we have also
$$\partial C/\partial r = 0$$
, $r = b$, (5.71)

so that $k_1 = k'_2 = 1$, $k_2 = -2D/a$, $k'_1 = k'_3 = k'_4 = k_3 = k_4 = 0$. Other cases, such as that of diffusion from a well-stirred solution in the region $0 \le r \le a$ with the surface r = b maintained at a constant concentration, or the surface r = a maintained at a constant concentration while there is loss by evaporation from the surface r = b, and other combinations of these boundary conditions are all deducible from the general solution. The derivation of the solution by the use of Laplace transforms is given by Jaeger [14]. The final result is

$$C = \frac{ak_4\{k'_2 - bk'_3 \log(r/b)\} - bk'_4\{k_2 - ak_3 \log(r/a)\}}{ak_3 k'_2 - bk_2 k'_3 - abk_3 k'_3 \log(a/b)} - \pi \sum_{n=1}^{\infty} e^{-D\alpha_n^3 t} F(\alpha_n) C_0(r; \alpha_n) \{k_4[A'_n J_0(b\alpha_n) - k'_2 \alpha_n J_1(b\alpha_n)] + -k'_4[A_n J_0(a\alpha_n) - k_2 \alpha_n J_1(a\alpha_n)]\}, \quad (5.72)$$

where

$$C_{0}(r;\alpha_{n}) = J_{0}(r\alpha_{n})[A_{n}Y_{0}(a\alpha_{n})-k_{2}\alpha_{n}Y_{1}(a\alpha_{n})] - -Y_{0}(r\alpha_{n})[A_{n}J_{0}(a\alpha_{n})-k_{2}\alpha_{n}J_{1}(a\alpha_{n})], \quad (5.74)$$

$$F(\alpha_n) = \frac{A_n J_0(\partial \alpha_n) - k_2 \alpha_n J_1(\partial \alpha_n)}{[A'_n J_0(\partial \alpha_n) - k'_2 \alpha_n J_1(\partial \alpha_n)]^2 (A_n^2 + k_2 B \alpha_n^2) - [A_n J_0(\partial \alpha_n) - k_2 \alpha_n J_1(\partial \alpha_n)] (A'_n^2 + k'_2 B' \alpha_n^2)}, \quad (5.75)$$

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and where the α_n 's are the positive roots of

$$[(k_{3}-k_{1}D\alpha^{2})J_{0}(a\alpha)-k_{2}\alpha J_{1}(a\alpha)][(k_{3}'-k_{1}'D\alpha^{2})Y_{0}(b\alpha)-k_{2}'\alpha Y_{1}(b\alpha)]- [(k_{3}'-k_{1}'D\alpha^{2})J_{0}(a\alpha)-k_{2}'\alpha Y_{1}(a\alpha)] = 0.$$

$$(5.76)$$



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5.5. The region bounded internally by the cylinder r = a

(i) If the initial concentration throughout the region r > a is C_0 , and the surface r = a is maintained at C_1 , then

$$\frac{C-C_0}{C_1-C_0} = 1 + \frac{2}{\pi} \int_0^\infty e^{-Du^3t} \frac{J_0(ur)Y_0(ua) - Y_0(ur)J_0(ua)}{J_0^2(ua) + Y_0^2(ua)} \frac{du}{u}.$$
 (5.77)

A solution useful for small times is

$$\frac{C-C_0}{C_1-C_0} = \left(\frac{a}{r}\right)^{\frac{1}{2}} \operatorname{erfe} \frac{r-a}{2\sqrt{(Dt)}} + \frac{(r-a)(Dt)^{\frac{1}{2}}}{4a^{\frac{1}{2}}r^{\frac{3}{2}}} \operatorname{ierfe} \frac{r-a}{2\sqrt{(Dt)}} + \frac{Dt(9a^2-2ar-7r^2)}{32a^{\frac{3}{2}}r^{\frac{3}{2}}} \operatorname{i}^{\frac{2}{2}}\operatorname{erfe} \frac{r-a}{2\sqrt{(Dt)}} + \dots \quad (5.78)$$

Fig. 5.12 shows how concentration depends on radius at successive times. The expression for the amount of diffusing substance, F, crossing unit area of the surface, r = a, in unit time is

$$F = -D\left(\frac{\partial C}{\partial r}\right)_{r=a} = \frac{4(C_1 - C_0)D}{\pi^2 a} \int_0^\infty e^{-Du^2 t} \frac{du}{u[J_0^2(au) + Y_0^2(au)]}.$$
(5.79)

Numerical values of the integral in (5.79) have been tabulated by Jaeger and Clarke [15] and are shown graphically by Carslaw and Jaeger [2, p. 283]. For small times we have

$$F = \frac{D(C_1 - C_0)}{a} \{ (\pi T)^{-\frac{1}{2}} + \frac{1}{2} - \frac{1}{4} (T/\pi)^{\frac{1}{2}} + \frac{1}{8} T - \dots \},$$
 (5.80)

and for large times

$$F = \frac{2D}{a} (C_1 - C_0) \left[\frac{1}{\log(4T) - 2\gamma} - \frac{\gamma}{\{\log(4T) - 2\gamma\}^2} - \dots \right], \quad (5.81)$$

where $T = Dt/a^2$ and $\gamma = 0.57722$ is Euler's constant.

(ii) If the region r > a is initially at a uniform concentration C_0 , and there is transfer of diffusing substance across r = a according to

$$-D \partial C/\partial r = \alpha (C - C_{1}), \quad r = a, \quad (5.82)$$

then we have
$$\frac{C - C_{1}}{C_{0} - C_{1}}$$
$$= -\frac{2h}{\pi} \int_{0}^{\infty} e^{-Du^{3}t} \frac{J_{0}(ur)[uY_{1}(ua) + hY_{0}(ua)] - Y_{0}(ur)[uJ_{1}(ua) + hJ_{0}(ua)]}{[uJ_{1}(ua) + hJ_{0}(ua)]^{2} + [uY_{1}(ua) + hY_{0}(ua)]^{2}} \frac{du}{u}, \quad (5.83)$$

where h = a/D. Graphs showing how $(C-C_1)/(C_0-C_1)$ at the surface r = a varies with time have been drawn by Carslaw and Jaeger [2, p. 283], for several values of ah. Clearly because of (5.82) these curves also show the rate of transfer across unit area of the surface r = a. Carslaw and Jaeger [2, p. 283] also give the solution of the corresponding problem when there is a constant rate of flow of diffusing substance across the surface r = a.

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DIFFUSION IN A SPHERE

6.1. Introduction

IF we restrict ourselves to cases in which the diffusion is radial, the diffusion equation for a constant diffusion coefficient takes the form

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right).$$
(6.1)

On putting

$$u = Cr, \tag{6.2}$$

(6.3)

(6.1) becomes $\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2}.$

Since this is the equation for linear flow in one dimension, the solutions of many problems in radial flow in a sphere can be deduced immediately from those of the corresponding linear problems.

6.2. Steady state

In this case the equation is

$$\frac{d}{dr}\left(r^2\frac{dC}{dr}\right) = 0, \qquad (6.4)$$

of which the general solution is

$$C = B + A/r, \tag{6.5}$$

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

$$C = \frac{aC_1(b-r) + bC_2(r-a)}{r(b-a)}.$$
 (6.6)

The quantity of diffusing substance, Q_t , which passes through the spherical wall in time t, is given by

ah

$$Q_l = 4\pi Dt \frac{a\sigma}{b-a} (C_2 - C_1). \tag{6.7}$$

If Q_l is measured in a concentration-dependent system, the mean value of the diffusion coefficient obtained from (6.7) is

$$\left(\int_{C_2}^{C_1} D \ dC\right) \Big/ (C_1 - C_2)$$

as for the plane sheet (see 4.11),

If the surface r = a is maintained at a concentration C_1 and at r = b there is evaporation according to the condition

$$\frac{dC}{dr} + h(C - C_2) = 0, \qquad r = b, \tag{6.8}$$

find
$$C = \frac{aC_1\{hb^2 + r(1-hb)\} + hb^2C_2(r-a)}{r\{hb^2 + a(1-hb)\}}.$$

The amount, Q_t , passing through the spherical wall in time t is now given by $4\pi Dthab^2(C-C)$

$$Q_t = \frac{4\pi D t hab^2 (C_1 - C_2)}{hb^2 + a(1 - hb)}.$$
 (6.10)

If ah > 2, the rate of diffusion decreases steadily as b increases, but if ah < 2 the rate first increases and later decreases, passing through a maximum when b = 2/h. As in the case of the cylinder, this maximum is due to the combination of a decreasing gradient and an increasing surface area as b is increased.

If the surface conditions are

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

(6.11)

the solutions are

$$C = \frac{C_1 a^2 h_1 \{ b^2 h_2 - r(bh_2 - 1) \} + C_2 b^2 h_2 \{ r(ah_1 + 1) - a^2 h_1 \}}{r\{ b^2 h_2 (ah_1 + 1) - a^2 h_1 (bh_2 - 1) \}}, \quad (6.12)$$

and
$$Q_{t} = \frac{4\pi a^{2}b^{2}h_{1}h_{2}Dt(C_{1}-C_{2})}{b^{2}h_{2}(ah_{1}+1)-a^{2}h_{1}(bh_{2}-1)}.$$
 (6.13)

6.3. Non-steady state

6.31. Surface concentration constant. Initial distribution f(r)

If we make the substitution u = Cr, suggested above, the equations for u are

$$\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial r^2}, \qquad (6.14)$$

$$u = 0, \quad r = 0, \quad t > 0,$$
 (6.15)

$$u = aC_0, \qquad r = a, \qquad t > 0,$$
 (6.16)

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(6.9)

$$u = rf(r), \quad t = 0, \quad 0 < r < a,$$
 (6.17)

where C_0 is the constant concentration at the surface of the sphere. These are the equations of diffusion in a plane sheet of thickness a, with its ends, r = 0 and r = a, kept at zero and aC_0 respectively, and with the initial distribution rf(r). This problem has been considered in § 4.31, and the solution follows immediately by making the appropriate substitutions in equation (4.16). If the sphere is initially at a uniform concentration, C_1 , and the surface concentration is maintained constant at C_0 , the solution becomes



FIG. 6.1. Concentration distributions at various times in a sphere with initial concentration C_1 and surface concentration C_0 . Numbers on curves are values of Dt/a^2 .

The concentration at the centre is given by the limit as $r \rightarrow 0$, that is by

$$\frac{C-C_1}{C_0-C_1} = 1 + 2\sum_{n=1}^{\infty} (-1)^n e^{-Dn^2 \pi^2 t/a^2}.$$
 (6.19)

[§ 6.3

The total amount of diffusing substance entering or leaving the sphere is given by $M = 6 - \frac{\infty}{2} - 1$

$$\frac{M_l}{M_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-Dn^2 \pi^2 l/a^2}.$$
 (6.20)

The corresponding solutions for small times are

$$\frac{C-C_1}{C_0-C_1} = \frac{a}{r} \sum_{n=0}^{\infty} \left\{ \operatorname{erfc} \frac{(2n+1)a-r}{2\sqrt{Dt}} - \operatorname{erfc} \frac{(2n+1)a+r}{2\sqrt{Dt}} \right\}, \quad (6.21)$$

and

$$\frac{M_t}{M_{\infty}} = 6 \left(\frac{Dt}{a^2}\right)^{\frac{1}{2}} \left\{\pi^{-\frac{1}{4}} + 2\sum_{n=1}^{\infty} \operatorname{ierfe} \frac{na}{\sqrt{(Dt)}}\right\} - 3\frac{Dt}{a^2}.$$
 (6.22)

These solutions 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 [1, p. 201], are reproduced in Fig. 6.1. The curve for zero fractional exhaustion on Fig. 6.4 shows M_t/M_{∞} as a function of Dt/a^2 .

6.32. Variable surface concentration

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

$$C = -\frac{2D}{ra} \sum_{n=1}^{\infty} (-1)^n e^{-Dn^2 \pi^2 l_j a^2} n\pi \sin \frac{n\pi r}{a} \int_0^t e^{Dn^2 \pi^2 \lambda' a^2} \phi(\lambda) \, d\lambda. \quad (6.23)$$

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$$\phi(t) = C_0(1 - e^{-\beta t}), \qquad (6.24)$$

(6.23) becomes

$$\frac{C}{C_0} = 1 - \frac{a}{r} e^{-\beta t} \frac{\sin\{(\beta a^2/D)^{\frac{1}{2}}r/a\}}{\sin\{\beta a^2/D\}^{\frac{1}{2}}} - \frac{2\beta a^3}{\pi Dr} \sum_{n=1}^{\infty} (-1)^n \frac{e^{-Dn^{\frac{1}{2}}\pi^{\frac{1}{2}}/a^2}}{n(n^2\pi^2 - \beta a^2/D)} \sin\frac{n\pi r}{a}, \quad (6.25)$$

and the sorption-time curve is given by

$$\frac{3M_{t}}{4\pi a^{3}C_{0}} = 1 - \frac{3D}{\beta a^{2}}e^{-\beta t} \left[1 - \left(\frac{\beta a^{2}}{D}\right)^{\frac{1}{2}} \cot\left(\frac{\beta a^{2}}{D}\right)^{\frac{1}{2}} \right] + \frac{6\beta a^{2}}{\pi^{2}D} \sum_{n=1}^{\infty} \frac{e^{-Dn^{2}\pi^{3}t/a^{2}}}{n^{2}(n^{2}\pi^{2} - \beta a^{2}/D)}.$$
 (6.26)

Fig. 6.2 shows uptake curves for different values of the parameter $\beta a^2/D$. (ii) If the surface concentration varies linearly with time, i.e.

$$\boldsymbol{\phi}(t) = kt, \tag{6.27}$$

§ 6.3]

the solutions are

$$C = k \left(t - \frac{a^2 - r_1^2}{6D} \right) - \frac{2ka^3}{D\pi^3 r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^3} e^{-Dn^2 \pi^2 t/a^2} \sin \frac{n\pi r}{a}, \qquad (6.28)$$

and $\frac{M_l}{\frac{4}{3}\pi a^3 k} = \left(t - \frac{a^2}{15D}\right) + \frac{6a^2}{\pi^4 D} \sum_{n=1}^{\infty} \frac{1}{n^4} e^{-Dn^3 \pi^3 l/a^3}.$ (6.29)

 $M_t D/(\frac{4}{3}\pi a^5 k)$ is plotted against Dt/a^2 in Fig. 6.3.



FIG. 6.2. Calculated sorption curves for surface concentration given by $C_0(1-e^{-\beta t})$. Numbers on curves are values of $\beta a^2/D$.

6.33. Diffusion from a well-stirred solution of limited volume

The problem and method of solution are very similar to those of the plane sheet and the results can be given without explanation. Suppose that the sphere occupies the space r < a, while the volume of the bath of solution (excluding the space occupied by the sphere) is V. The concentration of solute in the solution is always uniform and is initially C_0 . The sphere is initially free from solute. The total amount of solute, M_t , in the sphere after time t is expressed as a fraction of the corresponding quantity after infinite time by the relation

(6.30)

(6.31)

$$\frac{M_{l}}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha+1)e^{-Dq_{n}^{2}t/a^{2}}}{9 + 9\alpha + q_{n}^{2}\alpha^{2}},$$

where the q_n 's are the non-zero roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2}$$

and $\alpha = 3V/(4\pi a^3)$, the ratio of the volumes of solution and sphere, or if there is a partition factor, K, between solute in equilibrium in the sphere and the solution, $\alpha = 3V/(4\pi a^3K)$. The parameter α is expressed in terms of the final fractional uptake of solute by the sphere by the relation M

$$\frac{M_{\infty}}{VC_0} = \frac{1}{1+\alpha}.\tag{6.32}$$



FIG. 6.3. Sorption curve for sphere with surface concentration kt.

The roots of (6.31) are given in Table 6.1 for several values of α . An alternative solution suitable for small times given by Carman and Haul [2] is

4.1

$$\frac{M_{t}}{M_{\infty}} = (1+\alpha) \left[1 - \frac{\gamma_{1}}{\gamma_{1} + \gamma_{2}} e \operatorname{erfc} \left\{ \frac{3\gamma_{1}}{\alpha} \left(\frac{Dt}{a^{2}} \right)^{\frac{1}{2}} \right\} - \frac{\gamma_{2}}{\gamma_{1} + \gamma_{2}} e \operatorname{erfc} \left\{ -\frac{3\gamma_{2}}{\alpha} \left(\frac{Dt}{a^{2}} \right)^{\frac{1}{2}} \right\} \right] + \text{higher terms,} \quad (6.33)$$

 $\begin{array}{c} \gamma_1 = \frac{1}{2} \{(1+\frac{4}{3}\alpha)^{\frac{1}{2}}+1\}, \quad \gamma_2 = \gamma_1 - 1, \quad (6.34)\\ \text{and} \qquad e \operatorname{erfe} z \equiv \exp z^2 \operatorname{erfe} z. \quad (6.35)\\ \text{In Fig. 6.4, } M_t/M_{\infty} \text{ against } (Dt/a^2)^{\frac{1}{2}} \text{ is plotted for five final fractional}\\ \frac{5824}{6} \end{array}$

DIFFUSION IN A SPHERE



FIG. 6.4. Uptake by a sphere from a stirred solution of limited volume. Numbers on curves show percentage of solute finally taken up by sphere.

uptakes. Berthier [3] gives a table of M_l/M_{∞} for values of $1/\alpha$ between 0 and 1 at intervals of 0.1. His male are not always called by the terms

0 and 1 at intervals of 0.1. His values are not always reliable to three decimal places.

The concentration of solute C within the sphere is given by

$$C = C_{\infty} \left\{ 1 + \sum_{n=1}^{\infty} \frac{6(1+\alpha)e^{-Dq_n^2 t/\alpha^2}}{9+9\alpha+q_n^2 \alpha^2} \frac{a}{r} \frac{\sin(q_n r/a)}{\sin q_n} \right\}.$$
 (6.36)

The above equations also describe the course of desorption into a well-stirred solution, initially free from solute, from a sphere in which the concentration is uniform and equal to C_0 . The only modifications are that (6.32) is to be replaced by

$$\frac{3M_{\infty}}{4\pi a^3 C_0} = \frac{1}{1+1/\alpha},\tag{6.37}$$

and C_1 , $(C_1)_{\infty}$ replace C, C_{∞} in (6.36), where

$$C_1 = C_0 - C, \qquad (C_1)_{\infty} = C_0 - C_{\infty}.$$
 (6.38)

6.34. Surface evaporation

If the sphere is initially at a uniform concentration C_1 , and there is a surface condition

$$-D\partial C/\partial r = \alpha (C_s - C_0), \qquad (6.39)$$

where C_s is the actual concentration just within the sphere, and C_0 is the concentration required to maintain equilibrium with the surrounding atmosphere, the required solution is

$$\frac{C-C_0}{C_1-C_0} = \frac{2La}{r} \sum_{n=1}^{\infty} \frac{e^{-D\beta_n^2 t/a^2}}{\{\beta_n^2 + L(L-1)\}} \frac{\sin\beta_n r/a}{\sin\beta_n}.$$
 (6.40)

The β_n 's are the roots of

$$\beta_n \cot \beta_n + L - 1 = 0, \qquad (6.41)$$

and

$$L = a\alpha/D. \tag{6.42}$$

Some roots of (6.41) are given in Table 6.2. The expression for the total amount of diffusing substance entering or leaving the sphere is

$$\frac{M_l}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{6L^2 e^{-\beta_n^3 D l/a^2}}{\beta_n^2 \{\beta_n^2 + L(L-1)\}}.$$
(6.43)

Fig. 6.5 shows curves of M_l/M_{∞} plotted as functions of $(Dt/a^2)^{\frac{1}{2}}$ for several values of L for which Newman [4] gives tabulated solutions.

6.35. Constant flux F_0 at the surface

If the sphere is initially at a uniform concentration C_0 , and there is a constant rate of transfer F_0 per unit area of surface, i.e.

$$-D \partial C/\partial r = F_0, \qquad r = a, \qquad (6.44)$$

§ 6.3]

then we have

$$C_{0}-C = \frac{F_{0}a}{D} \left\{ \frac{3Dt}{a^{2}} + \frac{1}{2} \frac{r^{2}}{a^{2}} - \frac{3}{10} - 2\frac{a}{r} \sum_{n=1}^{\infty} \frac{\sin(\alpha_{n}r)}{\alpha_{n}^{2}a^{2}\sin(\alpha_{n}a)} e^{-D\alpha_{n}^{2}t} \right\}, \quad (6.45)$$

where the a_{α_n} 's are the positive roots of

$$a\alpha_n \cot a\alpha_n = 1.$$
 (6.46)
The amount of diffusing substance lost by the sphere in time t is $4\pi a^2 F_0 t$.

Some roots of (6.46) are given in Table 6.2 when L = 0. Fig. 6.6 shows curves of $D(C_0 - C)/(F_0 a)$ plotted against r/a for different values of Dt/a^2 .



Fig. 6.5. Sorption or desorption curves for the surface condition (6.39). Numbers on curves are values of $L = a\alpha/D$.

6.36. Impermeable surface

If the surface of the sphere is impermeable and there is an initial concentration f(r) then

$$C = \frac{3}{a^3} \int_{0}^{a} r^2 f(r) dr + \frac{2}{ar} \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t} \frac{\sin \alpha_n r}{\sin^2 \alpha_n a} \int_{0}^{a} r' f(r') \sin \alpha_n r' dr',$$
(6.47)

where the α_n 's are the positive roots of (6.46).

6.37. Composite sphere

Problems of diffusion into a composite sphere comprised of an inner core and an outer shell for which the diffusion coefficients are different

have been considered by Carslaw and Jaeger [1, p. 288], Bromwich [5], Carslaw [6], Carslaw and Jaeger [7], Bell [8], and others. The extraparameters involved make any attempt at general numerical evaluation too formidable to be attempted here.

6.4. Hollow sphere

Carslaw and Jaeger [1, p. 208] give the general solution to the problem of the hollow sphere with the surface r = a maintained at a constant



concentration C_1 , and r = b at C_2 , when the initial distribution is f(r) in the region $a \leq r \leq b$. Some special cases have been considered by



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FIG. 6.7. Uptake curves for hollow sphere.

Barrer [9] who also suggests a number of practical systems to which his solutions might be applied. In the special case of a constant initial concentration, $f(r) = C_0$, and when $C_1 = C_2$, the solution is

$$\frac{C-C_0}{C_1-C_0} = 1 + \frac{2}{\pi r} \sum_{n=1}^{\infty} \left(\frac{b \cos n\pi - a}{n} \right) \sin \frac{n\pi (r-a)}{b-a} e^{-Dn^2 \pi^2 t / (b-a)^2}.$$
 (6.48)

The total amount of diffusing substance entering or leaving the hollow

sphere $a \leq r \leq b$ in time t is given by

$$\frac{M_t}{M_{\infty}} = 1 - \frac{6}{\pi^2 (a^2 + ab + b^2)} \sum_{n=1}^{\infty} \left(\frac{b \cos n\pi - a}{n} \right)^2 e^{-Dn^2 \pi^2 l/(b-a)^2}.$$
 (6.49)

Graphs of M_t/M_{∞} against $\{Dt/(b-a)^2\}^{\frac{1}{2}}$ are shown in Fig. 6.7 for different values of b/a.

6.41. Flow through spherical wall

If the surface r = a is maintained at C_1 , and r = b at C_2 , and the region $a \leq r \leq b$ is initially at C_0 , the concentration approaches the steady-state distribution discussed in § 6.2, according to the expression

$$C = \frac{aC_1}{r} + \frac{(bC_2 - aC_1)(r - a)}{r(b - a)} + \frac{2}{r\pi} \sum_{n=1}^{\infty} \frac{b(C_2 - C_0)\cos n\pi - a(C_1 - C_0)}{n} \times \\ \times \sin \frac{n\pi(r - a)}{b - a} e^{-Dn^2\pi^2 l/(b - a)^2}. \quad (6.50)$$

The total amount which accumulates in the spherical wall in time t is M_t , where

$$M_{t} = \frac{4\pi}{3}(b-a) \left[\left(a^{2} + \frac{ab}{2} \right) C_{1} + \left(b^{2} + \frac{ab}{2} \right) C_{2} - (a^{2} + ab + b^{2}) C_{0} - \frac{6}{\pi^{2}} \sum_{n=1}^{\infty} \left\{ a^{2} C_{1} - (a^{2} + b^{2}) C_{0} + b^{2} C_{2} - 2ab \cos n\pi \left(\frac{C_{1} + C_{2}}{2} - C_{0} \right) \right\} \times \frac{e^{-Dn^{2}\pi^{4} \left((b-a)^{2} \right)}}{n^{2}} \right]. \quad (6.51)$$

The quantity which is usually of greater practical importance is Q_t , the amount escaping say from the outer surface r = b. In the simplest case, when $C_0 = C_2 = 0$, we find

$$\frac{Q_i}{4\pi ab(b-a)C_1} = \frac{Dt}{(b-a)^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=-1}^{\infty} \frac{(-1)^n}{n^2} e^{-Dn^2\pi^2 t/(b-a)^2}.$$
 (6.52)

As $t \to \infty$, the graph of (6.52) when plotted against $Dt/(b-a)^2$ approaches

10.000 10.000 10.000 10.000 10.000 10.000 10.000 10.000 10.000 10.000 10.000 10.000

a straight line which has an intercept on the time axis given by

$$\frac{Dt}{(b-a)^2} = \frac{1}{6}.$$
 (6.53)

As in the case of the plane sheet and the cylinder, this intercept can be used to determine the diffusion coefficient D experimentally [10, p. 31]. Fig. 6.8 shows the way in which the graph of (6.52) approaches the straight line.



Fig. 6.8. Approach to steady-state flow through the wall of a sphere.

6.42. Surface evaporation

Carslaw and Jaeger [1, p. 209] give a solution to the problem in which evaporation into an atmosphere of zero vapour pressure occurs at r = aand r = b according to the expressions

$$k_1 \frac{\partial C}{\partial r} - h_1 C = 0, \qquad r = a, \qquad (6.54)$$

$$k_2 \frac{\partial C}{\partial r} + h_2 C = 0, \qquad r = b. \tag{6.55}$$

If the initial concentration distribution in the spherical wall is f(r), the solution is

$$C = \frac{2}{r} \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t R_n(r)} \int_a^r r' R_n(r') f(r') dr', \qquad (6.56)$$

where
$$G = ah_1 + k_1, \qquad H = bh_2 - k_2, \qquad (6.57)$$
$$R_n(r) = \frac{(H^2 + b^2 k_2^2 \alpha_n^2)^{\frac{1}{2}} \{G \sin(r - a)\alpha_n + ak_1 \alpha_n \cos(r - a)\alpha_n\}}{\{(b-a)(a^2 k_1^2 \alpha_n^2 + G^2)(b^2 k_2^2 \alpha_n^2 + H^2) + (Hak_1 + Gbk_2)(GH + abk_1 k_2 \alpha_n^2)\}^{\frac{1}{2}}, \qquad (6.58)$$

and $\pm \alpha_n$, n = 1, 2, ..., are the roots of

$$(GH - abk_1 k_2 \alpha^2)\sin(b - a)\alpha + \alpha(ak_1 H + bk_2 G)\cos(b - a)\alpha = 0. \quad (6.59)$$

By putting either or both k_1 and k_2 zero we obtain the solutions for one or both surfaces maintained at zero concentration, and similarly h_1 or h_2 zero corresponds to an impermeable surface. If both h_1 and h_2 are zero, so that both surfaces are impermeable, a term

$$\frac{3}{(b^3-a^3)}\int\limits_a^b r^2f(r)\ dr$$

is to be added to (6.56).

If evaporation takes place into atmospheres of different vapour pressures the solution can be deduced from the above by following the method used by Carslaw and Jaeger [1, p. 97] for the plane sheet. Thus we write C = u + w, where u is a function of r only, satisfying

$$\frac{d}{dr}\left(r^2\frac{du}{dr}\right) = 0, \quad a < r < b,$$

$$k_1\frac{du}{dr} + h_1(C_1 - u) = 0, \quad r = a,$$

$$k_2\frac{du}{dr} + h_2(u - C_2) = 0, \quad r = b,$$

so that

$$u = \frac{C_1 a^2 h_1 [b^2 h_2 - r(bh_2 - k_2)] + C_2 b^2 h_2 [r(ah_1 + k_1) - a^2 h_1]}{r[b^2 h_2 (ah_1 + k_1) - a^2 h_1 (bh_2 - k_2)]},$$

and w is a function of r and t such that

$$egin{aligned} &rac{\partial w}{\partial t} = rac{D}{r^2} rac{\partial}{\partial r} \Big(r^2 rac{\partial w}{\partial r} \Big), & a < r < b, \ & k_1 rac{\partial w}{\partial r} - h_1 w = 0, & r = a, \ & k_2 rac{\partial w}{\partial r} + h_2 w = 0, & r = b, \end{aligned}$$

$$w=f(r)-u, \qquad t=0,$$

and hence w is given by (6.56) on using f(r) - u for f(r).

6.5. The region bounded internally by the sphere r = aSolutions of this problem follow readily from those of the corresponding problems of the semi-infinite sheet by using the transformation u = Cr.

(i) If the region r > a is initially at a uniform concentration C_0 , and the surface r = a is maintained at C_1 , the solution is

$$\frac{C-C_0}{C_1-C_0} = \frac{a}{r} \operatorname{erfc} \frac{r-a}{2\sqrt{Dt}},$$
 (6.60)

which is readily evaluated using Table 2.1.

(ii) If the initial concentration is C_0 , and there is a boundary condition

$$-\partial C/\partial r = h(C_1 - C), \qquad r = a, \qquad (6.61)$$

then we find

$$\frac{C-C_0}{C_1-C_0} = \frac{ha^2}{r(1+ah)} \left\{ \operatorname{erfe} \frac{r-a}{2\sqrt{Dt}} - e^{h'(r-a)+h'^2Dt} \operatorname{erfe} \left[\frac{r-a}{2\sqrt{Dt}} + h'\sqrt{Dt} \right] \right\},$$
(6.62)

where h' = h + (1/a). The ratio $(C - C_0)/(C_1 - C_0)$ on the surface, r = a, is ha (a set r = a) is ha (b) with c = 1 (b) ha (c) c = 1).

$$\frac{ha}{ha+1} \{1 - e^{h^{-1}Dt} \operatorname{erfc} h' \sqrt{(Dt)}\}, \qquad (6.63)$$

which again is readily evaluated from Table 2.1.

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DIFFUSION WITH A MOVING BOUNDARY

7.1. Introduction

In this chapter we consider a number of problems in which diffusion occurs in two distinct regions separated by a moving boundary or interface. Examples of such problems are (a) the absorption by a liquid of a single component from a mixture of gases; (b) tarnishing reactions in which a film of tarnish is formed at the surface of a metal by reaction with a gas, the diffusion of gas through the film being the rate-controlling process; (c) the progressive freezing of a liquid; (d) diffusion controlled by a diffusion coefficient which is a discontinuous function of concentration. The moving boundary may be marked by a discontinuous change in concentration as in examples (a) and (b) or by a discontinuity in the gradient of concentration as in (c) and (d). Furthermore, the movement of the boundary relative to the two regions it separates may be caused by the appearance or disappearance of matter at the boundary in one or both regions, which results in a bodily movement of the matter in one or both regions relative to the boundary, or it may be, as in example (d), that the boundary is associated with a certain concentration and this, of course, moves through the medium as diffusion proceeds. Nevertheless, these are all variants of a single mathematical problem which has been treated in a general way by Danckwerts [1].

7.2. Discontinuous diffusion coefficients

We shall first consider diffusion coefficients which change discontinuously from one constant value to another at certain concentrations. They may be zero or infinite over parts of the concentration range. Such coefficients provide examples of extreme types of concentration-dependence and are useful in that they enable limits to be set to the extent to which concentration-dependence of the diffusion coefficient can modify the course of diffusion as indicated, for example, by the shape of the concentration-distance curve. Discontinuities (or near discontinuities) have been observed in several practical systems, e.g. when two metals interdiffuse [2], and, as Hermans [3] points out, the phenomenon is general in all cases in which the diffusing substance reacts with the medium to form a precipitate. The sharp advancing boundary, familiar in many solvent-polymer systems [4], can be regarded as a discontinuity

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for some purposes. Some special cases which do not require detailed calculation are considered first, and afterwards solutions are developed for more general cases.



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FIG. 7.1. Sorption behaviour.

7.21. Special cases not requiring detailed calculation When the diffusion coefficient varies discontinuously with concentration in certain ways, the concentration-distance curves and the sorption- and desorption-time curves can be deduced by general reasoning from the known solutions for a constant diffusion coefficient. Some examples referring to unidirectional diffusion in a plane sheet are presented graphically in Fig. 7.1 and 7.2. These diagrams are largely selfexplanatory and need only brief comments. The nomenclature is as follows: c is the concentration of diffusing substance at a distance x measured from the surface of the sheet in the direction of diffusion at



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FIG. 7.2. Desorption behaviour.

time t, and D is the diffusion coefficient. Also M_l is the total amount of diffusing substance absorbed by or desorbed from unit area of a plane sheet of thickness l in time t. For sorption the sheet is initially free of diffusing substance and the surface is maintained at $c = C_1$ throughout; for desorption the initial concentration is C_1 throughout the sheet and the surface is maintained at zero concentration. In Fig. 7.1 a, over the

concentration range $C_1 > c > C_X$ for which D is zero, the concentration gradient is infinite and there is no penetration into the sheet. The sorption behaviour is identical with that for a constant diffusion coefficient D_1 and surface concentration C_X , and the equilibrium total content of the sheet is lC_X . When D is infinite over any finite interval of concentration at the upper end of the concentration range as in Fig. 7.1b, the existence of a finite concentration gradient anywhere in the range $C_1 > c > C_X$ would mean an infinite rate of transfer of diffusing substance. Consequently, the concentration must reach its final uniform value C_1 throughout the sheet infinitely rapidly, and this is true whatever the form of the D against c curve at low concentrations even if D is zero. When D is infinite at low concentrations but drops to a constant finite value $D_{\mathbf{i}}$ at $c = C_{\mathbf{X}}$ (Fig. 7.1 c), the sheet attains a uniform concentration, C_X , throughout, infinitely rapidly and the remainder of the sorption behaviour is as for a constant diffusion coefficient D_1 . The sorption behaviour is precisely the same for a diffusion coefficient which is infinite for intermediate concentrations and has a constant finite value at high concentrations, as in Fig. 7.1 d, whatever the form of D at low concentrations, again even if D is zero. The curves of Fig. 7.2 for desorption follow by similar arguments and need no comment.

7.22. Diffusion coefficients having a discontinuity at one concentration

The more general cases in which the diffusion coefficient changes discontinuously from one constant finite value to another at one or more concentrations require detailed calculation. At the concentration at which a discontinuous change in D occurs there is also a discontinuity in the concentration gradient and the way in which this moves has to be determined. The problem can be stated mathematically as follows.

Suppose that diffusion takes place into a semi-infinite medium and that the surface $\pi = 0$ is maintained at a constant of the surface π

that the surface x = 0 is maintained at a constant concentration C_1 . We shall consider first a diffusion coefficient in which a discontinuity occurs at a concentration C_X . For concentrations less than C_X , $D = D_2$, and for concentrations greater than C_X , $D = D_1$. Suppose that at time tthe discontinuity in concentration gradient occurring at C_X is at x = X(t); this is a function of t which has to be determined. At time t, let the concentration in the region 0 < x < X be denoted by c_1 , and in the region x > X by c_2 . At the discontinuity, the concentrations c_1 , c_2 must be the same and also the mass of diffusing substance must be conserved, so we have a - a - Cx = Y(7.1)

$$c_1 = c_2 = C_X, \quad x = A, \tag{7.1}$$

$$D_1 \partial c_1 / \partial x = D_2 \partial c_2 / \partial x, \qquad x = X.$$
 (7.2)

In the region 0 < x < X we have to satisfy

$$\partial c_1 / \partial t = D_1 \partial^2 c_1 / \partial x^2, \qquad 0 < x < X,$$
(7.3)

and

$$c_1 = C_1, \qquad x = 0.$$
 (7.4)

In the region x > X we must satisfy

$$\partial c_2/\partial t = D_2 \partial^2 c_2/\partial x^2, \qquad x > X.$$
 (7.5)

Also we suppose the concentration to be C_2 (constant) at large distances, i.e. С

$$c_2 = C_2, \qquad x = \infty. \tag{7.6}$$

The following method of solution of these equations is due to Neumann and is used by Carslaw and Jaeger [5, p. 71] to deal with an analogous problem in heat flow when heat is evolved or absorbed at the boundary. Neumann's method consists of writing down a particular solution of the differential equations and boundary conditions (7.1) to (7.6) and then seeing what initial condition this solution satisfies. The solution of (7.3) satisfying (7.4) is

$$c_1 = C_1 + A \operatorname{erf} \frac{x}{2\sqrt{D_1 t}},$$
 (7.7)

where A is a constant. Also if B is a constant,

$$c_2 = C_2 + B \operatorname{erfe} \frac{x}{2\sqrt{D_2 t}},$$
 (7.8)

Then (7.1) requires

$$A \operatorname{erf} \frac{X}{2\sqrt{D_1 t}} = C_X - C_1, \tag{7.9}$$

$$B \operatorname{erfc} \frac{X}{2\sqrt{D_2 t}} = C_X - C_2.$$
 (7.10)

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Since (7.9) and (7.10) have to be satisfied for all values of t, X must be proportional to t[‡], say, $X = kt^{4}$ (7.11)

where k is a constant to be determined. Using (7.7), (7.8), (7.9), (7.10), (7.11) in (7.2) we obtain

$$\frac{C_X - C_1}{g(k/2D_1^{\frac{1}{2}})} + \frac{C_X - C_2}{f(k/2D_2^{\frac{1}{2}})} = 0, \qquad (7.12)$$

where g and f are functions given by

$$g\left(\frac{k}{2D_{1}^{\dagger}}\right) = \pi^{\dagger} \frac{k}{2D_{1}^{\dagger}} e^{k^{\dagger}/4D_{1}} \operatorname{erf} \frac{k}{2D_{1}^{\dagger}}, \qquad (7.13)$$

$$f\left(\frac{k}{2D_{\frac{1}{2}}^{\frac{1}{2}}}\right) = \pi^{\frac{1}{2}} \frac{k}{2D_{\frac{1}{2}}^{\frac{1}{2}}} e^{k^{\frac{2}{4}D_{\frac{1}{2}}}} \operatorname{erfc} \frac{k}{2D_{\frac{1}{2}}^{\frac{1}{2}}}.$$
 (7.14)





When (7.12) is solved numerically, it gives k in terms of C_1 , C_2 , C_X , and the diffusion coefficients D_1 and D_2 . The numerical solution is greatly facilitated by using Figs. 7.3, 7.4, and 7.5 which show graphs of f and g. The same graphs were shown in Danckwerts's paper [1].

Substituting $k = X/t^{\dagger}$ in (7.9) and (7.10) we obtain

$$A \operatorname{erf} \frac{k}{2D_{1}^{k}} = C_{X} - C_{1}, \qquad (7.15)$$

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$$B\operatorname{erfc}\frac{k}{2D_2^{\dagger}} = C_X - C_2, \qquad (7.16)$$

from which A and B can be evaluated, knowing k, and hence the concentrations c_1 and c_2 follow from (7.7) and (7.8). This solution applies strictly only when the medium is semi-infinite, a condition which is effectively satisfied in the early stages of diffusion into a sheet of finite thickness. When the concentration at the centre


Fig. 7.5. g as a function of $k/2D_1^{\frac{1}{2}}$.

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of the sheet becomes appreciable, this solution must be replaced by one in which the finiteness of the sheet is recognized. In general, it is necessary to continue the solution by numerical methods such as are discussed later in Chapter X. In at least one interesting case, however, a formal solution is possible after the sheet has ceased to be semi-infinite. This is when the diffusion coefficient is zero at low concentrations, i.e. $D_2 = 0$. Since this case can be solved completely without excessive labour, and as it is a limiting case of a diffusion coefficient which is small at low concentrations and increases with concentration increasing, it justifies detailed consideration.

7.23. Diffusion coefficient zero for concentrations less than C_X and constant and finite above C_X

When D_2 approaches zero, $k/2D_2^2$ becomes large, and by applying the asymptotic expansion

$$\exp(z^2)\operatorname{erfc} z = \frac{1}{\pi^{\frac{1}{4}}} \left(\frac{1}{z} - \frac{1}{2z^3} + \dots \right)$$
 (7.17)

to (7.14) eqn. (7.12) reduces to

$$\frac{C_X - C_1}{g(k/2D_1^{\frac{1}{2}})} + C_X - C_2 = 0.$$
(7.18)

Equation (7.18) can be solved to give k and the solution follows from (7.7). From (7.2), $\partial c_2/\partial x \to \infty$ when $D_2 \to 0$, unless $\partial c_1/\partial x = 0$, which is the final steady state, and hence the concentration gradient is infinite at low concentrations. Examples of concentration curves, plotted against $x/2(D_1t)^{\ddagger}$, are shown in Fig. 7.6 for $C_X = \frac{1}{3}C_1$, $\frac{1}{2}C_1$, $\frac{2}{3}C_1$, and $\frac{6}{9}C_1$ respectively, and for $C_2 = 0$ in each case. They also apply to the problem of diffusion with precipitation discussed by Hermans [3], who gives a graph effectively of $k/2D_1^{\ddagger}$ as a function of $(C_X - C_1)/(C_X - C_2)$, so that the root of (7.18) can be read off for any desired combination of values of C_1 , C_2 , and C_X . This is the graph shown in Fig. 7.5.

It is clear from the way in which the concentration against distance curves of Fig. 7.6 terminate abruptly that, from the time the vertical advancing front reaches the centre of a finite sheet, the diffusion coefficient is constant at D_1 over the whole of the remaining concentration range. The solution required is thus the well-known one for diffusion into a plane sheet, with a constant diffusion coefficient and a given initial concentration distribution through the sheet. In the present nomenclature, the solution (4.16) given in § 4.31 is

$$c_{1} = C_{1} + \frac{2}{l} \sum_{n=0}^{\infty} e^{-D_{1}(2n+1)^{*}\pi^{2}(l-l_{0})/4l^{*}} \sin \frac{(2n+1)\pi x}{2l} \times \left\{ \frac{2(-1)^{n+1}lC_{1}}{(2n+1)\pi} + \int_{0}^{l} f(x) \sin \frac{(2n+1)\pi x}{2l} dx \right\}, \quad (7.19)$$



FIG. 7.6. Concentration-distance curves for D as in Fig. 7.6 (a). Numbers on curves are values of $C_{\mathbf{X}}/C_1$.

where the surface of the sheet x = 0 is maintained at C_1 , the centre of the sheet is at x = l, and f(x) is the concentration distribution through the sheet at time $t = t_0$. The total amount, M_t , of diffusing substance present in half the sheet at time t is obtained by integrating the righthand side of (7.19) with respect to x between the limits 0 and l and is

given by

$$\frac{M_l}{lC_1} = 1 + 2 \sum_{n=0}^{\infty} e^{-D_1(2n+1)^2 \pi^2 (l-t_0)/4l^2} \times \left\{ \frac{2(-1)^n}{(2n+1)\pi} \int_0^l \frac{1}{lC_1} f(x) \sin \frac{(2n+1)\pi x}{2l} \, dx - \frac{4}{(2n+1)^2 \pi^2} \right\}.$$
 (7.20)

In the present problem, f(x) is given by (7.7) evaluated at time t_0 , so that (A + x)

$$f(x) = C_1 \left\{ 1 + \frac{A}{C_1} \operatorname{erf} \frac{x}{2(D_1 t_0)^{\frac{1}{2}}} \right\},\tag{7.21}$$

where A is given by (7.9). The time t_0 is defined as that at which X = l, so that it is related to the solution of (7.7) by the expression

$$\left(\frac{D_1 t_0}{l^2}\right)^{\frac{1}{2}} = \frac{D_1^{\frac{1}{2}}}{k}.$$
(7.22)

By substituting in (7.20) from (7.21) and (7.22), M_l/lC_1 is expressed as a function of the single variable $D_1 t/l^2$. The integral in (7.20) is conveniently evaluated numerically. A family of curves showing M_l/lC_1 as a function of $(D_1 t/l^2)^{\frac{1}{2}}$ is shown in Fig. 7.7 for several values of C_X including $C_X = 0$, when the solution is simply that for a diffusion coefficient having the constant value D_1 . The linear parts of these curves follow readily from the solution (7.7) since we have

$$\frac{\partial M_{t}}{\partial t} = -\left(D_{1}\frac{\partial c_{1}}{\partial x}\right)_{x=0} = -\frac{AD_{1}^{\frac{1}{2}}}{(\pi t)^{\frac{1}{2}}},$$

$$\frac{M_{t}}{lC_{1}} = -\frac{2}{\pi^{\frac{1}{2}}}\frac{A}{C_{1}}\left(\frac{D_{1}t}{l^{2}}\right)^{\frac{1}{2}},$$
(7.23)

and hence

where A is given by (7.9) and is negative for sorption.

We may note that these curves, which are universal for all values of D_1 , are each linear at first, becoming concave downwards later though it might have been expected that they would show a different behaviour. Thus when the vertical front of a concentration against distance curve (Fig. 7.6) reaches the centre of the sheet, the region of zero diffusion coefficient is immediately removed and the subsequent sorption is governed by a constant and possibly high value of D, i.e. by D_1 . On these grounds it is not at first unreasonable to expect the sorption to proceed more rapidly at this stage, i.e. for the gradient of a curve of Fig. 7.7 to be first constant and then to increase. Detailed calculation shows that this is not so, however, even for this limiting case of a discontinuous diffusion coefficient which is zero at low concentrations.

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Fig. 7.7. Sorption curves for D as in Fig. 7.6 (a). Numbers on curves are values of C_X/C_1 .

7.24. Diffusion coefficients having discontinuities at two concentrations The above results can be extended to the case of a diffusion coefficient defined by

$$D = D_1, \qquad C_1 > c > C_X, \tag{7.24}$$

$$D = D_2, \quad c < C_Y,$$
 (7.25)

$$D = D_3, \qquad C_X > c > C_Y.$$
 (7.26)

It is convenient to refer to this as a two-step diffusion coefficient. At

the concentrations C_X and C_Y there are discontinuities in concentration gradient, and at each discontinuity conditions corresponding to (7.1) and (7.2) are to be satisfied. The method is so closely similar to that just described that the equations can be written down without explanation. Concentrations c_1 , c_2 , c_3 are associated with the ranges in which the diffusion coefficient has the values D_1 , D_2 , D_3 respectively. Then if A, B, and E are constants we have the following solutions:

$$c_1 = C_1 + A \operatorname{erf} \frac{x}{2(D_1 t)^{\frac{1}{2}}}, \quad 0 < x < X,$$
 (7.27)

$$c_2 = C_2 + B \operatorname{erfc} \frac{x}{2(D_2 t)^{\frac{1}{2}}}, \quad x > Y,$$
 (7.28)

$$c_{3} = C_{X} + E\left\{ \operatorname{erf} \frac{x}{2(D_{3}t)^{\frac{1}{2}}} - \operatorname{erf} \frac{X}{2(D_{3}t)^{\frac{1}{2}}} \right\}, \qquad X < x < Y. \quad (7.29)$$

The conditions

$$c_1 = c_3 = C_X, \qquad x = X,$$
 (7.30)

$$c_2 = c_3 = C_Y, \qquad x = Y,$$
 (7.31)

require that

$$C_X - C_1 = A \operatorname{erf} \frac{X}{2(D_1 t)^{\frac{1}{2}}},$$
 (7.32)

$$C_{\rm Y} - C_2 = B \, {\rm erfc} \, \frac{Y}{2(D_2 t)^{\frac{1}{2}}},$$
 (7.33)

$$C_Y - C_X = E \left\{ \operatorname{erf} \frac{Y}{2(D_3 t)^{\frac{1}{2}}} - \operatorname{erf} \frac{X}{2(D_3 t)^{\frac{1}{2}}} \right\},$$
(7.34)

from which it follows that

$$X = k_1 t^{\frac{1}{2}}, \quad Y = k_2 t^{\frac{1}{2}}, \quad (7.35)$$

where k_1 and k_2 are constants to be determined. By using the two conditions $D = 2e + 2\pi - D = 2e + 2\pi - \pi - V$ (7.26)

$$D_1 \partial c_1 / \partial x = D_3 \partial c_3 / \partial x, \quad x = X,$$
 (7.36)

$$D_2 \partial c_2 / \partial x = D_3 \partial c_3 / \partial x, \qquad x = Y,$$
 (7.37)

and equations (7.27), (7.28), (7.29), (7.32), (7.33), (7.34), (7.35) we derive the following two equations from which to evaluate k_1 and k_2 ,

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Once k_1 and k_2 are determined the whole solution follows as before, and it is easy to see that the same initial condition holds, namely, that the region x > 0 is at a uniform concentration C_2 . Equations (7.38) and (7.39) can be solved numerically without excessive labour, but for any further extension to a three-or-more step diffusion coefficient the numerical work would probably be prohibitive. However, the two-step form includes several interesting types of diffusion coefficient and by suitable choice of D_1 , D_2 , D_3 and C_X , C_Y a reasonable approximation to many continuously varying diffusion coefficients can be obtained. Some results for two-step diffusion coefficients are discussed in Chapter XII.

7.3. General problem of the moving boundary

We give now Danckwerts's [1] treatment of the more general problem in which a moving interface is involved. In all the cases considered the two regions are separated by a plane surface and diffusion takes place only in the direction perpendicular to this plane. The concentration is initially uniform in each region. The process of diffusion may cause changes which bring about the disappearance or appearance of matter at the interface in one or both regions and hence a resulting bodily movement of the matter in one or both regions relative to the interface. An example which is easy to visualize is afforded by the melting of ice in contact with water; as heat (here regarded as the diffusing substance) flows from water to ice, ice disappears and water appears at the interface, so that both ice and water are in bodily movement with respect to the interface. In all the cases considered the rates of bodily motion of the matter in the two regions with respect to the interface are directly proportional to each other, e.g. the volume of ice melted is proportional to the volume of water formed. Variations in specific volume or partial specific volume due to changes in concentration (or temperature) are ignored. The solutions derived below do not apply to systems in which convection currents are important or in which gradients of both concontration and temperature exist.

7.31. The problem

Consider two media which are free from convection currents but which may be in relative bodily motion along the x-axis, which is perpendicular

to the interface. Position in medium 1 is specified by a coordinate in the x_1 system which is stationary with respect to medium 1; position in medium 2 by a coordinate in the x_2 system, stationary with respect to medium 2. The media are separated at time t by the plane $x_1 = X_1$, $x_2 = X_2$, which is initially at $x_1 = x_2 = 0$. Medium 1 occupies all or part of the space $X_1 < x_1 < \infty$, medium 2 all or part of the space $-\infty < x_2 < X_2$.

In both media there is a substance which moves by diffusion relative to the x_1 and x_2 coordinates and is transferred from one medium to the other. The concentration of the diffusing substance at time t is denoted by c_1 at x_1 and by c_2 at x_2 . The following equations are obeyed in the two media,

$$\partial c_1 / \partial t = D_1 \partial^2 c_1 / \partial x_1^2, \tag{7.40}$$

$$\partial c_2/\partial t = D_2 \partial^2 c_2/\partial x_2^2, \tag{7.41}$$

where the diffusion coefficients D_1 and D_2 are assumed to be independent of c_1 and c_2 .

At any time the concentrations $c_1(X_1)$, $c_2(X_2)$ at either side of the interface are assumed to be related by an equilibrium expression

$$c_2(X_2) = Qc_1(X_1) + R, (7.42)$$

where Q and R are constants, e.g. for the absorption of a gas obeying Henry's law, Q is the solubility of the gas and R = 0. The diffusing substance is conserved at the interface so that

$$D_{1}(\partial c_{1}/\partial x_{1})_{x_{1}=X_{1}} - D_{2}(\partial c_{2}/\partial x_{2})_{x_{2}=X_{2}} + c_{1}(X_{1}) dX_{1}/dt - c_{2}(X_{2}) dX_{2}/dt = 0.$$
(7.43)

We have already said that there is constant proportionality between the rates of movement of the two media relative to the interface and hence it follows that

$$X_2 = PX_1, \tag{7.44}$$

where P is a constant determined by the conditions of the problem and may in some cases be zero.

We now proceed to build up solutions of these equations by what is essentially the same method as was used earlier for discontinuous diffusion coefficients, leaving till later an examination of the various ways in which the initial and boundary conditions can be specified.

Consider an infinite medium in which equation (7.40) holds. Then a solution takes the form

$$\frac{c_1(\infty) - c_1}{c_1(\infty) - c_1(0)} = 1 - \operatorname{erf} \frac{x_1}{2\sqrt{D_1 t}}, \qquad (7.45)$$

where $c_1(\infty)$ and $c_1(0)$ are given by the initial and boundary conditions, i.e. $c_{1} - c_{1}(\alpha)$ r > 0 t = 0(7 46)

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$$v_{\rm I} = v_{\rm I}(\omega), \quad x_1 > 0, \quad v = 0, \quad (7.40)$$

$$c_1 = c_1(0), \qquad x_1 = 0, \qquad t > 0.$$
 (7.47)

Similarly, the solution of (7.41) for corresponding conditions

$$c_2 = c_2(-\infty), \quad x_2 < 0, \quad t = 0,$$
 (7.48)

$$c_2 = c_2(0), \qquad x_2 = 0, \quad t > 0,$$
 (7.49)

$$\frac{c_2(-\infty) - c_2}{c_2(-\infty) - c_2(0)} = 1 + \operatorname{erf} \frac{x_2}{2\sqrt{D_2 t}}.$$

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For the same conditions, the total amounts of diffusing substance, V_1 and V_2 , crossing the planes $x_1 = 0$, $x_2 = 0$ respectively in time t in the direction of decreasing x are

$$V_1 = 2\{c_1(\infty) - c_1(0)\}(D_1 t/\pi)^{\dagger}, \qquad (7.51)$$

$$V_2 = 2\{c_2(0) - c_2(-\infty)\}(D_2 t/\pi)^{\frac{1}{2}}.$$
(7.52)

The solutions (7.45) and (7.50) apply to an infinite medium. Each can be applied equally well to a region bounded by one or two x-planes either stationary or moving, provided that (a) the initial concentration at every point in this restricted region is the same as for the same value of x_1 or x_2 in the infinite medium; and (b) the concentration at the boundary plane or planes is at all times the same as for the same value of x_1 or x_2 in the infinite medium. The problems to be discussed here concern media bounded by one or two planes, but they fulfil the above conditions and so the solutions for infinite media can be used. In other words we shall show that the solutions (7.45) and (7.50) are compatible with (a) equations (7.42), (7.43), (7.44) and (b) the conditions determined by the data of the problem which may be of one of two kinds described below as Class A and Class B. It should be noted that the values of c_1 outside medium 1 and of c_2 outside medium 2 have no physical significance.

7.32. Problems of Class A

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Here the movement of one or both media relative to the boundary is caused by the transfer of diffusing substance across the interface. The conditions are that two of the quantities $c_1(\infty)$, $c_1(0)$, $c_1(X_1)$, $c_2(-\infty)$, $c_2(0)$ are specified and also that the magnitudes of X_1 and X_2 are at all times proportional to the amount of diffusing substance which has crossed the interface ($x_1 = X_1, x_2 = X_2$). Hence we may write

$$\frac{dX_1}{dt} = S\left\{D_1\left(\frac{\partial c_1}{\partial x}\right) = + c_1(X_1)\frac{dX_1}{dt}\right\},\tag{7.53}$$

where S is a constant of proportionality characteristic of the system and is the ratio of the magnitude of X_1 to the amount of diffusing substance which has crossed the interface in the direction of decreasing x. Combining this with (7.43) and (7.44) we have

$$\frac{dX_2}{dt} = PS\left\{D_2\left(\frac{\partial c_2}{\partial x_2}\right)_{x_2=X_2} + c_2(X_2)\frac{dX_2}{dt}\right\}.$$
(7.54)

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Substituting (7.42), (7.44), (7.45), and (7.50) in (7.53) and (7.54) we find

$$\frac{dX_1}{dt} \left\{ \frac{1}{S} - c_1(X_1) \right\} = \left\{ c_1(\infty) - c_1(0) \right\} \left(\frac{D_1}{\pi t} \right)^{\frac{1}{2}} e^{-X_1^* (4D_1 t)}, \quad (7.55)$$

$$\frac{dX_1}{dt} \left\{ \frac{1}{S} - PR - PQc_1(X_1) \right\} = \left\{ c_2(0) - c_2(-\infty) \right\} \left(\frac{D_2}{\pi t} \right)^{\frac{1}{2}} e^{-P^* X_1^* (4D_0 t)}.$$
(7.56)

Also from (7.45), putting $x_1 = X_1$, $c_1 = c_1(X_1)$, we have

$$c_1(X_1) = c_1(0) + \{c_1(\infty) - c_1(0)\} \operatorname{erf}\left\{\frac{X_1}{2\sqrt{D_1 t}}\right\}.$$
 (7.57)

It is clear that (7.55), (7.56), and (7.57) can simultaneously be satisfied for all values of t, if and only if X_1/t^{\ddagger} is constant. Put

$$X_1 = 2\alpha (D_1 t)^{\frac{1}{2}}, \tag{7.58}$$

so that (7.55), (7.56), and (7.57) become respectively

$$c_1(\infty) - c_1(0) = \pi^{\frac{1}{2}} \alpha \left\{ \frac{1}{S} - c_1(X_1) \right\} \exp(\alpha^2), \tag{7.59}$$

$$c_{2}(0) - c_{2}(\infty) = \pi^{\dagger} \alpha \left(\frac{D_{1}}{D_{2}} \right)^{\frac{1}{2}} \left\{ \frac{1}{S} - PR - PQc_{1}(X_{1}) \right\} \exp \left\{ \frac{\alpha^{2} P^{2} D_{1}}{D_{2}} \right\},$$
(7.60)

$$c_1(X_1) = c_1(0) + \{c_1(\infty) - c_1(0)\} \text{erf} \alpha, \qquad (7.61)$$

while substituting $x_2 = X_2$ in (7.50) and using (7.58) and (7.44) gives

$$\frac{Qc_1(X_1) + R - c_2(-\infty)}{c_2(0) - c_2(-\infty)} = 1 + \operatorname{erf}\left\{P\alpha\left(\frac{D_1}{D_2}\right)^{\frac{1}{2}}\right\}.$$
 (7.62)

Equations (7.59) to (7.62) are independent and contain, besides physical constants and the parameters R and S, the six quantities $c_1(0)$, $c_1(\infty)$, $c_2(0)$, $c_2(-\infty)$, $c_1(X_1)$, and α . Hence if two of the concentrations are given, the four equations can be solved for the other three and α , and the concentrations c_1 and c_2 follow as functions of x and t from (7.45) and (7.50). The expressions so obtained for c_1 and c_2 satisfy both the initial and boundary conditions of the problem and the equation of diffusion, and therefore constitute the required solution. Substitution for α in (7.58) gives X_1 , and hence X_2 from (7.44), in terms of t and known

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quantities. Finally we notice that the concentrations $c_1(X_1)$ and $c_2(X_2)$ at the interface are necessarily constant from (7.61) and (7.42).

7.33. Problems of Class B

Here the movements of the media on either side of the interface are not related to the amount of diffusing substance which has crossed the interface by equations (7.53) and (7.54). Instead, three of the five concentrations $c_1(\infty)$, $c_1(0)$, $c_1(X_1)$, $c_2(0)$, $c_2(-\infty)$ are specified. § 7.3]

Substituting (7.42), (7.44), (7.45), and (7.50) into (7.43) gives

$$\begin{aligned} \{c_{1}(\infty)-c_{1}(0)\} \left(\frac{D_{1}}{\pi t}\right)^{\frac{1}{2}} \exp(X_{1}^{2}/4D_{1}t) + \\ +\{c_{2}(0)-c_{2}(-\infty)\} \left(\frac{D_{2}}{\pi t}\right)^{\frac{1}{2}} \exp(-P^{2}X_{1}^{2}/4D_{2}t) + \\ +\frac{dX_{1}}{dt} \{(1-PQ)c_{1}(X_{1})-PR\} = 0. \end{aligned}$$
(7.63)

Taken with (7.57) this can only be true for all values of t if $X_1/t^{\frac{1}{2}}$ is constant. On putting $X_1 = 2\beta t^{\frac{1}{2}}$, (7.64) (7.63) becomes

$$\begin{aligned} \{c_1(\infty) - c_1(0)\} \left(\frac{D_1}{\pi t}\right)^{\frac{1}{2}} \exp(-\beta^2/D_1) + \\ + \{c_2(0) - c_2(-\infty)\} \left(\frac{D_2}{\pi t}\right)^{\frac{1}{2}} \exp(-P^2\beta^2/D_2) + \\ + \beta\{(1 - PQ)c_1(X_1) - PR\} = 0. \end{aligned}$$
(7.65)

From (7.57) $c_1(X_1) = c_1(0) + \{c_1(\infty) - c_1(0)\} \operatorname{erf}(\beta/D_1^{\frac{1}{2}}),$ (7.66) while from (7.42) and (7.50)

$$c_2(X_2) = Qc_1(X_1) + R = c_2(0) + \{c_2(0) - c_2(-\infty)\} \operatorname{erf}(P\beta/D_2^{\ddagger}).$$
(7.67)

Equations (7.65), (7.66), and (7.67) are independent and so, since three of the five concentrations $c_1(\infty)$, $c_1(X_1)$, $c_1(0)$, $c_2(0)$, $c_2(-\infty)$ are known, the values of the other two and of β can be determined. Hence X_1 can be found as a function of t from (7.64), and c_1 and c_2 as functions of x and t from (7.45) and (7.50).

7.34. Examples of Class A problems

(i) Absorption by a liquid of a single component from a mixture of gases

An ideal mixture of a soluble gas A and an insoluble gas is in contact with a liquid. Let the gas be medium 1 and the liquid medium 2. Initially the mole fraction of A in the gas is $c_1(\infty)$ and the concentration of discolved A is the liquid back of A.

dissolved A in the liquid, expressed as volume of gas per unit volume of liquid, is uniform and equal to $c_2(-\infty)$; $c_1(\infty)$ and $c_2(-\infty)$ are given. There is always equilibrium between the gas and the liquid at the interface, where Henry's law is assumed to be obeyed. It is further assumed that there is no appreciable change in the partial volume or temperature of the liquid when A is absorbed and also that the diffusion of A in the liquid obeys the simple diffusion equation (7.41). If the origin of the x_1 system of coordinates moves so that there is no mass flow of the gaseous mixture across any plane of constant x_1 , then equation (7.40) is obeyed in the gas. For this to be so, X_1 must be equal at all times to the volume of component A absorbed by unit area of the liquid surface, i.e. $X_1 = V$. Thus the conditions of the problem correspond to those specified for Class A problems, with S = 1 in equations (7.53) and (7.54).

The x_2 coordinate of the liquid surface does not change, and hence $X_2 = 0$, $c_2(X_2) = c_2(0)$ for all t; in equation (7.44), P = 0. Equation (7.42) becomes

$$R = 0, \qquad c_2(X_2) = c_2(0) = Qc_1(X_1),$$

where Q is the solubility of A in the liquid expressed as volume of gaseous A in unit volume of liquid per unit mole fraction of A in the gas. Making the appropriate substitutions and eliminating the unknowns except α , equations (7.59), (7.60), and (7.61) reduce to

$$\frac{\alpha(\pi D_1/D_2)^{\dagger} - Qc_1(\infty) + c_2(-\infty)}{\alpha(\pi D_1/D_2)^{\dagger} - Q + c_2(-\infty)} = \pi^{\dagger} \alpha \exp(\alpha^2) \operatorname{erfc} \alpha = f(\alpha), \quad (7.68)$$

and putting $X_1 = V$ in (7.58) gives

$$V = 2\alpha (D_1 t)^{\frac{1}{2}}.$$
 (7.69)

The function f has already been shown in Figs. 7.3 and 7.4 and, using these curves, α is readily evaluated from (7.68) by trial and error for known values of D_1 , D_2 , Q, $c_1(\infty)$, and $c_2(-\infty)$. The rate V at which A is absorbed by the liquid follows immediately from (7.69). It is also easy to show that

$$c_1(X_1) = \frac{c_1(\infty) - f}{1 - f} = \frac{c_2(-\infty) + \alpha(\pi D_1 / D_2)^{\frac{1}{2}}}{Q}, \qquad (7.70)$$

$$c_{1} = \frac{c_{1}(\infty) + \{c_{1}(X_{1}) - c_{1}(\infty)\}}{\operatorname{erfc} \alpha} \operatorname{erfc} \frac{x_{1}}{2(D_{1}t)^{\frac{1}{2}}}, \quad (7.71)$$

$$c_{2} = Qc_{1}(X_{1}) + \{Qc_{1}(X_{1}) - c_{2}(-\infty)\} \operatorname{erf} \frac{x_{2}}{2(D_{2}t)^{\frac{1}{2}}}.$$
 (7.72)

The same equations may be used for the escape of dissolved gas A from solution. In this case α will be negative and the amount of A leaving the solution in time t is -V.

For further discussion of the physical conditions under which these solutions are applicable, Danckwerts's original paper [1] should be consulted.

A special case arises when $c_1(X_1)$, the concentration at the interface, is determined by some factor other than diffusion in a liquid. Examples quoted by Danckwerts are the isothermal evaporation of a liquid into still air, when $c_1(X_1)$ is determined by vapour pressure, and the sorption of a gas by a liquid which is rapidly stirred without deforming the surface, so that $Qc_1(X_1) = c_2(-\infty)$. For such cases it is easy to show that (7.59) and (7.61) become

$$\frac{c_1(X_1) - c_1(\infty)}{c_1(X_1) - 1} = f(\alpha), \tag{7.73}$$

where $f(\alpha)$ and α have the same significance as before.

(ii) Tarnishing reactions

A film of tarnish is formed on the surface of a metal by reaction with a gas. The reaction proceeds by diffusion of dissolved gas through the film to the surface of the metal, where its concentration $c_1(X_1)$ is assumed to be zero, i.e. the reaction is assumed to be so rapid that the rate of tarnishing is controlled entirely by the diffusion process. The outer surface of the film is constantly saturated with the gas.

Let the film be medium 1. Since $c_1(X_1)$ is not determined by diffusion in another medium, equations (7.60) and (7.62) are not required. Let W be the mass fraction of the gaseous component in the compound which it forms with the metal, ρ the density of this compound (which is assumed independent of the concentration of the dissolved gas), and c_1 the concentration of the dissolved gas (expressed as mass of gas per unit volume of the film) at a distance x_1 beneath the surface of the film. The outer surface of the film is at $x_1 = 0$, the metal surface at $x_1 = X_1$, the film thickness being X_1 . From (7.53)

$$S = -1/(W\rho).$$
 (7.74)

Furthermore, since $c_1(X_1) = 0$, $c_1(0)$, the saturated concentration of gas at the outer surface of the film, is given by

$$\frac{c_1(0)}{W\rho} = \pi^{\frac{1}{2}} \alpha \exp(\alpha^2) \operatorname{erf} \alpha = g(\alpha), \qquad (7.75)$$

from (7.59) and (7.61), and

$$X_1 = 2\alpha (D_1 t)^{\frac{1}{2}}, \tag{7.76}$$

where D_1 is the diffusion coefficient of the dissolved gas in the film. Fig. 7.5 gives g as a function of α , and so values of α corresponding to given values of $c_1(0)/(W\rho)$ can be read directly from that graph and used to calculate film thickness as a function of time from (7.76). If $c_1(0) \ll W\rho$, expansion of $\exp(\alpha^2)$ and $\operatorname{erf} \alpha$ shows that $g = 2\alpha^2$ approximately and therefore in this case

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$$X_{1} = \left(\frac{2D_{1}c_{1}(0)t}{W\rho}\right)^{\frac{1}{2}}.$$
(7.77)

This means that, if the solubility of the gas in the film is sufficiently

small, the film thickness is given without appreciable error by the formula obtained by assuming that the concentration gradient in the film is uniform. The problem of tarnishing was also solved by Booth [6] who points out that the form (7.77) is a good approximation for systems usually encountered in practice.

7.35. Examples of Class B problems

(i) Solution of gas in a liquid, followed by reaction with a solute

.The surface of the liquid is constantly saturated with the gas B, which is assumed to be undiluted with inert gases. The liquid contains a solute A which effectively reacts instantaneously and irreversibly with the dissolved gas. Diffusion of both A and B is assumed to obey the simple diffusion equation of the types (7.40) and (7.41). Any part of the liquid will contain A or B but not both. There will be a plane, $x_1 = X_1, x_2 = X_2$, at which the concentrations of both A and B will be zero. That part of the liquid containing A is taken to be medium 1, that containing B is medium 2. The surface of the liquid is permanently at $x_1 = x_2 = 0$, so that $X_1 = X_2$ and P = 1 from equation (7.44). Also

$$c_1(X_1) = c_2(X_2) = 0, (7.78)$$

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and hence R = 0 in equation (7.42). We assume n_1 moles of A to react with n_2 moles of B and so, in order to fulfil the conservation condition (7.43), we put $c_1 = -m_1 n_2/n_1$, where m_1 is the concentration of A at x_1 in moles per unit volume and c_2 the concentration of B at x_2 in the same units. Further, $c_2(0)$ is the saturated concentration of B at the surface of the liquid, and $m_1(\infty)$ the initial concentration of A in the liquid. Equations (7.65) and (7.67) then become

$$n_1 c_2(0) f(\beta/D_1^{\dagger}) - n_2 m_1(\infty) g(\beta/D_2^{\dagger}) = 0, \qquad (7.79)$$

where f and g are the functions of β/D_1^1 and β/D_2^1 given respectively, as functions of α , in equations (7.68) and (7.75) and plotted in Figs. 7.3, 7.4, and 7.5. Hence from (7.52) and (7.67) we find the volume of gaseous B absorbed in time t to be given by

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$$V = \frac{2c_2(0)}{\operatorname{erf}(\beta/D_2^{\dagger})} \left(\frac{D_2 t}{\pi}\right)^{\frac{1}{2}}.$$
 (7.80)

The value of β can be found from (7.79) by trial and error, using Figs. 7.3, 7.4, and 7.5, and substituted in (7.80) to obtain V. This problem is also treated by Hermans [3].

If the gas is diluted by an insoluble component, the surface concentration, $c_2(0)$, of B in the liquid is determined by diffusion in the gas. In this case, in order to obtain an exact solution, (7.69) and (7.73) must be used together with (7.79) and (7.80). A value of the concentration at the surface of the liquid must be found by trial and error such that the rate of absorption is the same when calculated from either set of equations. The quantities D_1 , $c_1(\infty)$, and $c_1(X_1)$ in (7.69) and (7.73) refer respectively to the diffusion coefficient of B in the gas and to the mole fractions of B in the bulk of the gas and at the interface.

(ii) Progressive freezing of a liquid

The solution to this problem, given previously by Carslaw and Jaeger [5, p. 71], assumes that no change of volume occurs on freezing. The present equations take such a volume change into account. Suppose liquid initially occupies the region x > 0 and that freezing proceeds progressively, due to the removal of heat from the surface, x = 0, which is maintained at a constant temperature T_0 . Subsequently, let the liquid be medium 1, and the solid, medium 2. Since no material crosses the surface maintained at T_0 this corresponds always to $x_2 = 0$. If there is a volume change on freezing there is relative movement of the planes $x_1 = 0$ and $x_2 = 0$. The diffuser in this case is heat. Take L to be the latent heat of fusion per unit mass, ρ_1 , ρ_2 the densities, σ_1 , σ_2 the specific heats, and D_1 , D_2 the thermal diffusivities of liquid and solid respectively, then

$$D_1 = K_1 / (\rho_1 \sigma_1); \qquad D_2 = K_2 / (\rho_2 \sigma_2).$$
 (7.81)

The temperature of the liquid is initially T_{∞} throughout and the solidliquid interface $(x_1 = X_1, x_2 = X_2)$ is always at the melting-point T_X . The heat content of the solid at T_X is taken to be zero, and hence that of the liquid at T_X is L. In this problem, concentration signifies the heat content, and hence, since $c_2(X_2) = 0$, we have from (7.42),

$$c_1(X_1) = -R/Q = L/\rho_1.$$
 (7.82)

Since $X_1/X_2 = \rho_2/\rho_1$, it follows from (7.44) that

$$P = \rho_1 / \rho_2. \tag{7.83}$$

We also have $c_1 = \rho_1 \sigma_1 (T_1 - T_N + L/\sigma_1),$

$$c_{1} = \rho_{1} \sigma_{1} (T_{1} - T_{X} + L/\sigma_{1}), \qquad (7.84)$$

$$c_{2} = \rho_{2} \sigma_{2} (T_{2} - T_{X}), \qquad (7.85)$$

where T_1 is the temperature at x_1 in the liquid and T_2 the temperature at x_2 in the solid.

Eliminating $c_1(0)$ and $c_2(-\infty)$ from (7.65) to (7.67) and substituting equations (7.81) to (7.85) we find

$$\frac{\sigma_1(T_{\infty} - T_X)}{f(\beta/D_1^{\dagger})} + \frac{\sigma_2(T_0 - T_X)}{g\{\rho_1\beta/(\rho_2 D_2^{\dagger})\}} + L = 0,$$
(7.86)

where f and g are the functions plotted with α as variable in Figs. 7.3, 7.4, and 7.5. The thickness of the solid formed up to time t is X_2 , where

$$X_2 = X_1' \rho_1 / \rho_2 = 2\beta t^{\frac{1}{2}} \rho_1 / \rho_2.$$
 (7.87)

The temperature at any point in the solid is T_2 , where

$$T_{2} = T_{X} - (T_{X} - T_{0}) \left[1 - \frac{\operatorname{erf}\{x_{2}/2(D_{2}t)^{\frac{1}{2}}\}}{\operatorname{erf}\{\rho_{1}\beta/(\rho_{2}D_{2}^{\frac{1}{2}})\}} \right], \quad (7.88)$$

while in the solid it is T_1 , where

$$T_{1} = T_{X} - (T_{X} - T_{\infty}) \left[1 - \frac{\operatorname{erfc}\{x_{1}/2(D_{1}t)^{\frac{1}{2}}\}}{\operatorname{erfc}\{\beta/D_{1}^{\frac{1}{2}}\}} \right].$$
(7.89)

Hence if (7.86) is solved by trial and error using Figs. 7.3, 7.4, and 7.5, . the resulting value of β can be used to calculate the thickness of the solid and the temperatures at any point as functions of time. The equations apply also, with suitable changes of nomenclature, to the melting of a solid which is at a uniform temperature.

It should be noted that a practical system only behaves in the way described by the above equations provided the density is uniform or increases steadily in a downward direction; otherwise convection currents arise.

7.4. Precipitation

The problem of rapid precipitation on a restricted number of sites, treated by Hermans [3], is characterized by the presence of a moving front which separates free from occupied sites. Hill [7] showed that an approximate solution can be obtained by assuming a steady state to be set up behind the moving front. Guided by Stefan [8], who treated the one-dimensional problem, Pekeris and Slichter [9] obtained the first-order correction to the steady-state solution of the analogous problem of ice formation round a cylinder.

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VIII

SIMULTANEOUS DIFFUSION AND CHEMICAL REACTION

8.1. Introduction

THE problem discussed in this chapter is that of the absorption of one substance by another through which it can diffuse and with which it can also react chemically. This can be regarded as a problem in diffusion in which some of the diffusing substance becomes immobilized as diffusion proceeds, or as a problem in chemical kinetics in which the rate of reaction depends on the rate of supply of one of the reactants by diffusion. There are numerous practical examples of processes involving simultaneous diffusion and chemical reaction of one sort or another. Thus diffusion may take place within the pores of a solid body which can absorb some of the diffusing substance, or we may have diffusion occurring through a gel and an immobile product resulting from the attraction of the diffusing molecules to fixed sites within the medium. Examples involving diffusion into living cells and micro-organisms can be cited from biology and biochemistry. In contrast with the sharp boundary problems of Chap. VII, here we assume that some unoccupied reacting sites are always available. Chemical reactions in high polymer substances are often considerably dependent on the mobility of the reactants as well as on the kinetics of the reaction itself.

8.2. Instantaneous reaction

If the reaction by which the immobilized reactant is formed proceeds very rapidly compared with the diffusion process, local equilibrium can be assumed to exist between the free and immobilized components of the diffusing substance. In the simplest case, the concentration, S, of

immobilized substance is directly proportional to the concentration C of substance free to diffuse, i.e.

$$S = RC. \tag{8.1}$$

In the particular case of diffusion with adsorption on to internal surfaces or sites (8.1) is referred to as a linear adsorption isotherm. When diffusion is accompanied by absorption, the usual equation for

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diffusion in one dimension has to be modified to allow for this, and becomes $\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial t^2} = \frac{\partial S}{\partial t}$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t}, \qquad (8.2)$$

if the diffusion coefficient D is constant. On substituting for S from (8.1) we have 2C = D - 22C

$$\frac{\partial C}{\partial t} = \frac{D}{R+1} \frac{\partial^2 C}{\partial x^2}, \qquad (8.3)$$

which is seen to be the usual form of equation for diffusion governed by a diffusion coefficient given by D/(R+1). Clearly the effect of the instantaneous reaction is to slow down the diffusion process. Thus if R+1 = 100, the overall process of diffusion with reaction is slower than the simple diffusion process alone by a hundredfold. In fact, if the linear relationship (8.1) holds, solutions of the diffusion-with-reaction problem for given initial and boundary conditions are the same as for the corresponding problem in simple diffusion, except that the modified diffusion coefficient D/(R+1) is to be used. This is true irrespectively of whether the diffusion-with-reaction occurs in a plane sheet, cylinder, or sphere, or any other geometric shape, and whether diffusion occurs in one dimension or more.

8.21. Non-linear isotherm

If the relationship between S and C is not linear but is of the form

$$S = RC^n, \tag{8.4}$$

for example, where R and n are constants, then (8.2) still holds but (8.3) becomes non-linear and solutions of the diffusion-with-reaction problem in this case can only be obtained by numerical methods of integration such as those described in Chapter X. Some numerical solutions have been obtained [1, 2] describing the uptake of a restricted amount of solute by a cylinder, when diffusion within the cylinder is accompanied by adsorption and where the concentrations of free and adsorbed solute are related by an equation such as (8.4). In this example, 90 per cent. of the total amount of solute is taken up by the cylinder in the final equilibrium state. Figs. 8.1 and 8.2 show the effect of the

(8.5)

exponent n on the overall rate of uptake of solute and on the way in which it is distributed through the cylinder at a given time. If R is large so that $\partial C/\partial t$ may be neglected compared with $\partial S/\partial t$, (8.2) may be written

$$\frac{\partial S}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = \frac{\partial}{\partial x} \left\{ \frac{D}{n} \left(\frac{1}{R} \right)^{1/n} S^{(1-n)/n} \frac{\partial S}{\partial x} \right\},$$



FIG. 8.1. Diffusion with adsorption into a cylinder of radius a. Numbers on curves are values of exponent n in (8.4).



---- concentration at surface of cylinder is constant.

on substituting for C from (8.4). Thus we see that diffusion accompanied by a non-linear reaction described by (8.4) is formally the same as diffusion governed by a diffusion coefficient which is not constant but which depends on the total concentration of diffusing substance, free and immobile. This statement holds whatever the relationship between the concentration of free and immobile components, provided it is non-linear. It need not necessarily be of the form of (8.4). If in (8.4) *n* is fractional, e.g. as in the well-known Freundlich type of adsorption isotherm, then the effective diffusion coefficient in (8.5), which is given by

$$(D/n)(1/R)^{1/n}S^{(1-n)/n},$$

increases as the concentration S is increased. If on the other hand n > 1, the effective diffusion coefficient decreases as the concentration is increased. Standing and others [3] have considered an extension of this argument to the case in which the product of the reaction is not immobile but can itself diffuse at a rate different from that of the free component.

8.3. Irreversible reaction

If the diffusing substance is immobilized by an irreversible first-order reaction so that the rate of removal of diffusing substance is kC, where k is a constant, then the equation for diffusion in one dimension becomes

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC, \qquad (8.6)$$

provided the diffusion coefficient D is assumed to be constant. This is also the equation representing the conduction of heat along a wire which loses heat from its surface at a rate proportional to its temperature. Some solutions relating to this latter problem are given by Carslaw and Jaeger [4, p. 111], where use is made of the transformation $C' = Ce^{-kt}$ which reduces (8.6) to the usual equation in one dimension with C' as dependent variable. Danckwerts [5] has shown how solutions of (8.6) and of the general equation

$$\frac{\partial C}{\partial t} = D\nabla^2 C - kC \tag{8.7}$$

can be deduced by simple transformation of the solutions of the corresponding problems in diffusion without reaction. He applies his method to two types of surface boundary condition. In the first case the surface is in equilibrium at all times with the surrounding atmosphere or solution, and the surface concentration has the constant value C_0 . In the second case the rate of evaporation or absorption at any time is given by

$$D \partial C / \partial N = \alpha (C_0 - C_s), \qquad (8.8)$$

where C_s is the actual concentration on the surface at that time, C_0 the equilibrium surface concentration attained after infinite time, and $\partial C/\partial N$ the concentration gradient measured in the outward direction along the

normal to the surface. Here α is a constant. For convenience in writing we put $h = \alpha/D$ in what follows.

In the problems to be considered, therefore, the initial and boundary conditions are

$$C = 0, t = 0, \text{ at all points in the medium,}$$
 (8.9)

and either

$$C = C_0, \quad t > 0, \quad \text{at all points on the surface,}$$
 (8.10)

or $\partial C/\partial N = h(C_0 - C), t > 0$, at all points on the surface. (8.11)

8.31. Danckwerts's method

Let C_1 be the solution of the equation for diffusion in one dimension in the absence of reaction, i.e. of

$$\frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2},\tag{8.12}$$

for the same boundary conditions as are imposed on C in (8.9), (8.10), and (8.11). We shall give the argument for diffusion in one dimension and it will be clear, as Danckwerts shows, that it can be applied equally well to the general equation (8.7). If C_1 is a solution of (8.12), the solution of (8.6) for the same boundary conditions of the above type is

$$C = k \int_{0}^{t} C_{1} e^{-kt'} dt' + C_{1} e^{-kt}. \qquad (8.13)$$

This is easily shown as follows. By differentiating (8.13) with respect to t we obtain aC = aC = aC

$$\frac{\partial C}{\partial t} = kC_1 e^{-kt} - kC_1 e^{-kt} + \frac{\partial C_1}{\partial t} e^{-kt} = \frac{\partial C_1}{\partial t} e^{-kt}, \qquad (8.14)$$

and on differentiating twice with respect to x we have

$$\frac{\partial^2 C}{\partial x^2} = k \int_0^t \frac{\partial^2 C_1}{\partial x^2} e^{-kt'} dt' + \frac{\partial^2 C_1}{\partial x^2} e^{-kt}.$$
(8.15)

Substituting from (8.12) in (8.15) gives

$$D\frac{\partial^2 C}{\partial x^2} = k \int_0^t \frac{\partial C_1}{\partial t} e^{-kt'} dt' + \frac{\partial C_1}{\partial t} e^{-kt}, \qquad (8.16)$$

and finally using (8.14) we find

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

(8.17)

so that (8.13) is a solution of (8.6)

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arthermore, when t = 0, we see from (8.13) that $C = C_1$ and so C is the required initial conditions. For points at which $C_1 = C_0$, for

$$C = kC_0 \int_0^t e^{-kt'} dt' + C_0 e^{-kt} = C_0.$$
 (8.18)

points at which $\partial C_1/\partial N = h(C_0 - C_1),$ (8.19)

 $\mathbf{n}\mathbf{d}$

$$\frac{\partial C}{\partial N} = k \int_{0}^{t} \frac{\partial C_{1}}{\partial N} e^{-kt'} dt' + \frac{\partial C_{1}}{\partial N} e^{-kt}$$

$$= hk \int_{0}^{t} (C_{0} - C_{1}) e^{-kt'} dt' + h(C_{0} - C_{1}) e^{-kt}$$

$$= h(C_{0} - C). \qquad (8.20)$$

solution (8.13) therefore satisfies the required initial and boundary itions if C_1 does.

the quantity, M_{t} , of diffusing substance absorbed in time t is required, se in general

$$F = \frac{\partial M_t}{\partial t} = \int \int D \frac{\partial C}{\partial N} dS = k \int_0^t F_1 e^{-kt} dt' + F_1 e^{-kt}. \quad (8.21)$$

area integral is taken over the whole surface of the absorbing um and F_1 is the corresponding rate of absorption when no chemical ion takes place, i.e.

$$F_1 = \frac{dM_1}{dt} = \int \int D \frac{\partial C_1}{\partial N} \, dS = \frac{d}{dt} \int \int \int C_1 \, dx \, dy \, dz. \tag{8.22}$$

volume integral is taken over the whole volume of the absorbing um.

ny of the solutions for diffusion without reaction are available in orm of infinite series which can be written

$$C_1/C_0 = 1 - \sum f(x, y, z)e^{-\nu t}.$$
 (8.23)

§ 8.3] where g is x, y, z, t, y

and M

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(i) *Sphe* We take without re

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erous examples have been given in Chapters III-VI. Here f and ν ifferent for each term in the series, but are not functions of t; ν is function of x, y, z. Applying (8.13) to (8.23) we find

$$\frac{C}{C_0} = 1 - \sum f(x, y, z) \left\{ \frac{k + \nu \exp[-t(k+\nu)]}{k + \nu} \right\}.$$
 (8.24)

arly, since in such cases F_1 is of the form

$$F_1/C_0 = \sum g e^{-\nu t}, \tag{8.25}$$



where g is different for each term in the series but is not a function of x, y, z, t, we obtain from (8.21)

$$\frac{F}{C_0} = \sum g \left[\frac{k + \nu \exp\{-t(k+\nu)\}}{k+\nu} \right], \quad (8.26)$$

and
$$M_t = \int_0^t F \, dt' = C_0 \sum g \left[\frac{kt(k+\nu) - \nu \exp\{-t(k+\nu)\} + \nu}{(k+\nu)^2} \right].$$
 (8.27)

8.32. Examples

The method can be applied generally for boundary conditions of the type (8.10) or (8.11). It will be illustrated by the examples quoted by Danckwerts.

(i) Sphere with surface evaporation condition

We take the sphere to be of radius a. Then the solution for diffusion without reaction is (Chapter VI, equation (6.40))

$$\frac{C_1}{C_0} = 1 - \frac{2ha^2}{r} \sum_{n=1}^{\infty} \frac{e^{-D\alpha_n^* t}}{\{a^2 \alpha_n^2 + ah(ah-1)\}} \frac{\sin r\alpha_n}{\sin a\alpha_n}, \quad (8.28)$$

where the α_n 's are the roots of

$$a\alpha \cot a\alpha + ah - 1 = 0, \qquad (8.29)$$

which are given in Table 6.2. Hence

$$F_1 = 4\pi a^2 D\left(\frac{\partial C_1}{\partial r}\right)_{r=a} = 8\pi h^2 C_0 D a^2 \sum_{n=1}^{\infty} \frac{e^{-D\alpha_n^2 t}}{a\alpha_n^2 + h(ah-1)}, \quad (8.30)$$

and from (8.26)

$$F = 8\pi h^2 C_0 Da^2 \sum_{n=1}^{\infty} \frac{k + D\alpha_n^2 \exp\{-t(k + D\alpha_n^2)\}}{(k + D\alpha_n^2)\{a\alpha_n^2 + h(ah - 1)\}},$$
(8.31)

and from (8.27)

$$M_{t} = 8\pi h^{2}C_{0} Da^{2} \sum_{n=1}^{\infty} \frac{kt(k+D\alpha_{n}^{2})-D\alpha_{n}^{2}[\exp\{-t(k+D\alpha_{n}^{2})\}-1]}{(k+D\alpha_{n}^{2})^{2}\{a\alpha_{n}^{2}+h(ah-1)\}}.$$
(8.32)

 (ii) Rectangular block or parallelepiped with constant surface concentration

We take the block to occupy the space -a < x < a, -b < y < b, -c < z < c, so that the edges are of lengths 2a, 2b, 2c. The solution

for diffusion without reaction is

$$\frac{C_1}{C_0} = 1 - \frac{64}{\pi^3} \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{(-1)^{l+m+n}}{(2l+1)(2m+1)(2n+1)} \cos\frac{(2l+1)\pi x}{2a} \times \cos\frac{(2m+1)\pi y}{2b} \cos\frac{(2n+1)\pi z}{2c} e^{-l\alpha_{l,m,n}}, \quad (8.33)$$

$$\alpha_{l,m,n} = \frac{\pi^2 D}{4} \left\{ \left(\frac{2l+1}{a} \right)^2 + \left(\frac{2m+1}{b} \right)^2 + \left(\frac{2n+1}{c} \right)^2 \right\}.$$
(8.34)

Hence

$$F_{1} = \frac{d}{dt} \int_{-a}^{a} \int_{-b}^{b} \int_{-c}^{c} C_{1} dx dy dz$$

= $\left(\frac{64}{\pi^{3}}\right)^{2} C_{0} abc \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{\alpha e^{-l\alpha}}{(2n+1)^{2}(2m+1)^{2}(2n+1)^{2}},$ (8.35)

and from (8.26)

$$F = \left(\frac{64}{\pi^3}\right)^2 C_0 abc \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{\alpha[k + \alpha \exp\{-t(k+\alpha)\}]}{(k+\alpha)(2l+1)^2(2m+1)^2(2m+1)^2},$$
(8.36)

where by α is understood $\alpha_{l,m,n}$ given by (8.34). Similarly M_t follows readily from (8.27).

(iii) Infinite cylinder with surface evaporation condition

We take the cylinder to have radius a and consider diffusion to be entirely radial. The expression for diffusion without reaction is (Chapter V, equation (5.46))

$$\frac{C_1}{C_0} = 1 - \frac{2h}{a} \sum_{n=1}^{\infty} \frac{J_0(r\alpha_n)e^{-D\alpha_n^2 t}}{(h^2 + \alpha_n^2)J_0(a\alpha_n)},$$
(8.37)

where the α_n 's are the roots of

$$\alpha J_1(a\alpha) = h J_0(a\alpha), \qquad (8.38)$$

and J_0 , J_1 are Bessel functions, of the first kind, of order zero and one

respectively. Values of α_n are to be found in Table 5.2. Hence

$$F_{1} = \frac{d}{dt} \int_{0}^{a} 2\pi r C_{1} dr = 4\pi h^{2} C_{0} D \sum_{n=1}^{\infty} \frac{e^{-D\alpha_{n}^{2}t}}{h^{2} + \alpha_{n}^{2}}, \qquad (8.39)$$

and from (8.26)

$$F = 4\pi h^2 C_0 D \sum_{n=1}^{\infty} \frac{k + D\alpha_n^2 \exp\{-t(k + D\alpha_n^2)\}}{(k + \alpha_n^2)(k + D\alpha_n^2)}.$$
 (8.40)

Also M_t is easily found from (8.27). Here M_t and F refer to unit length of cylinder.

Other results may be derived in this way or directly from (8.13) or (8.21). Some examples of expressions for F, the rate of uptake, are given below:

(iv) Sphere (radius a) with constant surface concentration

$$F = 8\pi a D C_0 \sum_{n=1}^{\infty} \frac{ka^2 + Dn^2 \pi^2 \exp\{-t(k + Dn^2 \pi^2/a^2)\}}{ka^2 + Dn^2 \pi^2}.$$
 (8.41)

(v) Infinite cylinder (radius a) with constant surface concentration

Here F is the rate of uptake through unit length of the curved surface of the cylinder:

$$F = 4\pi DC_0 \sum_{n=1}^{\infty} \frac{k + D\alpha_n^2 \exp\{-t(k + D\alpha_n^2)\}}{k + D\alpha_n^2}, \qquad (8.42)$$

where the α_n 's are the roots of $J_0(a\alpha) = 0$.

(vi) Finite cylinder (radius a, length 2l) with constant surface concentration

Here F is the rate of total uptake through the ends and the curved surface:

$$F = \frac{64DlC_0}{\pi} \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \left[\frac{\beta_{m,n}}{\alpha_m^2 (2n+1)^2} \right] \left[\frac{k + D\beta_{m,n} \exp\{-t(k + D\beta_{m,n})\}}{k + D\beta_{m,n}} \right],$$
(8.43)

where the α_n 's are the roots of $J_0(a\alpha) = 0$, and

$$\beta_{m,n} = \alpha_m^2 + (2n+1)^2 \pi^2 / (4l^2). \qquad (8.44)$$

(vii) Semi-infinite solid with surface evaporation condition

The solution is obtained by application of (8.21) to the corresponding solution without reaction (Chapter III, equation (3.35)). Here F is the rate of uptake per unit area of plane surface and

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$$F = \frac{hDC_0}{h^2D - k} [h(Dk)^{\dagger} \operatorname{erf}(kt)^{\dagger} + h^2D \operatorname{erfc} h(Dt)^{\dagger} \exp\{t(h^2D - k)\} - k].$$
(8.45)

(viii) Semi-infinite medium with constant surface concentration The mathematical problem and its solution are identical with those for the conduction of heat along a thin rod which loses heat from its surface at a rate proportional to its temperature [6; 4, p. 111]. The expression for the concentration is



F10. 8.3. Diffusion with an irreversible reaction into a semi-infinite medium with constant surface concentration.

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Also
$$\mathbf{F} = C_0 \sqrt{(Dk)} \left\{ \operatorname{erf} \sqrt{(kt)} + \frac{e^{-kt}}{\sqrt{(\pi kt)}} \right\}, \quad (8.47)$$

and
$$M_t = C_0 \sqrt{(D/k)} \{ (kt + \frac{1}{2}) \operatorname{erf} \sqrt{(kt)} + \sqrt{(kt/\pi)} e^{-kt} \}.$$
 (8.48)

The dimensionless quantity $M_t k^{\frac{1}{2}}/(C_0 D^{\frac{1}{2}})$ is plotted as a function of kt in Fig. 8.3. From this graph, M_t can be obtained at any time t for any combination of the variables C_0 , D, and k.

When kt is large so that erf $\sqrt{(kt)}$ approaches unity, (8.46), (8.47), and (8.48) become

$$C/C_0 = \exp(-xk^{\frac{1}{2}}/D^{\frac{1}{2}}),$$
 (8.49)

$$F = C_0(Dk)^{\frac{1}{2}},$$
 (8.50)

$$M_t = C_0 (Dk)^{\dagger} \left(t + \frac{1}{2k} \right). \tag{8.51}$$

Equations (8.49) and (8.50) show that the concentration at any point and the rate of sorption each tend to a steady value and the total amount taken up increases linearly with time as in Fig. 8.3.

When kt is very small we find by expanding $\operatorname{erf} \sqrt{kt}$ and $\exp(-kt)$ and neglecting powers of kt higher than the first, that (8.47) and (8.48) become

$$F = C_0(1+kt)\{D/(\pi t)\}^{\frac{1}{2}},$$
(8.52)

and

and the second second

$$M_{t} = 2C_{0}(1 + \frac{1}{2}kt)(Dt/\pi)^{\frac{1}{2}}, \qquad (8.53)$$

which reduce to the well-known solutions for diffusion without reaction when k = 0. Further solutions describing the uptake of a restricted amount of diffusing substance which is simultaneously destroyed by an irreversible reaction are given in § 8.44 below as special cases of more general solutions for a reversible reaction.

8.33. Steady-state solutions

As with the semi-infinite case just discussed so in all systems of the type under consideration, the rate of sorption and the concentration at any point tend to steady values at large times. The steady-state solutions may be obtained by putting $\partial C/\partial t$ equal to zero in the appropriate form of (8.7), which may then be solved to give the steady-state solution directly. When the expression for C or F takes the form of (8.24) or (8.26), the steady-state solution may be obtained merely by omitting the time-dependent term, which tends to zero as t tends to infinity. This leads to a solution in the form of a series which often is not readily evaluated.

In some cases the following method leads to a more convenient form of solution. On putting $t = \infty$ in (8.13) and (8.21) we find

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$$C_{\infty}/k = \int_{0}^{\infty} C_{1} e^{-kt} dt, \qquad (8.54)$$
$$F_{\infty}/k = \int_{0}^{\infty} F_{1} e^{-kt} dt. \qquad (8.55)$$

and

The expressions on the right-hand sides of these equations are the Laplace transforms of C_1 and F_1 respectively, the parameter (usually written as p or s in transform notation) taking the value k. Thus, as an example, for a semi-infinite solid with surface evaporation we have, in the absence of reaction,

$$F_1 = h D C_0 e^{h^* D t} \operatorname{erfc} \{ h(Dt)^{\dagger} \}.$$
(8.56)

The Laplace transform of the right-hand side of (8.56) is

and hence from (8.55)
$$F_{\infty} = \frac{hDC_0}{1 + h\sqrt{D/k}}.$$
 (8.57)

Some other steady-state solutions are given below, preceded by references to the corresponding expressions describing the approach to the steady state.

(i) Sphere with surface evaporation condition (equation (8.31))

$$\frac{F_{\infty}}{C_0} = 4\pi a^2 h D \left\{ \frac{(ka^2/D)^{\frac{1}{2}} \coth(ka^2/D)^{\frac{1}{2}} - 1}{ah + (ka^2/D)^{\frac{1}{2}} \coth(ka^2/D)^{\frac{1}{2}} - 1} \right\}.$$
(8.58)

(ii) Infinite cylinder with surface evaporation condition (equation (8.40))

$$\frac{F_{\infty}}{C_0} = 2\pi a h D \left\{ \frac{(k/D)^{\frac{1}{2}} I_1(ka^2/D)^{\frac{1}{2}}}{(k/D)^{\frac{1}{2}} I_1(ka^2/D)^{\frac{1}{2}} + h I_0(ka^2/D)^{\frac{1}{2}}} \right\}.$$
(8.59)

Here I_0 and I_1 are modified Bessel functions of the first kind of zero and first order respectively.

(iii) Sphere with constant surface concentration (equation (8.41))

$$\frac{F_{\infty}}{C_0} = 4\pi a D \{ (ka^2/D)^{\frac{1}{2}} \coth(ka^2/D)^{\frac{1}{2}} - 1 \}.$$
(8.60)

(iv) Infinite cylinder with constant surface concentration (equation (8.42))

$$\frac{F_{\infty}}{C_0} = 2\pi a (kD)^{\frac{1}{2}} \frac{I_1(ka^2/D)^{\frac{1}{2}}}{I_0(ka^2/D)^{\frac{1}{2}}}.$$
(8.61)

A further application of the use of (8.13), to the problem of the extraction of a dissolved substance from a drop of liquid which is rising or falling through another liquid, is described in Danckwerts's paper [5].

8.4. Reversible reaction

The most general case for which formal mathematical solutions have so far been obtained is that in which the reaction is first-order and reversible. The behaviour to be expected when the reaction is reversible depends on the relative rates of diffusion and reaction. Thus we have seen in § 8.2 that when the reaction is very rapid we can assume that the immobilized component is always in equilibrium with the component free to diffuse and diffusion is the rate-controlling process. At the other extreme is the case of diffusion being so rapid compared with the reaction that the concentrations of diffusing substance and immobilized product are effectively uniform throughout the medium and the behaviour is controlled solely by the reversible reaction. Solutions of the more general case in which the rates of diffusion and reaction are comparable have been obtained by Wilson [7] and Crank [8].

The general problem can conveniently be stated in terms of a solute diffusing from a solution into a plane sheet of material. The modifications necessary for corresponding, alternative problems, such as those of a sphere or cylinder suspended in a vapour, will be obvious. Suppose an infinite sheet of uniform material of thickness 2*a* is placed in a solution and that the solute is allowed to diffuse into the sheet. As diffusion proceeds, a first-order, reversible reaction occurs and a product, which is non-diffusing, is formed. The sheet occupies the space $-a \leq x \leq a$, and there is a restricted amount of solution which occupies the space $-l-a \leq x \leq -a$, $a \leq x \leq l+a$. The concentration of solute in the solution is always uniform and is initially C_0 , while initially the sheet is free from solute. Let *C* be the concentration of solute free to diffuse within the sheet and *S* that of the immobilized solute, each being expressed as amount per unit volume of sheet.

The diffusion is governed by the equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial S}{\partial t}, \qquad (8.62)$$

and we consider the simultaneous reaction to be of the type

$$\partial S/\partial t = \lambda C - \mu S. \tag{8.63}$$

Here D is the diffusion coefficient and λ and μ are the rate constants of the forward and backward reactions respectively. Thus the immobilized solute is formed at a rate proportional to the concentration of solute free to diffuse, and disappears at a rate proportional to its own concentration. We require solutions of (8.62) and (8.63) with the initial

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condition $S = C = 0, \quad -a < x < a, \quad t = 0,$ (8.64)

and with a boundary condition expressing the fact that the rate at which solute leaves the solution is equal to that at which it enters the sheet over the surfaces $x = \pm a$. This condition is

 $l \partial C/\partial t = \mp D \partial C/\partial x, \quad x = \pm a, \quad t > 0.$ (8.65)

We here assume that the concentration of solute free to diffuse just within the surface of the sheet is the same as that in the solution. This may not be so and there may be a distribution factor, K, which is not unity, such that the concentration just within the sheet is K times that in the solution. This can clearly be allowed for by using a modified length of solution, l/K, in place of l in (8.65) and elsewhere. Mathematical solutions follow for these equations and for corresponding equations for the cylinder and sphere.

8.41. Mathematical solutions

(i) Plane sheet

Solutions of the equations of § 8.4 can be obtained by the method of Laplace transforms. Writing \overline{C} and \overline{S} for the Laplace transforms of C and S respectively, so that

$$\overline{C} = \int_{0}^{\infty} C \exp(-pt) dt, \qquad \overline{S} = \int_{0}^{\infty} S \exp(-pt) dt, \qquad (8.66)$$

we have the following equations for \overline{C} and \overline{S} :

$$p\vec{C} = -p\vec{S} + D\,\partial^2\vec{C}/\partial x^2, \qquad (8.67)$$

$$p\overline{S} = \lambda \overline{C} - \mu \overline{S}, \qquad (8.68)$$

$$-lC_0 + pl\bar{C} = -D \,\partial \bar{C}/\partial x, \qquad x = a. \tag{8.69}$$

On eliminating \overline{S} from (8.67) and (8.68) and replacing the partial derivative by an ordinary derivative since t does not appear, we find

$$\frac{d^{2}\bar{C}}{dx^{2}} + k^{2}\bar{C} = 0, \qquad k^{2} = -\frac{p}{\bar{D}}\frac{p+\lambda+\mu}{p+\mu}, \qquad (8.70)$$

of which the solution that gives \overline{C} an even function of x is

$$\overline{C} = F(p)\cos kx. \tag{8.71}$$

The function F(p) is determined by the boundary condition (8.69) and it follows immediately that

$$\overline{C} = \frac{lC_0 \cos kx}{1 - 1 - 1 - 1} . \tag{8.72}$$

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$pl\cos ka - kD\sin ka$

The derivation of C is straightforward as in Chapter II, § 2.43 (ii), and after some reduction gives



where the p_n 's are the non-zero roots of

$$\frac{lp_n}{D} = k_n \tan k_n a, \qquad k_n^2 = -\frac{p_n}{D} \frac{p_n + \lambda + \mu}{p_n + \mu}, \qquad (8.74)$$

and $R = \lambda/\mu$ is the partition factor between immobilized and free solute. The expression for S differs from (8.73) only by having an extra factor $\lambda/(p_n + \mu)$ multiplying the *n*th term, including the term $p_n = 0$. Writing M_i for the total amount of solute, both free to diffuse and immobilized, in half the sheet at time *t*, and M_{∞} for the corresponding quantity in the final equilibrium state attained theoretically after infinite time, we have

$$\frac{M_{l}}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{(1+\alpha)\exp(p_{n}t)}{1 + \left\{1 + \frac{\lambda\mu}{(p_{n}+\mu)^{2}}\right\} \left\{\frac{a}{2l} + \frac{p_{n}}{2Dk_{n}^{2}} + \frac{p_{n}^{2}la}{2D^{2}k_{n}^{2}}\right\}}, \quad (8.75)$$

where the p_n 's are given by (8.74) and where

$$\alpha = l/(R+1)a, \qquad M_{\infty} = lC_0/(1+\alpha).$$
 (8.76)

(ii) Cylinder

The case of the cylinder was considered by Wilson [7], using a slightly different method. The final result for a cylinder of radius a, in a solution occupying a region of cross-sectional area A, is

$$\frac{M_l}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{(1+\alpha)\exp(p_n t)}{1 + \left\{1 + \frac{\lambda\mu}{(p_n+\mu)^2}\right\} \left\{\frac{\pi a^2}{A} + \frac{Ap_n^2}{4\pi D^2 k_n^2}\right\}},$$
(8.77)

where

$$\alpha = A / \{\pi a^2 (R+1)\}, \qquad M_{\infty} = A C_0 / (1+\alpha), \qquad (8.78)$$

and the p_n 's and k_n 's are given by

$$\frac{Ap_n}{2\pi Da} = k_n \frac{J_1(k_n a)}{J_0(k_n a)}, \qquad k_n^2 = -\frac{p_n}{D} \frac{p_n + \lambda + \mu}{p_n + \mu}.$$
 (8.79)

The expression for the concentration of free solute is

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The expression for S differs from (8.80) only by having an extra factor $\lambda/(p_n+\mu)$ multiplying the *n*th term, including the term $p_n = 0$.

(iii) Sphere

On introducing new variables rC and rS the equations for the spherical case take essentially the same form as those for the plane case, and the same method of solution leads to

$$\frac{M_{i}}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{(1+\alpha)\exp(p_{n}t)}{1 + \left\{1 + \frac{\lambda\mu}{(p_{n}+\mu)^{2}}\right\} \left\{\frac{2\pi a^{3}}{V} - \frac{p_{n}}{2Dk_{n}^{2}} + \frac{Vp_{n}^{2}}{8\pi a D^{2}k_{n}^{2}}\right\}},$$
(8.81)

where the p_n 's and k_n 's are given by

$$\frac{V}{4\pi Da} p_n - 1 = -k_n a \cot k_n a, \quad k_n^2 = -\frac{p_n}{D} \frac{p_n + \lambda + \mu}{p_n + \mu}, \quad (8.82)$$

$$lpha = rac{3V}{4\pi a^3(R+1)}, \qquad M_\infty = rac{VC_0}{1+lpha}.$$
 (8.83)

and

The expression for C is

$$C = \frac{3VC_0}{3V + 4\pi a^3(R+1)} + \sum_{n=1}^{\infty} \frac{-C_0 \exp(p_n t)}{1 + \left\{1 + \frac{\lambda\mu}{(p_n + \mu)^2}\right\} \left\{\frac{2\pi a^3}{V} - \frac{p_n}{2Dk_n^2} + \frac{Vp_n^2}{8\pi a D^2 k_n^2}\right\}} \frac{a}{r} \frac{\sin k_n r}{\sin k_n a}, \quad (8.84)$$

, and that for S differs from (8.84) only by having an extra factor $\lambda/(p_n + \mu)$ multiplying the *n*th term, including the term $p_n = 0$.

8.42. Physical significance of the mathematical solutions

When mathematical solutions are as complicated in form as those in § 8.41 their physical significance is not immediately obvious. Consider equations (8.74) and put

$$x = k^2 a^2, \qquad y = p a^2 / D, \qquad \xi = a^2 (\lambda + \mu) / D, \qquad \eta = a^2 \mu / D.$$

(8.85)

Then

$$ly/a = \sqrt{x} \tan \sqrt{x}, \qquad (8.86)$$

 $x = -rac{y(y+\xi)}{y+\eta}$

(8.87)

are the equations to be solved for the roots. Graphs of (8.86) and (8.87) are sketched in Fig. 8.4 to show the general location of the roots. The graph of (8.86) is the same for all ξ and η , and from the figure it is easy to see qualitatively how the roots vary with ξ and η . When corresponding transformations to those of (8.85) are applied to equations

(8.79) for the cylinder and (8.82) for the sphere, the resulting equations are of the same form as (8.86) and (8.87), so that Fig. 8.4 can be taken



FIG. 8.4. Location of roots of (8.86) and (8.87).

as showing qualitatively the location of the roots for all three cases. There is a root for which $k_n a$ is imaginary given by

$$ly/a = \sqrt{(-x)} \tanh \sqrt{(-x)}.$$
 (8.88)

The general expression for M_l/M_{∞} therefore comprises a unit term from $p_n = 0$, a term for which $k_n a$ is imaginary, and two infinite series of terms corresponding to the intersections of the two branches of (8.87) with successive branches of (8.86).

The relative importance of the various terms depends on the parameter η . It is interesting to see quantitatively what happens to the general solution for the extreme values of this parameter which correspond to very fast and very slow reactions. The roots of (8.87) are given by

$$2y = -(x+\xi) \pm \sqrt{\{(x+\xi)^2 - 4x\eta\}}, \qquad (8.89)$$

the two infinite series arising from the alternative sign. For extreme values of η the roots are readily obtained by using the appropriate ⁶⁸²⁴ K

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binomial expansion of the term under the square root sign in (8.89). Proceeding in this way with the aid of Fig. 8.4, it is not difficult to show that if η is very large, that is the reaction is very rapid compared with diffusion, the terms in the general solution for M_l/M_{∞} which arise by taking the negative sign in (8.89) vanish, as does also the term from the imaginary root. The terms from the positive sign lead to

$$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)\exp(-\beta k_n^2 a^2 t)}{1+\alpha+\alpha^2 k_n^2 a^2}, \qquad (8.90)$$

where the $k_n a$'s approach the roots of

$$\tan k_n a = -\alpha k_n a, \tag{8.91}$$

and

$$\beta = D/(R+1)a^2. \tag{8.92}$$

This is the solution obtained by Wilson [7] for the case of an immobilizing reaction which is rapid compared with diffusion.

If, however, η is small because the reaction is infinitely slow ($\mu = 0$) we find that the terms arising from the positive sign in (8.89) vanish provided a/l is not zero, which case is treated separately in § 8.43. The terms from the negative sign combine with that from the imaginary root to give

$$\frac{M_l}{M_{\infty}} = \left(1 - \frac{R}{R+1} \frac{l}{l+a}\right) \left\{1 - \sum_{n=1}^{\infty} \frac{2(l/a)(1+l/a)\exp(-Dk_n^2 t)}{1+l/a + (l/a)^2 k_n^2 a^2}\right\},$$
(8.93)

where the k_n 's are given by

$$\tan k_n a = -(l/a)k_n a. \tag{8.94}$$

The whole term in the second bracket in (8.93) is to be recognized as the expression for simple diffusion from a finite bath, i.e. diffusion in the absence of any immobilized component. Equation (8.93) also describes a simple diffusion process, therefore, and M_t/M_{∞} changes from zero at t = 0 to $1 - Rl/\{(R+1)(l+a)\}$ at $t = \infty$, which is easily shown to be the fractional uptake of solute to be expected in the absence of immobilized solute. Thus (8.93) indicates the behaviour to be expected on general argument, namely that for an infinitely slow reaction the sheet takes up, by simple diffusion, only the fraction of solute which it can accommodate

in the freely diffusing state and none in the immobilized state. If on the other hand $\mu a^2/D$ is small because D is very large, all terms in the general solution vanish except the one associated with the imaginary root and we are left with

$$\frac{M_l}{M_{\infty}} = 1 - \frac{R}{R+1} \frac{l}{l+a} \exp\left\{-\left(1 + \frac{Ra}{l+a}\right)\mu t\right\}.$$
(8.95)

This expression is readily deduced from elementary considerations when diffusion is so rapid that the concentration of solute is effectively uniform through the sheet at all times.

The type of behaviour observed in a practical system for which $\mu a^2/D$ is very small, depends on the time scale of the experiment. If this is such that the reaction occurs very slowly compared with the duration of the experiment the simple diffusion behaviour of (8.93) is observed. If on the other hand diffusion is very rapid compared with the time scale of the experiment the simple first-order reaction of (8.95) is observed.

8.43. Numerical evaluation

When equations (8.74) and (8.75) are written in terms of p_n/μ and $k_n a$ we see that M_l/M_{∞} can be calculated as a function of Dt/a^2 if three parameters are known. The parameters are l/a, that is the ratio of the volumes occupied by solution and sheet respectively, the partition factor R, and the modified rate constant for the reaction, $\mu a^2/D$. Alternatively, since $R = \lambda/\mu$, a solution is defined by l/a and the two rate constants $\mu a^2/D$ and $\lambda a^2/D$. In some cases it is more useful to relate R to the fraction of the total amount of solute which is in the sheet finally, i.e. to M_{∞}/lC_0 , by the relations (8.76). For the cylinder the corresponding parameters are $\pi a^2/A$, R, and $\mu a^2/D$, and for the sphere $4\pi a^3/3V$, R, and $\mu a^2/D$.

Once the roots p_n , $k_n a$ are obtained, the evaluation of each of the expressions for M_l/M_{∞} for the plane sheet, cylinder, and sphere is straightforward provided l, A, and V are finite. The cases of l, A, and V infinite, however, need further consideration because the convergence of terms for which p_n approaches $-\mu$ can be very slow and numerical evaluation becomes awkward and laborious, particularly for small $\mu a^2/D$. For the plane sheet when $\alpha = \infty$, (8.75) reduces to

$$\frac{M_l}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2D^2 k_n^2 (1 + p_n/\mu)^2 \exp(p_n t)}{(R+1)p_n^2 a^2 \{(1 + p_n/\mu)^2 + R\}}, \quad (8.96)$$

where now $k_n a = (n + \frac{1}{2})\pi$. As we saw in § 8.42 there are two infinite

series in the general expression for M_l/M_{∞} . We shall confine attention for the moment to the series associated with the positive square root in (8.89) since these are the terms for which p_n approaches $-\mu$ when Dk_n^2/μ is large. Substituting for $1+p_n/\mu$ from the second of (8.74) we find

$$\frac{M_{i}}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2(R+1+p_{n}/\mu)^{2} \exp(p_{n}t)}{(R+1)\{(1+p_{n}/\mu)^{2}+R\}k_{n}^{2}a^{2}}.$$
(8.97)

If $p_n = -\mu$ to the order of accuracy required, after the first r non-zero roots, we have

$$\frac{M_{t}}{M_{\infty}} = 1 - \sum_{n=1}^{r} \frac{2(R+1+p_{n}/\mu)^{2} \exp(p_{n}t)}{(R+1)\{(1+p_{n}/\mu)^{2}+R\}k_{n}^{2}a^{2}} - \frac{R}{R+1} \left\{1 - \sum_{n=1}^{r} \frac{2}{k_{n}^{2}a^{2}}\right\} \exp(-\mu t), \quad (8.98)$$

approximately, since

$$\sum_{n=1}^{\infty} \frac{2}{k_n^2 a^2} = 1.$$
 (8.99)

The relationship (8.99) follows, for example, from (8.90) when $\alpha = \infty$, since $M_t/M_{\infty} = 0$ when t = 0. The error involved in use of the approximate form (8.98) is less than

$$\left[\frac{(R+1+p_{r+1}/\mu)^2 \exp(p_{r+1}t)}{(R+1)\{(1+p_{r+1}/\mu)^2+R\}} - \frac{R}{R+1}\exp(-\mu t)\right] \left[1 - \sum_{n=1}^r \frac{2}{k_n^2 a^2}\right],$$
(8.100)

and can be made as small as desired by choice of r. We may note in passing that since in (8.97) p_n/μ and $1+p_n/\mu$ occur only with R, this is a more convenient form of expression for computation than (8.96) when p_n/μ is small or near -1, particularly for large R, since it is less sensitive to the accuracy of the roots p_n/μ .

When $l/a = \infty$, it follows from (8.88) that there is no root for which $k_n a$ is imaginary. The complete expression for M_l/M_{∞} is therefore that of (8.98) together with terms arising from the negative sign in the roots of (8.89). On using (8.98) numerical evaluation of M_l/M_{∞} for l/a infinite is straightforward. The corresponding formulae for the plane sheet and the sphere are easily derived.

8.44. Irreversible reaction

A special case of the above solutions of particular interest is that of an irreversible reaction, when the rate of formation of immobilized solute

is directly proportional to the concentration of free solute. In this case $\mu = 0$, but λ is non-zero so that $R = \infty$, $\alpha = 0$, $M_{\infty} = lC_0$. The solution for the plane sheet, for example, for these values follows immediately from (8.74) and (8.75) provided l is finite. The solution for the case of $l = \infty$ is less obvious. When $\mu = 0$, the imaginary root (p_i, k_i) is given by

$$lp_i = -Dk'_i \tanh k'_i a, \qquad k'^2_i = (p_i + \lambda)/D,$$
 (8.101)
where $k_i = ik'_i$, and so when $l = \infty$,

$$p_i = 0, \qquad k_i^{\prime 2} = \lambda/D.$$
 (8.102)

When $\alpha = 0$, $\mu = 0$, and p_i is small, we can expand $\exp(p_i t)$ in powers of $p_i t$ and write (8.75) as

$$M_{i} = lC_{0} - \frac{lC_{0}(1+p_{i}t)}{1+\frac{a}{2l} - \frac{p_{i}}{2Dk_{i}^{\prime 2}} - \frac{p_{i}^{2}la}{2D^{2}k_{i}^{\prime 2}}} - \sum_{n=1}^{\infty} \frac{lC_{0}\exp(p_{n}t)}{1+\frac{a}{2l} + \frac{p_{n}}{2Dk_{n}^{2}} + \frac{p_{n}^{2}la}{2D^{2}k_{n}^{2}}},$$
(8.103)

from which, when $l = \infty$, so that lp_i is given by (8.101) and (8.102), we have finally

$$\frac{M_{l}}{aC_{0}} = \frac{Dt}{a^{2}}q \tanh q + \frac{1}{2} \operatorname{sech}^{2}q + \frac{1}{2q} \tanh q - \sum_{n=1}^{\infty} \frac{2D^{2}k_{n}^{2} \exp(p_{n}t)}{a^{2}p_{n}^{2}},$$
(8.104)

where

 $k_n a = (n + \frac{1}{2})\pi, \quad k_n^2 = -(p_n + \lambda)/D, \quad q = \sqrt{(\lambda a^2/D)}.$ (8.105)

The first term on the right-hand side of (8.104) gives the rate of uptake of solute due to the chemical reaction in the final steady state.

The forms of (8.77) and (8.79) for the cylinder, and of (8.81) and (8.82) for the sphere when $\mu = 0$, $\alpha = 0$, are obvious. When $A = \infty$ we have for the cylinder

$$\frac{M_{t}}{\pi a^{2}C_{0}} = 1 + \frac{2Dt}{a^{2}}q\frac{I_{1}(q)}{I_{0}(q)} - \frac{I_{1}^{2}(q)}{I_{0}^{2}(q)} - \sum_{n=1}^{\infty} \frac{4D^{2}k_{n}^{2}\exp(p_{n}t)}{p_{n}^{2}}, \quad (8.106)$$

where

$$J_0(k_n a) = 0, \qquad k_n^2 = -(p_n + \lambda)/D, \qquad q = \sqrt{(\lambda a^2/D)}.$$
 (8.107)

When $V = \infty$ we have for the sphere

$$\frac{3M_t}{4\pi a^3 C_0} = \frac{3Dt}{a^2} (q \coth q - 1) - \frac{3}{2} \operatorname{cosech}^2 q + \frac{3}{2} \coth q - \sum_{n=1}^{\infty} \frac{6D^2 k_n^2 \exp(p_n t)}{a^2 p_n^2},$$

(8.108)

where

$$k_n a = n\pi, \qquad k_n^2 = -(p_n + \lambda)/D, \qquad q = \sqrt{(\lambda a^2/D)}.$$
 (8.109)

The solutions (8.104), (8.106), (8.108) can of course be obtained directly by use of the Laplace transform or otherwise. When $A = \infty$ the concentration at the surface of the cylinder is constant and (8.106) is the integrated form of (8.42). Similarly (8.108) is the integrated form of (8.41).

8.45. Desorption

We have considered diffusion into a plane sheet initially free of solute. There is the complementary problem in which all the solute is at first uniformly distributed through the sheet and subsequently diffuses out into the solution. If free and immobilized solute are considered to be initially in equilibrium everywhere in the sheet, it is easily seen that the mathematical solutions presented above for sorption also describe desorption, provided M_t is taken to mean the amount of solute leaving the sheet up to time t, and M_{∞} the corresponding amount after infinite time. For desorption from a plane sheet, for example, we want solutions of the equations (8.62) and (8.63) satisfying the condition (8.65) but with (8.64) replaced by

$$C = C_0, \qquad S = S_0, \qquad -a < x < a, \qquad t = 0.$$
 (8.110)

Writing

$$C_1 = C_0 - C, \qquad S_1 = S_0 - S, \tag{8.111}$$

it is easy to see that (8.110) and the other equations for desorption are identical with (8.62), (8.63), (8.64), (8.65) with C_1 , S_1 written for C, S respectively, remembering only that $\lambda C_0 - \mu S_0 = 0$, if we have equilibrium throughout the sheet at t = 0. Hence the solutions for C_1 for desorption are readily deduced from those for C for sorption, as are also the expressions for M_t/M_{∞} relating to desorption.

8.46. Calculated results

Evaluation of the expressions of § 8.44 for the irreversible reaction and any particular set of parameters is comparatively simple and straightforward. On the other hand a considerable amount of painstaking labour is involved in the evaluation of the formulae for the reversible reaction even when there is an infinite amount of solute, and it is therefore worth while to present some numerical values. In Tables 8.1, 8.2, 8.3, 8.4 calculated values of M_l/M_{∞} are tabulated for the plane sheet, cylinder, and sphere. The arrangement of the tables was decided by ease of presentation. Three values of the partition factor R are included and for each Rthree rates of reaction. All tabulated solutions refer to an infinite amount

of diffusing substance. The values of M_t/M_{∞} are believed to be correct to within ± 1 in the third decimal place.

Solutions for the plane sheet are illustrated in Figs. 8.5, 8.6, and 8.7. Those for the cylinder and sphere show the same general features, differing only in detail. Fig. 8.5 shows how the sorption curves change in shape and position as $\mu a^2/D$ is varied between the two extremes given by $\mu = \infty$ (infinitely rapid reaction) and $\mu = 0$ (simple diffusion with no reaction). By plotting against $(\mu t)^{\frac{1}{2}}$ as in Fig. 8.6 we can show the



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FIG. 8.5. Plane sheet, R = 10. Numbers on curves are values of $\mu a^*/D$.



F10. 8.6. Plane sheet, R = 10. Numbers on curves are values of $\mu a^2/D$.

approach to the curve for $D = \infty$ (purely reaction controlled) as $\mu a^2/D$ tends to zero because of D becoming large. We see also in Fig. 8.6 that the discontinuity in the gradient of the curve for D infinite appears as a 'shoulder' when $\mu a^2/D = 0.01$. As $\mu a^2/D$ is increased further the shoulder disappears leaving a sorption curve with a point of inflexion.





At still higher $\mu a^2/D$ the inflexion becomes less noticeable as in Fig. 8.5 and the curves have the simple shape commonly associated with diffusion. Fig. 8.7 shows the influence of the parameter R, the partition factor between immobilized and free solute. As R is increased the height of the shoulder decreases, and if curves for R = 100 were plotted on the present scale no shoulder would be detected for any value of $\mu a^2/D$.

One interesting feature of these results is that they indicate limits to the relative rates of diffusion and reaction outside of which the reaction is effectively infinitely rapid or infinitely slow as the case might be. Thus for the plane sheet, the values of M_i/M_{∞} for $\mu a^2/D = 10$ differ by only a few per cent. from those for an infinitely rapid reaction. The differences are greatest for R = 1 where they are about 5 per cent. At the other extreme the solution for $\mu a^2/D = 0.01$, R = 1, is the same as that for an infinitely slow reaction to the same degree of accuracy except at small times (see Fig. 8.7 for example). The differences increase in this case as R increases, being about 20 per cent. for R = 100.

The significance of these limits is perhaps easier to appreciate when they are expressed in terms of the half-times of the simple diffusion and simple reaction processes respectively. For simple diffusion into the plane sheet from an infinite amount of solution it is easy to show that the half-time, t_d , that is the time at which $M_l/M_{\infty} = \frac{1}{2}$, is given by

$$Dt_d/a^2 = -(4/\pi^2) \ln \pi^2/16 = 0.2, \qquad (8.112)$$

approximately. On the other hand if immobilized solute is formed from a uniform, constant concentration, C_0 , of free solute according to the equation

$$\partial S/\partial t = \lambda C_0 - \mu S,$$
 (8.113)

this reaction has a half-time, t_r , given by

$$\mu t_r = \ln 2 = 0.7, \qquad (8.114)$$

approximately, and combining (8.112) and (8.113) we have for the ratio of the half-times,

$$t_r/t_d = 3.5D/(\mu a^2). \tag{8.115}$$

Thus we can say roughly that if the diffusion is more than a thousand times faster than the reaction, the behaviour of the diffusion-reaction process is roughly the same as it would be if diffusion were infinitely rapid. On the other hand if the half-times for diffusion and reaction are comparable, the behaviour approximates to that for an infinitely rapid reaction. These statements indicate orders of magnitude only. They apply also to the cylinder and sphere.

8.5. A bimolecular reaction

Katz and others [9] and also Reese and Eyring [10] have considered the problem of diffusion accompanied by an immobilizing reaction which is bimolecular. They consider diffusion in a cylinder, representing a textile fibre in which there are a number of active groups to which the diffusing molecules can become attached. The process is described by the equation

$$\partial C/\partial t = D\nabla^2 C - knC, \qquad (8.116)$$

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where n(r, t) is the number of active groups unattacked at radius r and time t. Both treatments are approximate only, because (8.116) is nonlinear and not amenable to formal solution. Katz and others [9] first neglect the term knC in (8.116) and then use the known solution of the simplified diffusion equation which yields C as a function of r and t, to obtain an approximation to n through the equation

$$\partial n/\partial t = -knC. \tag{8.117}$$

Reese and Eyring [10] make the assumption that the rate of reaction depends on the average concentration of diffusing molecules throughout the fibre and not on the concentration C, as in (8.117), which depends on the radial coordinate r.

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SOME METHODS OF SOLUTION FOR VARIABLE DIFFUSION COEFFICIENTS

9.1. Time-dependent diffusion coefficients

IN Chapters III-VIII mathematical solutions were presented for various problems in which the diffusion coefficient was taken to be constant. These solutions can also be used if the diffusion coefficient, D, depends on the time, t, for which diffusion has been proceeding but is independent of other variables, i.e. if D is a function of t only. In this case the equation for diffusion in one dimension becomes

$$\frac{\partial C}{\partial t} = D(t) \frac{\partial^2 C}{\partial x^2}, \qquad (9.1)$$

$$dT = D(t) dt, (9.2)$$

and on writing

equation (9.1) reduces to

$$T = \int_{0}^{t} D(t') dt', \qquad (9.3)$$

that is

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial x^2}.$$
(9.4)

The solutions for constant D can therefore be used to give C as a function of x and T, and T is then converted into t using the relationship (9.3). If the integral in (9.3) cannot be evaluated formally, the relationship between T and t has to be obtained by graphical or numerical integration. If the boundary conditions involve time explicitly, e.g. if the surface concentration is a given function of t, this function must be rewritten in terms of T in order to obtain the appropriate solution of (9.4) in x and T. The transformation (9.2) can, of course, be used for all forms of the diffusion equation, e.g. for diffusion in a plane sheet, cylinder, or sphere.

9.2. Non-homogeneous media

Little attention has been paid to diffusion in non-homogeneous media in which the diffusion coefficients vary with distance measured in the direction of diffusion, apart from the special cases relating to composite sheets, cylinders, and spheres. Some examples in which the diffusion coefficient has one constant value in the surface layer and another constant value below the surface layer have been referred to in Chapters III-VI. Other cases in which the diffusion coefficient is concentrationdependent in the surface layer are discussed later in § 12.6. The numerical methods discussed in Chapter X can be used to handle a particular problem in which D depends on x in a known way and for which formal solutions are not available.

9.3. Concentration-dependent diffusion. Infinite and semiinfinite media

A case of great practical interest is that in which the diffusion coefficient depends only on the concentration of diffusing substance. Such a concentration dependence exists in most systems, but often, e.g. in dilute solutions, the dependence is slight and the diffusion coefficient can be assumed constant for practical purposes. In other cases, however, such as the diffusion of vapours in high-polymer substances, the concentration dependence is a very marked, characteristic feature. A number of methods have been used to obtain numerical solutions, some applicable to any type of concentration-dependent diffusion coefficient, and others restricted to particular types, e.g. exponential or linear dependence. In other cases, algebraic solutions have been expressed in terms of a single integral and these will be referred to as formal solutions even though the integral has to be evaluated numerically.

9.31. Boltzmann's transformation

The equation for one-dimensional diffusion when the diffusion coefficient D is a function of concentration C is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right). \tag{9.5}$$

In 1894 Boltzmann [1] showed that for certain boundary conditions, provided D is a function of C only, C may be expressed in terms of a single variable $x/2t^{\ddagger}$ and that (9.5) may therefore be reduced to an ordinary differential equation by the introduction of a new variable, η , where

$$\eta = \frac{1}{2}x/t^{\frac{1}{2}}.\tag{9.6}$$

$$\frac{\partial C}{\partial x} = \frac{1}{2t^{\frac{1}{2}}} \frac{dC}{d\eta}, \qquad (9.7)$$

Thus we have

and
$$\frac{\partial C}{\partial t} = -\frac{x}{4t^{\dagger}} \frac{dC}{d\eta},$$
 (9.8)
and hence $\frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = \frac{\partial}{\partial x} \left(\frac{D}{2t^{\dagger}} \frac{dC}{d\eta} \right) = \frac{1}{4t} \frac{d}{d\eta} \left(D \frac{dC}{d\eta} \right),$ (9.9)
so that finally (9.5) becomes
 $-2\eta \frac{dC}{d\eta} = \frac{d}{d\eta} \left(D \frac{dC}{d\eta} \right),$ (9.10)

an ordinary differential equation in C and η . The transformation (9.6) can be used when diffusion takes place in infinite or semi-infinite media provided the concentration is initially constant in the regions $x \ge 0$ or x > 0 as the case may be. For the problem defined by

$$C = C_1, \qquad x < 0, \qquad t = 0,$$
 (9.11)

$$C = C_2, \qquad x > 0, \qquad t = 0,$$
 (9.12)

equation (9.10) is to be solved for the boundary conditions

$$C = C_1, \qquad \eta = -\infty, \tag{9.13}$$

$$C = C_2, \qquad \eta = +\infty. \tag{9.14}$$

Similarly, the conditions for a semi-infinite medium

$$C = C_0, \qquad x = 0, \qquad t > 0,$$
 (9.15)

$$C = C_1, \quad x > 0, \quad t = 0,$$
 (9.16)

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$$C = C_0, \qquad \eta = 0,$$
 (9.17)

$$C = C_1, \qquad \eta = \infty. \tag{9.18}$$

It is only when the initial and boundary conditions are expressible in terms of η alone, and x and t are not involved separately, that the transformation (9.6) and the equation (9.10) can be used. They cannot be used, for example, when diffusion occurs in a finite sheet of thickness l, and the boundary conditions are

$$C = C_0, \quad x = 0, \quad x = l,$$
 (9.19)

because the second condition becomes

$$C = C_0, \qquad \eta = \frac{1}{2}l/t^{\frac{1}{2}},$$
 (9.20)

which is not expressible in terms of η only but involves t explicitly. In general the transformation can be used for diffusion in infinite and semiinfinite media when the initial concentrations are uniform and may be zero.

9.32. Iterative solution

In this method we estimate a first approximation to the solution and

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then evaluate a succession of better approximations, each of which satisfies all the boundary conditions, but only when two successive approximations agree to the accuracy of working is the differential equation satisfied as well. We shall illustrate the method by considering diffusion in a semi-infinite medium for which

$$c = 1, \quad x = 0, \quad t > 0,$$
 (9.21)

$$c = 0, \quad x > 0, \quad t = 0,$$
 (9.22)

and the diffusion coefficient is of the form $D_0 e^{kc}$. Here c denotes a nondimensional concentration convenient for purposes of calculation. It will be obvious that the method can be used for any relationship between the diffusion coefficient and concentration provided it is known, and that furthermore a graphical or numerical relationship is sufficient in the absence of an algebraic formula. In practice we can always make c = 1 on the surface by expressing the concentration as a fraction of the actual concentration on the surface, expressed for example in g. cm, -3

On writing
$$y = \frac{1}{2}x/(D_0 t)^{\frac{1}{2}}$$
, (9.23)

 $D = e^{kc}$.

the diffusion equation becomes

$$-2y\frac{dc}{dy} = \frac{d}{dy}\left(D\frac{dc}{dy}\right),\tag{9.24}$$

where now

On rewriting (9.24) as

$$-\frac{2y}{D}D\frac{dc}{dy} = \frac{d}{dy}\left(D\frac{dc}{dy}\right),\tag{9.26}$$

and integrating, we find

$$D\frac{dc}{dy} = A \exp\left(-\int_{0}^{y} \frac{2y'}{D} \, dy'\right),\tag{9.27}$$

where A is a constant of integration to be determined later by the boundary conditions. A further integration gives

$$c = 1 - A \int_{0}^{y} \frac{1}{D} \exp\left(-\int_{0}^{y} \frac{2y'}{D} \, dy'\right) dy'. \tag{9.28}$$

The condition, c = 1 at y = 0, is satisfied by taking the integral to be zero at the lower limit y = 0. The condition c = 0, $y = \infty$, can be satisfied by choosing A such that

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$$A \int_{0}^{\infty} \frac{1}{D} \exp\left(-\int_{0}^{y} \frac{2y'}{D} \, dy'\right) dy' = 1, \qquad (9.29)$$

[§ 9.3

(9.25)

so that finally we have

$$c = 1 - \frac{\int_{0}^{y} (1/D) \exp\left\{-\int_{0}^{y} (2y'/D) \, dy'\right\} \, dy'}{\int_{0}^{\infty} (1/D) \exp\left\{-\int_{0}^{y} (2y'/D) \, dy'\right\} \, dy'}.$$
(9.30)

This may seem an elaborate form of solution of (9.24) but it contains

the boundary conditions as well and is in fact quite convenient for numerical evaluation.

In the absence of anything better, a first approximation from which to start the evaluation of (9.30) is afforded by the solution for which Dis constant and equal to its value when c = 0, i.e. D = 1, in this example. The first approximation is then (see Chapter II (2.14))

$$c = 1 - \operatorname{erf} y. \tag{9.31}$$

The error function, $\operatorname{erf} y$, is unity to four decimal places when y exceeds 3.0, so that, when working to this order of accuracy, y = 3.0 replaces $y = \infty$ as the practical upper limit of integration. A danger in using this sort of method when the upper limit of the range in y is not known exactly till the solution is completed, is that c may have been made zero at some value of y smaller than the correct one. In such a case dc/dy will not be zero to the desired order of accuracy and a further approximation is necessary, extending further in y. It is always desirable to overestimate rather than to under-estimate the range in y for the first approximation. A check which is found very useful in practice is based on the comparison of the two expressions for the total amount, M_{t} , of diffusing substance which has crossed y = 0 at time t. Thus

$$M_{t} = \int_{0}^{\infty} c \, dx = 2(D_{0} t)^{\frac{1}{2}} \int_{0}^{\infty} c \, dy, \qquad (9.32)$$

and also

$$\frac{dM_t}{dt} = -D_0 D\left(\frac{\partial c}{\partial x}\right)_{y=0} = -\frac{D_0^{\frac{1}{2}}D}{2t^{\frac{1}{2}}}\left(\frac{dc}{dy}\right)_{y=0},$$

so that on integrating we have

$$M_{t} = -D(D_{0}t)^{i} \left(\frac{dc}{dy}\right)_{y=0}.$$
 (9.33)

Thus if any one of the successive approximations is the correct solution, to the accuracy of working, we must have

$$2\int_{-\infty}^{\infty} c \, dy = -D\left(\frac{dc}{t}\right) \quad . \tag{9.34}$$

$\int_0^{J} |dy|_{y=0}$

The iterative method of solution is therefore as follows:

- 1. Using (9.31), obtain values of c at equal intervals in y. The range is determined by the value of y at which c = 0 to the accuracy of working. Intervals of 0.1 in y are usually small enough if three decimal places in c are being taken.
- 2. Evaluate D from (9.25) at each value of y.

- 3. Evaluate (9.30) by numerical integration to give new values of c at each y. Any of the standard formulae for numerical integration can be used and the interval in y clearly depends on the accuracy required in the integration.
- 4. Repeat the steps (2) and (3) starting from the new values of c.
- 5. When two successive approximations yield the same values of ceverywhere to the order of accuracy required see if (9.34) is satisfied.
- 6. If not, the range in y is usually too small and needs to be increased so that a further approximation can be evaluated.

9.33. A useful alternative variable

In the steady-state flow through a membrane between two fixed concentrations, the shape of the concentration-distance curve is very dependent on how the diffusion coefficient varies with concentration (see § 12.1), but the product $D \partial c / \partial x$ is constant throughout the membrane. This suggests that although in the non-steady state $D \partial c / \partial x$ at a given time cannot be exactly the same at all points of the medium, nevertheless the results may assume a simpler form in terms of a variable which includes such a product. We therefore introduce a new variable sdefined by

$$s = \left(\int_{0}^{c} D dc'\right) / \int_{0}^{1} D dc', \qquad (9.35)$$

so that

 $s=1, \quad c=1, \quad y=0,$ (9.36)

$$s = 0, \quad c = 0, \quad y = \infty.$$
 (9.37)

Then (9.24) becomes
$$-2y\frac{ds}{dy} = D\frac{d^2s}{dy^2}$$
, (9.38)

and (9.30) takes the slightly simpler form

$$s = 1 - \frac{\int_{0}^{y} \exp\left\{-\int_{0}^{y} (2y'/D) \, dy'\right\} dy'}{\int_{0}^{\infty} \exp\left\{-\int_{0}^{y} (2y'/D) \, dy'\right\} dy'}.$$
(9.39)

The transformation (9.35) is essentially that used by Eyres, Hartree, and others [2]. The iterative solution of (9.39) follows closely that of (9.30)with slight modification due to the disappearance of the factor 1/D. Apart from this simplification, the advantages of using s instead of care clear from Fig. 9.1 which shows s and c as functions of y for a diffusion coefficient increasing exponentially from 1 to 200 in the range $0 \le c \le 1$. Because of the simpler shape of the s against y curve, numerical integration is quicker when s is the variable because larger intervals in y can



Fig. 9.1. Concentration distribution during sorption for exponential diffusion coefficient $D = D_0 e^{5.3c}, \dots error$ function solution (9.41).



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be taken and the same size of interval is more likely to suffice throughout. Also it is easier to get a better first approximation to s than to c. Thus a possible improvement on (9.31) is to use an integrated mean value for D over the whole range in c, instead of using the value D = 1 at c = 0, i.e. to use D_I , where 1

$$D_I = \int_0^1 D \, dc. \tag{9.40}$$

For this mean value of D, s = c and the solution of (9.24) and (9.38) is

$$c = s = 1 - \operatorname{erf} y/D_I^{\dagger},$$
 (9.41)

which is shown as a broken line on Fig. 9.1. This is clearly a better approximation to the final solution in s than to that in c shown in Fig. 9.1.

On the other hand, for some D-c relationships s may be a slowly varying function of c over part of the concentration range, so that a small error in s corresponds to a large error in c. For this reason, when the values of s in two successive approximations agree to the order of accuracy required it may be desirable to convert the values of s into c values and to continue the iteration in terms of c.

The iterative method can be applied equally well to a problem of desorption from a semi-infinite sheet, for which

$$c = 0, \quad x = 0, \quad t > 0,$$
 (9.42)

$$c = 1, \quad x > 0, \quad t = 0,$$
 (9.43)

though the advantages of using the variable s are less marked because of the different shapes of the concentration-distance curves for sorption and desorption. This is clear from Figs. 9.1 and 9.2, which also illustrate the considerable difference in the ranges of y involved in the two solutions for the same diffusion coefficient-concentration relationship.

The corresponding problem in an infinite medium for which

$$c = 1, \quad x < 0, \quad t = 0,$$
 (9.44)

 $c = 0, \quad x > 0, \quad t = 0,$ (9.45)

can be treated similarly. Here the simplest first approximation is $c = \frac{1}{2} \operatorname{erfe} y, \qquad (9.46)$

for which the practical range in y is -3 < y < 3 if four decimal places are taken in c. The variable s and the approximation

$$c = s = \frac{1}{2} \operatorname{erfc} y/D_I^4,$$
 (9.47)

corresponding to (9.41), are also useful.

9.34. Forward integration

An alternative method of obtaining numerical solutions of (9.38) is to assume a value for ds/dy at y = 0 and to integrate forwards, using either a differential analyser or one of the established methods for the numerical solution of ordinary differential equations [3]. In general, the solution obtained for the first trial of ds/dy will not satisfy the end condition $s = 0, y = \infty$. Successive trial values are tried till this end condition is satisfied, and then we have a solution satisfying the differential equation and both the boundary conditions. Philip† has described a method, using c as independent variable, which converges rapidly.

9.35. Some special cases

By using the methods described above a solution of (9.10) can be obtained for any diffusion coefficient-concentration relationship, provided numerical values of D are known over the relevant concentration range. For the two cases of diffusion coefficients which depend linearly or exponentially on concentration, equation (9.10) has been transformed so that the relationship between D and c is removed from the differential equation and appears instead in one of the boundary conditions. A solution of the transformed equation, which satisfies the boundary condition at y = 0, is obtained by forward numerical integration for a postulated value of a second condition, e.g. a concentration gradient, at y = 0. The particular linear or exponential diffusion coefficient to which this solution corresponds is determined afterwards from the value to which the solution tends as y approaches infinity. By repeating the integration for different values of the unknown condition at y = 0, a family of solutions of (9.10) is built up for the given type of diffusion coefficient-concentration relationship. The solution for a given diffusion coefficient of the particular type can be obtained afterwards by interpolation on the family of solutions.

(i) Exponential diffusion coefficients. Infinite medium

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Wagner [4] has given the following method of dealing with a diffusion coefficient which varies exponentially with concentration, according to the expression $D = D \exp[\beta(C - 1/C + C)]$

$$\mathcal{V} = D_a \exp[\beta \{C - \frac{1}{2}(C_1 + C_2)\}], \qquad (9.48)$$

where D_a is the diffusion coefficient for the average concentration $C_a = \frac{1}{2}(C_1 + C_2)$, and β is a constant given by

$$\beta = d \ln D/dC. \tag{9.49}$$

† Philip J. R., Trans. Faraday Soc. 51 (1955) 885.

Wagner deals first with the problem in an infinite medium for which the diffusion equation is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \tag{9.50}$$

and the initial conditions are

$$C = C_1, \quad x < 0, \quad t = 0,$$
 (9.51)

$$C = C_2, \qquad x > 0, \qquad t = 0.$$
 (9.52)

For purposes of tabulating the final results it is convenient to take new variables

$$y = \frac{1}{2}x/(D_0 t)^{\frac{1}{2}}, \tag{9.53}$$

where D_0 is the diffusion coefficient for the concentration C_0 at x = 0, and

$$\psi = \frac{C - \frac{1}{2}(C_1 + C_2)}{\frac{1}{2}(C_2 - C_1)},$$
(9.54)

so that

$$C = \frac{1}{2}(C_1 + C_2) + \frac{1}{2}(C_2 - C_1)\psi.$$
(9.55)

To compute numerical values of the function ψ , we introduce another dimensionless variable (9.56) $\gamma = \beta (C - C_0),$

$$D = D_0 e^{\gamma}, \qquad (9.57)$$

with D_0 as diffusion coefficient for $C = C_0$. Substitution of (9.53), (9.56), and (9.57) in (9.50) gives

$$\frac{d}{dy}\left(e^{\gamma}\frac{d\gamma}{dy}\right) + 2y\frac{d\gamma}{dy} = 0.$$
(9.58)

Introducing the auxiliary variable

$$u = e^{\gamma} \tag{9.59}$$

 $u\frac{d^2u}{dy^2} + 2\frac{du}{dy} = 0.$ (9.60)into (9.58), we have

Solutions of (9.60) from $y = -\infty$ to $y = +\infty$ for the initial conditions

$$\gamma = 0, \quad u = 1, \quad y = 0,$$
 (9.61)

(9.62) $g \equiv (d\gamma/dy)_{y=0} \equiv (du/dy)_{y=0} = 0.2, 0.4, ..., 2.4$ were obtained with the aid of a differential analyser. For each auxiliary parameter g there are two limiting values of γ , γ_1 at $y = -\infty$ and γ_2 at $y = +\infty$, with opposite signs. In view of (9.56) these values are related to the initial concentrations C_1 and C_2 by

> (9.63) $\gamma_1 = \beta(C_1 - C_0),$ (9.64) $\gamma_2 = \beta(C_2 - C_0).$

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On subtracting corresponding sides of (9.63) and (9.64) we have

$$\boldsymbol{\gamma}_2 - \boldsymbol{\gamma}_1 = \boldsymbol{\beta}(C_2 - C_1), \qquad (9.65)$$

which according to (9.49) is the natural logarithm of the ratio of the diffusion coefficients for the concentrations C_2 and C_1 . Fig. 9.3 shows the relation between $\gamma_2 - \gamma_1$ and the parameter g.



FIG. 9.3. Auxiliary parameter g as a function of $(\gamma_2 - \gamma_1) = \beta(C_2 - C_1)$.

Moreover, it follows from (9.63) and (9.64) that

$$C_0 = \frac{1}{2}(C_1 + C_2) - \frac{1}{2}(\gamma_1 + \gamma_2)/\beta.$$
(9.66)

Substitution of (9.66) in (9.48) gives

$$D_0 = D_a \exp\{-\frac{1}{2}(\gamma_1 + \gamma_2)\}.$$
 (9.67)

To facilitate the computation of D_0 , a graph of $\frac{1}{2}(\gamma_1 + \gamma_2)$ as a function of g is shown in Fig. 9.4.

According to (9.56) and (9.54) we obtain the values of ψ from the



$$\psi = \frac{\gamma - \frac{1}{2}(\gamma_1 + \gamma_2)}{\frac{1}{2}(\gamma_2 - \gamma_1)}.$$
(9.68)

Numerical values of the function $\psi(y,g)$ are compiled in Table 9.1. For negative values of the parameter g the relationship

$$\psi(y, -g) = -\psi(y, g) \tag{9.69}$$

can be used and the sign of y must be reversed.

In view of the regularity of the differences between the ψ values for different g values but equal y values, it is believed that the error in ψ is in general not greater than one figure in the last decimal place, except



for g = -1.6 to g = -2.4 for which the accuracy is less because of rather sudden changes in the values of the first derivative of ψ as a function of y.

In order to obtain the concentration distribution for a diffusion coefficient with given initial concentrations C_1 and C_2 and known values of D_a and β , we proceed as follows.

- 1. Read the value of the auxiliary parameter g for the known value of $(\gamma_2 \gamma_1) = \beta(C_2 C_1)$ from Fig. 9.3.
- 2. Read the value of $\frac{1}{2}(\gamma_1 + \gamma_2)$ for the auxiliary parameter g from Fig. 9.4.
- 3. Calculate the value of D_0 from (9.67).
- 4. Plot ψ for the auxiliary parameter g as a function of y with the

aid of Table 9.1.

In view of (9.53) and (9.55) the plot of ψ versus y gives the concentration C at any point x at time t.

Instead of using Figs. 9.3 and 9.4, the values of g and $\frac{1}{2}(\gamma_1 + \gamma_2)$ may be calculated from the empirical interpolation formulae

$$g = 0.564(\gamma_2 - \gamma_1) - 5(\gamma_2 - \gamma_1)^3 10^{-3} + 64(\gamma_2 - \gamma_1)^5 10^{-5}, \quad (9.70)$$

$$\frac{1}{2}(\gamma_1 + \gamma_2) = -0.144g^2 - 0.0038g^4. \quad (9.71)$$

Thus far it has been assumed that the diffusion coefficient is an exponential function of the concentration in accordance with (9.48). If this assumption does not hold strictly, we may use the foregoing analysis as an approximation. Wagner [4] recommends that the analysis be based on the diffusion coefficients for the concentrations

$$C_{-\frac{1}{2}} = \frac{1}{2}(C_1 + C_2) - \frac{1}{4}(C_2 - C_1)$$
 and $C_{\frac{1}{2}} = \frac{1}{2}(C_1 + C_2) + \frac{1}{4}(C_2 - C_1)$

as the most representative values, corresponding to the average concentration $\frac{1}{2}(C_1+C_2)\pm 25$ per cent. of the total concentration difference (C_2-C_1) . Thus $2 = D(C_1)$

$$\beta = \frac{2}{C_2 - C_1} \ln \frac{D(C_4)}{D(C_{-4})}, \qquad (9.72)$$

$$D_a = \{ D(C_{\frac{1}{2}}) D(C_{-\frac{1}{2}}) \}^{\frac{1}{2}}.$$
(9.73)

(ii) Exponential diffusion coefficients. Semi-infinite medium

If a substance diffuses from the interior of a sample, with uniform initial concentration C_0 , to the surface (or vice versa) we need solutions of (9.50) with the initial and boundary conditions

$$C = C_0, \qquad x > 0, \qquad t = 0,$$
 (9.74)

$$C = C_s, \qquad x = 0, \qquad t > 0,$$
 (9.75)

where x is the distance from the surface and C_s denotes the surface concentration for t > 0.

In this case we consider an exponential dependence of the diffusion coefficient, D, on concentration given by

$$D = D_s \exp\{\beta(C - C_s)\},$$
(9.76)

where D_s is the diffusion coefficient for the surface concentration C_s .

Upon introduction of (9.76) and the auxiliary variables

$$y_s = \frac{1}{2}x/(D_s t)^{\frac{1}{2}},\tag{9.77}$$

$$c = (C - C_s) / (C_0 - C_s), \qquad (9.78)$$

and

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$$\gamma = \beta(C - C_s), \qquad (9.79)$$

into (9.50) we obtain (9.58) with y_s instead of y. In view of (9.75), (9.77), (9.79) the integration is to be performed with $\gamma = 0$ at $y_s = 0$. Thus we can use the values of γ calculated above in § 9.35 (i). In view of (9.74), (9.78), and (9.79) we have

$$\gamma = \beta(C_0 - C_s) = r, \qquad y_s = \infty, \qquad (9.80)$$

$$c = \gamma/r. \tag{9.81}$$

Here r is the natural logarithm of the ratio of the diffusion coefficients for the concentrations C_0 and C_s . Fig. 9.5 shows the values of r, i.e. the

limiting values of γ at $y = \infty$, as a function of the auxiliary parameter g used for the integration of (9.60). Numerical values of c are compiled in Table 9.2.



Fig. 9.5. Auxiliary parameter g as a function of $r = \beta(C_0 - C_s)$.

In order to obtain the concentration distribution for diffusion from the surface to the interior of a sample (or vice versa) one therefore proceeds as follows:

- 1. Read the value of the parameter g for the value of $r = \beta(C_0 C_g)$ from Fig. 9.5.
- 2. Plot c for this value of g as a function of y_s using Table 9.2.

The concentration C at any distance x and any time t follows, since from (9.78) C = C + (C - C)

$$C = C_s + (C_0 - C_s)c, (9.82)$$

and y_s is given by (9.77).

Instead of using Fig. 9.5 one may calculate the values of g with the aid of the empirical interpolation formula

$$g = \frac{1 \cdot 128r}{1 - 0 \cdot 177r}.$$
 (9.83)
Using (9.77) and (9.82), the flux across the surface, $x = 0$, becomes
 $-D_s(\partial C/\partial x)_{x=0} = -\frac{1}{2}(D_s/t)^{\frac{1}{2}}(C_0 - C_s)(dc/dy_s)_{y_s=0}$: (9.84)
and from (9.62), (9.81), and (9.83) it follows that

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$$\left(\frac{dc}{dy_s}\right) = g/r = \frac{1 \cdot 128}{1 - 0 \cdot 177r}, \qquad y_s = 0. \tag{9.85}$$

till wor of ulead are of vby § If β is positive (i.e. the diffusion coefficient increases with concentration) and if the substance diffuses from the surface into the interior of a sample with zero initial concentration (i.e. $C_0 - C_s < 0$), the value of g is negative.

(iii) Linear diffusion coefficients

Using a method similar to Wagner's, R. H. Stokes [5] has obtained solutions for the infinite medium and conditions (9.51), (9.52) for a diffusion coefficient depending linearly on concentration according to the expression $D = D\{1 + \frac{1}{2}a(C + C) - aC\}$

$$D = D_a \{1 + \frac{1}{2}a(C_1 + C_2) - aC\}.$$
(9.86)

Here D_a is the value of D when $C = \frac{1}{2}(C_1 + C_2)$, the mean concentration. By using the substitutions

$$v = \left\{\frac{1 + \frac{1}{2}a(C_1 + C_2) - aC}{1 + \frac{1}{2}a(C_1 - C_2)}\right\}^2$$
(9.87)

and

$$= \frac{x}{2\{1+\frac{1}{2}a(C_1-C_2)\}^{\frac{1}{2}}(D_a t)^{\frac{1}{2}}},$$
(9.88)

the diffusion equation (9.50) reduces to

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$$\frac{d^2v}{dw^2} = -\frac{2w}{v^4}\frac{dv}{dw},\tag{9.89}$$

with the boundary conditions

$$v = 1, \qquad w = +\infty, \tag{9.90}$$

$$v = \left\{ \frac{1 - \frac{1}{2}a(C_1 - C_2)}{1 + \frac{1}{2}a(C_1 - C_2)} \right\}^2, \qquad w = -\infty.$$
(9.91)

For convenience, we denote by b^2 the value of v at $w = -\infty$. From (9.86) we see that b is the ratio of the diffusion coefficient at C_1 to that at C_2 . Stokes obtained numerical solutions of (9.89) by starting at w = 3, v = 1 (the value w = 3 is suggested by the known solution for a constant diffusion coefficient) and a chosen *small* value of dv/dw, say less than 0.01. The integration proceeds in the direction of decreasing w

till a value of v is reached which is constant to within the accuracy of working. This value of v is b^2 , and is reached at some negative value of w between -2 and -5. Different values of the initial gradient dv/dwlead to different values of b^2 which are known only when the solutions are completed. This family of solutions gives, for different b's, values of v and dv/dw at closely-spaced intervals in w (the usual interval used by Stokes was 0.1 in w). From these solutions, values of concentration and concentration gradient are readily obtained. They are conveniently expressed in terms of a new independent variable y_a defined by

$$y_a = \frac{x}{2(D_a t)^4} = w \sqrt{\left(\frac{2}{1+b}\right)},$$
 (9.92)

so that we have

$$\frac{dC}{dy_a} = -\frac{(C_1 - C_2)\{\frac{1}{2}(1+b)\}^{\frac{1}{2}}}{2(1-b)} \frac{1}{v^{\frac{1}{2}}} \frac{dv}{dw}, \qquad (9.93)$$

$$C = C_2 + (C_1 - C_2)(1 - v^{\frac{1}{2}})/(1 - b).$$
(9.94)

Tables 9.3 and 9.4 show $-(dC/dy_a)/(C_1-C_2)$ and $(C-C_2)/(C_1-C_2)$ as functions of y_a for different values of b. All the solutions shown correspond to b < 1, i.e. to diffusion coefficients which decrease as the concentration increases. The corresponding solutions for b > 1 may be obtained by reversing the sign of y_a ; thus, for example, the solution for b = 0.1407 becomes the solution for b = 1/0.1407 = 7.106 when the sign of y_a is changed. Solutions for intermediate values of b can be obtained by interpolation. If higher accuracy is required the interpolated values can be improved by the iterative method described earlier in § 9.32.

(iv) Diffusion coefficient directly proportional to concentration

The problem treated by Wagner [6] of a diffusion coefficient given by

$$D = D_0 C/C_0, (9.95)$$

has some features of particular interest. Considering first the semiinfinite medium in which

$$C = C_0, \qquad x = 0, \qquad t > 0,$$
 (9.96)

$$C = 0, \qquad x > 0, \qquad t = 0,$$
 (9.97)

and introducing the variables

$$y = \frac{1}{2}x/(D_0 t)^{\frac{1}{2}}, \tag{9.98}$$

$$c = C/C_0, \tag{9.99}$$

the diffusion equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D_0 \frac{C}{C_0} \frac{\partial C}{\partial x} \right), \qquad (9.100)$$
becomes
$$c \frac{d^2 c}{dy^2} + \left(\frac{dc}{dy} \right)^2 + 2y \frac{dc}{dy} = 0. \qquad (9.101)$$
Further simplification is achieved by substituting

$$\nu = c^2, \qquad (9.$$

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 $\frac{d^2\nu}{dy^2} = -\frac{2y}{\nu^{\frac{1}{2}}}\frac{d\nu}{dy},$

with boundary conditions

when (9.101) becomes

$$\nu = 1, \quad y = 0,$$
 (9.104)

$$y = 0, \qquad y = \infty. \tag{9.105}$$



FIG. 9.6. Schematic solutions of (9.103).

Using numerical methods of integration and disregarding temporarily the second condition (9.105), a family of solutions of (9.103) can be obtained for arbitrarily chosen values of $(d\nu/dy)_{\nu=0} = \nu'_0$. Clearly if the condition (9.105) at $y = \infty$ is to be satisfied, ν'_0 must be negative. Then from (9.103) the second derivative of ν with respect to y is positive. If $|\nu'_0| \ll 1$, the curve of ν against y tends to a constant value at large yas shown in Fig. 9.6, curve A. A solution of this kind does not satisfy (9.105), however. On the other hand, if $|\nu'_0| \gg 1$, curves which approach the axis $\nu = 0$ with finite slopes as shown schematically by curve B in

(9.103)

Fig. 9.6 are obtained. Tentatively we assume that a special value of $|\nu'_0|$ yields a solution for which ν vanishes at a certain abscissa, $y = y_0$, and satisfies the additional condition

$$\frac{d\nu}{dy} = 0, \quad \nu = 0, \quad y = y_0.$$
 (9.106)

This is the condition that the rate of transport of diffusing substance shall be zero when C = 0, since by equations (9.98), (9.99), and (9.102)

we have for the rate of transport

$$D_0 \frac{C}{C_0} \frac{\partial C}{\partial x} = \frac{D_0^{\dagger} C_0}{4t^{\dagger}} \frac{d\nu}{dy}.$$
(9.107)

A function satisfying (9.103), (9.104), and (9.106) can then be combined with the trivial solution $\nu = 0$, $y \ge y_0$, so that a solution for the whole range $y \ge 0$ results.

With the tentative assumption that condition (9.106) is satisfied at a finite value $y = y_0$, the factor y on the right side of (9.103) can be replaced approximately by y_0 if $v \ll 1$. Thus

$$\frac{d^2\nu}{dy^2} = -\frac{2y_0}{\nu^*} \frac{d\nu}{dy},$$
(9.108)

if $\nu \ll 1$, with the boundary conditions

 $\nu = 0, \qquad y = y_0, \qquad (9.109)$

$$d\nu/dy = 0, \quad y = y_0.$$
 (9.110)

Integration yields

$$\nu = \{2y_0(y_0 - y)\}^2, \quad \nu \ll 1.$$
(9.111)

Consequently, in the vicinity of $y = y_0$, where $\nu \ll 1$ and hence $c \ll 1$ and $C \ll C_0$, the function $\nu(y)$ is represented approximately by a parabola and the concentration ratio $c = \nu^{\frac{1}{2}}$ by a straight line.

To obtain a solution of (9.103) for the whole range $0 < y < y_0$, numerical integration is required. Since the boundary conditions (9.104) and (9.106) refer to different values of y it is useful to make the substitutions

$$\zeta = \nu / y_0^4, \tag{9.112}$$

$$\xi = 1 - (y/y_0), \tag{9.113}$$

whereupon equations (9.103), (9.109), and (9.110) become

$$\frac{d^2\zeta}{d\xi^2} = \frac{2}{\zeta^{\frac{1}{2}}}(1-\xi)\frac{d\zeta}{d\xi},$$
(9.114)

$$\zeta = 0, \qquad \xi = 0, \qquad (9.115)$$

$$\frac{d\zeta}{d\xi} = 0, \qquad \xi = 0.$$
 (9.116)

In order to integrate (9.114) from $\xi = 0$, the second derivative $d^2\zeta/d\xi^2$ at $\xi = 0$ must be known. This cannot be obtained directly from (9.114) because for $\xi = 0$ the right side is indeterminate. By substituting (9.112) and (9.113) in (9.111) and differentiating twice, we obtain

$$d^2\zeta/d\xi^2 = 8, \qquad \xi = 0. \tag{9.117}$$

On carrying out the numerical integration of (9.114) starting with

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conditions (9.115), (9.116), (9.117) at $\xi = 0$, we obtain $\zeta = 2.34$ when $\xi = 1$, i.e. when y = 0. Then it follows from (9.112) and (9.104) that $y = (\xi_1, y) - \xi = 0.81$. (9.118)

$$y_0 = (\zeta_{\xi=1})^{-1} = 0.81. \tag{9.112}$$

Transforming (9.113) and substituting (9.118) we have

$$y = y_0(1-\xi) = 0.81(1-\xi). \tag{9.119}$$



FIG. 9.7. Concentration distributions. Curve I, $D = D_0 C/C_0$; curve II, error function solution (9.121).

Finally it follows from (9.99), (9.102), (9.112), and (9.118) that

$$C/C_0 = c = \nu^{\frac{1}{2}} = \zeta^{\frac{1}{2}} y_0^2 = (\zeta/\zeta_{y=1})^{\frac{1}{2}}.$$
 (9.120)

A graph of C/C_0 against $\frac{1}{2}x/(D_0t)^{\frac{1}{2}}$ is shown as curve I in Fig. 9.7.

In Fig. 9.7 curve II shows the corresponding graph for a constant diffusion coefficient, calculated from

$$C/C_0 = \operatorname{erfc}\{\frac{1}{2}x/(D_0 t)^{\frac{1}{2}}\}.$$
(9.121)

Curve II approaches the abscissa asymptotically whereas curve I reaches the abscissa at the finite value y = 0.81 with a finite slope. Thus, in this special case, an advancing velocity of the diffusing component is strictly definable, and from (9.98) and (9.118) it is given by

$$(dx/dt)_{c=0} = y_0 D_0^{\frac{1}{2}}/t^{\frac{1}{2}} = 2y_0^2 D_0/x = 1.31 D_0/x.$$
(9.122)

Furthermore, (9.114) may be integrated up to $\xi = +\infty$, i.e. $x = -\infty$, when the solution approaches a limiting value ζ_1 , where $\zeta_1 = 6.82$. We

then have the solution of the problem in an infinite medium for the initial conditions C = C

$$y = C_1, \quad x < 0,$$
 (9.123)

[§ 9.3

$$C = C_2, \quad x > 0,$$
 (9.124)



where C_1 and C_2 are both constant, and the diffusion coefficient D is given by $D = D_1 C/C_1$.

where
$$D_1$$
 is the diffusion coefficient when $C = C_1$. Then from equations 9.99), (9.102), (9.112), and (9.113) we find

$$C/C_1 = (\zeta/\zeta_{\xi=\infty})^{\frac{1}{2}} = (\zeta/\zeta_1)^{\frac{1}{2}}.$$
 (9.125)

This concentration ratio can be related to the non-dimensional variable $\frac{1}{2}x/(D_1t)^{\frac{1}{2}}$, which through (9.98) is given by

$$\frac{x}{2(D_1 t)^{\frac{1}{2}}} = y \left(\frac{D_0}{D_1}\right)^{\frac{1}{2}} = y \left(\frac{\zeta_{\xi=1}}{\zeta_{\xi=\infty}}\right)^{\frac{1}{2}} = 0.585\xi, \qquad (9.126)$$

where y is calculated from ξ using (9.119). A graph of C/C_1 as a function of $\frac{1}{2}x/(D_1t)^{\frac{1}{2}}$ is shown in Fig. 9.8. The concentration at x = 0 is $0.59C_1$

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instead of $0.50C_1$ which is the value obtained when the diffusion coefficient is constant.

9.36. Formal solutions

Hiroshi Fujita [7, 8, 9] has obtained formal solutions for diffusion in a semi-infinite medium when the diffusion coefficient depends on concentration in certain ways. As far as is known, these are the only formal A

solutions to have been obtained for concentration-dependent diffusion coefficients. His method is reproduced here in full for one example and his results are quoted for the others.

(i) $D = D_0 / (1 - \lambda C)$

Consider the unidimensional diffusion of a substance in a semi-infinite medium, the surface concentration of diffuser being C_0 . The diffusion equation is then

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right),$$
 (9.127)

where C is the concentration of the diffuser at any point and at any time, D(C) is the diffusion coefficient (assumed to be a function of C only), t is the time, and x is the space coordinate, whose origin is taken to be on the surface of the medium. We deal here with the case in which

$$D(C) = D_0 / (1 - \lambda C), \qquad (9.128)$$

where D_0 is the value of D when C = 0. The initial and boundary conditions are

$$C = 0, \quad x > 0, \quad t = 0,$$
 (9.129)

$$C = C_0, \qquad x = 0, \qquad t > 0.$$
 (9.130)

It is assumed that C_0 is kept constant throughout.

By making the changes of variables,

$$C/C_0 = c, \qquad D(C)/D_0 = K(c), \qquad \frac{1}{2}x/(D_0 t)^{\frac{1}{2}} = y, \qquad (9.131)$$

the partial differential equation (9.127) reduces to an ordinary differential equation in y of the form

$$\frac{d}{dy}\left\{K(c)\frac{dc}{dy}\right\} = -2y\frac{dc}{dy},\qquad(9.132)$$

and the conditions (9,129) and (9.130) become

$$c = 0, \qquad y = \infty, \tag{9.133}$$

$$c = 1, \quad y = 0.$$
 (9.134)

Also,
$$K(c) = 1/(1 - \alpha c)$$
, (9.135)

 $\alpha = \lambda C_0.$

where

(9.136)

(9.137)

As in § 9.33 we introduce the new variable, s, defined by

$$s = \frac{\int\limits_{0}^{c} K(c') dc'}{\int\limits_{0}^{1} K(c) dc},$$

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which gives, on substitution of (9.135),

$$\frac{\ln(1-\alpha c)}{\ln(1-\alpha)} = s. \tag{9.138}$$

With the new variable, s, thus defined, the system of equations for c transforms to $d^{2}c$ $d^{2}c$

$$\frac{d^2s}{dy^2} = -2ye^{-\beta_s}\frac{ds}{dy}, \qquad (9.139)$$

$$s = 0, \qquad y = \infty, \tag{9.140}$$

$$s = 1, \quad y = 0,$$
 (9.141)

where β is connected with α by the relationship

$$\beta = -\ln(1-\alpha). \tag{9.142}$$

In the present analysis, λ and α are assumed to be positive, and $0 < \alpha < 1$. Hence, $\beta > 0$.

The substitutions defined by

$$ds/dy = -\phi, \tag{9.143}$$

$$e^{-\beta s}/\beta = q, \qquad (9.144)$$

transform equation (9.139) to

$$q\frac{d^2\phi}{dq^2} = -\frac{2}{\beta\phi}.$$
(9.145)

This equation can be integrated, giving as a general solution appropriate to the present problem

$$\ln q + b = -\int_{0}^{\phi/q^{2}} \left(a + \frac{1}{4}z^{2} - \frac{4}{\beta}\ln z\right)^{-\frac{1}{2}} dz, \qquad (9.146)$$

where a and b are integration constants, the determination of which proceeds as follows.

First, it is seen from (9.140), (9.143), and (9.144) that $\phi \to 0$ as $q \to 1/\beta$. This condition makes the determination of b possible, and we then have

$$\ln q\beta = -\int_{0}^{\phi/q^{3}} \left(a + \frac{1}{4}z^{2} - \frac{4}{\beta}\ln z\right)^{-\frac{1}{2}} dz. \qquad (9.147)$$

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Next, from (9.141), the following condition is derivable:

$$d\phi/dq = 0, \qquad q = e^{-\beta}/\beta.$$
 (9.148)

Substituting this and the above-mentioned first condition into equation (9.147), it follows after some reduction that

$$a = (4/\beta) \ln \epsilon, \qquad (9.149)$$

where ϵ is a quantity defined by

$$\epsilon = (\phi/q^{\frac{1}{2}})_{q=e^{-\beta}/\beta}.$$
(9.150)

Thus, equation (9.147) is put into the form

$$\ln r = -\int_{0}^{\theta} (\theta_{1}^{2} - \mu \ln \theta_{1}^{2})^{-\frac{1}{2}} d\theta_{1}, \qquad (9.151)$$

with the introduction of the following new variables:

$$r = (q\beta)^{\frac{1}{2}},$$
 (9.152)

$$\theta = \phi/(\epsilon q^{\frac{1}{2}}),$$
 (9.153)

$$\mu = 8/(\beta \epsilon^2). \tag{9.154}$$

The equation used to determine μ and hence the unknown parameter ϵ as a function of the given parameter β is as follows:

$$\beta = 2 \int_{0}^{1} (\theta^{2} - \mu \ln \theta^{2})^{-\frac{1}{2}} d\theta, \qquad (9.155)$$

which is derived from equation (9.151) by inserting the conditions that $\phi/q^4 = \epsilon$ at $q = e^{-\beta}/\beta$. The integral in equation (9.155) appears not to be evaluated in a closed form, so that for practical purposes it is convenient to treat μ as a given parameter.

From equation (9.139) and the subsequent equations, the following expression for y in terms of θ and r is obtained:

$$y = -\frac{1}{(2\mu)^{\frac{1}{2}}} \left(\frac{\theta}{r} + \frac{1}{r^2} \frac{d\theta}{dr} \right).$$
 (9.156)

By eliminating r from this with the aid of equation (9.151) there results

$$y = \frac{1}{(2\mu)^{\frac{1}{2}}} \{ (\theta^2 - \mu \ln \theta^2)^{\frac{1}{2}} - \theta \} \exp \left\{ \int_{0}^{\theta} (\theta_1^2 - \mu \ln \theta_1^2)^{-\frac{1}{2}} d\theta_1 \right\}.$$
(9.157)

On the other hand, by combining equations (9.144), (9.151), and (9.152), the corresponding expression for s is derived, namely

$$s = (2/\beta) \int_{0}^{\theta} (\theta_{1}^{2} - \mu \ln \theta_{1}^{2})^{-\frac{1}{2}} d\theta_{1}. \qquad (9.158)$$

§ 9.3]

Correspondingly, from equation (9.138) a final expression for c is obtained in the form

õ

$$c = \frac{1}{1 - e^{-\beta}} \left[1 - \exp\left\{-2 \int_{0}^{\theta} (\theta_{1}^{2} - \mu \ln \theta_{1}^{2})^{-\frac{1}{2}} d\theta_{1} \right\} \right]. \quad (9.159)$$

Equations (9.157) and (9.159) thus obtained constitute a parametric representation of the required solution c = c(y), or C = C(x, t), of the

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problem under investigation. It should be noted that the parameter μ in these equations is related to the given parameter β according to equation (9.155). In his original paper Fujita [7] shows that his solution reduces to the well-known error-function solution for a constant diffusion



FIG. 9.9. Relationship between the parameters α and μ .

coefficient when $\lambda = \alpha = \beta = 0$. The method of solution for a given μ is therefore as follows:

- 1. Evaluate β by numerical integration of (9.155) and hence find α from (9.142).
- 2. Evaluate y and c by numerical integration of (9.157) and (9.159) respectively.

The relationship between α and $\log_{10}\mu$ expressed by (9.142) and (9.155) is shown graphically in Fig. 9.9, so that if a solution is required for a given α the corresponding value of μ can be obtained immediately. Some solutions evaluated by the method of this section are given in Fig. 12.12.

(ii)
$$D = D_0/(1 - \lambda C)^2$$

[§ 9.3

(9.160)

Here the equation to be solved is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left\{ \frac{D_0}{(1-\lambda C)^2} \frac{\partial C}{\partial x} \right\},$$

subject to the conditions:

$$C = 0, \quad x > 0, \quad t = 0,$$
 (9.161)
 $C = C_0, \quad x = 0, \quad t > 0,$ (9.162)

where the notation used is identical with that in the previous example. Introducing the non-dimensional variables

$$C/C_0 = c, \qquad \frac{1}{2}x/(D_0 t)^{\frac{1}{2}} = y, \qquad C_0 \lambda = \alpha, \qquad (9.163)$$

the partial differential equation (9.160) reduces to an ordinary differential equation in y of the form

$$\frac{d}{dy}\left\{\frac{1}{(1-\alpha c)^2}\frac{dc}{dy}\right\} = -2y\frac{dc}{dy},\qquad(9.164)$$

and the conditions (9.161) and (9.162) are transformed, respectively, to

$$c = 0, \qquad y = \infty, \tag{9.165}$$

$$c = 1, \quad y = 0.$$
 (9.166)

The problem is thus reduced to solving equation (9.164) with the conditions (9.165) and (9.166) to obtain the relationship between c and y.

The results of the mathematical analysis to be found in full in Fujita's paper [8] are summarized as follows:

$$c = \frac{f(\theta, \beta)}{\alpha \{1 - \alpha + f(\theta, \beta)\}},$$
(9.167)

$$y = \frac{\beta}{1-\alpha} [\{1-\alpha+f(\theta,\beta)\}\theta - \exp\{\beta^2(1-\theta^2)\}], \qquad (9.168)$$

where $f(\theta, \beta)$ is given by

$$f(\theta,\beta) = \pi^{\frac{1}{2}}\beta\{1 - \operatorname{erf}(\beta\theta)\}\exp(\beta^{2}), \qquad (9.169)$$

and β is a constant to be determined as a function of the given parameter, α , by the equation $f(1,\beta) = \alpha$ (0.170)

$$f(1,\beta) = \alpha. \tag{9.170}$$

It is assumed that $0 < \alpha < 1$. Equations (9.167) and (9.168) give the required solution c = c(y) with θ as an intermediate parameter, where θ varies in the range $1 \leq \theta < \infty$.

Some solutions evaluated by the method of this section are given in Fig. 12.13.

(iii)
$$D = D_{1}/(1 \pm 2aC \pm bC^{2})$$

 $(-1)^{2} = D_{0}(1 + 2a0 + 00)^{2}$

In the two previous examples the diffusion coefficients have increased continuously with concentration increasing. Fujita [9] has extended his method of solution to include a diffusion coefficient of the form

$$D = \frac{D_0}{1 + 2aC + bC^2},\tag{9.171}$$

where a and b are arbitrary constants. This form (9.171) includes the previous forms (9.128) and that involved in (9.160) as special cases. It

also includes other types of diffusion coefficient which (1) decrease continuously as concentration increases, (2) have a minimum value at some intermediate concentration, (3) have a maximum value at some intermediate concentration. Fujita restricts his analysis to the last of these three, i.e. to diffusion coefficients which increase, pass through a maximum, and finally decrease as concentration is increased.

Retaining the nomenclature of the two previous examples and introducing the dimensionless variables defined by

 $C/C_0 = c,$ $\frac{1}{2}x/(D_0t)^{\frac{1}{2}} = y,$ $aC_0 = \alpha,$ $bC_0^2 = \beta,$ (9.172) the equation to be solved is

$$\frac{d}{dy}\left\{\frac{1}{1+2\alpha c+\beta c^2}\frac{dc}{dy}\right\} = -2y\frac{dc}{dy},\qquad(9.173)$$

subject to the conditions

$$c = 0, \qquad y = \infty, \tag{9.174}$$

$$c = 1, \quad y = 0.$$
 (9.175)

As has been noted, we are concerned only with particular cases in which D passes through a maximum value between C = 0 and $C = C_0$. The condition for this must first be sought. This condition is equivalent to that for which the function, f(c), defined by

$$f(c) = 1 + 2\alpha c + \beta c^2, \qquad (9.176)$$

has a minimum between c = 0 and c = 1. It can easily be shown that such a condition is satisfied by

$$0 < -\alpha/\beta < 1, \tag{9.177}$$

$$\alpha < 0. \tag{9.178}$$

Hence, β must necessarily be positive, i.e.

$$\beta > 0. \tag{9.179}$$

(9.180)

Physically, any maximum of D appearing in the concentration range concerned must remain finite, and this demands that the corresponding minimum of f(c) must be positive. This is fulfilled by the condition

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$0<\alpha^2/\beta<1.$

Equations (9.177), (9.178), (9.179), (9.180) express the conditions required for D to pass through a maximum value. For convenience, writing $\alpha = -\gamma$, the conditions in question are summarized, in terms of the positive quantities of β and γ , as follows:

$$0 < \gamma/\beta < 1,$$
 (9.181)
 $0 < \gamma^2/\beta < 1.$ (9.182)

The final solution is given as follows:

$$\beta c = (\beta - \gamma^2)^{\frac{1}{2}} \tan\{F(\theta, \epsilon) - \tan^{-1}k\} + \gamma, \qquad 0 < c < c_1, \quad (9.183)$$

$$\beta c = (\beta - \gamma^2)^{\frac{1}{2}} \tan\{\tan^{-1}m - F(\theta, \epsilon) + F(\theta_m, \epsilon)\} + \gamma, \qquad c_1 < c < 1,$$

$$(9.184)$$

where

$$\beta c_1 = (\beta - \gamma^2)^{\frac{1}{2}} \tan\{F(1,\epsilon) - \tan^{-1}k\} + \gamma.$$
 (9.185)

Also,

$$y = \left\{\frac{\beta}{\epsilon(\beta - \gamma^2)(1 + z^2)}\right\}^{\frac{1}{2}} \{z\theta + (1 - \theta^2 - \epsilon \ln \theta)^{\frac{1}{2}}\}, \qquad -k < z < z_1,$$
(9.186)

$$y = \left\{ \frac{\beta}{\epsilon(\beta - \gamma^2)(1 + z^2)} \right\}^{\frac{1}{2}} \{ z\theta - (1 - \theta^2 - \epsilon \ln \theta)^{\frac{1}{2}} \}, \qquad z_1 < z < m, \quad (9.187)$$

where

$$\tan^{-1}z_1 = F(1,\epsilon) - \tan^{-1}k,$$
 (9.188)

$$\tan^{-1}z = F(\theta, \epsilon) - \tan^{-1}k, \quad -k < z < z_1,$$
 (9.189)

and
$$\tan^{-1}z = \tan^{-1}m - F(\theta, \epsilon) + F(\theta_m, \epsilon), \quad z_1 < z < m.$$
 (9.190)

The auxiliary variables in these equations are evaluated as follows. First, $\theta = (-1)$

$$k = \frac{\gamma}{(\beta - \gamma^2)^{\frac{1}{2}}}, \qquad m = \frac{\beta}{(\beta - \gamma^2)^{\frac{1}{2}}} \left(1 - \frac{\gamma}{\beta}\right), \qquad (9.191)$$

where $\gamma = -\alpha$ and β are the constants in the diffusion coefficientconcentration relationship. Furthermore, ϵ and θ_m are related to k and m by the expressions

$$\epsilon \ln \theta_m + (m^2 + 1)\theta_m^2 = 1,$$
 (9.192)

and

$$\tan^{-1}k + \tan^{-1}m = 2F(1,\epsilon) - F(\theta_m,\epsilon), \qquad (9.193)$$

where

$$F(\theta,\epsilon) = \int_{0}^{\theta} (1-\theta_{1}^{2}-\epsilon\ln\theta_{1})^{-\frac{1}{2}} d\theta_{1}. \qquad (9.194)$$

In evaluating (9.183) and (9.184) as functions of θ , it should be noted that in (9.183) θ can vary between 0 and 1, but in (9.184) it is restricted

to the range $\theta_m < \theta < 1$. As an example of the use of this method, consider a diffusion coefficient for which $\alpha = -\gamma = -1.646$, $\beta = 2.877$. Fig. 9.10 shows this coefficient as a function of c. The value of D/D_0 is 1.710 when c = 1, and D/D_0 has a maximum value of 17.20 when c = 0.572. The values of k and m calculated from (9.191) are k = 4.025, m = 3.010. Fig. 9.11 shows graphs of ϵ against θ_m calculated from (9.192) and (9.193) respectively, the point of intersection giving the solution of these equations, i.e.







FIG. 9.11. Auxiliary graphs to find the roots of (9.192) and (9.193).



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FIG. 9.12. Concentration distribution for diffusion coefficient shown in Fig. 9.10.

9.4. Hopkins's method of successive approximations

Hopkins [10] showed that a problem of heat flow in a medium of variable thermal properties can be related to the corresponding problem in a medium of constant properties in which heat is generated at a certain rate. He used the known solution of the problem for constant thermal properties to obtain a first estimate of the heat generation term, and so obtained a second approximation. By repeating this process, successively better approximations can be obtained in theory, but in practice the algebra is usually cumbersome after two steps. The general method in terms of diffusion nomenclature is as follows.

Consider a region V of the medium, extending to infinity or confined by given boundaries. The general diffusion equation assuming the medium to be isotropic is

medium to be isotropic is

$$\frac{\partial c}{\partial t} = \operatorname{div}(D\operatorname{grad} c). \tag{9.195}$$

Let C(x, y, z, t) be the solution of the problem obtained by assuming that D has a constant value D_0 , when (9.195) reduces to

$$\frac{\partial C}{\partial t} = D_0 \operatorname{div} \operatorname{grad} C.$$
 (9.196)

The solution, C, is, of course, one of the well-known solutions worked out in Chapters III-VI.

Let us write

$$D = D_0 \{1 + \mu F(c)\}. \tag{9.197}$$

Then (9.195) can be written

$$\frac{\partial c}{\partial t} - \operatorname{div}\{D_0 \operatorname{grad} c\} = \mu D_0 \operatorname{div}\{F(c) \operatorname{grad} c\}.$$
(9.198)

If we denote the right-hand side by $\mu G(x, y, z, t)$ we see that (9.198) is the equation for diffusion in a medium having a diffusion coefficient D_0 and to which diffusing substance is being supplied at the rate μG per unit volume. The rate of supply to any element of volume is a function of its position and of time. If we denote by $g(x, y, z, x', y', z', t-\tau)$ the concentration at coordinates x, y, z and time t due to the introduction of unit amount of diffusing substance at x', y', z' and τ into the medium whose diffusion coefficient is D_0 , the boundaries being kept at zero, then the solution of the original problem is

$$c = C + \mu \int_{v} \int_{0}^{t} g \cdot G(x', y', z', \tau) \, dx' dy' dz' d\tau. \qquad (9.199)$$

The function g is known as the Green's function and is to be found for standard boundary conditions in textbooks on heat flow [11, p. 291]. Regarding the term in μ as a correction term we evaluate it approximately by writing the known function C instead of c in G.

Clearly, if this process is repeated we shall have a term involving μ^2 and the solution can be thought of as a power series in μ . In a few simple cases the equations determining the coefficients of the powers of μ can be solved directly without the aid of a Green's function. Examples are given in Hopkins's original paper. The method is of very limited application because the algebra is exceedingly tedious even if two steps in the approximation process suffice.

9.5. Linear form of the diffusion equation

Storm [12] has transformed the non-linear diffusion equation (9.5) into a linear equation by a number of successive changes of variable. The conditions under which the transformation is effective are, (1) that the rate of transfer of diffusing substance, F, across the surface x = 0 is known as a function of time; (2) that the diffusion coefficient is given by

$$1/D^{\frac{1}{2}} = A(C - C_0) + 1/D^{\frac{1}{2}}, \qquad (9.200)$$

where A is a constant, and D_0 is the value of D when the concentration C
has the value C_0 . On writing $A = a/D_0^{\dagger}$ with a another constant, (9.200) becomes

$$1/D^{\frac{1}{2}} = (1/D_0^{\frac{1}{2}})\{1 + a(C - C_0)\}, \qquad (9.201)$$

and for small variations in D this can be regarded as an approximation to $D = D_0 e^{-2\alpha(C_0-C)}$. (9.202)

The linear form of the diffusion equation obtained by Storm [12] is

$$\frac{\partial^2 \zeta}{\partial X^2} = \frac{\partial \zeta}{\partial t} + AF \frac{\partial \zeta}{\partial X}, \qquad (9.203)$$

where A and F have already been defined and where

$$X = \int_{0}^{x} (1/D^{\frac{1}{2}}) \, dx', \qquad (9.204)$$

and

$$\log \zeta = -AQ^*, \tag{9.205}$$

where

$$Q^*\{X(x,t),t\} = Q(x,t), \qquad (9.206)$$

and Q(x,t) is given by

$$Q = \int_{C_0}^{C} \{D(C')\}^{\frac{1}{2}} dC', \qquad (9.207)$$

with C_0 an arbitrary reference concentration. Storm uses this method to handle the problem of diffusion into a semi-infinite medium when there is a constant rate of transfer across the surface x = 0.

9.6. Method of moments. Plane sheet

Fujita has made use of a method developed by Yamada [13] for obtaining approximate solutions of non-linear differential equations. A brief account of this method, and of its application to a diffusion problem in which the diffusion coefficient depends linearly on concentration, has been published [14]. Professor Fujita has very kindly supplied an English translation of another paper of his, written in Japanese, dealing with the general case of a concentration-dependent diffusion coefficient. The account that follows is based on his translation.

The method is illustrated by the problem of diffusion into a plane sheet

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of thickness 2l, when each surface is maintained at a constant concentration, C_0 , and the sheet is initially at zero concentration throughout. If therefore we take non-dimensional variables

 $C/C_0 = c$, x/l = X, $D_0 t/l^2 = T$, $D(C)/D_0 = F(c)$, (9.208) where $D = D_0$ when $C = C_0$, the problem is defined by the equations

$$\frac{\partial c}{\partial T} = \frac{\partial}{\partial X} \left\{ F(c) \frac{\partial c}{\partial X} \right\},\tag{9.209}$$

$$c = 0, \quad 0 < X < 1, \quad T = 0,$$
 (9.210)

$$c = 1, \quad X = 1, \quad T > 0,$$
 (9.211)

$$\partial c/\partial X = 0, \qquad X = 0, \qquad T > 0.$$
 (9.212)

Yamada's [13] method consists in replacing the original differential equation by a set of moment equations. Fujita uses the zero and first moments only and the problem is reduced to that of finding c(X, T) satisfying the two moment equations derived from (9.209), which are

$$\int_{0}^{1} \left[\frac{\partial c}{\partial T} - \frac{\partial}{\partial X} \left\{ F(c) \frac{\partial c}{\partial X} \right\} \right] dX = 0, \qquad (9.213)$$

and

$$\int_{0}^{1} \left[\frac{\partial c}{\partial T} - \frac{\partial}{\partial X} \left\{ F(c) \frac{\partial c}{\partial X} \right\} \right] X \, dX = 0, \qquad (9.214)$$

together with the conditions (9.210) to (9.212). We proceed by considering that in the early stages of diffusion the concentration-distance curve may be represented approximately by a curved portion near the surface of the sheet, followed by a horizontal part coinciding with the x-axis as in Fig. 9.13. Strictly, according to the diffusion equation, the concentration becomes finite, though it may be small, everywhere in the sheet at the instant diffusion commences. The region over which the concentration may be assumed zero depends, of course, on the accuracy of working. For a prescribed accuracy, we denote by x_0 the point at which the concentration becomes zero as in Fig. 9.13, and clearly x_0 is a function of time. Thus $x_0 = l$ when t = 0 and $x_0 = 0$ when $t = t_1$, say. The time, t_1 , is that at which the concentration first becomes finite at the centre of the sheet to the prescribed accuracy of working. Denoting by X_0 the value of X corresponding to x_0 , i.e. $X_0 = x_0/l$, we assume that in the region $X_0 \leq X \leq l$ the concentration is given by a cubic expression of the form

$$c(X,T) = B(T)\{X - X_0(T)\}^2 + E(T)\{X - X_0(T)\}^3, \quad (9.215)$$

where B(T), E(T), and $X_0(T)$ are functions of T to be determined. We

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have furthermorec = 0, $0 \leq X \leq X_0$.(9.216)The condition (9.212) is satisfied by (9.215). Also (9.210) may be writtenas $X_0 = 1$, T = 0.(9.217)Introducing (9.211) into (9.215) and putting

$$B(1-X_0)^2 = U, \qquad E(1-X_0)^3 = V, \qquad (9.218)$$

we obtain the relation between U and V,

$$U+V = 1.$$
(9.219)

FIG. 9.13. Concentration distribution in the early stage of diffusion into a plane sheet.

Inserting (9.215) and (9.216) into (9.213), integrating, and using (9.211) we obtain

$$\frac{d}{dT}\{(1-X_0)(\frac{1}{3}U+\frac{1}{4}V)\} = \frac{(2U+3V)}{1-X_0}F(1). \tag{9.220}$$

which, on eliminating V by equation (9.219), becomes

$$\frac{d}{dT}\left\{(1-X_0)(1+\frac{1}{3}U)\right\} = \frac{12}{1-X_0}(1-\frac{1}{3}U)F(1). \quad (9.221)$$

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Similarly from the first-moment equation (9.214) we find

$$\frac{d}{dT}\left\{(1-X_0)^2(1+\frac{2}{3}U)\right\} = 20G(1), \qquad (9.222)$$

where

$$G(c) = \int_{0}^{c} F(c') dc'. \qquad (9.223)$$

Here F(1) and G(1) denote the values of F and G when c = 1. On integrating, (9.222) becomes

$$(U+\frac{3}{2})\xi^2 = \alpha T, \tag{9.224}$$

where $\alpha = 30G(1), \quad \xi = 1 - X_0,$ (9.225)

and the integration constant has been determined by (9.217). Inserting (9.224) into (9.221) we find

$$\frac{d}{dT}\left(\frac{1}{2}\xi + \frac{\alpha T}{3\xi}\right) = \frac{12}{\xi}\left(\frac{3}{2} - \frac{\alpha T}{3\xi^2}\right)F(1).$$
(9.226)

The solution of (9.226) which satisfies the condition $\xi = 0$, T = 0, in accordance with (9.225) and (9.217), is

$$\xi = \sqrt{(T/\beta)},\tag{9.227}$$

where β is a constant determined from the quadratic equation

$$24\alpha\beta^2 F(1) + \{\alpha - 108F(1)\}\beta + \frac{3}{2} = 0.$$
 (9.228)

Clearly for (9.227) to have a physical meaning β must be positive. The question as to which of the two possible roots of (9.228) should be taken. if both are positive is decided in Fujita's treatment by considering the special case of a constant diffusion coefficient. When the solution (9.233) below, derived by the method of moments, is evaluated for a constant diffusion coefficient it is found that better agreement with the formal solution is obtained by taking the larger of the two roots (actually $\beta = \frac{1}{12}$ of (9.228). When the diffusion coefficient is concentration-dependent we take that root of (9.228) which tends to the value $\frac{1}{12}$ as the range in the diffusion coefficient is decreased and we approach a constant coefficient. Denoting by T_1 the time at which $X_0 = 0$, i.e. at time T_1 the advancing front of the diffusion reaches the centre of the sheet, we have $\xi = 1, T = T_1$ and hence from (9.227) $\beta = T_1.$ (9.229)Inserting (9.227) into (9.224) yields $U=\alpha\beta-\frac{3}{2},$ (9.230) $V = -\alpha\beta + \frac{1}{2}.$ and then (9.231)

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Thus both U and V are found to be constants. The expression for X_0 is

$$X_0 = 1 - \sqrt{(T/\beta)}.$$
 (9.232)

Substituting these equations into (9.215) and remembering (9.218) we find

$$c(X,T) = (\alpha\beta - \frac{3}{2})\{X - 1 + \sqrt{(T/\beta)}\}^{2}(\beta/T) - (\alpha\beta - \frac{5}{2})\{X - 1 + \sqrt{(T/\beta)}\}^{3}(\beta/T)^{\frac{3}{2}},$$
$$1 - \sqrt{(T/\beta)} \leq X \leq 1, \qquad (9.233)$$

and

$$c(X,T) = 0, \qquad 0 \leq X \leq 1 - \sqrt{(T/\beta)}.$$
 (9.234)

From (9.233) we readily obtain an expression for the concentration distribution when the concentration just ceases to be zero at the centre of the sheet. It is

$$c(X,T) = (\alpha \beta + \frac{3}{2})X^2 - (\alpha \beta - \frac{5}{2})X^3, \quad 0 \leq X \leq 1.$$
 (9.235)

The next step is to derive an approximate solution which holds for later times when the concentration at the centre of the sheet has become appreciable, according to the accuracy of working. Such a solution must satisfy (9.212) and (9.210), and must also agree with (9.235) when $T = T_1$. We therefore assume a cubic equation again of the form

$$c(X,T) = A_1(T) + X^2 B_1(T) + X^3 E_1(T), \qquad 0 \le X \le 1, \quad (9.236)$$

where $A_1(T)$, $B_1(T)$, $E_1(T)$ are functions of T to be determined. They are of course different from the corresponding functions in (9.215). We see immediately that $A_1(T)$ in (9.236) is the concentration at the centre of the sheet. Proceeding as before, by inserting (9.211) in (9.236) we obtain $A_1 + B_1 + E_1 = 1.$ (9.237)

$$\frac{d}{dT}(A_1 + \frac{1}{3}B_1 + \frac{1}{4}E_1) = (2B_1 + 3E_1)F(1), \qquad (9.238)$$

$$\frac{d}{dT}(\frac{1}{2}A_1 + \frac{1}{12}B_1 + \frac{1}{20}E_1) = G(1) - G(A_1).$$
(9.239)

Eliminating E_1 by using (9.237) and putting^{*}

 $dA_1/dT = \phi, \qquad (9.240)$

we have

$$\begin{array}{ll} \frac{3}{4}\phi + \frac{1}{12}\phi \frac{dB_1}{dA_1} = (3 - B_1 - 3A_1)F(1), & (9.241) \\ \\ \frac{9}{20}\phi + \frac{1}{30}\phi \frac{dB_1}{dA_1} = G(1) - G(A_1). & (9.242) \end{array}$$

We can eliminate B_1 from these two equations, remembering that $dG/dA_1 = F$, and obtain

$$-\frac{d\phi}{dA_1} = 28F(1) + \frac{20}{3}F(A_1) + \frac{80}{\phi} \{G(A_1) - G(1)\}F(1). \quad (9.243)$$

This can be simplified to the form

$$\psi \frac{d\psi}{d\phi} = \frac{49}{5} \{ \psi r(f) - q(f) \}, \qquad (9.244)$$

by introducing the following variables

$$f = 1 - A,$$
 (9.245)

$$\psi = 7\phi/\{20F(1)\},\tag{9.246}$$

$$r(f) = 1 + \frac{5}{21} \frac{F(A_1)}{F(1)}, \qquad (9.247)$$

$$q(f) = \int_{0}^{f} \frac{F(A_1)}{F(1)} \, df'. \tag{9.248}$$

In order that the solution (9.236) should reduce to (9.235) when $T = T_1$, over the whole range of X, we must have

$$A_1(T_1) = 0, (9.249)$$

$$B_1(T_1) = \alpha \beta - \frac{3}{2}, \qquad (9.250)$$

$$E_1(T_1) = -\alpha \beta + \frac{5}{2}. \tag{9.251}$$

Eliminating the term $\phi dB_1/dA_1$ from (9.241) and (9.242) we obtain, in terms of the new variables just introduced,

$$B_1 = \frac{15}{14}\psi(f) + 3f - \frac{5}{2}q(f). \tag{9.252}$$

From (9.245), (9.249), and (9.250) it follows that $B_1 = \alpha \beta - \frac{3}{2}$ when f = 1, and so from (9.252) we have

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 $\psi(1) = \frac{14}{15} \{ \alpha \beta - \frac{9}{2} + \frac{5}{2}q(1) \}.$ (9.253)

For any given concentration-dependent diffusion coefficient the quantities r(f) and q(f) can be evaluated from (9.247) and (9.248), the relevant range of f being $0 \leq f \leq 1$ since f = 1 corresponds to $T = T_1$ and f = 0 to $T = \infty$. Thus (9.253) gives the initial condition to be satisfied by the solution of the differential equation (9.244). In general, numerical integration of (9.244) will be necessary. When the solution of (9.244) is known, $\phi(A_1)$ follows from (9.246). Also by integrating (9.240) and using the condition $A_1 = 0$, $T = T_1$ we obtain

$$T = T_1 + \int_0^{A_1} \frac{dA_1'}{\phi(A_1')}, \qquad (9.254)$$

which can be evaluated once $\phi(A_1)$ has been obtained from (9.246). Since from (9.236) A_1 represents the concentration at the centre of the sheet, from (9.254) we can calculate how this concentration varies with time. Once the relationship between A_1 and T, and hence between f and T is known, B_1 is easily determined as a function of T from (9.252) using (9.246). Finally, knowing $A_1(T)$ and $B_1(T)$, $E_1(T)$ is obtained from (9.237), and hence all functions of T on the right-hand side of (9.236) are known.

The total amount of diffusing substance, M_t , taken up by the sheet per unit area at time, t, is given by

$$M_{t} = 2 \int_{0}^{t} C(x,t) dx, \qquad (9.255)$$

which in terms of the non-dimensional variables becomes

$$M_t = 2lC_0 \int_0^1 c(X, T) \, dX. \tag{9.256}$$

For early times, when the concentration at the centre of the sheet is effectively zero, i.e. $T < T_1$, c is given by (9.233) and (9.234), and so we have

$$M_{t} = 2lC_{0} \left(\frac{1}{8\beta^{\frac{1}{2}}} + \frac{\alpha\beta^{\frac{1}{2}}}{12} \right) T^{\frac{1}{2}}, \qquad 0 < T < T_{1}.$$
(9.257)

For later times we find

$$M_{t} = 2lC_{0}\{1 - \frac{2}{3}B_{1}(T) - \frac{3}{4}E_{1}(T)\}.$$
(9.258)

We note from (9.257) that, in the early stages, M_i is proportional to the square root of time, irrespectively of how the diffusion coefficient depends on concentration. We shall see later, in § 12.6, that this is a characteristic feature of concentration-dependent diffusion.

9.61. Semi-infinite medium

Clearly the solution developed for the early stages of diffusion into a plane sheet describes diffusion in a semi-infinite medium. It is convenient to write it in terms of the original space variable x measured

FINITE-DIFFERENCE METHODS

10.1. Introduction

A NUMBER of methods have been devised whereby numerical solutions of the diffusion equation are obtained by replacing some or all of the derivatives by finite-difference approximations. Some of these methods will be described in terms of the problem of one-dimensional diffusion in a plane sheet in which the concentration is initially zero and whose surfaces are maintained at constant concentration. The diffusion coefficient will be assumed constant for the preliminary description. Afterwards, corresponding formulae will be given for the cylinder and the sphere and for alternative boundary conditions. An example will then be discussed in some detail, in order to illustrate the treatment of a concentration-dependent diffusion coefficient. Finally, ways of starting a finite-difference solution from t = 0 when a singularity exists in the solution there, are discussed, and the accuracy and convergence of the solutions are considered.

10.2. Non-dimensional variables

A worth-while preliminary step in all numerical methods of the kind about to be considered is to introduce non-dimensional variables of length, time, concentration, etc. For diffusion in a plane sheet when the diffusion coefficient, D, is constant, convenient variables are

$$X = x/l, \qquad T = Dt/l^2, \qquad c = C/C_0,$$
 (10.1)

where l is the half-thickness of the sheet and where C_0 is some standard concentration. If the concentration at the surface of the sheet is constant it is usually taken as the standard. The advantages are that numbers occurring in the computation cover roughly the same ranges for all calculations, e.g. the variable X lies between 0 and 2 whatever the thickness of the sheet in cm. Also the basic independent parameters of

the problem are isolated and it is often possible to deduce many solutions in ordinary dimensions from one non-dimensional solution, simply by inserting values for the appropriate physical properties. The labour of repeating the whole process of numerical solution is thus avoided. In terms of the variables of (10.1), the problem we are using as an example becomes $\frac{\partial}{\partial t}$

$$\frac{\partial c}{\partial T} = \frac{\partial^2 c}{\partial X^2},$$

n h

(10.2)

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$$c = 1, \qquad X = \pm 1, \qquad T > 0,$$
 (10.3)

$$c = 0, \quad -1 < X < 1, \quad T = 0,$$
 (10.4)

the central plane of the sheet being taken as X = 0.

10.3 Finite-difference approximations

Let the range in X be divided into a number of equal intervals δX , and the time into intervals δT . We denote by c_{m-1} , c_m , c_{m+1} the concentrations at the points $(m-1)\delta X$, $m\delta X$, $(m+1)\delta X$ respectively at time $T = n\delta T$, and by c_m^+ , c_m^- the corresponding values at $X = m\delta X$ at times $(n+1)\delta T$ and $(n-1)\delta T$ respectively. Then using Taylor's expansion theorem we obtain

$$c_{m+1} = c_m + \delta X \left(\frac{\partial c}{\partial X} \right)_m + \frac{1}{2} (\delta X)^2 \left(\frac{\partial^2 c}{\partial X^2} \right)_m + \dots,$$
(10.5)

$$c_{m-1} = c_m - \delta X \left(\frac{\partial c}{\partial \overline{X}} \right)_m + \frac{1}{2} (\delta X)^2 \left(\frac{\partial^2 c}{\partial \overline{X}^2} \right)_m - \dots, \qquad (10.6)$$

so that an approximation to $\partial^2 c/\partial X^2$ at the point $m \, \delta X$ and time T, neglecting second-order terms in $(\delta X)^2$ is

$$\left(\frac{\partial^2 c}{\partial X^2}\right)_m = \frac{(c_{m+1} - 2c_m + c_{m-1})}{(\delta X)^2}.$$
(10.7)

Corresponding approximations for $\partial c/\partial T$ are

$$\left(\frac{\partial c}{\partial T}\right)_m = \frac{c_m^+ - c_m}{\delta T},\qquad(10.8)$$

for which the leading term in the error is $\frac{1}{2}(\delta T)(\partial^2 c/\partial T^2)_m$, or

$$\left(\frac{\partial c}{\partial T}\right)_m = \frac{c_m^+ - c_m^-}{\delta T},\qquad(10.9)$$

which is more accurate since it only neglects $\frac{1}{6}(\delta T)^2(\partial^3 c/\partial T^3)_m$ and higher terms. In (10.9) the finite-difference ratio is an approximation to the derivative at the mid-point of the interval $(n-1)\delta T$ to $(n+1)\delta T$, whereas in (10.8) the approximation relates to the derivative at the beginning of the interval over which the difference is taken. In the

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methods to be described the approximations (10.7), (10.8), (10.9) are used in different ways.

10.4. Schmidt method

A method usually attributed to Schmidt [1] has been widely used for the solution of heat-flow problems. Recently Jakob [2] stated that the method was used earlier by Binder [3]. It is described in textbooks on heat transfer [4, p. 39]. Schmidt replaces the right-hand side of (10.2) by the approximation (10.7) and the left-hand side by the approximation (10.8) and so obtains



FIG. 10.1. Schmidt's graphical method.

If we put in the value

$$\delta T/(\delta X)^2 = D \, \delta t/(\delta x)^2 = \frac{1}{2},$$
 (10.11)

(10.10) reduces to

$$c_m^+ = \frac{1}{2}(c_{m+1} + c_{m-1}). \tag{10.12}$$

This result means that the concentration at the point X at time $T + \delta T$ is the arithmetic mean of the concentrations at the neighbouring points $X \pm \delta X$ at time T. Thus if the concentration is plotted against the distance through the sheet at time T, the value of the concentration at time $T + \delta T$ at the point X is given according to (10.12) by the point at which the line joining c_{m+1} and c_{m-1} meets the ordinate at X. This leads to the graphical method of solution originally suggested by Schmidtand which is illustrated in Fig. 10.1. Alternatively the arithmetic mean can be found numerically and its value entered in a table which is progressively extended as suggested by McAdams [4, p. 41]. The table is drawn up with a row for each step in T and a column for each step in X. A section of such a table is shown for half the sheet in Table 10.1. Here

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half the sheet is divided into eight layers and the first row of values is obtained from the formal solution

$$c = 1 - \operatorname{erf}\{(1 - X)/2T^{\frac{1}{2}}\}, \qquad (10.13)$$

which holds as long as the concentration at X = 0 is zero to the accuracy of working. The second row is obtained by applying (10.12) successively to each point of the first row, and so on for succeeding rows. On the surface, X = 1, c = 1 at all times. Furthermore, since there is symmetry about the central plane of the sheet, X = 0, (10.12) becomes

$$c_0^+ = c_1, \tag{10.14}$$

and (10.14) is to be used instead of (10.12) to obtain c_0^+ , the concentration at the centre of the sheet. The figures in brackets in the final row of Table 10.1 are calculated for T = 29/256 from the formal solution given in equation (4.17), and indicate the accuracy of the Schmidt method in this case.

Equation (10.10) can of course be used with values other than

$$\delta T/(\delta X)^2 = \frac{1}{2}.$$

Dusinberre [5, p. 114], for example, points out that $\delta T/(\delta X)^2 = \frac{1}{3}$ leads to

$$c_m^+ = \frac{1}{3}(c_{m+1} + c_m + c_{m-1}), \qquad (10.15)$$

which is almost as convenient as (10.12) and gives values at slightly smaller intervals in time.

Jaeger [6] has shown that the Schmidt method is a satisfactory one in that it is not subject to any cumulative error, and it yields an accuracy which is adequate for many practical purposes. It has the great advantage of simplicity. Nevertheless, the approximations leading to (10.12)can easily be improved upon.

10.5. Crank-Nicolson method

In this method [7] finite-difference approximations are made to both derivatives at the time $T + \frac{1}{2}\delta T$ for the interval T to $T + \delta T$. Thus $\partial c/\partial T$ is given by a formula of the type (10.9) applied to a single step, i.e.

$$\left(\frac{\partial c}{\partial T}\right)_{m} = \frac{c_{m}^{+} - c_{m}}{\delta T} \quad \text{at } T + \frac{1}{2}\delta T, \qquad (10.16)$$

and $\partial^2 c / \partial X^2$ by the mean of (10.7) and the corresponding result at $T + \delta T$. This leads to the equation

$$c_{m}^{+} = c_{m}^{+} + \frac{\delta T}{2(\delta X)^{2}} \{ (c_{m+1}^{+} + c_{m+1}) - 2(c_{m}^{+} + c_{m}) + (c_{m-1}^{+} + c_{m-1}) \}.$$
(10.17)

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If $\delta T/(\delta X)^2 = 1$, (10.17) takes the particularly simple form

$$c_m^+ = \frac{1}{4} (c_{m+1}^+ + c_{m+1}^+ + c_{m-1}^+ + c_{m-1}).$$
(10.18)

There is one equation of this type for each point in the sheet, i.e. each value of m. For the centre of the sheet, m = 0, because of symmetry (10.17) reduces to

$$c_0^+ = c_0 + \frac{\delta T}{(\delta X)^2} \{ (c_1^+ + c_1) - (c_0^+ + c_0) \}.$$
 (10.19)

In this method the values of c at $T + \delta T$ are not determined by the repeated application of a single equation as in the Schmidt method but by the solution of a set of simultaneous equations of the type (10.17). Thus if the half-sheet is divided into eight layers so that $0 \leq m \leq 8$, then there are six equations obtained by putting m = 1, 2, ..., 7 in (10.17). These six, together with (10.18) for m = 0 and the given boundary condition on the surface of the sheet, m = 8 (in this example $c_8 = 1$ for all T), suffice to determine values of c_m^+ for all m, i.e. concentrations can be evaluated at $T + \delta T$ if the corresponding values c_m at T are already known. The fact that the equations are simultaneous leads to an iterative method of solution applied at successive times so that the solution proceeds in steps δT . Table 10.2 shows a section of the scheme of computation adopted. A table is drawn up with a row for each step in Tand a column for each step in X and values of c are recorded. In this case eight steps are taken in X. Leaving till later the question of starting the integration from T = 0 and assuming the solution has been taken as far as the nth step in time, i.e. $T = n \delta T$, the following operations are performed successively in order to evaluate the (n+1)th step.

- (i) Estimate values of $c_0^+, c_1^+, ..., c_7^+$ by inspection of previous differences in each column. By the boundary condition we have $c_8 = 1$.
- (ii) Evaluate c_7 by substituting known and estimated values in the right-hand side of (10.18) since we are using $\delta T/(\delta X)^2 = 1$ in this example. If the general equation (10.17) is used, i.e. $\delta T/(\delta X)^2 \neq 1$,

then this is best written as

$$c_m^+ \left(1 + \frac{\delta T}{(\delta X)^2} \right) = c_m \left(1 - \frac{\delta T}{(\delta X)^2} \right) + \frac{\delta T}{(\delta X)^2} (c_{m+1}^+ + c_{m+1}^+ + c_{m-1}^+),$$
(10.20)

from which c_m^+ is directly calculable. (iii) Evaluate $c_6^+, c_5^+, ..., c_0^+$ by solving the appropriate equations (10.18) or (10.20), remembering that an alteration in c_m^+ may necessitate resolving the equations for c_{m-1}^+ and c_{m+1}^+ . (iv) Repeat for successive steps δT .

The iteration of a whole line may appear prohibitive but in practice the method has proved very easy to carry out. If $\delta T/(\delta X)^2 = 1$ is used, it is clear from (10.18) that a change of 4 in c_m^+ produces a change of 1 in c_{m-1}^+ which affects c_m^+ itself by only one-quarter and these adjustments are quickly made without solving the whole equation again. In terms of Southwell's relaxation terminology [8] we have a relaxation pattern 1, --4, 1. It is also clear that the process of adjusting successive values converges more rapidly the smaller $\delta T/(\delta X)^2$ is. The values after five steps in Table (10.2) are compared with values from the solution (4.17) to indicate the accuracy obtained.

10.6. Relaxation methods

Southwell's relaxation methods for the solution of certain types of differential equations have been adequately described elsewhere [8, 9]. The relaxation method is a process of steadily improved approximation for the solution of simultaneous algebraic equations, and any problem that can be formulated in terms of simultaneous equations can, theoretically, be solved by this method. It has been widely applied to obtain solutions in two dimensions of various second-order partial differential equations. A typical example is Laplace's equation of which solutions are required to satisfy a single boundary condition at all points of a closed boundary. Steady-state diffusion for a constant diffusion coefficient is described by the Laplace equation

$$\frac{\partial^2 c}{\partial X^2} + \frac{\partial^2 c}{\partial Y^2} + \frac{\partial^2 c}{\partial Z^2} = 0, \qquad (10.21)$$

and solutions are obtainable for given boundary conditions by a direct application of relaxation methods [10]. The application of relaxation techniques to non-steady diffusion problems is, however, more recent. The basic difficulty lies in the difference between what Richardson [11] calls 'jury' and 'marching' problems. Diffusion in one dimension is an

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example of a marching problem. Here the initial concentration distribution is given at zero time and the solution can proceed step-by-step as we have seen, there being no prescribed condition to be satisfied at some later time. In other words there is an 'open' boundary in time on which conditions are not specified but are determined by the solution. Relaxation techniques on the other hand were devised to deal with jury problems, in which the solution must satisfy conditions at both ends of the range of integration, just as the verdict has to satisfy all the jurymen together. In order to apply relaxation techniques to a diffusion problem, therefore, it must first be transformed into one of the jury type. Two ways of doing this have been suggested.

10.61. The steady-state solution as a boundary condition

Continuing to think of the example of diffusion into a plane sheet with constant surface concentrations, we know that after a sufficiently long time the solution approaches a steady state which in this case is one of uniform concentration. This steady-state solution can be taken as a condition to be satisfied by the non-steady state solution at large times, and as such it provides the missing condition necessary to turn the diffusion problem into one of the 'jury' type. This is the approach suggested by Gilmour [12].

Taking intervals δX and δT as before, and using the approximations (10.7) and (10.9) to the derivatives at the point $m \delta X$ at time T, we obtain for the finite difference form of (10.2), if $\delta T/(\delta X)^2 = 1$,

$$\frac{1}{2}(c_m^+ - c_m^-) = c_{m+1} - 2c_m + c_{m-1}, \qquad (10.22)$$

i.e.

(10.23) $-c_m^+ + 2c_{m+1} + c_m^- + 2c_{m-1} - 4c_m = 0.$

Putting $R_m = -c_m^+ + 2c_{m+1} + c_m^- + 2c_{m-1} - 4c_m$, then R_m is called the residual at the point m, and such a residual exists for each point of the network comprised of rectangles of sides δX , δT as in Fig. 10.2. After substituting initial trial values of the c's at each point of the network, the corresponding residuals are evaluated and the relaxation process consists in the systematic reduction of these residuals. When they are zero, or as near zero as possible to the accuracy of working, the process is complete. Clearly if we alter the value of c_m by +1, R_m is altered by -4 and the residuals at the surrounding points by 1, +2, -1, +2respectively. This is what is known as the relaxation pattern and it is by repeated and judicious application of this pattern at all points of the network that the residuals are reduced and the final solution obtained. Accounts of relaxation methods [8, 9] describe specialized techniques by which this reduction is accomplished most easily and quickly.

Although we are free to start from any set of estimated values of the c's at the points of the network, the nearer these are to the correct values the less the computation involved. Thus in the example under consideration the steady-state values are c = 1 everywhere. In other problems the steady-state solution is obtained by equating the time derivative to zero. The relaxation process may then be carried out as follows. Insert the initial and boundary values, i.e. c = 0, T = 0, $0 < X < 1; c = 1, X = \pm 1$, at points of the network on the boundaries, and at every other point insert the steady-state values (in this example c = 1). The residuals will be zero except for the first row. If these points are relaxed the residuals will spread and the process is carried on until residuals everywhere are so small that no more relaxation is possible.



FIG. 10.2. Rectangular grid.

In practice, however, the labour can usually be considerably reduced by estimating at what time the steady-state is reached to within the accuracy of working. Between this estimated time and T = 0 intermediate values of c are inserted from which to start the relaxation process.

In many problems there is little to choose between this relaxation method and one of the forward integration methods described earlier (§§ 10.4, 10.5), if the solution is to be carried as far as the steady state. If, however, the solution is required only for a limited period of time, forward integration is likely to be quicker. Furthermore, the ease and speed with which a relaxation process can be carried out depend very much on there being a simple relaxation pattern which can be applied over the whole region. If the diffusion coefficient is not constant, however, the relaxation pattern changes from point to point in the network. This is particularly troublesome in dealing with concentration-dependent diffusion because the relaxation pattern then depends on the values of concentration which are to be determined.

10.62. Relaxation of a transformed equation A more sophisticated method of applying relaxation techniques to a diffusion problem has been suggested by Allen and Severn [13]. In general, the number of boundary conditions which can be imposed on

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an ordinary differential equation is equal to the order of the equation. Thus the solution of the second-order equation, $d^2c/dx^2 = 0$, can be made to satisfy two boundary conditions. When these are imposed one at each end of the range in x, the problem is of the 'jury' type, but when both are imposed at one end we have a 'marching' problem. If in the latter case the equation is transformed so that its order is increased, then additional arbitrary conditions can be imposed so that the problem becomes of jury type. Allen and Severn [13] show that, in general, if m conditions are given at one end of the range of integration and p at the other, and if p < m, the governing equation must be transformed so that its order is increased by m-p to become 2m. In the extreme case of a marching problem, m conditions are given at one end but none at the other, and the transformation must double the order of the original equation from m to 2m.

The diffusion equation (10.2) is of marching type in the time coordinate only and must be transformed in such a way as to double the order of the derivatives in T if it is to be of the jury type. The transformation may be accomplished by substituting in place of c, a differential function of a new dependent variable s. In any particular case there are several possible ways of doing this and the aim is firstly to make the substitution itself as simple as possible, thus keeping to a minimum the work which has to be done to return to the original variable after the transformed equation has been solved, and secondly to make the transformed equation as convenient as possible for solution by relaxation. Allen and Severn used the substitution

$$c = \frac{\partial s}{\partial T} + \frac{\partial^2 s}{\partial X^2}, \qquad (10.24)$$

by which (10.2) is transformed into

$$\frac{\partial^2 s}{\partial T^2} - \frac{\partial^4 s}{\partial X^4} = 0. \tag{10.25}$$

The finite difference approximation to this equation is

$$(s_m^+ + s_m^- - 2s_m)(\delta X)^4/(\delta T)^2 + 4s_{m-1} + 4s_{m+1} - s_{m-2} - s_{m+2} - 6s_m = 0.$$

By choosing $\delta T/(\delta X)^2 = \sqrt{2/2}$, residuals are defined by (10.26)

$$R_m = 2s_m^+ + 2s_m^- + 4s_{m-1} + 4s_{m+1} - 10s_m - s_{m-2} - s_{m+2}, \quad (10.27)$$

and the relaxation pattern is of corresponding form. The illustrative example used by Allen and Severn [13] is that of diffusion in the medium 0 < x < l, initially at zero concentration throughout, and in which the surface x = 0 is maintained at zero conFINITE DIFFERENCE METHODS

centration and the surface x = l at a concentration of 100 on an arbitrary scale. In terms of s, the problem requires the solution of (10.25) over a rectangular region in the (X, T) plane bounded by the lines X = 0, X = 1, T = 0, and $T = \tau$, where τ measures the extent in time for which the solution is required. The boundary conditions to be imposed, remembering the transformation (10.24), are

$$\frac{\partial s}{\partial T} + \frac{\partial^2 s}{\partial X^2} = 0, \quad X = 0$$

$$\frac{\partial s}{\partial T} + \frac{\partial^2 s}{\partial X^2} = 100, \quad X = 1$$

$$\frac{\partial s}{\partial T} + \frac{\partial^2 s}{\partial X^2} = 0, \quad T = 0$$
(10.28)

When a solution for s has been found from (10.25) satisfying these conditions, then c calculated from (10.24) automatically satisfies all requirements. To find a solution for s, however, some extra boundary conditions are needed, one on each of the lines X = 0, X = 1, $T = \tau$. These are arbitrarily chosen to be

$$s = 0, \qquad X = 0, \qquad X = 1 \\ \frac{\partial s}{\partial T} = 0, \qquad T = \tau$$
 (10.29)

These extra conditions can be chosen in any way provided they do not imply any condition on c or its derivatives and provided they are everywhere consistent with one another and with the other conditions (10.28). In actual fact, by this choice of (10.29) the conditions (10.28) simplify to become

$$\begin{array}{c} \partial^2 s / \partial X^2 = 0, \quad X = 0 \\ \partial^2 s / \partial X^2 = 100, \quad X = 1 \\ \partial s / \partial T + \partial^2 s / \partial X^2 = 0, \quad T = 0 \end{array} \right\}.$$
(10.30)

In finite-difference terms, the second of (10.30) becomes

$$(s_{m-1} + s_{m+1} - 2s_m)/(\delta X)^2 = 100, \qquad (10.31)$$

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so that it is convenient to work numerically in terms of $s/(\delta X)^2 = v$, say. The finite-difference expressions for the boundary conditions (10.29) and (10.30) are then

$$\begin{cases} v_m = 0, \quad v_{m-1} + v_{m+1} = 0, \quad X = 0 \\ v_m = 0, \quad v_{m-1} + v_{m+1} = 100, \quad X = 1 \\ v_m^+ - v_m^- + (v_{m-1} + v_{m+1} - 2v_m)\sqrt{2} = 0, \quad T = 0 \\ v_m^+ = v_m^-, \quad T = \tau \end{cases} \right\}.$$
(10.32)

These conditions are just sufficient for the elimination of all the fictitious values which occur in calculating the residuals at points near the boundaries from the expression (10.27) with s replaced by v. In this way, v can be found as a purely numerical quantity. Afterwards c can be found without specifying particular values for l and D since on replacing (10.24) by its finite-difference approximation, substituting for s in terms of v, and using $\delta T/(\delta X)^2 = \sqrt{2}/2$, we find

0	ю	23	39	56	78	100	$T = \sqrt{2/8}$
0	10	21	36	54	76	100	1-02/0
0	9	/9	33	5Z	74	100	
0	7	16	30	49	73	100	
0	5	/3	25	44	70	100	
0	3	9	20	39	66	100	
0	2	5	14	31	61	100	
0	1	2	7	2Z	<i>52</i>	100	
0	0	0	2	8	33	100	
0	о	о	0	о	0		T≠O
X = O						X =	1

$$c_m = v_{m-1} + v_{m+1} - 2v_m + (v_m^+ - v_m^-)/\sqrt{2}.$$
(10.33)



The value of δX serves only to determine δT , i.e. the time interval at which values are determined on the rectangular network. Fig. 10.3 shows the final values of c deduced by dividing the space-range into six

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intervals $(\delta X = \frac{1}{6})$ so that the time interval is given by $\delta T = \sqrt{2/72}$. The total range in time T covered in the nine steps shown in Fig. 10.3 is therefore $\sqrt{2/8}$.

10.7 Finite-difference formulae for the cylinder and the sphere In terms of the variables

 $R = r/a, \qquad T = Dt/a^2,$ (10.34)

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the equation for radial diffusion in a cylinder of radius a becomes

$$\frac{\partial c}{\partial T} = \frac{1}{R} \frac{\partial}{\partial R} \left(R \frac{\partial c}{\partial R} \right) = \frac{\partial^2 c}{\partial R^2} + \frac{1}{R} \frac{\partial c}{\partial R}.$$
 (10.35)

The finite-difference approximations corresponding to (10.7) for the plane-case are

$$\frac{1}{R}\frac{\partial}{\partial R}\left(R\frac{\partial c}{\partial R}\right) = \frac{1}{2m(\delta R)^2}\{(2m+1)c_{m+1} - 4mc_m + (2m-1)c_{m-1}\},$$
(10.36)

for
$$m \neq 0$$
, and $\frac{1}{R} \frac{\partial}{\partial R} \left(R \frac{\partial c}{\partial R} \right) = \frac{4}{(\delta R)^2} (c_1 - c_0),$ (10.37)

for m = 0, where the nomenclature is as before, namely c_m is the concentration at the point $m \,\delta R$, the range $0 \leq R \leq 1$ having been divided into equal intervals δR . By using one or other of the approximations (10.8) and (10.9) the various finite-difference equations follow as in the plane case. They are slightly more laborious to use because of the factors (2m+1), (2m-1), etc., which are different for each point in the cylinder.

An alternative method of dealing with a hollow cylinder of internal radius b, suggested by Eyres, Hartree *et al.* [14] is to use

$$X_1 = \log(R/b) \tag{10.38}$$

as independent variable. Then (10.35) becomes

$$\frac{\partial c}{\partial T} = \frac{e^{-2X_1}}{b^2} \frac{\partial^2 c}{\partial X_1^2},\tag{10.39}$$

and we have a problem in one-dimensional flow but with a variable diffusion coefficient depending on the new space variable X_1 .

On using (10.34) the equation for radial diffusion in a sphere of radius *a* becomes

$$\frac{\partial c}{\partial T} = \frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial c}{\partial R} \right) = \frac{\partial^2 c}{\partial R^2} + \frac{2}{R} \frac{\partial c}{\partial R}, \qquad (10.40)$$

and the finite-difference approximations corresponding to (10.36) and

(10.37) are

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial c}{\partial R} \right) = \frac{1}{m(\delta R)^2} \{ (m+1)c_{m+1} - 2mc_m + (m-1)c_{m-1} \},$$
(10.41)
for $m \neq 0$, and
$$\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial c}{\partial R} \right) = \frac{6}{(\delta R)^2} (c_1 - c_0),$$
(10.42)
for $m = 0$.

10.8. Other boundary conditions

10.81. Surface concentration given as a function of time

The way in which the concentration at the surface of the sheet varies with time may be given either in the form of an algebraic relationship, a graph, or a set of tabulated values. These data can be put directly into the appropriate finite-difference equation of the set (10.12) or (10.18) for example.

10.82. Surface evaporation

A boundary condition involving the rate of transfer of diffusing substance across the surface needs further consideration. In terms of the variable X such a condition is of the form

$$-\partial c/\partial X = \alpha(c_e - c_s), \qquad (10.43)$$

where c_s is the surface concentration at time t and c_c its value after infinite time. The argument will be presented for this case, and its extension to include other expressions on the right-hand side of (10.43) will be obvious. Imagine the sheet extended one interval, δX , beyond the real surface X_s to $X_s + \delta X$, so that applying (10.7) to (10.2) for the point on the surface (m = s) we have

$$\frac{\partial c_s}{\partial T} = \frac{c_{s+1} - 2c_s + c_{s+1}}{(\delta X)^2}.$$
(10.44)

To the same order of approximation

$$\left(\frac{\partial c}{\partial X}\right)_s = \frac{c_{s+1} - c_{s-1}}{2\delta X}.$$
(10.45)

Elimination of the fictitious concentration, c_{s+1} , outside the sheet, between (10.44) and (10.45) using (10.43) yields

$$\frac{\partial c_s}{\partial T} = \frac{2}{\delta X} \left\{ \frac{c_{s-1} - c_s}{\delta X} - \alpha (c_e - c_s) \right\}.$$
 (10.46)

Here we are measuring X as increasing outwards from the surface and so $\alpha(c_c - c_s)$ is a measure of the rate of evaporation. Substituting now for $\partial c_s / \partial T$ from (10.8) we find

$$c_{s}^{+} = c_{s} + \frac{2\delta T}{(\delta X)^{2}} \{c_{s-1} - c_{s} - \alpha \,\delta X(c_{e} - c_{s})\}. \tag{10.47}$$

On putting $\delta T/(\delta X)^2 = 1$, we have

$$c_s^+ = c_{s-1} - \alpha \, \delta X(c_e - c_s),$$
 (10.48)

and this is the equation by which the surface concentration is to be

calculated when using the Schmidt method. Applying (10.9) over the interval T to $T + \delta T$ we find for the Crank-Nicolson method

$$c_s^+ = \frac{1}{2} \{ c_{s-1}^+ + c_{s-1}^+ - \alpha (2c_e^- - c_s^- - c_s^+) \,\delta X \}, \tag{10.49}$$

when $\delta T/(\delta X)^2 = 1$. Corresponding formulae are readily deduced for use with relaxation techniques.

If the surface is impermeable (10.46) becomes

$$\frac{\partial c_s}{\partial T} = \frac{2}{(\delta X)^2} (c_{s-1} - c_s), \qquad (10.50)$$

with corresponding simplification of the subsequent expressions for c_s^+ .

For the cylinder, the corresponding equation to (10.46) is

$$\frac{\partial c_s}{\partial T} = \frac{2}{\delta R} \left\{ \frac{c_{s-1} - c_s}{\delta R} - \alpha \left(1 + \frac{1}{2s} \right) (c_e - c_s) \right\},\tag{10.51}$$

for the outer surface $R = s \,\delta R$, and

$$\frac{\partial c_p}{\partial T} = \frac{2}{\delta R} \left\{ \frac{c_{\rho+1} - c_p}{\delta R} + \alpha \left(1 - \frac{1}{2p} \right) (c_e - c_s) \right\},\tag{10.52}$$

for the inner surface $R = p \, \delta R$.

The equations for the sphere corresponding to (10.51) and (10.52) are

$$\frac{\partial c_s}{\partial T} = \frac{2}{\delta R} \left\{ \frac{c_{s-1} - c_s}{\delta R} - \alpha \left(1 + \frac{1}{\delta} \right) (c_e - c_s) \right\},\tag{10.53}$$

for the outer surface, $R = s \delta R$, and

$$\frac{\partial c_p}{\partial T} = \frac{2}{\delta R} \left\{ \frac{c_{p+1} - c_p}{\delta R} + \alpha \left(1 - \frac{1}{p} \right) (c_e - c_s) \right\},\tag{10.54}$$

for the inner surface $R = p \, \delta R$. The above formulae and other ways of treating this type of boundary condition are suggested by Eyres, Hartree *et al.* [14].

10.83. A restricted amount of diffusing substance

A different type of boundary condition arises if we have a limited amount of diffusing substance. Some solutions have already been given in § 4.35 for the problem in which a sheet of thickness 2l is placed in a well stimud solution in which the solution of the solution l

well-stirred solution in which the solute concentration is C_0 initially and which occupies the spaces $-a-l \leq x \leq -l$ and $l \leq x \leq l+a$. The sheet occupies the space $-l \leq x \leq l$. The boundary condition at the surface of the sheet, x = l, can be written in terms of the variables (10.1) either as

$$ac + l \int_{0}^{1} c \, dX = a, \qquad X = 1, \qquad T > 0,$$
 (10.55)

 $-l(\partial c/\partial X)_s = a \,\partial c_s/\partial T, \qquad X = 1, \qquad T > 0, \qquad (10.56)$

assuming the concentration in the solution to be uniform and the same as the concentration, c_s , at the surface of the sheet. The condition (10.55) expresses the fact that the total amount of solute in the sheet and in the solution is constant and equal to the total amount originally in the solution. In (10.56) the rate at which solute enters the sheet is equated to that at which it leaves the solution. If in the Schmidt or Crank-Nicolson method an estimated value of the surface concentration

 c_s^+ is used to evaluate the row $T + \delta T$, and hence $\int_0^{\tilde{s}} c \, dX$, then a revised estimate of c_s^+ is obtained from (10.55) and the process repeated if necessary [15]. Alternatively, by eliminating c_{s+1} from (10.44) and (10.45) as above and substituting for $(\partial c/\partial X)_s$ from (10.56) we obtain

$$\frac{\partial c_s}{\partial T} \left(1 + \frac{2a}{l\,\delta\,\overline{X}} \right) = \frac{2}{(\delta\overline{X})^2} (c_{s-1} - c_s). \tag{10.57}$$

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By making appropriate substitutions for $\partial c_s/\partial T$, the finite-difference formula for use with either of the forward integration methods of §§ 10.4 and 10.5 or the relaxation methods of § 10.6 follow immediately. The corresponding boundary conditions for the cylinder and the sphere are obtained in the same way.

10.9. Solutions for small times

It is possible to start any finite-difference method from T = 0 by taking, as the first row on the computation sheet, the prescribed initial values of concentration. In some cases, e.g. when surface concentration is a continuously varying function of time which is known, starting in this way will probably be satisfactory. In other cases, however, the conditions are often such that a singularity exists in the solution at T = 0. This is so, for example, when the surface concentration rises discontinuously from zero to a finite value at zero time and we have

$$c = 0, \quad 0 < X < 1, \quad T = 0,$$
 (10.58)

$$c = 1, \qquad X = 1, \qquad T \ge 0. \tag{10.59}$$

 \mathbf{or}

It is undesirable to replace a derivative by a finite-difference ratio in the neighbourhood of such a discontinuity. Nevertheless, surprisingly good accuracy is achieved after a few steps of the Crank-Nicolson method, § 10.5, even if it is applied directly from T = 0 under these stringent conditions.

Alternatively, it may be possible to use a formal solution or a solution in series to get away from T = 0. This is particularly so since diffusion

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into a medium of any geometric shape obeys the solution for a semiinfinite medium in the early stages. Thus the formal solution (10.13) can often be used to obtain a row of values of c on the computation sheet for some small, non-zero time, and the solution can then be continued by finite-difference methods. If the diffusion coefficient is a function of concentration, the iterative method described in § 9.32 can be used to obtain a solution for small times, provided the concentration at the surface of the sheet is constant. This is elaborated in an example discussed below in § 10.13.

Sometimes it is preferable to transform the diffusion equation in such a way that the singularity is removed and finite-difference methods can then be applied. An example is discussed in reference (16) where the use of the variables $T^{\frac{1}{2}}$ and $X/T^{\frac{1}{2}}$ in place of T and X is effective. Other transformations may be necessary for different boundary conditions. In some examples it is desirable to use the transformed equation only for a few steps in the neighbourhood of the singularity and then to return to the original variables. In others, the solution proceeds more satisfactorily in the new variables throughout. Much depends on the relative degree of complication of the original and transformed equations when expressed in finite-difference form, and on the boundary conditions.

10.10. Accuracy and convergence of finite-difference solutions

The ease with which a finite-difference solution can be evaluated depends very largely on the ratio $\delta T/(\delta X)^2$. Clearly, the smaller this is the more rapidly does an iterative technique, based for example on (10.17), converge. Questions of convergence and cumulative errors have been discussed by Fowler [17], and various other authors [5, 6, 7, 18]. It suffices to say here that the methods proposed above behave satisfactorily provided the ratio $\delta T/(\delta X)^2$ is taken small enough. Usually a value 1 or $\frac{1}{2}$ can be used for this ratio. If in practice too large a value is tried this is immediately obvious from the way the results behave. Usually a pronounced oscillation develops or else values calculated from successive stages in the iterative process diverge.

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The accuracy of a finite-difference solution can be estimated and improved in one of the following ways.

(i) h^2 -extrapolation

Clearly, the accuracy depends on the sizes of the intervals δX and δT , and can be improved by taking smaller intervals. In many cases the only practicable way of estimating the accuracy of a finite-difference solution is to repeat the process using, for example, half the interval in 5824 0

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both X and T. If the same result is obtained to within the desired accuracy the solution is complete. If there is a difference, however, a good estimate of the true solution can often be obtained by using what Richardson [11] called the ' h^2 -extrapolation process'.

Examination of the leading terms in the errors of the approximations (10.7) and (10.9) reveals that these are proportional to $(\delta X)^2$ and $(\delta T)^2$ respectively. Thus if both δX and δT are altered in the same ratio and a second solution obtained, a good estimate of the true solution (corresponding to $\delta X = \delta T = 0$ is given by extrapolating linearly in $(\delta X)^2$ or $(\delta T)^2$ on the two approximate values of c obtained at each point (X, T). If the concentration distribution through the sheet is wanted only at one time, the extrapolation need only be performed on the two sets of values of concentration obtained at this time by carrying out the solution with the two sizes of interval. Thus if at any point and time a value C_1 is obtained with intervals δX , δT , and C_2 is the corresponding value obtained with intervals $\frac{1}{2}\delta X$, $\frac{1}{2}\delta T$, a good estimate of the true solution is given by $C_2 + \frac{1}{3}(C_2 - C_1)$. This h^2 -extrapolation process has been examined by Hartree and Womersley [19], who showed that the justification for its use depends on the boundary conditions. They found that for certain boundary conditions, including those of constant surface concentration and of surface evaporation, the extrapolation removes not only the leading term in the error but the next term also. Thus only an error of the order of the fourth power of the interval remains.

(ii) Higher-order differences

Success in using the simple finite-difference formulae such as (10.10) and (10.17) depends essentially on choosing intervals δX and δT so small that the higher-order terms present in (10.5), (10.6), etc., can be neglected. An alternative approach is to extend the formulae (10.7), (10.9) for example to take account of the higher-order differences. In this way the accuracy can be both estimated and improved. The method was developed by Fox [20] in connexion with relaxation techniques. Making use of well-known formulae in the theory of finite differences we find

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$$\delta T \frac{\partial c_m}{\partial T} = \frac{1}{2} (c_{m+1} - c_{m-1}) - \frac{1}{6} \delta_{m,T}^{m} + \frac{1}{30} \delta_{m,T}^{\nabla} - \dots, \qquad (10.60)$$

$$(\delta X)^{2} \frac{\partial^{2} c_{m}}{\partial X^{2}} = (c_{m+1} - 2c_{m} + c_{m-1}) - \frac{1}{12} \delta_{m,X}^{iv} + \frac{1}{90} \delta_{m,X}^{vi} - \dots$$
(10.61)

Here δ_m^n is the *n*th central difference at the points $m \, \delta X$ and time $n \, \delta T$, the suffixes T and X denoting difference 'in the T or X direction'

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respectively. The differences in the T direction, for example, take the form

The full finite-difference form of the diffusion equation (10.2) therefore takes the form

$$\frac{1}{2}(c_{m+1}-c_{m-1}) - \frac{\delta T}{(\delta X)^2}(c_{m+1}-2c_m+c_{m-1}) = \nabla, \qquad (10.62)$$

where ∇ is a difference correction given by

$$\nabla = \frac{1}{6} \delta_{m,T}^{\prime\prime\prime} - \frac{1}{30} \delta_{m,T}^{v} - \frac{\delta T}{(\delta X)^2} \{ \frac{1}{12} \delta_{m,X}^{iv} - \frac{1}{90} \delta_{m,X}^{vi} + \ldots \}.$$
(10.63)

The method of solution is then as follows. First, the difference correction on the right-hand side of (10.62) is ignored and a first approximation is obtained by relaxation methods as in § 10.6. The values so obtained are then differenced and, if the differences are converging, the difference corrections ∇ are calculated for each point and entered as new residuals to be relaxed in turn. This is continued until the full finite-difference equation is satisfied with all significant differences included. Differences near the boundaries which are not known can be obtained with sufficient accuracy by extrapolation, fairly large inaccuracies usually being permissible because of the way such differences enter into the difference correction. For further details and examples of the use of this method the reader is referred to the original paper [20]. Clearly the same technique can be applied to a method of forward integration such as that of Schmidt, § 10.4.

In many problems, it is a matter of personal choice on the part of the computer as to whether small intervals and simple formulae or larger intervals and more complicated formulae are used. In non-linear systems, however, e.g. where the diffusion coefficient is a function of concentration, formulae involving higher-order differences soon become unwieldy and the only practical approach is to use the simpler formulae with a fine network.

(iii) A formal solution as a check If a family of solutions is required it may be that one of the family has a formal solution. The sizes of the intervals δX and δT needed to

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secure agreement to prescribed accuracy between the formal solution and the corresponding finite-difference solution for this special case are often good guides to the sizes of intervals to be used for the other solutions in the same family. For example, if solutions are wanted for a set of diffusion coefficients which depend exponentially on concentration, an idea of the interval sizes to be used can be obtained by evaluating a finite-difference solution for a constant diffusion coefficient and comparing this with the formal solution for the same boundary conditions.

10.11. Composite media

Conditions at the surface of separation of two different media can be dealt with by a slight extension of the treatment of the boundary condition (10.43). The method was suggested by Eyres, Hartree et al. [14].

Considering the plane case first, let $x = x_s$ be the surface separating two media, and let the suffixes a, b indicate reference to the left-hand $(x < x_s)$ and right-hand $(x > x_s)$ sides of the boundary respectively. The interval δx may be taken as different in the two media if desired. If $F(c_s, t)$ denotes the flux across the boundary then the conditions to be satisfied there are

$$c_a = c_b = c_s, \qquad D_a \frac{\partial c_a}{\partial x} = D_b \frac{\partial c_b}{\partial x} = -F(c_s, t), \qquad x = x_s.$$
(10.64)

By imagining the medium to the left of the boundary to be extended one step, δx_a , to the right of x_s and eliminating the fictitious concentration there as in § 10.82 above but using (10.64), we obtain

$$\frac{\partial c_s}{\partial t} = \frac{2D_a}{\delta x_a} \left\{ \frac{c_{s-1} - c_s}{\delta x_a} - \frac{F}{D_a} \right\}.$$
(10.65)

Similarly, by extending the medium to the right of the boundary one step, δx_b , to the left of x_s , we find

$$\frac{\partial c_s}{\partial t} = \frac{2D_b}{\delta x_b} \left\{ \frac{c_{s+1} - c_s}{\delta x_b} + \frac{F}{D_b} \right\}.$$
 (10.66)

On eliminating F from (10.65) and (10.66) we have

$$\frac{1}{2}\left\{\delta x_a + \delta x_b\right\}\frac{\partial c_s}{\partial t} = \frac{D_b}{\delta x_b}\left(c_{s+1} - c_s\right) - \frac{D_a}{\delta x_a}\left(c_s - c_{s-1}\right). \tag{10.67}$$

This equation can be written in terms of non-dimensional variables such as those of (10.1) and by appropriate substitution for $\partial c_s/\partial t$ can be expressed in a finite-difference form suitable for use with any of the methods described above.

A composite cylinder of outer radius a and having an inner core of radius b can be treated similarly. Let the range $0 \le r \le a$ be divided into n equal intervals, δr_a , and the range $0 \le r \le b$ into l equal intervals, δr_b , such that $l \delta r_b = m \delta r_a = b$, with l, m, and n integers. On the boundary surface, r = b, we have $c_l = c_m = c_s$. The relationship at the boundary corresponding to (10.67) is

$$\frac{1}{2}\left\{\left(1-\frac{1}{2m}\right)\delta r_{b}+\left(1+\frac{1}{2l}\right)\delta r_{a}\right\}\frac{\partial c_{s}}{\partial t}$$

$$=\left\{\left(1+\frac{1}{2l}\right)\left(c_{m+1}-c_{s}\right)\frac{D_{a}}{\delta r_{a}}-\left(1-\frac{1}{2m}\right)\left(c_{s}-c_{l-1}\right)\frac{D_{b}}{\delta r_{b}}\right\}.$$
(10.68)

With the same nomenclature the corresponding expression for a composite sphere is

$$\frac{1}{2}\left\{\left(1-\frac{1}{m}\right)\delta r_{b}+\left(1+\frac{1}{l}\right)\delta r_{a}\right\}\frac{\partial c_{a}}{\partial t} = \left\{\left(1+\frac{1}{l}\right)(c_{m+1}-c_{s})\frac{D_{a}}{\delta r_{a}}-\left(1-\frac{1}{m}\right)(c_{s}-c_{l-1})\frac{D_{b}}{\delta r_{b}}\right\}.$$
(10.69)

Solutions for the uptake of solute from a limited volume of solution by a composite cylinder have been obtained [21] using (10.68).

10.12. Two-dimensional diffusion

The finite-difference methods have been described as they are applied to uni-directional diffusion. They can readily be extended to diffusion in two dimensions, though in general the labour is correspondingly greater. Consider, as an example, the problem of diffusion in a prism having a rectangular section, the surface of which is maintained at constant unit concentration and in which the concentration is initially zero. We shall assume for simplicity of explanation that the section can be divided into a network of squares each of side h. Taking the sides to be parallel to the axes x, y respectively, we denote the concentration at the point x = jh, y = kh by $c_{j,k}$. Diffusion is governed by the equation

$$rac{\partial c}{\partial t} = D igg(rac{\partial^2 c}{\partial x^2} + rac{\partial^2 c}{\partial y^2} igg),$$

(10.70)

if the diffusion coefficient is constant. Replacing each derivative on the right-hand side of (10.70) by its finite-difference approximation (10.7) we find $\partial c_{11} = D$

$$\frac{\partial c_{j,k}}{\partial t} = \frac{D}{h^2} (c_{j+1,k} + c_{j-1,k} + c_{j,k+1} + c_{j,k-1} - 4c_{j,k}).$$
(10.71)

On using the approximation (10.8) for $\partial c_{j,k}/\partial t$, and putting $D \,\delta t/\hbar^2 = \frac{1}{4}$, (10.71) becomes

$$c_{j,k}^{+} = \frac{1}{4} (c_{j+1,k} + c_{j-1,k} + c_{j,k+1} + c_{j,k-1}), \qquad (10.72)$$

which is the equivalent of the Schmidt formula (10.12) in two dimensions. Given values of concentration at time t, values at $t + \delta t$ can be built up by applying (10.72) to each point of the network successively. In Fig. 10.4



FIG. 10.4. Two-dimensional Schmidt pattern.

the values required to deal with the point marked by a circle are shown by crosses. A difficulty is that of recording on paper a calculation which in reality should take place on a threedimensional lattice. Richardson [11] suggested using a separate sheet of paper, possibly transparent, for each step in time. A much neater method due to Allen and Dennis [22], which enables the work to be carried out on a single sheet of paper, is to draw an 'isometric projection' of the threedimensional lattice and to insert

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numerical values on this as in Fig. 10.5. The diagram shows onequarter of a rectangular block of sides 2a and $\frac{3}{2}a$. The origin, x = y = 0, is taken at the centre of the block and the surfaces are all maintained at unit concentration. The solution starts from zero concentration throughout the sheet at the top of the lattice and, since $h = \frac{1}{4}a$, the horizontal planes in the network correspond to successive times differing by equal intervals $\frac{1}{64}$ in Dt/a^2 . The values at $Dt/a^2 = \frac{1}{64}$ are obtained from the formal product solution, § 2.5,

$$c = 1 - \frac{16}{\pi^2} \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \frac{(-1)^{l+m}}{(2l+1)(2m+1)} \cos \frac{(2l+1)\pi x}{2a} \times \cos \frac{2(2m+1)\pi y}{2a} \exp(-\alpha - t) = (10.73)$$

where
$$\alpha_{l,m} = \frac{D\pi^2}{4} \left\{ \frac{(2l+1)^2}{a^2} + \frac{4}{9} \frac{(2m+1)^2}{a^2} \right\}.$$
 (10.74)

For successive steps in time, values are obtained using (10.72), and they are compared in Fig. 10.5 after four steps with corresponding values calculated from (10.73) to indicate the accuracy obtained with a network of this size.



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FIG. 10.5. Diffusion into a rectangular prism $2a \times \frac{3}{2}a$. Values of 1000c are tabulated.

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10.13. Example: a problem involving a concentration-dependent diffusion coefficient

Suppose a sample of material in the form of an infinite plane sheet of thickness 2l is immersed in a bath of vapour of infinite extent. We shall assume that the rate-determining step controlling the uptake of vapour is diffusion within the sheet and that this is governed by a diffusion

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coefficient D_1 , which increases with concentration increasing according to the expression $D_1 = D_0 e^{2\cdot 303C/C_0}$. (10.75)

Here C_0 is the concentration at each surface of the sheet, assumed constant, and the sheet is taken to be free of vapour initially. We thus require solutions of aC = a (-aC)

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D_1 \frac{\partial C}{\partial x} \right), \qquad (10.76)$$

subject to the boundary conditions

$$C = C_0, \quad x = -l, \quad x = +l, \quad t > 0,$$
 (10.77)

$$C = 0, \quad -l < x < l, \quad t = 0.$$
 (10.78)

It is convenient to introduce the non-dimensional variables

$$c = C/C_0, \qquad X = x/l, \qquad T = D_0 t/l^2, \qquad D = D_1/D_0, \quad (10.79)$$

where D is thus a function of c given by

$$D = e^{2 \cdot 303c}, \tag{10.80}$$

and D_0 is the value of D_1 when c = 0. Equations (10.76), (10.77), and (10.78) then reduce to

$$\frac{\partial c}{\partial T} = \frac{\partial}{\partial X} \left(D \, \frac{\partial c}{\partial X} \right), \tag{10.81}$$

$$c = 1, \quad X = -1, \quad X = 1, \quad T > 0,$$
 (10.82)

$$c = 0, \quad -1 < X < 1, \quad T = 0.$$
 (10.83)

In the early stages, when the concentration of vapour has not yet become appreciable at the centre of the sheet, the problem reduces to one of diffusion into a semi-infinite medium, with constant surface concentration. By use of the variable y, where

$$y = (1 - X)/2T^{\frac{1}{2}},$$
 (10.84)

(10.81) is reduced to

$$-2y\frac{dc}{dy} = \frac{d}{dy}\left(D\frac{dc}{dy}\right),$$
(10.85)

which is equation (9.24) of § 9.32. A solution satisfying

$c = 1, \quad y = 0; \quad c \to 0, \quad y \to \infty,$ (10.86)

and with D given by (10.80) can be obtained as described in § 9.32. This solution was evaluated at intervals of 0.1 in y. It is shown graphically in Fig. 10.6, and is considered to hold till the concentration at the centre of the sheet reaches the value c = 0.001. The time at which this happens is determined as follows. Let y_{lim} be the value of y at which c = 0.001. In this example $y_{\text{lim}} = 2.90$. The condition that the value

c = 0.001 occurs at the centre of the sheet, X = 0, is given from (10.84) by $2T^{\frac{1}{2}}y_{\lim} = 1$, (10.87)



FIG. 10.6. Concentration distribution calculated from (10.85) for $D = e^{1.303C}$. The X-scale refers to the time T = 0.0297.

and the limiting value of T above which (10.85) no longer applies follows at once. It is T = 0.0297. For later times the equation (10.81) must be used. Approximate numerical solutions can be evaluated by the method of § 10.5 for example. Because the diffusion coefficient is concentrationdependent, it is useful to introduce the variable

$$s = \int_{0}^{c} D \, dc \Big/ \int_{0}^{1} D \, dc, \qquad (10.88)$$

previously used in § 9.33. For D given by (10.80), s becomes

$$s = (e^{2 \cdot 303c} - 1)/(e^{2 \cdot 303} - 1) = \frac{1}{9}(e^{2 \cdot 303c} - 1).$$
 (10.89)

In terms of s, equation (10.81) may be written

$$\frac{\partial s}{\partial \bar{T}} = D \frac{\partial^2 s}{\partial X^2},$$
 (10.90)

and a solution is wanted for

$$s = 1, \qquad X = \pm 1, \qquad T > 0 \\ s = 0, \qquad -1 < X < 1, \qquad T = 0 \ \right\}.$$
 (10.91)

Using the nomenclature of \S 10.3, the appropriate finite-difference form of (10.90) is

$$s_m^+ = s_m + \frac{(D_m^+ + D_m)(\delta T)}{4(\delta X)^2} \{ (s_{m+1}^+ + s_{m+1}) - 2(s_m^+ + s_m) + (s_{m-1}^+ + s_{m-1}) \},$$
(10.92)

with the special form

$$s_0^+ = s_0 + \frac{(D_0^+ + D_0)(\delta T)}{2(\delta X)^2} \{ (s_1^+ + s_1) - (s_0^+ + s_0) \}$$
(10.93)

at the centre of the sheet by virtue of the symmetry about the central plane. In this example, half the sheet was divided into eight intervals δX , and $\delta T/(\delta X)^2$ was taken to be $\frac{1}{10}$. When the values of X at the points $m \delta X$, i.e. $\xi = 0, \frac{1}{8}, \frac{1}{4}, \frac{3}{8}, ..., 1$, are converted into y values at the time T = 0.0297, by using (10.84), the solution of (10.85) shown in Fig. 10.6 provides values of c at each point. The values of s calculated from these, using (10.89), are inserted in the first row of the computation sheet shown in Table 10.3. By combining (10.80) and (10.89) we find that D = 9s+1 and this is used to evaluate D_m^+ and D_m for use in (10.92) and (10.93). Apart from this slight modification the evaluation of (10.92) and (10.93) proceeds exactly as described in § 10.5. Five steps are shown in Table 10.3 and for the fifth row the values of s are converted back into c's. If M_t denotes the total amount of vapour absorbed by the sheet at time t, and M_{∞} denotes the equilibrium uptake attained theoretically after infinite time, then

$$\frac{M_t}{M_x} = \frac{\int\limits_0^1 C \, dx}{lC_0} = \int\limits_0^1 c \, dX = 2T^{\frac{1}{2}} \int\limits_0^\infty c \, dy. \tag{10.94}$$

Thus the overall rate of uptake is easily obtained from the computation

sheet at any time. It is shown graphically as a function of $(D_0 t/l^2)^1$ in Fig. 12.17.

10.14. A step-wise diffusion coefficient

In the previous section, the diffusion coefficient was a continuous function of concentration. The variable s introduced in (10.88) is also useful in dealing with a diffusion coefficient which changes discontinuously from one value to another at one or more concentrations, as in

Fig. 10.7. If (10.88) is used only on the right-hand side of (10.81) we obtain, instead of (10.90),





FIG. 10.8. Graph of s against c for the step-wise diffusion coefficient in Fig. 10.7.

of which the finite-difference form corresponding to (10.92) is

$$c_{m}^{+} = c_{m} + \frac{\delta T}{2(\delta X)^{2}} \{ (s_{m+1}^{+} + s_{m+1}) - 2(s_{m}^{+} + s_{m}) + (s_{m-1}^{+} + s_{m+1}) \}.$$
(10.96)

The relationship (10.88) is used at each stage of the computation to convert c_m^+ into s_m^+ . For a relationship between D and c of the type shown in Fig. 10.7, the graph of s against c is as in Fig. 10.8. Since D does not appear explicitly in (10.96), the computational difficulties arising from the discontinuities are considerably lessened.

10.15. Analogues and other machines

Most of the instrumental methods of solving the diffusion equation depend on 'lumping' the medium in a way which is equivalent to the use of finite-differences and so they are considered briefly in this chapter.

(i) Differential analyser

This machine [23, 24] was designed originally for the solution of ordinary differential equations, but two methods of using it to obtain solutions of the diffusion equation have been devised by Hartree and co-workers. In the first method [19, 23, 24] the time derivative is replaced by a finite-difference ratio to give an equation of the type

$$\frac{1}{2}\frac{d^2}{dX^2}\{c(T+\delta T)+c(T)\} = \frac{1}{\delta T}\{c(T+\delta T)-c(T)\},$$
 (10.97)

for the simple diffusion equation (10.2). This is an ordinary differential equation for $c(T+\delta T)$ as a function of X, where c(T) is a given function of X, and (10.97) can be solved by the differential analyser, subject to given boundary conditions. The solution $c(T+\delta T)$ becomes the known function c(T) for the next interval δT and the solution proceeds in steps δT . As there is one condition to be fulfilled at each end of the range in X, a trial and error process is necessary for each interval δT , and so the method is clearly somewhat cumbersome and except for special circumstances has been superseded by a second method [14, 23, 24] in which the X-derivative is replaced by the finite-difference ratio (10.7). Then for each point, $m \delta X$, we have an equation

$$\frac{\partial c_m}{\partial T} = \frac{c_{m+1} - 2c_m + c_{m-1}}{(\delta X)^2}.$$
 (10.98)

If, for example, the sheet is divided into four layers of thickness δX , then there are four equations of the type (10.98). Apart from limitations imposed by machine capacity, the solution of such a set of simultaneous equations by the differential analyser is straightforward, the concentrations at the surfaces of the sheet being fed into the machine as it operates, if they are known. The treatment of other boundary conditions follows the lines discussed above in connexion with finite-difference methods, and details are given by Eyres, Hartree *et al.* [14]. If a differential

analyser with twenty or thirty integrating units is available, this is an attractive and practical method of handling many problems. The boundary conditions are satisfied exactly and continuously and no trial and error process is involved. It makes considerable demands on machine capacity, however, for all but the simpler problems and geometrical shapes.

(ii) Analogue machines

The use of analogue methods has received a good deal of attention with reference to complicated problems in heat flow. The methods are



Fig. 10.9. Ladder network.

based on the identity between the equations of heat flow or diffusion and those governing the behaviour of the model analogue. In the case of the electrical resistance and capacity analogues, the flow of diffusing substance is simulated by the flow of electrical charge, and gradient of electric potential corresponds to concentration gradient. Fig. 10.9 shows a simple 'ladder network' consisting of resistance and capacities. In such a circuit, the rate of accumulation of charge on any one condenser depends on the voltage V_m across it and on the voltages V_{m-1} and V_{m+1} across the neighbouring condensers. Thus if all the resistances have the same value, R, and all the capacities are C, charge enters the *m*th con-

denser at a rate $(V_{m-1} - V_m)/R$ and leaves at a rate $(V_m - V_{m+1})/R$. For this condenser we have the equation

$$\frac{\partial V_m}{\partial t} = \frac{V_{m+1} - 2V_{m-1} + V_{m-1}}{CR}.$$
 (10.99)

This is of the same form as (10.98) and becomes identical with it if

$$\frac{c = aV}{T = t(\delta X)^2/(CR)} \bigg\},$$
(10.100)

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where a is an arbitrary constant which can be chosen to give suitable voltages. Thus the concentration distribution produced by one-dimensional diffusion in a plane sheet can be represented by the voltage distribution in a ladder network of the type shown in Fig. 10.9. By

-Applied pressure change



F1G. 10.10. Air-flow analogue.

imposing conditions at the ends of the network corresponding to those at the faces of the sheet, the concentration distribution at any time is obtained by reading the voltages. Clearly, the accuracy depends on the number of resistances and condensers used, in the same way as that of finite-difference solutions depends on the number of intervals δX , δT . Instruments based on this principle have been developed, for example, by Paschkis and Baker [25], by Jackson et al. [26], and no doubt there are others.

Redshaw [27] and Liebmann [28] have developed two-dimensional resistance networks based essentially on the same analogy but for use in steady-state problems only. Here the connexion with relaxation methods is very close, and Liebmann [28] claims that because of certain averaging properties of the network very high accuracy is possible. The Liebmann type of network has since been extended to include transient problems [29]. The diffusion process can also be simulated by the flow of liquid or
gas through a series of reservoirs connected by small-bore flow tubes or resisting ducts. The analogy is precisely that of the electrical network (Fig. 10.9), with capacities replaced by reservoirs and electrical resistances by flow-tube resistances. The Hydrocal designed by A. D. Moore



F1G. 10.11. Mechanism for Schmidt method.

[30] is a well-known example of an analogue machine using water, and an air-flow analogy has been developed by M. B. Coyle [31]. The principle of the latter instrument is clear from Fig. 10.10. Problems in which the diffusion coefficient is concentration-dependent can be handled automatically by constructing each reservoir in such a way that its cross-sectional area is a function of the liquid level. Details are given in Coyle's paper [31].

(iii) A Schmidt mechanism

Jaeger [32] has described a simple link mechanism by which Schmidt's graphical process discussed in § 10.4 can be carried out mechanically for a medium in which the diffusion coefficient is a function of concentra-

tion. Using the nomenclature of § 10.3 and the variable s defined by (10.88) the Schmidt approximation to the diffusion equation (10.90) is

$$s_m^+ - s_m = \frac{D\,\delta T}{(\delta X)^2} (s_{m+1} - 2s_m + s_{m-1}). \tag{10.101}$$

If we put $D\delta T/(\delta X)^2 = \frac{1}{2}$, (10.102)

we have the same Schmidt formula as for a constant D, i.e.

$$s_m^+ = \frac{1}{2}(s_{m+1} + s_{m-1}),$$
 (10.103)

but now, if the time interval δT is fixed, δX is no longer constant but is a function of s determined by the relationship between D and c, through (10.88) and (10.102). Jaeger's mechanism is a device for automatically adjusting δX as the solution proceeds. The principles may be understood from Fig. 10.11. The concentration curves are to be plotted on a board which slides in the X direction below the mechanism. ABCDEF is a pantograph with joints at D, B, E, F, and in which AD = DF = BE = CE = EF = BD, so that B is always the midpoint of AC. The point C of the pantograph carries a pointer with which a curve can be followed and is attached to a nut which can be traversed perpendicular to the X direction by rotation of the screw RS. The point A of the pantograph carries a pointer. The point B carries a pen and is also hinged to a rod BK, parallel to the X direction, which slides through a nut H which can be traversed at right angles to the X direction by the screw PQ. The end K of the rod BK carries a small roller which slides on a curve LM cut to represent δX as a function of s, where

$$\delta X = \sqrt{\{2\delta TD(s)\}},$$

for the chosen value of δT and the known function D(s). In plotting the curve, s is measured perpendicular to the direction of X and δX along it. Thus the projections of BC and AB on the X direction both have the required value δX appropriate to each value of s. The curve s(X, T) at time T is drawn on the drawing-board and traversed under the machine. Then if the pointers A and C are made to follow the curve, the construction ensures that the pen at B will trace the concentration curve

$s(X,T\!+\!\delta T)$

at the time $T + \delta T$. In practice a convenient choice of δT and the order of magnitude of δX is made; if there is a sudden change in surface concentration at T = 0, the concentration distribution at $T = \delta T$ is worked out independently by one of the methods in Chapter IX or otherwise, and the solution is then continued in steps δT by using the mechanism. For other surface conditions the mechanism can be used directly from T = 0, though the accuracy may be poor.

(iv) High-speed automatic digital machines and the Monte Carlo method

High-speed automatic digital machines [24] can carry out a large number of oft-repeated operations very rapidly. The most obvious way of applying them to the solution of the diffusion equation therefore is to use a simple formula like Schmidt's (10.12) and to take very small $\{10.15\}$

,我们不是一个的,我们不是不是一个,我们就是这个人的,我们就是我们就是我们就是我们就是我们就是我们的人,我们就是我们的人,我们是我们的,我们也能有什么。""你就不是你,我们不是不是我们的,我们就是我们

intervals δX and δT . A quite different approach is that of the 'Monte Carlo method', in which the basic feature of diffusion, namely random molecular motions, is simulated on the digital calculating machine by actually counting the result of a succession of random events. The idea is illustrated by King [33] with reference to a simple diffusion problem in which dye is supplied to the centre of a capillary tube filled with water and diffuses in both directions along the tube. This problem can be supplied directly to a calculating machine without the necessity of going through the intermediate step of the usual diffusion equation, in the following way. The dye molecules are subject to Brownian movement and move a mean distance Δx along the tube in time Δt . The movement is completely random so that Δx may be positive or negative. Suppose now that a counter in the calculating machine is assigned to x and a succession of quantities, each representing Δx (usually unity in any appropriate decimal position) is fed to the counter. Let the counter be impulsed to add or subtract the quantities Δx by some random process. A convenient method is to supply random digits which the machine can examine for oddness or evenness, and the counter is activated to subtract or add accordingly. For example, if the random numbers supplied are 5, 7, 7, 0, 5, 1, 3, 0, 9, 4 then the particle moves backwards or forwards according to the signs -, -, -, +, -, -, -, +, -, +. Its successive positions are -1, -2, -3, -2, -3, -4, -5, -4, -5, -4, and its final position after ten steps (at time $10\Delta t$) is -4. After 1,000 jumps the particle has moved a certain distance, say x_1 , in the time $1,000\Delta t$. If now another particle is examined on another counter for 1,000 random jumps it will follow a different course and finally arrive at a different point x_2 . If this is done for each of 1,000 different particles, and the numbers of particles are counted at $x = \Delta x$, $2\Delta x$, $3\Delta x$, $-\Delta x$, $-2\Delta x$, etc., we obtain the distribution of the particles at time

$t=1,000\Delta t,$

and this is the concentration of diffusing dye molecules at this time. This simple example serves to illustrate the principle of the Monto Carlo method. Ways of elaborating it to include a random distribution of

molecular jumps, Δx , and to apply it to different boundary conditions and to three-dimensional problems are described by King [33].

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THE DEFINITION AND MEASUREMENT OF DIFFUSION COEFFICIENTS

11.1. Definitions

QUANTITATIVE measurements of the rate at which a diffusion process occurs are usually expressed in terms of a diffusion coefficient. Before describing some methods of measurement, we shall examine the definition of the diffusion coefficient a little more carefully than in § 1.2. Confining attention to one dimension only, the diffusion coefficient is defined as the rate of transfer of the diffusing substance across unit area of a section, divided by the space gradient of concentration at the section. Thus, if the rate of transfer is F, and C the concentration of diffusing substance, and if x denotes the space coordinate, then

$$F = -D \,\partial C / \partial x, \tag{11.1}$$

and (11.1) is a definition of the diffusion coefficient *D*. In using this definition in practice, it is necessary to specify carefully the section used and the units in which *F*, *C*, and *x* are measured. Only the simplest system of practical importance is considered, which is a two-component system, since it is not possible to set up and observe a concentration gradient of a single substance in itself without introducing complicating features such as pressure gradients, etc. The diffusion of isotopes is best regarded as a special case of a two-component system.

11.2. A frame of reference when the total volume of the system remains constant

Consider the inter-diffusion of two liquids A and B in a closed vessel and assume that there is no overall change of volume of the two liquids on mixing. Two diffusion coefficients, D_A^V , D_B^V , one for each liquid, may

be defined by the relationships

$$F_A = -D_A^V \partial C_A / \partial x, \qquad (11.2)$$

$$F_B = -D_B^V \partial C_B / \partial x. \qquad (11.3)$$

 C_A and C_B are the concentrations of A and B respectively, each expressed in the usual way in any convenient unit of amount (e.g. g. or, in the case of simple molecular substances, g. mole) per unit overall volume. F_A and F_B are the rates of transfer of A and B measured in the same units of amount per unit time, across a section which is defined by the condition that the total volume on either side of it remains constant as diffusion proceeds. In the particular case under consideration it is therefore fixed with respect to the containing vessel. The origin from which x is measured is such that the x-coordinate of the section is constant; x is measured in normal units of length, e.g. cm., and the same unit of length is used in measuring the volume which appears in the definition of concentration. If the unit of time adopted is the second it follows that the units of D_A^V and D_B^V are each cm.² sec.⁻¹ These somewhat obvious statements are made here in full because it will be seen later in § 11.3 below that other scales of length and alternative ways of measuring concentration are more suitable in some circumstances.

Let V_A and V_B denote the constant volumes of the unit amounts used in defining the concentrations of A and B. Thus if C_A is expressed in g. per unit volume, V_A is the volume of 1 g. of A. In dilute solutions, where the volume changes in the range of concentration concerned can be considered negligible, V_A and V_B will be the partial specific or molar volumes. That of the solute may be very different from the specific volume in the pure state. The volume transfer of A per unit time across unit area of the section defined is therefore

and that of B is
$$-D_B^V V_A \partial C_A / \partial x$$
,
 $-D_B^V V_B \partial C_B / \partial x$.

By definition of the section as one across which there is no net transfer of volume we have immediately

$$D_A^V V_A \frac{\partial C_A}{\partial x} + D_B^V V_B \frac{\partial C_B}{\partial x} = 0.$$
 (11.4)

The volume of A per unit overall volume of solution is $V_A C_A$ and of B is $V_B C_B$, so that, since only molecules of A and B are present, we have

$$V_A C_A + V_B C_B = 1, (11.5)$$

which, following differentiation with respect to x, becomes

$$V_A \frac{\partial C_A}{\partial A} + V_B \frac{\partial C_B}{\partial A} = 0. \tag{11.6}$$

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$\partial x \partial x \partial x$

In order that (11.4) and (11.6) shall both be satisfied it follows that $D_A^V \equiv D_B^V$. (11.7) or else that $V_A = 0$ or $V_B = 0$. (11.8) If $V_A = 0$ and $V_B \neq 0$, it follows from (11.6) that $\partial C_B / \partial x = 0$, (11.9)

and further reference is made to this case in §11.64 below. In either

OF DIFFUSION COEFFICIENTS § 11.2]

case the behaviour of a two-component system, satisfying the condition of zero volume change on mixing, may be described in terms of a single diffusion coefficient, which may vary with composition. It is convenient to refer to it as the mutual diffusion coefficient denoted henceforth by D^{V} . This coefficient is familiar in the interdiffusion of gases [1]. Its physical significance is considered later in §11.4.

11.3. Alternative frames of reference

The definition of the volume-fixed section used in § 11.2 above is unambiguous only as long as the total volume of the diffusion system remains constant. If there is an overall change of volume of the two components on mixing, the side of the section on which the volume is to remain constant must be chosen arbitrarily, and the diffusion coefficient becomes equally arbitrary. In such a case some alternative frame of reference must be used in defining the section across which transfer of diffusing substance is to be measured. There are clearly several possible alternatives. Thus, for example, the total mass of the system will always be conserved even though volume is not, and a section can be defined consistently such that the mass of the system on either side of the section remains constant during diffusion.

Where a convention other than that of constant volume on either side is used in defining a section, the second-order differential equation describing diffusion may not take the standard form of (9.5). It is clearly convenient if it can be made to do so since the standard form has frequently been used as the starting-point in calculations of diffusion behaviour. This can always be arranged by departing from the orthodox linear scale, e.g. cm., for measurement of the spatial coordinate so far denoted by x, and by measuring concentration in a certain way. Let some modified scale of length be denoted by ξ , and consider two sections, fixed on the same convention, at ξ and $\xi + d\xi$. The rate of entry of A into the volume enclosed between these sections is F_A and that of departure is $F_A + (\partial F_A / \partial \xi) d\xi$. The rate of accumulation is therefore

 $-(\partial F_A/\partial\xi) d\xi,$

and this is always true independently of how F_A and ξ are measured. It can only be equated to $(\partial C_A/\partial t) d\xi$, however, when C_A and ξ are measured in certain consistent units. Thus, if the sections are fixed with respect to total mass, then ξ must be measured so that equal increments of ξ always include equal increments of total mass, and $C_{\!\!A}$ must be defined as the amount of A per unit total mass. Similarly, if

the sections are fixed with respect to volume or mass of component B, equal increments of ξ must include equal increments of amount of B, and C_A must be expressed as the amount of A per unit amount of B. In general, for all values of ξ and t, the element of unit length in terms of ξ , and of unit cross-sectional area, is that which contains an amount of A equal to the unit used in defining the concentration C_A . When the quantities C_A and ξ satisfy this condition the usual relationship

$$\frac{\partial C_A}{\partial t} d\xi = -\frac{\partial F_A}{\partial \xi} d\xi \qquad (11.10)$$

follows at once, and by substituting for F_A from the relationship

$$F_A = -D \partial C_A / \partial \xi \tag{11.11}$$

we derive the familiar form of the diffusion equation

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial \xi} \left(D \frac{\partial C_A}{\partial \xi} \right). \tag{11.12}$$

It is convenient that ξ should have the dimension of length and D the usual dimensions of $(\text{length})^2(\text{time})^{-1}$. This can be arranged without interfering with the generality or simplicity of (11.12), by multiplying the mass of component B (or the total mass of A and B together if this is the reference system being used) by an arbitrary constant specific volume. The volume represented by the product of a mass of B, for example, and this arbitrary specific volume will be referred to for convenience as the basic volume of that mass of B.

The concentration of A was defined above as the amount of A per unit amount of B. We now redefine the concentration of A as the amount per unit basic volume of B, and unit ξ to contain unit basic volume of B per unit area. A convenient arbitrary specific volume is that of the pure component B, so that the basic volume of a certain mass of B is the volume that mass of B would occupy in the pure state.

The same arbitrary specific volume is used for concentrations expressed in the original definition per unit mass of A and B together, i.e. the basic volume of a mass of A and B together is obtained by multiplying the mass by the same arbitrary specific volume. This is true also for deriving the basic volume of A alone, so that the basic volume has a simple physical significance only in the case of the basic volume of B. Nevertheless, the use of this particular basic volume has the convenience that all the concentrations measured in the different frames of reference tend to the same value in dilute solutions. Concentration is, of course, frequently expressed in a number of different ways and so the symbol C_A is retained, but the appropriate index V, B, or M as superscript is added, so that the concentration of Ais written C_A^V , C_A^B , or C_A^M according as the amount of A is contained in unit volume of solution, or in unit basic volume of B or in unit basic volume of total mass. According as unit ξ contains, per unit area, unit basic volume of B or of A and B together, the symbol ξ_B or ξ_M is used. The diffusion coefficients D_A^V , D_A^B , D_A^M also carry an index to indicate the frame of reference to which they refer. The arbitrary specific volume may be denoted by V_B^0 , and then ξ_B and ξ_M are defined formally by the respective relationships

$$d\xi_B = V_B^0 C_B^V dx, (11.13)$$

$$d\xi_M = V_B^0(C_A^V + C_B^V) \, dx. \tag{11.14}$$

11.31. Sections fixed with respect to total mass and mass of one component

It was found in § 11.2 that the behaviour of a two-component system satisfying the condition of zero volume change on mixing can be represented in terms of a single diffusion coefficient D^{ν} . A similar result follows readily for a system in which volume changes occur, provided the diffusion coefficients are defined with respect to a mass-fixed section. Thus the equation defining such a section is

$$D_A^M \frac{\partial C_A^M}{\partial \xi_M} + D_B^M \frac{\partial C_B^M}{\partial \xi_M} = 0, \qquad (11.15)$$

and the definitions of C_A^M and C_B^M lead immediately to the equation

$$C_A^M + C_B^M = 1/V_B^0.$$
 (11.16)

On differentiating (11.16) with respect to ξ_M and comparing with (11.15) we find $D^M_A \equiv D^M_B$. (11.17)

If a section fixed with respect to one component, say B, is used, then clearly $D_B^B = 0$ and only the coefficient D_A^B is needed to describe the diffusion behaviour. Thus the statement that the diffusion behaviour of a two-component system can be described in terms of a single diffusion coefficient, is valid whether there is a change of volume of the whole

system or not, provided the appropriate frame of reference is used in defining the diffusion coefficient. Frames of reference could be so chosen that the two coefficients are not identical and neither is zero, but they would be related through some function of the partial volumes and would not be independent measures of two separate diffusion processes. The possibility of measuring the diffusion of the two molecular species independently is discussed in § 11.4.



11.32. Relations between the diffusion coefficients D_A^V , D_A^M , D_A^B

The rate of transfer of A through a B-fixed section is greater than that through a total-mass-fixed section by an amount given by the concentration of A per unit mass of B multiplied by the flux of B across the mass-fixed section. Thus the flux of A across a B-fixed section in the direction of ξ increasing is

$$-D^{M}\frac{\partial C^{M}_{A}}{\partial \xi_{M}} + D^{M}\frac{C^{M}_{A}}{C^{M}_{B}}\frac{\partial C^{M}_{B}}{\partial \xi_{M}} = -\frac{D^{M}}{C^{M}_{B}}\frac{\partial C^{M}_{A}}{\partial \xi_{M}}, \qquad (11.18)$$

using (11.16).

But the rate of transfer across a *B*-fixed section is $-D_A^B \partial C_A^B / \partial \xi_B$ so that we have $D^M - \partial C^M - \partial \xi_B$.

$$D_A^B = \frac{D^M}{V_B^0 C_B^M} \frac{\partial C_A^m}{\partial \xi_M} \frac{\partial \xi_B}{\partial C_A^B}.$$
 (11.19)

From the definitions of C_A^M and C_A^B it is easy to show that

$$\frac{dC_A^M}{dC_A^R} = (V_B^0 C_B^M)^2. \tag{11.20}$$

Also since

$$d\xi_{M} = V_{B}^{0}(C_{A}^{\nu} + C_{B}^{\nu}) \, dx, \qquad d\xi_{B} = V_{B}^{0} \, C_{B}^{\nu} \, dx, \qquad (11.21)$$

$$\frac{\partial \xi_B}{\partial \xi_M} = V_B^0 C_B^M, \qquad (11.22)$$

we have

so that finally, by substituting (11.22) and (11.20) in (11.19), we find

$$D^B_A = D^M (V^0_B \, C^M_B)^2, \tag{11.23}$$

since rearrangement of the partial derivatives in (11.19) is permissible. For a system in which there is zero volume change on mixing, so that V_A and V_B are constant, the relation between D_A^B and D^V can be similarly established. Thus the flux of A across a B-fixed section in the direction of ξ increasing is

$$-D^{\nu}\frac{\partial C_{A}^{\nu}}{\partial x} + D^{\nu}\frac{C_{A}^{\nu}}{C_{B}^{\nu}}\frac{\partial C_{B}^{\nu}}{\partial x} = -\frac{D^{\nu}}{V_{B}C_{B}^{\nu}}\frac{\partial C_{A}^{\nu}}{\partial x}, \qquad (11.24)$$

using (11.5) and (11.6). But the rate of transfer of A across a B-fixed

section is $-D_A^B \partial C_A^B / \partial \xi_B$, so that we have

$$D_{A}^{B} = \frac{D^{V}}{V_{B} C_{B}^{V}} \frac{\partial C_{A}^{V}}{\partial x} \frac{\partial \xi_{B}}{\partial C_{A}^{B}}.$$
 (11.25)

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(11.26)

From the definition of $C^{\mathcal{V}}_{\mathcal{A}}$ and $C^{\mathcal{B}}_{\mathcal{A}}$ it follows that

$$\frac{dC^V_A}{dC^B_A} = (V_B C^V_B)^2,$$

and from the second of (11.21) we have immediately

$$\frac{\partial \xi_B}{\partial x} = V_B C_B^V, \qquad (11.27)$$

so that on substituting (11.26) and (11.27) in (11.25) we find

$$D_A^B = D^V (V_B C_B^V)^2 = D^V (\text{volume fraction of } B)^2.$$
(11.28)

Since (11.28) applies only when V_B is constant, and therefore $V_B = V_B^0$, comparison of (11.28) and (11.23) shows that when there is no overall volume change accompanying diffusion

$$D^M = D^V (C_B^V / C_B^M)^2 = D^V$$
 (basic total volume/true total volume)².
(11.29)

11.4. Intrinsic diffusion coefficients

We saw in § 11.31 that any two-component system can be described by a single or mutual diffusion coefficient, which may be a function of composition but will be the same function for both components. In the simplest case, where the molecules of the components A and B are identical in mass and size, the rates of transfer of A and B due to random motion across a volume-fixed section may reasonably be expected to be equal and opposite. In general, however, differences of mass and size of A and B molecules result in the transfer of A by random motions being greater or less than that of B. Consequently, a hydrostatic pressure tends to be built up in the region of the solution which contributes least to the volume rate of transfer. This pressure is relieved by a compensating mass-flow of A and B together, that is of the whole solution [1, 2]. This existence of mass flow can be demonstrated in the case of gases, when diffusion occurs across a porous plate which offers considerable viscous resistance. In this case, an increased pressure is found to arise in that part of the vessel occupied initially by the slower diffusing component. It has been demonstrated in metal systems [3] and in polymer-solvent systems [4] by the insertion of marker particles.[†] In the latter case, the large polymer molecules will diffuse far more slowly, as a result of random motions, than the small solvent molecules. Thus

the polymer movement measured by the mutual diffusion coefficient is almost entirely a mass-flow.

Thus the overall rate of transfer, say of component A, across a volume-fixed section may be expressed as the combined effect of mass-flow and

[†] The marker movement is often referred to as the Kirkendall effect, since it was first observed in metals by Kirkendall, E. O., *Trans. Am. Inst. Mining Met. Engrs.* **147** (1942) 104.



true diffusion resulting from the random motion of non-uniformly distributed A molecules. From the point of view of interpreting diffusion coefficients in terms of molecular motions, the mutual diffusion coefficient $D^{\mathcal{P}}$ thus appears to be unnecessarily complicated by the presence of the mass-flow. It is desirable to define new diffusion coefficients, \mathscr{D}_A and \mathscr{D}_B , in terms of the rate of transfer of A and B, respectively, across a section fixed so that no mass-flow occurs through it. Such a section may be impossible to determine in practice, except in special conditions mentioned below. It is fixed in a different way from any of the other sections previously dealt with, and it must follow the mass-flow although this flow is not normally directly observable. These new diffusion coefficients will be referred to as 'intrinsic diffusion coefficients'. When the partial volumes are constant they are related to the mutual diffusion coefficient in the following way.

On one side of a section fixed so that no mass-flow occurs through it, there is a rate of accumulation of total volume of solution, which may be denoted by ϕ , where

$$\phi = V_{A} \mathscr{D}_{A} \frac{\partial C_{A}^{V}}{\partial x} + V_{B} \mathscr{D}_{B} \frac{\partial C_{B}^{V}}{\partial x}.$$
 (11.30)

As thus defined, ϕ is actually the rate of increase of volume on the side of smaller x, and this must be equal to the rate of transfer of total volume by mass-flow across a volume-fixed section. Such a mass-flow involves a rate of transfer of A of ϕC_A^{ν} , so that, equating two expressions for the net rate of transfer of A across the volume-fixed section, we find

$$D^{\nu}\frac{\partial C^{\nu}_{A}}{\partial x} = \mathscr{D}_{A}\frac{\partial C^{\nu}_{A}}{\partial x} - \phi C^{\nu}_{A}. \qquad (11.31)$$

On substituting for ϕ from (11.30) and using (11.6) we have finally

$$D^{V} = V_{\mathcal{A}} C^{V}_{\mathcal{A}} (\mathscr{D}_{\mathcal{B}} - \mathscr{D}_{\mathcal{A}}) + \mathscr{D}_{\mathcal{A}}.$$
(11.32)

If the molal volumes vary with composition, the coefficient D^{ν} has no physical significance, but \mathscr{D}_{A} , \mathscr{D}_{B} can still be defined in terms of the rates of transfer of A and B respectively across a section which moves so that there is no mass-flow, of A and B together, through it. It is convenient in this case to relate the intrinsic diffusion coefficients to D_{A}^{B} . Since the net rate of transfer of B through a B-fixed section is, by definition, zero, it follows that the contributions to the transfer of Bresulting from the overall mass-flow and from the true diffusion of Brelative to the mass-flow, must be equal and opposite. The rate of transfer of B by true diffusion relative to the mass-flow is

 $-\mathcal{D}_{B}\partial C_{B}^{V}/\partial x,$

in the direction of x increasing, and hence the volume transfer of the whole solution accompanying mass-flow with respect to the *B*-fixed section is given by $\mathcal{D}_{-} \partial C \mathcal{U}$

$$\frac{\mathscr{D}_B}{C_B^V}\frac{\partial C_B^V}{\partial x},$$

in the direction of x increasing. This produces a rate of transfer of A through the *B*-fixed section of

$$\frac{C_{A}^{V}}{C_{B}^{V}}\mathscr{D}_{B}\frac{\partial C_{B}^{V}}{\partial x},$$

due to the mass-flow. This is to be combined with the rate of transfer of A relative to the mass-flow which is given by

$$-\mathscr{D}_{A}\partial C^{V}_{A}/\partial x$$

to give the net rate of transfer of A across a B-fixed section, which is simply $-D_A^B \partial C_A^B / \partial \xi_B$.

Thus we have the equation

$$-D^B_{\mathcal{A}} \frac{\partial C^B_{\mathcal{A}}}{\partial \xi_B} = -\mathscr{D}_{\mathcal{A}} \frac{\partial C^V_{\mathcal{A}}}{\partial x} + \frac{C^V_{\mathcal{A}}}{C^V_B} \mathscr{D}_B \frac{\partial C^V_B}{\partial x}.$$
 (11.33)

When the molal volumes are not constant, the relationship

$$V_{\mathcal{A}}C_{\mathcal{A}} + V_{\mathcal{B}}C_{\mathcal{B}} = 1$$

still holds, but the differentiated form (11.6) is to be replaced by

$$\begin{pmatrix} V_A + C_A^V \frac{dV_A}{dC_A^V} \end{pmatrix} \frac{\partial C_A^V}{\partial x} + \begin{pmatrix} V_B + C_B^V \frac{dV_B}{dC_B^V} \end{pmatrix} \frac{\partial C_B^V}{\partial x} = 0.$$
 (11.34)
$$\frac{dC_A^V}{dC_A^B} = V_B^0 V_B (C_B^V)^2,$$

Since

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it follows immediately from (11.27), (11.33), and (11.34) that

$$D_{\mathcal{A}}^{B} = V_{B} C_{B}^{V} (V_{B}^{0} C_{B}^{V})^{2} \left\{ \mathscr{D}_{\mathcal{A}} + \mathscr{D}_{B} \frac{C_{\mathcal{A}}^{V}}{C_{B}^{V}} \frac{V_{\mathcal{A}} + C_{\mathcal{A}}^{V} dV_{\mathcal{A}} / dC_{\mathcal{A}}^{V}}{V_{E} + C_{B}^{V} dV_{E} / dC_{B}^{V}} \right\}.$$
(11.35)

This reduces to (11.32) when V_A and V_B are constant.

It is clear from (11.32) or (11.35) that the values of \mathscr{D}_A and \mathscr{D}_B cannot be deduced separately, unless some information other than D^{ν} or D^B_A is available. One possibility is to use an observation of the mass-flow, as suggested by Darken [3] and by Hartley and Crank [5]. Sometimes, e.g. in solvent-polymer systems, the intrinsic diffusion for one component, e.g. the polymer, is so much smaller than for the other that it can be assumed to be zero. With the assumption that $\mathscr{D}_B = 0$ we have from (11.32)

$$\mathscr{D}_{A} = D^{V}/(1-V_{A}C_{A}^{V}) = D^{V}/(V_{B}C_{B}^{V}) = D^{V}/(\text{volume fraction of } B),$$
(11.36)

which allows the intrinsic diffusion coefficient of component A and its dependence on concentration to be deduced from observations of D^{ν} . The ideas discussed above in §§ 11.1–11.4 have been the subjects of papers by Darken [3], Hartley and Crank [5], Kuusinen [6], and Lamm [7].

11.5. 'Self'-diffusion coefficients

By using radioactively-labelled molecules it is possible to observe the rate of diffusion of one component in a two-component system of uniform chemical composition. Since what is involved is an interchange of labelled and unlabelled molecules which are otherwise identical there is no mass-flow and the true mobility of the labelled molecules with respect to stationary solution is measured. Nevertheless, the diffusion coefficient so deduced will in general differ from the corresponding intrinsic diffusion coefficient for the same chemical composition. Johnson [8] has found this to be so in metal systems. Seitz [9], regarding the diffusion process as a jumping of molecules from one equilibrium position to another, accounts for the difference on the basis that when there is a gradient of chemical composition the frequency with which a molecule jumps to the right is not the same as that with which it jumps to the left. For the labelled molecules, however, the two frequencies are identical. Darken [3] and Prager [10] have related the diffusion coefficient measured by an experiment using radioactive molecules to the intrinsic diffusion coefficient in terms of the thermodynamic properties of the system. Their result can be anticipated as follows.

Consider a two-component system comprising molecules A and B and let the gradient of concentration C_A of A be maintained in an equilibrium

condition by the application of a force F_A per g. mole of A in the direction of increasing x. This is purely a hypothetical operation but it can be realized in the case of large molecules, much different in density from the solvent, by a centrifugal field. The generalized form of the condition for this thermodynamic equilibrium is

$$F_{A} = \partial \mu_{A} / \partial x,$$
 (11.37)

where μ_A is the chemical potential of component A. The rate of transfer

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of A due to the force F_A is

$$\frac{F_A C_A}{\sigma_A \eta} = \frac{C_A}{\sigma_A \eta} \frac{\partial \mu_A}{\partial x}, \qquad (11.38)$$

where $\sigma_A \eta$ is a resistance coefficient. But in the equilibrium condition (11.38) is also the rate of transfer by diffusion relative to a section through which there is no mass-flow and so we have

$$\mathscr{D}_{A}\frac{\partial C_{A}}{\partial x} = \frac{C_{A}}{\sigma_{A}}\frac{\partial \mu_{A}}{\partial C_{A}}\frac{\partial C_{A}}{\partial x}, \qquad (11.39)$$

$$\mathscr{D}_{A} = \frac{C_{A}}{\sigma_{A} \eta} \frac{\partial \mu_{A}}{\partial C_{A}}.$$
 (11.40)

and hence

On applying the same treatment to the labelled molecules in a system of uniform chemical composition we have

$$F_A^* = \frac{\partial \mu_A^*}{\partial x} = \frac{RT}{\overline{C}_A^*} \frac{\partial C_A^*}{\partial x}, \qquad (11.41)$$

because of the ideality of the system, where asterisks denote properties of labelled molecules. Instead of (11.40), therefore, we obtain

$$\mathscr{D}_{A}^{*} = \frac{1}{\sigma_{A} \eta}, \qquad (11.42)$$

it being legitimate to equate the resistance coefficients at the same chemical composition. Thus finally

$$\mathscr{D}_{A} = \mathscr{D}_{A}^{*} C_{A} \partial \mu_{A} / \partial C_{A}. \tag{11.43}$$

11.6. Methods of measurement

Most of the earlier methods of measurement assumed the diffusion coefficient to be constant. When such methods are applied to systems in which this is not so, a mean value for the conditions of the experiment is obtained. Methods are basically of two types according to whether the flow is steady or transient. When the steady-state flow is observed through a membrane or sintered disk, for example, the diffusion coefficient is given immediately as the quotient of the flow-rate through unit area divided by the concentration gradient. In some non-steady state experiments, the concentration distribution is observed at a known time t after the commencement of diffusion. Solution of the diffusion equation for the appropriate boundary conditions leads to a theoretical concentration-distance curve in terms of the variable Dt. Comparison of experimental and theoretical curves yields the diffusion coefficient, D. Various ways of carrying out the comparison are reviewed by Alexander and Johnson [11], Chapter X. A variant is to observe the overall rate

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of uptake or loss of diffusing substance by a specimen of known size and shape, and to compare this with the calculated rate of uptake expressed as a function of Dt. In some cases, special tables have been constructed to facilitate the calculations. Stefan's tables [12], to which reference was made earlier in § 4.38, refer to the diffusion of solute from a column of solution into a column of water. They give the amount of diffusing substance contained in successive layers of equal height. These tables and others of a similar nature are reproduced and discussed by Jost [13, p. 63]. In all these methods, the difficulties lie in the experimental techniques rather than in the subsequent mathematics. Adequate accounts are already available [13, 14]. It suffices to say here, following the discussion of the alternative definitions of diffusion coefficients, that in the early measurements it is usually assumed that the total volume of the system remains constant as diffusion proceeds and so the mutual diffusion coefficient D^{ν} is measured. A notable exception is that of Clack [15], who introduced a correction for mass-flow and obtained in effect the coefficient D_A^B of solute with respect to stationary solvent. A number of examples are discussed in more detail in reference [5].

We shall now confine attention to some of the mathematical methods by which the concentration-dependence of the diffusion coefficient has been deduced from experimental data.

11.61. Steady-state method

Experimental methods of realizing steady-state conditions have been reviewed by Newns [16]. Suppose, as an example, that we have a membrane of thickness l separating a region of high vapour pressure from one of low vapour pressure. Provided the vapour pressures are maintained constant, a steady-state transfer of vapour through the membrane is set up. The concentrations C_0 and C_1 , just within the two surfaces of the membrane, are constant and are the equilibrium uptakes for the high and low vapour pressures respectively. The rate of transfer, F, of vapour through the membrane in the steady state is given by

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$$F = -D_C dC/dx, \qquad (11.44)$$

which on integration becomes

$$\int_{0}^{l} F \, dx = \int_{C_1}^{C_0} D_C \, dC. \tag{11.45}$$

In (11.44) and (11.45) D_C is the value of the diffusion coefficient for a concentration C. Since we are concerned with a steady state, F is the

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same through each section of the membrane, i.e. F is independent of x. Hence i i

$$\int_{0}^{1} F \, dx = F \int_{0}^{1} dx = Fl, \qquad (11.46)$$

and therefore

$$F = \frac{1}{l} \int_{C_1}^{C_0} D_C \, dC. \tag{11.47}$$

By determining F experimentally for a fixed low vapour pressure C_1 (it may be zero) and different values of the high vapour pressure C_0 , and differentiating the curve relating F and C_0 , the diffusion coefficient D_C is obtained for different concentrations C. Alternatively we may proceed as follows, taking for simplicity the case in which $C_1 = 0$. If we neglect the concentration-dependence of D_C we obtain a mean diffusion coefficient D_I given from (11.45) by

$$Fl = \int_{0}^{l} F \, dx = \int_{0}^{C_{0}} D_{I} \, dC = D_{I} \, C_{0}. \tag{11.48}$$

Thus equating (11.48) and (11.45) we have

$$C_0 D_I = \int_0^{C_0} D_C \, dC, \qquad (11.49)$$

so that

$$D_{C=C_0} = D_I + C_0 \, dD_I / dC_0 \tag{11.50}$$
nction D_C can be deduced by observing D_I for different values

and the function D_C can be deduced by observing D_I for different values of C_0 and differentiating.

Barrer [17] points out that the concentration-dependence can be deduced from one experiment provided the concentration distribution through the membrane in the steady state is observed, as well as the rate of flow through. Clearly it is possible to obtain D_C from (11.44) if both dC/dx and F are observed experimentally. The method can equally well be applied to a medium in the form of a spherical or cylindrical shell [17]. Also, of course, if the diffusion coefficient is known to be a function of distance through the sheet or shell, i.e. the medium is nonhomogeneous, the variation of D can be deduced from (11.44) or from the corresponding equations for the shell [17]. If the membrane swells as the steady state is established, and this is very likely to occur, then the thickness of the membrane in ordinary units of length, e.g. cm., will vary with time. In such a case, the modified scale of length ξ_B , introduced in equation (11.13), may usefully be used, since the thickness on this scale, being the basic volume of the membrane per unit area, remains constant and equal to its unswollen value. We are then measuring the rate of flow relative to a section fixed with respect to the membrane which, using the nomenclature of § 11.31, is the component *B* of a two-component system. Provided the concentration of the vapour is expressed as the amount of vapour per unit basic volume of the substance of the membrane and *l* is the unswollen thickness, the diffusion coefficient obtained from (11.47) is D_A^B , where *A* is the vapour and *B* the membrane. If there is no overall change of volume of the whole system when the vapour enters the membrane, D_A^B is related to the mutual coefficient D^V by equation (11.28).

11.62. Analysis of concentration-distance curves

There are a number of optical methods for observing how either the refractive index or its gradient depends on distance measured in the direction of diffusion at a given time. Numerous references are given by Hartley and Crank [5], Jost [13], and others. Concentration-distance curves can also be obtained in the case of two metals interdiffusing [14, p. 239]. If two infinite media are brought together at t = 0, e.g. two long columns of liquid or two metal bars, the diffusion coefficient and its concentration-dependence can readily be deduced from the concentration distribution observed at some known subsequent time. The conditions of the experiment are

$$C = C_{\infty}, \quad x < 0, \quad t = 0,$$
 (11.51)

(11.53)

$$C = 0, \qquad x > 0, \qquad t = 0, \tag{11.52}$$

where C is the concentration of the component in which we are interested, and x = 0 is the position of the initial interface between the two components at time t = 0. Assume for the moment that there is no overall change of volume on mixing and that C is measured as mass per unit volume of the system. Then we may use the Boltzmann variable $\eta = x/2t^{\frac{1}{2}}$ and as in § 9.31 we obtain the ordinary differential equation

$$dC = d (dC)$$

$$-2\eta \frac{d\sigma}{d\eta} = \frac{d}{d\eta} \left(D \frac{d\sigma}{d\eta} \right).$$

On integration with respect to η (11.53) becomes

$$-2\int_{0}^{C_{1}}\eta \, dC = \left[D\frac{dC}{d\eta}\right]_{C=0}^{C=C_{1}} = \left(D\frac{dC}{d\eta}\right)_{C=C_{1}}, \qquad (11.54)$$

since $D dC/d\eta = 0$ when C = 0. Here C_1 is any value of C between 0

and C_{∞} . Finally, by rearrangement of (11.54) and introducing x and t, we have

$$D_{C=C_1} = -\frac{1}{2t} \frac{dx}{dC} \int_{0}^{0} x \, dC.$$
 (11.55)

Since $(D dC/d\eta)_{C=C_{\infty}} = 0$ also, it follows from (11.54) that



F10. 11.1. Evaluation of D from a concentration-distance curve using (11.55).

and in order that the boundary conditions shall be satisfied the origin from which x is measured must be such that (11.56) is satisfied. In other words, the plane, x = 0, must be chosen so that the two shaded areas in Fig. 11.1 (a) are equal. In a constant volume system (11.56) is a conservation of mass condition and it is clearly satisfied if x is measured from the initial position of the boundary between the two components at time t = 0. In this case, therefore, the procedure is to plot the concentration-distance curve for a known time as in Fig. 11.1 (b), to locate the plane x = 0 by use of (11.56), and then to evaluate D at

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various concentrations C_1 from (11.55). The integrals can be obtained by using a planimeter or by counting squares and the gradients dx/dCby drawing tangents. In Fig. 11.1 (b) the area representing $\int_{0}^{C_1} x \, dC$ is snown shaded. Diffusion coefficients in metal systems were obtained by Matano [18] using this method, and since then it has been widely used. Alternative ways of using (11.55) have been suggested.

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(i) One development has been found useful in dilute solutions [19]. On integrating by parts (11.55) becomes

$$D_{C=C_{1}} = -\frac{1}{2t} \frac{dx}{dC} \left(x_{1}C_{1} - \int_{\infty}^{x_{1}} C \, dx' \right)$$

$$= -\frac{1}{4t} \frac{x_{1}}{(\log C_{1})^{\frac{1}{2}}} \frac{dx}{d(\log C)^{\frac{1}{2}}} \left(1 + \frac{1}{x_{1}C_{1}} \int_{x_{1}}^{\infty} C \, dx' \right), \quad (11.57)$$

where x_1 is the value of x at which $C = C_1$ and the derivatives are to be measured at the point $x = x_1$. The determination of the gradients at various concentrations is made simpler by this modification if the graph of x against $(\log C)^{\frac{1}{2}}$ is nearly linear as it is in some systems [19].

A corresponding analysis can be applied to the penetration of diffusing substance into an effectively semi-infinite sheet, provided the concentration-distance curve can be obtained. An example is the diffusion of dye molecules from a well-stirred solution into a cellulose sheet [20]. Equation (11.55) still holds if x is measured from the surface of the sheet.

(ii) Graphical or numerical methods of evaluating the diffusion coefficient from (11.55) have certain disadvantages. They entail the measurement of slopes and areas under curves and it is clear from the behaviour of the concentration-distance curves in Fig. 11.1 that considerable uncertainty arises for concentrations near the limiting values. Often the values of diffusion coefficients for very small concentrations of one component are of great importance and so it is desirable to be able to calculate them as accurately as the experimental data permit. A method of improving the accuracy of the calculations near the extremes of the concentration-range has been suggested by Hall[21]. He examines some experimental data of da Silva and Mehl [22] for the copper-silver system. Using the nomenclature of the previous section, he takes C to be the concentration of copper and C_{∞} to be 100 per cent. copper. Fig. 11.2, taken from Hall's paper, is a probability plot of C/C_{∞} against $x/t^{\frac{1}{2}}$, i.e. the variable u which is used as ordinate is given by

 $\frac{1}{2}(1+\operatorname{erf} u) = C/C_{\infty}.$ (11.58)

Other relationships involving error functions can of course be used. Hall finds (11.58) convenient for purposes of calculation. We avoid his use of the function erfc for the left-hand side of (11.58) because it is not standard notation. The point of interest is that when plotted in this way the concentration-distance curve becomes linear at the two ends of the concentration range. Now a straight line on this plot corresponds to an equation of the type





so that, from (11.58) and (11.59), we have

$$C/C_{\infty} = \frac{1}{2} \{1 + \operatorname{erf}(h\eta + k)\}.$$
(11.60)

It readily follows that

and

$$\frac{d\eta}{dC} = \frac{\pi^{\frac{1}{2}}}{hC_{\infty}} \exp(u^{2}),$$
(11.61)
$$\int_{0}^{C} \eta \, dC' = \frac{hC_{\infty}}{\pi^{\frac{1}{4}}} \int_{-\infty}^{\eta} \eta' \exp\{-(h\eta'+k)^{2}\} \, d\eta'$$

$$= -\frac{C_{\infty}}{2h\pi^{\frac{1}{4}}} \exp(-u^{2}) - \frac{kC}{h}.$$
(11.62)

If now we write (11.55) in terms of η and substitute from (11.61) and (11.62) we obtain

$$D(C) = \frac{1}{h^2} + k \frac{\pi^{\dagger}}{h^2} (1 + \operatorname{erf} u) \exp(u^2).$$
 (11.63)

The differences between (11.63) and Hall's final expression are because the η used here differs from his λ by a factor of 2. The quantities h and k are obtained respectively as the slope and intercept of the linear portion of the probability plot, and D is evaluated from (11.63) simply by substituting these values and that of u which through (11.58) corresponds to the C/C_{∞} for which D is required. The relationship (11.63) can be applied at each end of the concentration range with appropriate values for h and k. In the intermediate curved portion of Fig. 11.2, slopes and areas must be measured on a plot of the type shown in Fig. 11.1 and the diffusion coefficient deduced from (11.55). Evidence of the improved accuracy resulting from the use of (11.63) is advanced by Hall [21].

11.63. Systems in which there is a volume change on mixing

The interdiffusion of two components forming a system in which volume changes occur on mixing has been considered by Prager [10] as follows. The rates at which the concentrations of the two components C_A and C_B change at a point are given by

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\mathscr{D}_A \frac{\partial C_A}{\partial x} \right) - \frac{\partial}{\partial x} (v C_A), \qquad (11.64)$$

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x} \left(\mathscr{D}_B \frac{\partial C_B}{\partial x} \right) - \frac{\partial}{\partial x} (v C_B), \qquad (11.65)$$

where \mathscr{D}_{A} and \mathscr{D}_{B} are the intrinsic diffusion coefficients introduced in § 11.4, and v is the velocity of the mass-flow assumed to be in the xdirection and dependent only on the x coordinate and the time t. There is a relationship between C_{A} and C_{B} at constant temperature and pressure which is (11.66)

$$V_{\mathcal{B}}C_{\mathcal{B}}+V_{\mathcal{A}}C_{\mathcal{A}}=1,$$

where the V's are the partial molal volumes of the two components, and also we have $(\partial C_B/\partial C_A)_{P,T} = -V_A/V_B.$ (11.67)

Using (11.66) and (11.67) in (11.65) we find

$$-\frac{V_A}{V_B}\frac{\partial C_A}{\partial t} = -\frac{\partial}{\partial x}\left(\mathscr{D}_B\frac{V_A}{V_B}\frac{\partial C_A}{\partial x}\right) - C_B\frac{\partial v}{\partial x} + \frac{V_A}{V_B}\frac{\partial C_A}{\partial x},\qquad(11.68)$$

and combining (11.68) with (11.64) yields

$$\frac{\partial v}{\partial x} = V_{\underline{A}} \frac{\partial}{\partial x} \left(\mathscr{D}_{\underline{A}} \frac{\partial C_{\underline{A}}}{\partial x} \right) - V_{\underline{B}} \frac{\partial}{\partial x} \left(\mathscr{D}_{\underline{B}} \frac{V_{\underline{A}}}{V_{\underline{B}}} \frac{\partial C_{\underline{A}}}{\partial x} \right).$$
(11.69)

Integration by parts from $-\infty$ to x transforms (11.69) into

$$v = V_{A}(\mathscr{D}_{A} - \mathscr{D}_{B})\frac{\partial C_{A}}{\partial x} + \int_{-\infty}^{\infty} \frac{C_{B}}{C_{A}} \left(\mathscr{D}_{A} + \mathscr{D}_{B}\frac{V_{A}C_{A}}{V_{B}C_{B}}\right) \left(\frac{\partial V_{B}}{\partial C_{A}}\right) \left(\frac{\partial C_{A}}{\partial x}\right)^{2} dx',$$
(11.70)

where v and $\partial C_A/\partial x$ have been assumed zero at $x = -\infty$. Substituting (11.70) into (11.64) and (11.65) we find

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(D^V \frac{\partial C_A}{\partial x} \right) - \frac{\partial}{\partial x} \left\{ C_A \int_{-\infty}^x \frac{D^V}{V_B C_A} \left(\frac{\partial V_B}{\partial C_A} \right) \left(\frac{\partial C_A}{\partial x} \right)^2 dx' \right\}, \quad (11.71)$$

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x} \left(D^V \frac{\partial C_B}{\partial x} \right) - \frac{\partial}{\partial x} \left\{ C_B \int_{-\infty}^x \frac{D^V}{V_B C_A} \left(\frac{\partial V_B}{\partial C_A} \right) \left(\frac{\partial C_A}{\partial x} \right)^2 dx' \right\}, \quad (11.72)$$

where D^{V} is related to \mathscr{D}_{A} and \mathscr{D}_{B} by

$$D^{\nu} = \mathscr{D}_{A} V_{B} C_{B} + \mathscr{D}_{B} V_{A} C_{A}, \qquad (11.73)$$

which is equation (11.32). We should note that we are here defining D^{ν} by (11.73). It has the significance of a mutual diffusion coefficient as defined in § 11.2 only if there is no volume change on mixing. The second terms on the right-hand sides of (11.71) and (11.72) arise because of the volume changes on mixing, and they vanish when such changes do not occur, i.e. when $(\partial V_A/\partial C_A)_{P,T} = 0$, in which case (11.71) and (11.72) reduce to the usual diffusion equations.

If the initial distribution is such that

 $C_{A} = 0, \qquad x < 0, \qquad t = 0,$ (11.74)

$$C_A = C_{\infty}, \quad x > 0, \quad t = 0,$$
 (11.75)

then we can make the Boltzmann substitution [23] even if $(\partial V_A/\partial C_A)_{P,T}$

is not zero. Thus if we suppose $C_{\underline{A}}$ to be a function of $\eta = x/2t^{\underline{1}}$ only, equation (11.71) becomes

$$-2\eta \frac{dC_A}{d\eta} = \frac{d}{d\eta} \left(D^V \frac{dC_A}{d\eta} \right) - \frac{d}{d\eta} \left\{ C_A \int_{-\infty}^{\eta} \frac{D^V}{V_B C_A} \left(\frac{\partial V_B}{\partial C_A} \right) \left(\frac{dC_A}{d\eta} \right)^2 d\eta' \right\}, \quad (11.76)$$

with boundary conditions

$$C_{\underline{A}} = 0, \qquad \eta = -\infty; \qquad C_{\underline{A}} = C_{\infty}, \qquad \eta = \infty.$$
 (11.77)

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If the concentration distribution $C_{A}(\eta)$ is known from experiment, (11.76) can be solved for D^{V} to give

$$D_{C_{A}=C_{1}}^{V} = -2 \frac{d\eta}{dC_{1}} \left[\int_{0}^{C_{1}} \eta \ dC_{A} + C_{1} \int_{0}^{C_{1}} \frac{\int_{0}^{C_{1}} \eta \ dC_{A}}{C_{A} V_{B}} \left(\frac{\partial V_{B}}{\partial C_{A}} \right) dC_{A} \right]. \quad (11.78)$$

The first term on the right-hand side of (11.78), when written in terms of x and t, is the expression (11.55) for calculating D from the concentration distribution when there is no volume change on mixing. The second term is a small correction term in which we have substituted for D^{V} from (11.55) written in terms of η as an approximation.

It is of interest to examine what diffusion coefficient is obtained by the Matano procedure [18], as described in § 11.62, when there is a volume change on mixing. Continuing to denote by η the distance coordinate measured from the initial position of the boundary between the two components, Matano introduces a new coordinate η_1 measured from a new origin chosen so that $\int_{0}^{C_{\infty}} \eta_1 \, dC_A = 0$. If the new origin be at $\eta = -\delta$ then we have $\eta_1 = \eta + \delta$ and hence

$$\int_{0}^{C_{\infty}} (\eta - \delta) dC_{\mathbf{A}} = 0, \qquad (11.79)$$

so that

$$\delta = \frac{1}{C_{\infty}} \int_{0}^{C_{\infty}} \eta \, dC_A. \tag{11.80}$$

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Furthermore, Matano deduces a diffusion coefficient from the expression

$$D_{C_{A}=C_{1}} = -2 \frac{d\eta_{1}}{dC_{A}} \int_{0}^{C_{1}} \eta_{1} dC_{A}. \qquad (11.81)$$

Now $\int_{0}^{C_{1}} \eta_{1} dC_{A} = \int_{0}^{C_{1}} (\eta + \delta) dC_{A} = \int_{0}^{C_{1}} \eta dC_{A} + C_{1} \delta,$ (11.82)

and hence the diffusion coefficient calculated in this way is

$$D_{C_{A}=C_{1}} = -2\frac{d\eta}{dC_{A}} \left[\int_{0}^{C_{1}} \eta \ dC_{1}' + C_{1} \delta \right], \qquad (11.83)$$

since $d\eta_1/dC_A = d\eta/dC_A$ and where δ is given by (11.80). Comparing (11.83) with (11.78) shows that this procedure does not yield exactly the coefficient D^V related to the intrinsic diffusion coefficients by

(11.73) but only an approximation to it. It assumes

$$\int_{0}^{C_{1}} \frac{\int_{0}^{C_{1}} \eta \, dC_{A}}{C_{A} V_{B}} \left(\frac{\partial V_{B}}{\partial C_{A}} \right) dC_{A} = \text{constant}, \qquad (11.84)$$

the constant being δ , the displacement of the origin. Prager [10] suggests that a better approximation is to treat V_B and $(1/C_A)(\partial V_B/\partial C_A)$ as constants, in which case (11.78) becomes

$$D_{C_{A}=C_{1}} = -2 \frac{d\eta}{dC_{A}} \Big[\int_{0}^{C_{1}} \eta \ dC_{A} + BC_{1} \int_{0}^{C_{1}} \left(\int_{0}^{C_{1}} \eta \ dC_{A} \right) dC_{A}, \qquad (11.85)$$

where B is given by

$$B = -\left[\int_{0}^{C_{\infty}} \eta \, dC_{A}\right] / \left[C_{\infty} \int_{0}^{C_{\infty}} \left(\int_{0}^{C_{\infty}} \eta \, dC_{A}\right) \, dC_{A}\right]. \tag{11.86}$$

This procedure, like Matano's, requires no data on the partial molal volumes. If such data are available it is of course possible, though more laborious, to use the complete equation (11.78) to evaluate D^{V} .

We can now see what is the physical significance of the diffusion coefficient deduced by the Matano procedure when there is a volume change on mixing. Returning to equation (11.76) and writing ϕ for the flow velocity due to volume change, we have

$$-2\eta \frac{dC_A}{d\eta} = \frac{d}{d\eta} \left(D^{\nu} \frac{dC_A}{d\eta} \right) - \frac{d}{d\eta} (C_A \phi), \qquad (11.87)$$

and on integrating from $C_{A} = 0$ to $C_{A} = C_{\infty}$, this becomes

$$-2\int_{0}^{C_{\infty}}\eta \, dC_{\mathcal{A}} = \left[D^{\mathcal{V}}\frac{dC_{\mathcal{A}}}{d\eta}\right]_{0}^{C_{\infty}} - \left[C_{\mathcal{A}}\phi\right]_{0}^{C_{\infty}}.$$
 (11.88)

Since $dC_A/d\eta = 0$ at both ends of the range of integration, we see that

$$C_{\infty}\phi_{\infty} = -2\int_{0}^{C_{\infty}}\eta \, dC_{A}, \qquad (11.89)$$

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where ϕ_{∞} is the value of ϕ when $C_A = C_{\infty}$. Thus by choosing the origin of η such that the right-hand side of (11.89) is zero, we select a frame of reference such that, provided C = 0 at one end of the system, there is no flux of component A at either end due to volume change. It must be emphasized that the removal of the effect of volume change is complete only at the ends of the system, and so the diffusion coefficient deduced by using the Matano procedure is not the mutual diffusion coefficient. In fact, it is not a diffusion coefficient which is readily related to those obtained by other methods.

An alternative treatment of a system in which a volume change occurs makes use of the frame of reference fixed with respect to the total mass of the system. Thus in terms of the variables C_A^M and ξ_M introduced in § 11.3, equation (11.55) becomes

$$D_{C_{A}=C_{1}}^{M} = -\frac{1}{2t} \frac{d\xi_{M}}{dC_{A}^{M}} \int_{0}^{C_{1}} \xi_{M} dC_{A}^{M}, \qquad (11.90)$$

and according to the Matano procedure the origin of ξ_M is to be chosen such that $1/V_{k}^{k}$

$$\int_{0}^{d_{F}} \xi_{M} \, dC_{A}^{M} = 0. \tag{11.91}$$

The upper limit of integration for C_A^M comes from (11.16) since when $\xi_M = \infty$, $C_B^M = 0$. Choosing the origin of ξ_M so that (11.91) holds ensures that the boundary conditions are satisfied as in § 11.62. Thus, provided concentrations and distance scales are expressed in the new units as described in § 11.3, the coefficient D^M is obtained from (11.90) and (11.91).

By combining (11.23) and (11.35) we have a relationship between $D^{\mathcal{M}}$ and the intrinsic diffusion coefficients, $\mathscr{D}_{\mathcal{A}}$ and $\mathscr{D}_{\mathcal{B}}$, which takes the place of (11.73) in Prager's method.

11.64. Analysis of sorption data by a method of successive approximations

A different approach is to deduce the diffusion coefficient from observations of the overall rate of uptake of component A by a plane sheet of component B. Such a method has been used, for example, to determine the diffusion coefficient of direct dyes in cellulose sheet [24] and of oxygen in muscle [25]. In each case the diffusion coefficient was assumed constant.

We shall describe the method in terms of the uptake of vapour by a plane sheet, first on the assumptions that the diffusion coefficient is constant and the sheet does not swell, and then for cases in which the sheet swells and the diffusion coefficient is concentration-dependent. Its application to other systems will be obvious. The experimental procedure is to suspend a plane sheet of thickness l in an atmosphere of vapour maintained at constant temperature and pressure, and to observe the increase in weight of the sheet and hence the rate of uptake of vapour. This can be done most conveniently by hanging the sheet on a spring of known stiffness. The appropriate solution of the diffusion equation may be written

$$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\{-D(2m+1)^2 \pi^2 t/l^2\}, \quad (11.92)$$

if the uptake is considered to be a diffusion process controlled by a constant diffusion coefficient D. Here M_t is the total amount of vapour absorbed by the sheet at time t, and M_{∞} the equilibrium sorption attained theoretically after infinite time. The application of (11.92) is based on the assumption that immediately the sheet is placed in the vapour the concentration at each surface attains a value corresponding to the equilibrium uptake for the vapour pressure existing, and remains constant afterwards. The sheet is considered to be initially free of vapour. The value of t/l^2 for which $M_t/M_{\infty} = \frac{1}{2}$, conveniently written $(t/l^2)_t$, is given by

$$\left(\frac{t}{l^2}\right)_{\frac{1}{2}} = -\frac{1}{\pi^2 D} \ln\left\{\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9\right\}$$
(11.93)

approximately, the error being about 0.001 per cent. Thus we have

$$D = 0.049/(t/l^2)_{\frac{1}{2}},\tag{11.94}$$

and so, if the half-time of a sorption process is observed experimentally for a system in which the diffusion coefficient is constant, the value of this constant can be determined from (11.94). The extension of this method to less simple systems is as follows.

(i) Sorption by a swelling sheet

In deriving (11.92) the thickness l of the sheet is assumed to remain constant as diffusion proceeds. In practice it often happens, however, that the sheet swells and the thickness increases as the vapour enters. Equation (11.92) can still be used in such cases, provided we take a frame of reference fixed with respect to the substance of the sheet, and concentration and thickness are measured in the units discussed in § 11.3. Thus we take the basic volume of the sheet to be its volume in the absence of vapour and use the unit of length, ξ_R , such that unit ξ_B contains, per unit area, unit basic volume of the substance of the sheet, B. Then the thickness of the sheet, measured in these units, is constant and equal to the original unswollen thickness, and the diffusion coefficient deduced from (11.92) by substituting the original thickness for l is that for the diffusion of vapour relative to stationary sheet (denoted by D_A^B in § 11.3). If there is no overall volume change on mixing, i.e. if the increase in volume of the sheet is equal to the volume of vapour sorbed

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at the vapour pressure existing in the experiment, the coefficient obtained by this sorption method is related to the mutual diffusion coefficient D^{ν} , deduced by the Matano procedure, by equation (11.28), i.e.

$$D^B_A = D^V (1 - \text{volume fraction of vapour})^2.$$
 (11.95)

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(ii) Concentration-dependent diffusion coefficients

Clearly from (11.92) and (11.94) the value of t/l^2 for which M_t/M_{∞} has any given value, and in particular the value of $(t/l^2)_{\downarrow}$, is independent of



FIG. 11.3. Rate of uptake of chloroform by polystyrene sheet at 25° C.

 M_{∞} when the diffusion coefficient is constant. Fig. 11.3 shows a set of curves obtained experimentally by Park [26] for the uptake of chloroform by a polystyrene sheet, each curve corresponding to a different vapour pressure and hence a different M_{∞} . It is evident that $(t/l^2)_{i}$ decreases considerably the greater the value of the final uptake M_{∞} and therefore the diffusion coefficient is not constant but increases as the concentration of chloroform is increased. The problem is to deduce quantitatively how the diffusion coefficient is related to concentration, given the half-times of sorption experiments carried out for a number of different vapour pressures.

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Application of (11.94) to each of the curves of Fig. 11.3 yields some mean value \overline{D} , say, of the variable diffusion coefficient averaged over

the range of concentration appropriate to each curve. The method devised by Crank and Park [26] depends on the fact that, for any experiment, \overline{D} provides a reasonable approximation to $(1/C_0) \int_0^{C_0} D \, dC$, where 0 to C_0 is the concentration range existing in the sheet during that



experiment. This was shown to be so [27] by evaluating numerical solutions of the diffusion equation for a number of variable diffusion coefficients. By applying (11.94) to the sorption-time curves so calculated, values of \overline{D} were obtained and compared with corresponding values of $(1/C_0) \int_{0}^{C_0} D \, dC$. Thus by deducing a value of \overline{D} from each of the experimental curves of Fig. 11.3 using (11.94), and assuming the

approximate relationship

$$\overline{D} = (1/C_0) \int_0^{C_0} D \, dC, \qquad (11.96)$$

a graph showing $\overline{D}C_0$ as a function of C_0 can be drawn as in Fig. 11.4 and numerical or graphical differentiation of the curve with respect to C_0 gives a first approximation to the relationship between D and C. Numerical data are given in Table 11.1.

TABLE 11.1

Diffusion coefficients for chloroform in polystyrene at 25° C. All diffusion coefficients are in $cm.^2/sec. \times 10^{-10}$

% Regain at equi- librium = C ₀	$(t/l^3)_{\frac{1}{2}}$ sec./cm. ³ $\times 10^{10}$	D expt.	1st Approximation			2nd Approximation		
			$ \frac{\frac{1}{C_0} \int_{0}^{C_0} D dC}{cm.^{1/sec.}} $	D	D calc,	$\frac{1}{C_0} \int_{0}^{C_0} D dC$ $\frac{1}{C_0} \int_{0}^{C_0} D dC$ $\frac{1}{cm.^2/sec.}$ 10^{-10}	D	D calc.
5.0	••	0.024	0.024	0.024	0.024	0.024	0.024	0.024
7·5 9·9 12·9 13·2 15·1 16·3 16·8	1.130 0.620 0.288 0.248 0.151 0.0583 0.0481	(extrap.) 0.0437 0.0797 0.171 0.199 0.326 0.846 0.972	0.0437 0.0797 0.171 0.199 0.326 0.846 0.972	(extrap.) 0.116 0.288 0.780 0.970 3.36 10.5 16.0 approx.	0.0504 0.103 0.238 0.276 0.585 1.20 	0.039 0.062 0.125 0.144 0.216 0.583	0.12 0.29 0.40 0.54 1.6 6.6	0.044 0.080 0.17 0.20 0.33 0.85

In many cases this first approximation may be sufficiently accurate, but successively better approximations can be obtained as follows. Sorptiontime curves are calculated numerically for the D-C relationship obtained as the first approximation, there being one calculated curve for each experimental curve of Fig. 11.3. The \overline{D} values derived by applying (11.94) to the calculated curves are shown in Table 11.1, column 6. Comparison of these calculated \overline{D} values with the experimental ones and therefore with the first estimate of $(1/C_0) \int_0^{C_0} D \, dC$ shows the errors involved in use of (11.96) for this particular type of diffusion coefficient. The correct relationship between \overline{D} and $(1/C_0) \int_0^{C_0} D \, dC$ for the D-Crelationship given by the first approximation can be plotted, and from this improved values of $(1/C_0) \int_0^{C_0} D \, dC$ can be read off for the experi「「「「「「「「「「「「「「」」」」」」

mental values of \overline{D} . By repeating the differentiation, a second approximation to the diffusion coefficient D is obtained. The process can be repeated till the calculated and experimental values of \overline{D} agree to the accuracy desired. Results are shown in Table 11.1. In this form the method can be used whatever the relationship between D and C but the calculations involved in evaluating successive

approximations are tedious and laborious.

(iii) Exponential and linear diffusion coefficients

In many systems the diffusion coefficient is found to depend either linearly or exponentially on concentration, and so for these cases correction curves have been produced showing the difference between



FIG. 11.5. Correction curves for sorption method. Percentage difference is $(\bar{D}/D_0) - (1/C_0) \int_0^{C_0} (D/D_0) dC$ expressed as a percentage of \bar{D}/D_0 . These curves can be applied to both half-times and initial gradients.

 $(1/C_0) \int_0^{C_0} (D/D_0) dC$ and \overline{D}/D_0 , where D_0 is the value of D at zero concentration of vapour or whatever the diffusing substance is. The correction curves are shown in Fig. 11.5. By using the appropriate curve, the diffusion coefficient-concentration relationship can be deduced as readily from sorption experiments as from steady-state measurements

using (11.47) or (11.50). In each case, differentiation of $\int D \, dC$ to obtain D is the only mathematical operation involved. Park [28], incidentally, has used a method of differentiation which is considerably more accurate than direct graphical differentiation if D is an exponential function of C. Denoting $\int_{0}^{C_0} (D/D_0) \, dC$ by I, he plots $\log_{10} I$ against C_0 to obtain a curve which approximates to a straight line. Then $d \log I/dC_0$

is easily obtained by graphical differentiation and D follows from the expression D(D) = M(D)

$$D/D_0 = dI/dC_0 = 2.303Id \log_{10} I/dC_0.$$
(11.97)

The method for exponential and linear diffusion coefficients is therefore as follows:

- 1. Plot sorption-time curves for different vapour pressures as in Fig. 11.3.
- 2. Calculate \overline{D} for each curve using (11.94).
- .3. Extrapolate \overline{D} to zero concentration to give D_0 .
- 4. Read off from the appropriate correction curve of Fig. 11.5 the 'value of $(1/C_0) \int_{0}^{C_0} (D/D_0) dC = I/C_0$ for each \overline{D}/D_0 .
- 5. Differentiate I using (11.97) or otherwise to obtain D/D_0 and hence D.

A second approximation may be necessary due to the uncertainty in the first estimate of D_0 . It is, of course, necessary to have some idea of the type of diffusion coefficient involved before the choice of correction curve can be made. For example, if the initial choice is exponential, but the final result is nothing like an exponential function, and if use of the linear correction curve also fails, then the method of successive approximations has to be carried out as described above in § 11.64 (ii).

11.65. Sorption-desorption method

An extension of the sorption method, which uses both sorption and desorption data, is very quick and simple to use in cases to which it is applicable. If \overline{D}_s is calculated using (11.94) from the half-time for sorption and \overline{D}_d from the half-time for desorption over the same concentration range, then $\frac{1}{2}(\overline{D}_s + \overline{D}_d)$ is a better approximation to $(1/C_0) \int_0^{C_0} D \, dC$ than either \overline{D}_s or \overline{D}_d separately. Often it is a very good approximation and

has been used without correction in some instances [29, 30]. If the range in D is small enough for this to give the accuracy required, the method is particularly simple since there is no need even to extrapolate to obtain D_0 at zero concentration. Kokes, Long, and Hoard [30] have applied the sorption-desorption method to successive small concentration ranges so that the approximation $\frac{1}{2}(\overline{D}_s + \overline{D}_d)$ can be used with more confidence than it could if applied to the complete concentration range. Should it be necessary to obtain higher accuracy, the correction curves of Fig. 11.6 can be used to obtain better estimates of $(1/C_0) \int_0^{C_0} D \, dC$. These are then differentiated as in the sorption method to obtain D.



F10. 11.6. Correction curve for sorption-desorption method. Percentage difference is $(1/C_0) \int_{-\infty}^{C_0} (D/D_0) dC = \frac{1}{2} (\bar{D}_s + \bar{D}_d) / D_0$ expressed as a percentage of

$\frac{1}{2}(\bar{D}_s+\bar{D}_d)/D_0$

[N.B. The differences here are opposite in sign to those of Fig. 11.5.]

11.66. Use of initial rates of sorption and desorption

In § 11.64 we deduced an average diffusion coefficient from the halftime of a sorption curve by using (11.94). It is also possible to deduce an average diffusion coefficient from the initial gradient of the sorption curve when plotted against the square root of time. Thus, in the early stages, for a constant diffusion coefficient D and a sheet of thickness l, we have (§ 4.32) M = A(Dt) t

$$\frac{M_{l}}{M_{\infty}} = \frac{4}{\pi^{\frac{1}{2}}} \left(\frac{Dt}{l^{2}}\right)^{\frac{1}{2}}.$$
(11.98)

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If the initial gradient, $R = d(M_t/M_{\infty})/d(t/l^2)^{\frac{1}{2}}$, is observed in a sorption experiment in which D is concentration-dependent, then the average diffusion coefficient, \overline{D} , deduced from (11.98) is

$$\bar{D} = \frac{\pi}{16} R^2. \tag{11.99}$$

This, too, provides an approximation to $(1/C_0) \int_0^{C_0} D \, dC$, and the sorption method can proceed as above but starting with the new values of \overline{D} given by (11.99) as original data. Initial rates of desorption can be used similarly. Correction curves for exponential and linear diffusion coefficients are shown for the sorption method in Fig. 11.5 and for sorption-desorption in Fig. 11.6.

If the sorption curve when plotted against $(t/l^2)^{\frac{1}{2}}$ is approximately linear as far as $M_t/M_{\infty} = \frac{1}{2}$, and this is often true in practice, then it is easy to see that (11.94) and (11.99) yield roughly the same diffusion coefficient. Thus for a linear sorption curve we have

$$R = \frac{1}{2} / \sqrt{(t/l^2)_{\frac{1}{2}}}, \qquad (11.100)$$

and so from (11.99) we find

$$\overline{D} = \frac{\pi}{64} / (t/l^2)_{\frac{1}{2}} = 0.049 / (t/l^2)_{\frac{1}{2}}, \qquad (11.101)$$

which is the same as (11.94).

11.67. A step-function approximation to the diffusion coefficient

Prager [31] has described an alternative method of deducing the diffusion coefficient-concentration relationship from sorption data. The principle of the method is to approximate to the actual concentration-dependence by a step function. For such a function the differential equations can be solved analytically (Chapter VII) and the heights of the individual steps computed. The step function is then smoothed out by an averaging process. The concentration range to be studied is divided into a number of intervals and we assume that the diffusion coefficient D(C) has a constant (although as yet unknown) value in each. For a diffusion experiment covering only the first concentration interval D is constant throughout and may be calculated if M_i is known as a function of t, using the solution (11.98). For a diffusion experiment covering the first two intervals, D(C) is given by a step function whose value in the first interval is now known from the first calculation. The value in the second interval may be calculated as described below using the equations of § 7.22. This procedure may be continued so as to calculate the value of D(C) in the third interval, its value in the first two being known, and so on, until the entire concentration range has been covered. The method as described here is based on the treatment of diffusion with discontinuous boundaries given in §§ 7.22 and 7.24. An alternative treatment is given in Prager's original paper [31].

Before the concentration in the centre of the film attains an appreciable value we may consider diffusion to take place into a semi-infinite medium. If we have a two-step diffusion coefficient such that for concentrations greater than C_X , $D = D_1$, and for concentrations less than C_X , $D = D_2$, then the diffusion process can be described by the equations of § 7.22 if D_1 and D_2 are known. In particular, $\partial M_i/\partial t^{\frac{1}{2}}$ is given using the nomenclature of that section by

$$\frac{\partial M_l}{\partial t^{\frac{1}{2}}} = -\frac{2AD_1^{\frac{1}{2}}}{\pi^{\frac{1}{2}}}.$$
(11.102)

Here we have the opposite problem, i.e. given $\partial M_i/\partial t^{\dagger}$ from an experiment and D_2 having been calculated from the previous experiment, to find D_1 . If M_i is measured as a function of t^{\dagger} this means essentially that AD_1^{\dagger} is measured. Hence if we estimate D_1 , k is determined from (7.15) of § 7.22 and a new D_1 follows from (7.12) of the same section. Successive estimates of D_1 are made till agreement is obtained between estimated and final values of D_1 . The graphs shown in Figs. 7.3, 7.4, and 7.5 of Chapter VII can be used to help the calculation.

The method is readily extended to a three-step diffusion coefficient and then to higher numbers of steps. Thus if

$$D = D_1, \qquad C_1 > C > C_X, \qquad (11.103)$$

 $D = D_2, \qquad C < C_Y,$ (11.104)

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$D = D_3, \qquad C_X > C > C_Y,$ (11.105)

the process is described by the equations of §7.24. Again AD_1^{\uparrow} is measured and D_2 , D_3 are known from previous experiments. We estimate D_1 and calculate k_1 from (7.32) and k_2 from (7.38). Finally we check k_1 , k_2 , D_1 in (7.39), repeating if necessary as before. The number of equations of the type (7.38) and (7.39) increases with the number of steps in the diffusion coefficient but the method still holds.

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The function D(C) obtained in this fashion, being a step function, does not correspond to physical reality. Prager suggests a way of smoothing it by calculating the average values D_I given by

$$D_I = (1/C_k) \int_0^{C_k} D \, dC = (1/k) \sum_{i=1}^k D_i, \qquad (11.106)$$

where $C_1, C_2, ..., C_k, ..., C_N$ are the concentrations at which the calculated D changes from one constant value to another. Then D_I is fitted by a polynomial in C and D(C) is recalculated from the equation

$$D(C) = D_I + C \, dD_I / dC. \tag{11.107}$$

Prager [31] has applied this method to the isobutane-polyisobutylene system, taking five intervals in concentration. His result agrees quite well with that obtained from sorption and desorption experiments using the approximation

$$D_I = (1/C_k) \int_{0}^{C_k} D \, dC = \frac{1}{2} (\overline{D}_s + \overline{D}_d), \qquad (11.108)$$

discussed in §11.65 and applied here to successive concentration intervals 0 to C_k .

11.68. Analysis of sorption data by the method of moments

Fujita and Kishimoto [32] have described an alternative method of analysing sorption data based on the method of moments discussed earlier in § 9.6. This method is restricted to diffusion coefficients which increase monotonically throughout the relevant range of concentration. In many systems this is not a serious restriction. The method ceases to be reasonably accurate if the diffusion coefficient increases by more than thirtyfold. Subject to these limitations, however, the method has the double attraction of being fairly simple to use and of avoiding the need for graphical differentiation at any stage. Fujita and Kishimoto express the amount of diffusing substance taken up by a sheet at time t, when the concentrations at the surfaces are constant and denoted by C_0 , in the form

(11.109) $M_t = 2K(C_0)t^{\frac{1}{2}}.$

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This is the same as (11.98) remembering that $M_{\infty} = lC_0$. The sheet is assumed to be behaving semi-infinitely. In (11.109), $K(C_0)$ is a function of C_0 only, and its form is given by sorption experiments carried out for different values of C_0 , i.e. different vapour pressures or different concentrations in the solution in which the sheet is placed. The problem is to deduce the diffusion coefficient-concentration relationship from the experimental data given in the form of the function $K(C_0)$.
It was shown in § 9.6, when discussing solution of the diffusion equation by the method of moments, that

$$K(C_0) = C_0 D^{\frac{1}{2}}(0) \left(\frac{1}{8\beta^{\frac{1}{2}}} + \frac{1}{12} \alpha \beta^{\frac{1}{2}} \right), \qquad (11.110)$$

where α is given by

$$\alpha = \frac{30}{C_0} \int_0^{C_0} \frac{D(C)}{D(0)} dC, \qquad (11.111)$$

and β is the larger, positive root of the quadratic equation

$$24\alpha \frac{D(C_0)}{D(0)}\beta^2 + \left\{\alpha - 108 \frac{D(C_0)}{D(0)}\right\}\beta + \frac{3}{2} = 0.$$
 (11.112)

Here D(C) is the value of the diffusion coefficient when the concentration is C, $D(C_0)$ and D(0) being the values for concentrations C_0 and zero respectively. Introducing the quantities f(C) and g(C) defined by

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$$f(C) = D(C)/D(0)$$
 (11.113)

$$g(C) = (1/C) \int_{0}^{C} \{D(C')/D(0)\} dC', \qquad (11.114)$$

and then writing

and

$$x = \beta g(C_0) = \alpha \beta/30,$$
 (11.115)

$$y = g(C_0)/f(C_0),$$
 (11.116)

equation (11.112) reduces to

$$720x^2 + (30y - 108)x + \frac{3}{2}y = 0. \tag{11.117}$$

By solving (11.117) for x and using the larger positive root we obtain

$$x = \frac{54 - 15y}{720} \left[1 + \left\{ 1 - \frac{1080y}{(54 - 15y)^2} \right\}^{\frac{1}{2}} \right].$$
 (11.118)

If now we confine attention to diffusion coefficients which increase monotonically with concentration increasing we have the condition

$$0 < y < 1. \tag{11.119}$$

With this in mind, the right-hand side of (11.118) may be expanded in

powers of y to give $x = \frac{3}{20} \left(1 - \frac{10y}{27}\right)$, (11.120)

if we neglect terms in y^2 and higher terms. But from (11.110) and (11.115) we have $F(C_0) = (1 + 20^{-13})^2$

$$64\frac{T(C_0)}{g(C_0)}x = (1+20x)^2, \qquad (11.121)$$

where

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$$F(C_0) = \{K(C_0)\}^2 / \{D(0)C_0^2\}.$$
(11.122)

Substituting for x from (11.118) and rearranging in a series of powers of y we find $3 F(C_0)$

$$\frac{3}{5} \frac{F(C_0)}{g(C_0)} = 1 - \frac{5}{27}y, \qquad (11.123)$$

which becomes on using (11.116)

$$f(C_0) = \frac{\frac{5}{279}g(C_0)}{1 - \frac{3}{5}F(C_0)/g(C_0)}.$$
 (11.124)

From (11.113) and (11.114) we have

$$f(C_0) = \frac{d}{dC_0} \{ C_0 g(C_0) \}, \qquad (11.125)$$

and so (11.124) can be transformed into the following differential equation for g,

$$\frac{dg(C_0)}{dC_0} = \frac{g(C_0)}{C_0} \left\{ \frac{5/27}{1 - \frac{3}{5}F(C_0)/g(C_0)} - 1 \right\}.$$
 (11.126)

$$g(C_0) = \exp\{q(C_0)\},\tag{11.127}$$

(11.126) becomes

On substituting

$$\frac{dq}{dC_0} = \frac{1}{C_0} \left\{ \frac{5/27}{1 - \frac{3}{5}F(C_0)e^{-q}} - 1 \right\}.$$
 (11.128)

It follows from (11.114) that $g(C_0)$ tends to unity as C_0 approaches zero and hence the starting condition for the integration of (11.128) is

$$q = 0, \quad C_0 = 0.$$
 (11.129)

Since, in general, dq/dC_0 must remain finite for any C_0 it follows from (11.128) that (5/27)

$$\lim_{C_0\to 0} \left\{ \frac{5/27}{1-\frac{3}{5}F(C_0)e^{-q}} - 1 \right\} = 0, \qquad (11.130)$$

from which, because of (11.129) we have

$$\lim_{C_0 \to 0} F(C_0) = 110/81. \tag{11.131}$$

(11.132)

(11.133)

From (11,131) and (11,122) we deduce an equation determining D(0), i.e.

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$$D(0) = \frac{81}{110} \lim_{C_0 \to 0} \left\{ \frac{K(C_0)}{C_0} \right\}^2.$$

It is easy to see from (11.98) and (11.109) that the ratio 81/110 is an approximation to $\frac{1}{4}\pi$. Combining (11.125) and (11.128), and using (11.113) we obtain

$$D(C_0) = \frac{\frac{5}{27}D(0)\exp(q)}{1 - \frac{3}{5}F(C_0)\exp(-q)}$$

from which D can be deduced for a given C_0 if q has been obtained by solving (11.128). The successive steps in the method are as follows:

- 1. Plot $\{K(C_0)/C_0\}^2$ against C_0 from the given sorption data and extrapolate to $C_0 = 0$.
- 2. Determine D(0) from (11.132).
- 3. Substitute this value of D(0) in (11.122) and draw a graph of $F(C_0)$ against C_0 .
- 4. Integrate equation (11.128) either graphically or numerically, using this function $F(C_0)$, with the initial condition (11.129), and so obtain $q(C_0)$.
- 5. Substitute $q(C_0)$, together with D(0) and $F(C_0)$ in (11.133), to give $D(C_0)$.

Clearly this method is more accurate the smaller y is, but the main limitation is the range of application of the method of moments. Fujita and Kishimoto have applied their method to the polyisobutyleneisobutane system and obtained a diffusion coefficient in good agreement with that found by Prager [31] using his step-function analysis.

11.69. A polynomial approximation to the diffusion coefficient

Jenn Linn Hwang [33] has proposed a method of calculating diffusion coefficients from sorption data in which he first develops a series solution of the diffusion equation for $D = D_0(1 + \alpha c + \beta c^2 + ...)$. By inserting the experimental data he obtains a set of linear equations from which, in theory at least, the constants D_0 , α , β ... can be determined. He draws attention to the need to tabulate a number of subsidiary functions to facilitate the use of his method but he does not develop this approach numerically.

11.610. Sorption by sheets initially conditioned to different uniform concentrations

Barrer and Brook [34] have used a method of measuring the concentration dependence of the diffusion coefficient based on a series of sorption

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experiments. The concentration, C_0 , at the surface of the specimen is kept constant throughout the series but the initial uniform concentration, C_1 , through the sheet, is different for each experiment. Denoting again by M_i the amount of diffusing substance taken up by the sheet in time t, we may write as in (11.98) and (11.109) for the initial stages of sorption,

$$M_t = K(C_1)t^{\frac{1}{2}}.$$
 (11.134)

Here K is different for each experiment, being a function of C_1 , the initial

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concentration through the sheet. A curve showing K as a function of C_1 must cut the axis of C, at the point $C_1 = C_0$ because then the initial rate of sorption, and hence K, is zero, there being no concentration gradient.



FIG. 11.7. Curve of K against C_1 approaching asymptote from above because D decreases as C increases.



F10. 11.8. Curve of K against C_1 approaching asymptote from below because D increases as C increases.

Thus the experimental curve of K against C_1 , when extrapolated, must always pass through $C_1 = C_0$ when K = 0. Furthermore, as the interval $C_0 - C_1$ is decreased progressively in successive experiments the sorption process can more and more nearly be described by the diffusion equation and its solution for a constant diffusion coefficient, i.e. by

$$M_t = 4(C_0 - C_1)(D_0 t/\pi)^{\frac{1}{2}}, \qquad (11.135)$$

where D_0 is the value of the diffusion coefficient at the concentration C_0 .

Hence, as C_1 approaches C_0 , the curve of K against C_1 approaches asymptotically a tangent of slope $-4D_0^{\dagger}/\pi^{\frac{1}{2}}$. This differs by a factor of two from the expression given by Barrer and Brook, because they consider the amount entering through one face of the sheet, whereas we



FIG. 11.9. Curve of K against C_1 using data from both sorption and desorption experiments.

include both. If the experimental curve is sufficiently well defined by the data obtained from the sorption experiments, the tangent can be drawn and D_0 deduced from its gradient using (11.135). By repeating the series of experiments for different values of the surface concentration C_0 , the relationship between the diffusion coefficient and concentration is obtained. If, as in some zeolites, D decreases as C increases, then the curve of K against C_1 approaches the tangent from above as in Fig. 11.7. If, however, D increases as C increases, which is often the case in solventpolymer systems, then the tangent is approached from below as in Fig. 11.8. Thus the curves of K against C_1 show at a glance the nature of the concentration-dependence of D. If it is practicable to carry out desorption experiments as well as sorption, that is to include values of C_1 which are higher than the surface concentration C_0 , the curve of K against C_1 will cross the C_1 axis at $C_1 = C_0$, as in Fig. 11.9. This should allow the tangent to be drawn more accurately since extrapolation is avoided.

11.7. Weighted-mean diffusion coefficients

In § 11.66 we looked upon the average diffusion coefficient deduced from the initial rate of sorption by (11.99) as an approximation to $(1/C_0) \int_{0}^{C_0} D \, dC$. Subsequent calculations have revealed that the initial rate of sorption is much more closely controlled by a weighted-mean diffusion coefficient, namely $(\frac{5}{3}/C_0^1) \int_{0}^{C_0} C^{\frac{1}{2}} D \, dC$, where 0 to C_0 is the concentration range involved. This is found to hold to within an accuracy of 1 per cent. for diffusion coefficients increasing with concentration increasing (over ranges varying from 1 to 200-fold) in one or other of the ways shown by the curves 1, 3, 4 in Fig. 12.4.

For the same diffusion coefficients the initial rate of desorption is determined to the same accuracy by a different weighted-mean,

$$(1.85/C_0^{1.85}) \int_0^{C_0} (C_0 - C)^{0.85} D \ dC.$$

It is a matter of some interest that a single type of weighted mean represents sorption rates and another single one desorption rates for such a wide variety of diffusion coefficient-concentration relationships. These weighted-means are useful both from the point of view of the evaluation of D from sorption or desorption data in concentrationdependent systems, and also in estimating what initial rate of sorption or desorption is to be expected in a system for which the diffusion coefficient-concentration relationship is known.

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XII

SOME CALCULATED RESULTS FOR VARIABLE DIFFUSION COEFFICIENTS

12.1. Steady state

In the steady state the concentration distribution through a plane sheet, in which diffusion is assumed to be one-dimensional, is given by the solution of the equation

$$\frac{d}{dx}\left(D\frac{dC}{dx}\right) = 0, \qquad (12.1)$$

where D is the diffusion coefficient, not necessarily constant. The corresponding equations for the hollow cylinder and sphere are obvious.

12.11. D a function of concentration

If D is a given function of concentration, i.e.

$$D = D_0\{1+f(C)\},$$

the general solution of (12.1) can be written as

$$D_0 \int \{1 + f(C)\} dC = Ax + B, \qquad (12.2)$$

where A and B are constants to be determined by the boundary conditions. The corresponding solution for the hollow cylindrical tube is

$$D_0 \int \{1 + f(C)\} dC = A \log r + B, \qquad (12.3)$$

and for the hollow spherical shell,

$$D_0 \int \{1 + f(C)\} \, dC = -\frac{A}{r} + B. \tag{12.4}$$

When the boundary conditions for the plane sheet are

$$C = C_1, \qquad x = 0,$$
 (12.5)

$$C = C_{2}, \quad x = l, \quad (12.6)$$
equation (12.2) becomes, using Barrer's [1] nomenclature,

$$\frac{C_{1} + F(C_{1}) - C - F(C)}{C_{1} + F(C_{1}) - C_{2} - F(C_{2})} = \frac{x}{l}, \quad (12.7)$$
where

$$F(C) = \int_{0}^{C} f(C') dC'. \quad (12.8)$$

Similarly, for the cylindrical tube or spherical shell with boundary conditions

$$V = C_1, \quad r = r_1, \quad (12.9)$$

$$C = C_2, \quad r = r_2, \quad (12.10)$$



FIG. 12.1. Typical steady-state concentration distributions across a membrane when $D = D_0\{1+f(C)\}$. $C_1 = 1, C_2 = 0$.

Curve 1; f(C) = aC; a = 100, Curve 4: f(C) = 0 (simple Fick law obeyed). Curve 2: f(C) = aC; a = 10. Curve 5: f(C) = -aC; a = 0.5, Curve 3: f(C) = aC; a = 2. Curve 6: f(C) = -aC; a = 1.0,

we find for the cylinder

$$\frac{C_1 + F(C_1) - C - F(C)}{C_1 + F(C_1) - C_2 - F(C_2)} = \frac{\log r_1 - \log r}{\log r_1 - \log r_2},$$
(12.11)

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and for the sphere

$$\frac{C_1 + F(C_1) - C - F(C)}{C_1 + F(C_1) - C_2 - F(C_2)} = \frac{r_2}{r_1 - r_2} \frac{r_1 - r_2}{r_1}.$$
 (12.12)

For any given relationship between D and C, the integrals F(C) are readily evaluated either analytically, graphically, or numerically, and the concentration distribution follows immediately from the above equations. Some typical examples calculated by Barrer [1] are reproduced in Figs. 12.1 and 12.2. They illustrate the general conclusion that

when D increases as C increases the concentration-distance curves in the steady state are convex away from the distance axis; but when Ddecreases as C increases the curves are convex towards that axis. If Dfirst increases and then decreases or vice versa, with increasing C, a point of inflexion appears in the concentration-distance curves.



FIG. 12.2. Typical steady-state concentration distributions across a membrane when $D = D_0(1+f(C))$. $C_1 = 1, C_2 = 0$.

Curve 1: $f(C) = ae^{bC}$; a = 1, b = 3. Curve 2: $f(C) = \frac{aC}{1+bC}$; a = 100, b = 1. Curve 3: $f(C) = -aC^{\frac{1}{2}} + bC^{\frac{1}{2}}$; a = 1, b = 2. Curve 4: $f(C) = \frac{aC}{1+bC}$; a = 1, b = 1. Curve 4: $f(C) = \frac{aC}{1+bC}$; a = 1, b = 1. Curve 5: f(C) = 0 (simple Fick law obeyed). Curve 6: $f(C) = \frac{-aC}{1+bC}$; a = 0.9, b = 1. Curve 7: $f(C) = -aC^{\frac{1}{2}}$; a = 1. Curve 8: $f(C) = -aC^{\frac{1}{2}}$; a = 1.

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12.12. D a function of distanceIf we have
$$D = D_0\{1+f(x)\},$$
or $D = D_0\{1+f(r)\},$ (12.13)

for the sheet or cylinder and sphere, the general solutions (12.2), (12.3), and (12.4) are to be replaced by

$$D_0 C = A \int \frac{dx}{1+f(x)} + B, \qquad (12.15)$$

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$$D_0 C = A \int \frac{dr}{r\{1+f(r)\}} + B, \qquad (12.16)$$

$$D_0 C = A \int \frac{dr}{r^2 \{1 + f(r)\}} + B, \qquad (12.17)$$



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FIG. 12.3. Typical steady-state concentration distributions when $D = D_0\{1+f(x)\}, C_1 = 1, C_1 = 0.$

Curve 1: f(x) = -ax; a = 0.99. Curve 2: f(x) = -ax; a = 0.90. Curve 3: f(x) = 0 (simple Fick law obeyed). Curve 4: f(x) = ax; a = 1.0. Curve 5: f(x) = ax; a = 2.0. Curve 6: $f(x) = bx + ax^{i}$; a = 1, b = 2. Curve 7: $f(x) = bx + ax^{i}$; a = 2.25, b = 3. Curve 8: f(x) = ax; a = 9. Curve 9: f(x) = ax; a = 99.

respectively. Denoting by I the integral on the right-hand side of each

of these equations, taking x = 0 or r = 0 as the lower limit and I_1 , I_2 the values of I at the two boundary surfaces, we find

$$\frac{C_1 - C}{C_1 - C_2} = \frac{I_1 - I}{I_1 - I_2}.$$
(12.18)

Concentration distributions follow immediately for given f(x) or f(r). Barrer [1] shows typical curves for f(x) = ax and $f(x) = bx + ax^2$. They are reproduced in Fig. 12.3. When D is an increasing function of x the curves are convex towards the axis of x and when D is a decreasing function of x they are convex away from that axis.

12.13. Rate of flow

We saw in § 11.61 that the rate of flow, F, through unit area of a plane membrane of thickness l, when the concentrations at the two faces are C_1, C_2 , is given by C_1 .

$$F = (1/l) \int_{C_1}^{C_1} D \, dC, \qquad (12.19)$$

where D is a function of concentration C. The corresponding argument for a cylindrical shell of inner radius r_1 and outer radius r_2 is as follows. Let F denote the rate of flow per unit length of cylinder. Then

$$F = -2\pi r D \, dC/dr, \qquad (12.20)$$

which on integration becomes

$$\int_{1}^{r_{1}} \frac{F}{2\pi r} dr = \int_{C_{1}}^{C_{1}} D \, dC. \tag{12.21}$$

But in the steady state F is independent of r and hence we find

$$F = \{2\pi/\log(r_2/r_1)\} \int_{C_1}^{C_1} D \, dC.$$
 (12.22)

The corresponding result for a spherical shell is

$$F = 4\pi \frac{r_1 r_2}{r_2 - r_1} \int_{C_1}^{C_1} D \, dC, \qquad (12.23)$$

where F now refers to the total flow through the shell. When D is a function of x or r given by (12.13) or (12.14) it is easy to see from (12.18) that

$$F = -D \, dC/dx = -D_0 \frac{C_1 - C_2}{I_1 - I_2}$$
, for the plane sheet, (12.24)

$$F = -2\pi D_0 \frac{C_1 - C_2}{I_1 - I_2}$$
, for the cylindrical tube, (12.25)

and $F = -4\pi D_0 \frac{C_1 - C_2}{I_1 - I_2}$, for the spherical shell. (12.26)

12.14. Asymmetrical diffusion through membranes Hartley [2] has indicated that in any membrane for which the diffusion coefficient depends both on concentration and on distance through the membrane, different rates of penetration in the forward and backward

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direction are to be expected in general. Writing D = f(x, C) we have for the rate of flow, F,

$$F = -f(x, C) \, dC/dx. \qquad (12.27)$$

If the function f(x, C) is expressible as the product of two separate functions $f_1(x)$ and $f_2(C)$, (12.27) becomes

$$F\int_{0}^{l} \frac{dx}{f_{1}(x)} = \int_{C_{1}}^{C_{1}} f_{2}(C) dC, \qquad (12.28)$$

where the boundaries of the sheet are at x = 0, x = l. In this case, since

$$\int_{0}^{l} \frac{dx}{f_{1}(x)} = \int_{0}^{l} \frac{dx}{f_{1}(l-x)}, \qquad (12.29)$$

the permeability of the membrane will be symmetrical. The function f(x, C) will not usually be separable in this way, however, except in the simple cases in which $f_1(x)$ or $f_2(C)$ is constant, and so it is unlikely that the membrane will be symmetrical unless D is constant or a function of either x or C alone.

12.15. Diffusion of one substance through a second substance which is confined between membranes

A point of considerable interest concerning steady-state diffusion was raised by Hartley and Crank [3]. Let a substance B be confined between membranes which are impermeable to B. Also let the concentrations of A in contact with the membranes be maintained by supply and removal of A through the membranes from and to reservoirs of vapour or of solutions of A in B or in any other substance which cannot penetrate the membranes. It is convenient here to use the ideas and nomenclature of § 11.3. Then in the steady state, sections at fixed distances from the membranes are fixed with respect to amount of component B, and the rates of transfer of A across all such sections must be equal so that

$$-D_A^B \partial C_A^B / \partial \xi_B = \text{constant.}$$
(12.30)

We will assume that the partial volumes are constant. Equations

(11.21), (11.26), (11.28) are $d\xi_B = V_B^0 C_B^V dx; \quad dC_A^V / dC_A^B = (V_B C_B^V)^2; \quad D_A^B = D^V (V_B C_B^V)^2,$ (12.31)

and on substituting these relationships in (12.30) we have

$$\frac{-D^{\nu}}{V_B C_B^{\nu}} \frac{\partial C_A^{\nu}}{\partial x} = \text{constant.}$$
(12.32)

On using

$$V_{A}\frac{\partial C_{A}^{V}}{\partial x} + V_{B}\frac{\partial C_{B}^{V}}{\partial x} = 0, \qquad (12.33)$$

(12.32) becomes
$$\frac{D^{\nu}}{V_{\mathcal{A}} C_{B}^{\nu}} \frac{\partial C_{B}^{\nu}}{\partial x} = \text{constant.}$$
(12.34)

If, instead, we maintain the steady state by substituting membranes permeable only to B and supplying and removing B in the reverse direction we find, by interchanging A and B in (12.32) and reversal of signs to allow for the reversal of direction,

$$\frac{D^{V}}{V_{A} C_{A}^{V}} \frac{\partial C_{B}^{V}}{\partial x} = \text{constant.}$$
(12.35)

It is evident that equations (12.34) and (12.35) require different concentration-distance functions. The steady state is therefore different, even between the same concentration limits, according to which component is constrained and which is free to diffuse.

This difference is particularly evident in dilute solutions. We shall assume here, in the interests of simplicity, that D^{ν} is constant. The concentration of A being very low, $V_B C_B^{\nu}$ can be assumed to be unity. Equation (12.32) now becomes

$$D^{V} \frac{\partial C_{A}^{V}}{\partial x}$$
 = the constant rate of transfer of A. (12.36)

This is valid for A diffusing and B restrained.

Substituting from (12.33) we may modify (12.35) to

$$\frac{D^{\nu}}{V_B C_A^{\nu}} \frac{\partial C_A^{\nu}}{\partial x} = \frac{D^{\nu}}{V_B} \frac{\partial}{\partial x} (\log C_A^{\nu}) = \text{constant rate of transfer of } B. \quad (12.37)$$

This is valid for A restrained and B diffusing between the same concentration limits.

It will be seen that when the dilute component is diffusing its concentration gradient under these simple conditions is linear. When the same limits are maintained by diffusing the 'solvent' through membranes impermeable to the 'solute', the gradient of the logarithm of concentration of the latter is linear and hence the concentration itself varies exponentially with distance.

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When the total fall of concentration, $\Delta C_{\mathcal{A}}^{\mathcal{V}}$, of the dilute constituent is small compared with its mean concentration, (12.36) becomes

rate of transfer of
$$A = \frac{D^{\nu}}{l} \Delta C^{\nu}_{A}$$
, (12.38)

and (12.37) becomes

equivalent rate of transfer of
$$B = \frac{D^V}{l} \frac{\Delta C_A^V}{C_A^V V_B}$$
, (12.39)

where l is the distance between the membranes. The rate of diffusion of water in such a system down a given, small, mean vapour pressure gradient is therefore not expected to be constant but to be inversely proportional to the mean concentration of the solute. It will further be proportional to the diffusion rate of the solute given by (12.38). Thus if water diffuses from 99.1 to 99.0 per cent. relative humidity through a layer containing hydrogen chloride, it will do so about twice as rapidly as when the layer contains sodium chloride. If the diffusion occurs from 90.1 to 90.0 per cent. relative humidity, each rate will fall to one-tenth of its former value.

These conclusions refer to the case where the membranes are separated by a fixed distance. If, as is more likely to be true in practice, the membranes confine a given amount of component A so that the volume between them will vary inversely as the mean concentration of A, the distance l in (12.39) will be more nearly inversely proportional to C_A than constant. In this case the rate of transfer of B will be, to a first approximation, dependent on ΔC_A only and not on the mean value of C_A . This result would be obtained directly, of course, from equations in ξ as in the treatment already given of the swelling membrane, § 11.61. Diffusion of solvent through a constant amount of solute per unit area thus behaves more simply than diffusion through a constant thickness. This conclusion is not at once obvious and may have some important applications in physiological processes.

A second conclusion of interest may be drawn when we consider what happens in such a steady-state system if the membranes are suddenly rendered completely impermeable. Sections fixed with respect to the membranes are now fixed with respect to volume of solution. The change of concentration with time will therefore from now on be governed by

$$\frac{\partial C_{\mathcal{A}}^{\mathcal{V}}}{\partial t} = \frac{\partial}{\partial x} \left(D^{\mathcal{V}} \frac{\partial C_{\mathcal{A}}^{\mathcal{V}}}{\partial x} \right), \qquad (12.40)$$

but, at the instant of change of membranes, (12.32) still holds if A has been the diffusing component, whence

$$\frac{\partial}{\partial x} \left(D^{V} \frac{\partial C^{V}}{\partial x} \right) = -\operatorname{constant} \times V_{B} \frac{\partial C_{B}^{V}}{\partial x} = \operatorname{constant} \times V_{A} \frac{\partial C_{A}^{V}}{\partial x}.$$
 (12.41)

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Combining (12.40) and (12.41) we obtain

$$\left(\frac{dx}{dt}\right)_{C} = -\operatorname{constant} \times V_{A}, \qquad (12.42)$$

$$\left(\frac{\partial C_{\mathcal{A}}^{\mathcal{V}}}{\partial t}\right)dt + \left(\frac{\partial C_{\mathcal{A}}^{\mathcal{V}}}{\partial x}\right)dx = dC_{\mathcal{A}}^{\mathcal{V}} = 0, \qquad (12.43)$$

for C_A^{ν} constant. Now the constant in (12.30) and (12.42) is the rate of transfer of A at the steady state in standard units of amount. Multiplied by V_A it represents the volume rate of transfer of A, or, since we are always considering transfer across unit area, the linear velocity with which A appeared to pass through the system.

We thus find that, at the instant when A ceases to flow through, the whole concentration-distance distribution commences to move backwards at the velocity with which substance A previously passed through the membrane. With increasing time, the distribution will, of course, flatten out from the low concentration upwards as the substance A, diffusing down the gradient now, accumulates.

It is evident, therefore, that in the steady state during the passage of substance A there was superimposed on the true diffusion process a real flow of the whole system.

12.2. Non-steady-state conditions

We present here, in graphical form, a collection of solutions of the equation for diffusion in one dimension. They have been evaluated by one or other of the methods described in Chapters IX and X, and refer to various types of concentration-dependent diffusion coefficients and three simple boundary conditions. Solutions for the infinite medium refer to the initial condition

$$C = C_1, \qquad x < 0, \qquad (12.44)$$

$$C = C_2, \qquad x > 0. \tag{12.45}$$

For sorption in a semi-infinite medium the conditions are

$$C = C_0, \qquad x = 0, \qquad t > 0, \qquad (12.46)$$

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since

and for desorption
$$C = 0, \quad x > 0, \quad t = 0,$$
 (12.47)
 $C = 0, \quad x = 0, \quad t > 0,$ (12.48)
 $C = C_0, \quad x > 0, \quad t = 0.$ (12.49)

One example of each type of diffusion coefficient considered is shown in Figs. 12.4 (a) and 12.4 (b).



FIG. 12.5. Concentration-distance curves for $D = D_a \exp \beta \{C - \frac{1}{2}(C_1 + C_2)\}$, where β is positive and given by $\beta(C_2 - C_1) = \log_e(D_1/D_1)$. Numbers on curves are values of D_1/D_2 . D_1 and D_2 are values of D at C_1 and C_2 respectively.

12.3. Concentration-distance curves

The shapes of the concentration-distance curves are characteristic of the diffusion coefficient and of the boundary conditions. They do not conform to quite such a simple classification as do the corresponding curves in the steady state. Thus, as we saw earlier in § 12.11, Barrer [1] was able to write, with regard to the results of his steady-state calculations, that whenever D increases as C increases, concentration-distance curves are convex away from the distance axis. Figs. 12.8 and 12.10



FIG. 12.7. Concentration-distance curves for linear diffusion coefficients during sorption for $D = D_0(1 + aC/C_0)$. Numbers on curves are values of a.

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show that this is true also for curves relating to desorption from a semiinfinite medium when D is a linearly or exponentially increasing function of concentration. Figs. 12.7 and 12.9 show that for these diffusion coefficients the statement holds also for sorption by a semi-infinite medium over the greater part of the concentration range, but that there is an important difference in behaviour in the region of low concentration.



FIG. 12.8. Concentration-distance curves for linear diffusion coefficients during desorption for $D = D_0(1 + aC/C_0)$. Numbers on curves are values of a.

This difference is a direct consequence of the boundary condition. In the steady state, the condition is that the concentration shall have some fixed value, possibly zero, at the face of the membrane through which the diffusing substance emerges. When diffusion occurs into a semiinfinite medium, however, the condition that the concentration shall approach zero at infinity means that the gradient of concentration tends to zero at the limit of penetration into the medium. This produces a point of inflexion in any concentration-distance curve which is convex away from the distance axis at high concentrations. The curves of Fig. 12.11 relate to a diffusion coefficient which increases as C increases but does so at a steadily decreasing rate (see Fig. 12.4 (a)). We see that in this case the concentration-distance curves may be convex downwards. The curves of Figs. 12.12 and 12.13 conform with these statements. In Fig. 9.12 we had an example of a concentration-distance curve associated with a diffusion coefficient which passes through a maximum value.



FIG. 12.9. Concentration distance curves for exponential diffusion coefficients during sorption for $D = D_0 e^{kC/C_0}$. Numbers on curves are values of e^k , being the ratio of D at $C = C_0$ to D at C = 0.

The curves shown in Figs. 12.5 and 12.6 for infinite media follow the same general pattern as for the semi-infinite media, except that the boundary conditions ensure that the concentration gradient becomes zero at each end.

12.31. Correspondence between sorption and desorption If (C_0-C) is written for C, the diffusion equation in one dimension is unchanged but the conditions (12.46) and (12.47) become respectively (12.48) and (12.49). This means that the solution for sorption when Dis a given function of C is also the solution for desorption when D is the



F10. 12.10. Concentration distance curves for exponential diffusion coefficients during desorption for $D = D_0 e^{kC/C_0}$. Numbers on curves are values of e^k , being the ratio of D at $C = C_0$ to D at C = 0.

This allows general statements corresponding to those of § 12.3 to be made for diffusion coefficients which decrease as concentration increases.

12.32. Common points of intersection

Stokes [4] has drawn attention to the fact that if a large-scale graph is prepared from the data of Table 9.3 an interesting property emerges. Two concentration-gradient curves are shown in Fig. 12.14, one for a constant diffusion coefficient and the other for a diffusion coefficient varying linearly with concentration, the value at the higher concentration being 0.1406 of that at the lower concentration. The other curves are omitted to avoid confusion of the diagram but on his largescale plot Stokes found that whatever the value of b, all his curves passed through the point P (Fig. 12.14) of coordinates

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$$y_a = 1.205, \ (dC/dy_a)/(C_1 - C_2) = -0.133.$$





Numbers on curves are values of $1+50 \log_e(1+k)$, being the ratio of D at $C = C_0$ to D at C = 0.







$$D = \frac{D_0}{(1 - \alpha C U C)}.$$

 $(1 - \alpha C / C_0)$

Numbers on curves are values of $1/(1-\alpha)$, being ratio of D at $C = C_0$ to D at C = 0.



FIG. 12.13. Concentration-distance curves during sorption for

$$D = rac{D_{\mathbf{Q}}}{(1 - lpha C/C_{\mathbf{0}})^{\mathbf{2}}}$$

Numbers on curves are values of $1/(1-\alpha)^2$, being ratio of D at $C = C_{\bullet}$ to D at C = 0.

The nomenclature here is that of § 9.35 (iii). If a similar large-scale graph of $(C-C_2)/(C_1-C_2)$ be prepared from the data of Table 9.4 it is found that two common points appear, with coordinates





Curve I. For a constant diffusion coefficient. Curve II. For a diffusion coefficient varying linearly with concentration, the value at the higher concentration being 0-1406 of that at the lower concentration.

If the sorption curves of Fig. 12.7 for linear D's are replotted against the variable y_a they too pass through a common point of coordinates $y_a = 1.00, C/C_0 = 0.157$. For the replotted desorption curves of Fig. 12.8 the common point is $y_a = 1.09, C/C_0 = 0.872$. When the curves of Figs. 12.9 and 12.10 for exponential diffusion coefficients and Figs. 12.12 and

§ 12.3]

12.13 for $D = D_0/(1-\alpha c)$ and $D_0/(1-\alpha c)^2$ are replotted in the same way with D_a replaced by the integrated mean-value no such common points are found.

Stokes [4] suggests that this common-point property may have a useful practical application as follows. Suppose, for example, that values of $(x dC/dx)/(C_1-C_2)$ are obtained experimentally and plotted against x for points in the vicinity of the common point P of Fig. 12.14, and the value of x for which $(x dC/dx)/(C_1-C_2) = -1.205 \times 0.133 = -0.1603$

is determined. Calling this value x_P we have, since $x_P^2/(4D_a t) = (1.205)^2$, $D_a = x_P^2/(5.81t).$ (12.50)

Thus, by observing the rate of penetration of the common point in experiments covering different concentration ranges, the concentration-dependence of D_a and hence of D can be deduced. This was not referred to in the chapter on methods because it has not yet been exploited in a practical case.

So far it has not been possible to deduce the existence of the common points as a fundamental property of the diffusion equation. The existence of a common point in the concentration-distance curves had been noted by Crank and Henry [5] previously to Stokes, though their method of plotting their results against an independent variable, $x/\{2(D_0t)^{\dagger}\}$ (where D_0 is the diffusion coefficient at zero concentration), did not bring the common point into prominence as clearly as does the use of the variable y_a . They pointed out, however, that there is some concentration whose rate of penetration is governed by

$$\left\{\int_{C_1}^{C_1} D \, dC\right\} / (C_1 - C_2) = D_a$$

for a linear diffusion coefficient. They also discussed in some detail the effect of the relationship between the diffusion coefficient and concentration on the rates of penetration of concentrations other than that at which the common point occurs.

12.4. Sorption- and desorption-time curves

On the basis of the sorption and desorption curves shown in Figs. 12.15, 12.16, and 12.17 and of corresponding curves published elsewhere [9] we may draw the following general conclusions for a system in which the diffusion coefficient increases as concentration is increased but does not depend on any other variable.

(i) In the early stages, when diffusion takes place essentially in a semi-infinite medium, the amount sorbed or desorbed is directly proportional to the square root of time. This is true, incidentally, whatever the relationship between the diffusion coefficient and concentration, and follows directly from the fact that for the prescribed boundary conditions concentration depends on the single variable $x/t^{\frac{1}{2}}$ (§ 9.31). When D increases with concentration increasing, the linear behaviour may extend well beyond 50 per cent. of the final equilibrium uptake in the case of sorption. The same is true for desorption when D decreases with concentration increasing.

(ii) When they cease to be linear, the sorption and desorption curves

plotted against $(time)^{i}$ each become concave towards the $(time)^{i}$ axis, and steadily approach the final equilibrium value. This is true for all the calculated results obtained for the initial and boundary conditions (12.46), (12.47), (12.48), (12.49) and it is reasonable to conclude that it





is a quite general result though no satisfactory general proof has yet been produced. It is an important property because sorption curves have been observed experimentally [7, 8] which show points of inflexion when plotted against (time)[‡], i.e. there is a region in which the curve is convex to the (time)[‡] axis. This has been taken as evidence either that the boundary condition (12.46) does not describe the experimental conditions, or that the diffusion coefficient is a function of some variable other than concentration. Prager [6] has given a general proof that sorption and desorption curves when plotted against *time* can never become convex to the time axis, but this is a less stringent restriction than the one just put forward. His proof is as follows.

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We wish to show that the integral

$$M_t = \int_0^t C(x,t) \, dx, \qquad (12.51)$$

obtained as a solution of

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right), \qquad (12.52)$$



with the conditions

$$C = C_0 = \text{constant}, \quad x = 0, \quad x = l, \quad t > 0,$$
 (12.53)
 $C = 0, \quad 0 < x < l, \quad t = 0,$ (12.54)

cannot yield an inflexion point when plotted against t. The diffusion coefficient, D, is a function of concentration C only and is always positive. On writing

$$s(C) = \int_{0}^{b} D(C') dC', \qquad (12.55)$$

$$(12.52) \text{ becomes} \qquad D(s) \frac{\partial^2 s}{\partial x^2} = \frac{\partial s}{\partial t}, \qquad (12.56)$$
with conditions $s = S_0, \quad x = 0, \quad x = l, \quad t > 0, \qquad (12.57)$

$$s = 0, \quad 0 < x < l, \quad t = 0. \qquad (12.58)$$

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Furthermore, since the rate of transfer across unit area normal to the x-direction is given by $-D\partial C/\partial x = -\partial s/\partial x$, we have

$$\frac{\partial M_t}{\partial t} = -2\left(\frac{\partial s}{\partial x}\right)_{x=0} \tag{12.59}$$

allowing for the symmetry of the problem. Because dM_t/dt is infinite when t = 0, it follows that if there is to be a point of inflexion at some later time, dM_t/dt must



FIG. 12.17. Sorption and desorption curves for exponential diffusion coefficient $D = D_0 e^{kC/C_0}$. Numbers on curves are values of e^k , being ratio of D at $C = C_0$ to D at C = 0.

go through a minimum, and so $(\partial s/\partial x)_{x=0}$ must go through a maximum as a function of t. This in turn requires that there is some finite length of time, extending just

beyond that at which the inflexion is supposed to occur, during which

$$\frac{d}{dt} \left(\frac{\partial s}{\partial x} \right)_{x=0} < 0. \tag{12.60}$$

Also, since $s = S_0$ is constant at x = 0 and x = l, $\partial s/\partial t$ must also be negative during that time near x = 0 and x = l. We now show that this is impossible for the given initial and boundary conditions.

For very small t, the condition $\partial C/\partial t \ge 0$ holds for all x, because we cannot have negative concentrations. Since D is positive everywhere this means that $\partial s/\partial t = D \partial C/\partial t$ must also be positive or zero everywhere for sufficiently small t.

But $\partial C/\partial t$, and hence $\partial s/\partial t$, is continuous everywhere and $\partial s/\partial t$ must therefore first be zero if it is to become negative. Let x = X be the first point at which $\partial s/\partial t = 0$ excepting x = 0 or x = l where this is always true. Then $\partial s/\partial t$ will be positive or zero on both sides of X, i.e. it will show a minimum at X when plotted against x so that $\left\{\frac{\partial^2}{\partial x^2} \begin{pmatrix} \partial s \\ \partial t \end{pmatrix}\right\}_{x=0} \ge 0,$

$$\mathbf{or}$$

$$\left\{\frac{\partial}{\partial t} \left(\frac{\partial^2 s}{\partial x^2}\right)\right\}_{x=X} \ge 0.$$
(12.61)

But it follows from (12.56) that since $\partial s/\partial t = 0$ at x = X, so also $\partial^2 s/\partial x^2 = 0$ there. Equation (12.61) then indicates that in the next instant $(\partial^2 s/\partial x^2)_{x=X}$ is positive or zero, and so using (12.56) again and remembering that D > 0 we see that $(\partial s/\partial t)_{x=X}$ becomes positive or zero. Thus $\partial s/\partial t$ can never become negative and so there can never be a point of inflexion in the plot of M_t against t, i.e. in the uptake curve plotted against time.

(iii) If D increases as concentration increases, the shape of the sorption curve when plotted against *time* is not very sensitive to the form of the diffusion coefficient. It is often not significantly different from the corresponding curve for a constant diffusion coefficient. This is, of course, because the sorption curves are parabolic, i.e. linear against (time)[‡], over most of their length. The desorption curves when plotted against time are much more sensitive to the form of the diffusion coefficient if this increases as concentration increases. If the diffusion coefficient *decreases* as concentration increases, then the *desorption* curve will approximate to that for a constant diffusion coefficient.

(iv) When D increases with concentration increasing throughout the relevant range of concentration, desorption is always slower than sorption, and conversely if D decreases with concentration increasing. This is illustrated by Fig. 12.17. In particular, the last stages of desorption are much slower than those of sorption if D increases with concentration increasing, and vice versa.

Crank and Henry [9] have examined the sorption and desorption curves associated with a diffusion coefficient which passes through a maximum value at some intermediate concentration. Three such diffusion coefficients are shown in Fig. 12.18, where $c = C/C_0$ as usual. They correspond to the clumber in the distance of the standard states of the clumber in the standard states of the states of the standard states of the states

(12.62) is a symmetrical form in which this maximum occurs at c = 0.5, while the maximum values for (12.63) and (12.64) are at c = 0.3 and 0.7 respectively, since (12.64) follows immediately from (12.63) by writing (1-c) for c. The sorption and desorption curves for these diffusion coefficients are presented in Fig. 12.19. Since (12.62) is





symmetrical in c and (1-c) it follows from what was said above that for the boundary conditions considered the sorption- and desorptiontime curves are coincident, and this is, of course, true for any symmetrical relationship between D and c. The results show that for D given by (12.63) with a maximum at c = 0.3 the desorption curve lies wholly above that for sorption, while the opposite is true for the relation (12.64) where the maximum value of D occurs at c = 0.7.

The relative behaviour of the sorption- and desorption-time curves is affected by the relative values of the diffusion coefficient at c = 0 and c = 1, and also by the position of the maximum in the *D*-*c* curve if one occurs. This suggests that, in some cases, the desorption curve may be above the sorption curve in the early stages of diffusion but later may cross it so that the final stages of desorption are again slower than those of sorption. This is likely to occur when there is a maximum in the diffusion coefficient-concentration relationship and when the value of *D* at c = 1 is greater than at c = 0. In order to study this behaviour a diffusion coefficient-concentration relationship and the sum of the stages of the study the study the stages of th

relationship of the form

 $D/D_0 = 1 + \alpha \operatorname{erf}(\beta c) + \gamma c^{\uparrow}$ (12.65) was used, where α , β , γ are constants for any one curve. There is no 5824 T



significance in the precise form of (12.65) except that it leads to diffusion coefficient-concentration curves of the desired form and is convenient



FIG. 12.19. Sorption and desorption curves.

to handle numerically. From (12.65) we have

$$\frac{d(D/D_0)}{dc} = \frac{2\alpha\beta}{\pi^{\frac{1}{2}}} e^{-\beta^2 c^2} + \gamma = 0, \qquad (12.66)$$

when D has a maximum value. All curves given by (12.65) pass through the point $D/D_0 = 1$, c = 0. The three further conditions that D/D_0 shall have a prescribed value at c = 1 and a given maximum value at

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a prescribed value of c, can be satisfied by suitable choice of the parameters α , β , γ , the desired values being readily determined by use of (12.65) and (12.66). A typical curve of this family, actually the one given by $D/D_0 = 1 + 4.62 \operatorname{erf}(6.10c) - 3.12c$, (12.67)



FIG. 12.22. $D/D_0 = 1 + 29.86 \operatorname{erf}(0.98c) - 23.40c$.

which satisfies the conditions

is shown in Fig. 12.21 together with the sorption- and desorption-time curves. The curves intersect at

$$(D_0 t/l^2)^{\frac{1}{2}} = 0.29.$$

For values of $(D_0 t/l^2)^{\frac{1}{2}}$ less than this, desorption proceeds more rapidly than sorption but after the intersection the desorption curve lies below that for sorption. This to be contrasted with the sorption and desorption curves shown in Fig. 12.22 which do not intersect and which are for a diffusion coefficient of the form

$$D/D_0 = 1 + 29.86 \operatorname{erf}(0.98c) - 23.40c. \tag{12.69}$$

This diffusion coefficient is also shown in Fig. 12.22 where it is seen to differ from that defined by (12.67) in that it has a maximum value at c = 0.6 instead of c = 0.25. Fig. 12.20 shows further curves for a diffusion coefficient of the same general shape having a maximum value at c = 0.125. It is clear from inspection of these curves that, keeping the end points of the diffusion coefficient-concentration curves fixed at $D/D_0 = 1$ and $D/D_0 = 2.5$ and the maximum value of $D/D_0 = 4.7$, as the position of the maximum value moves back from c = 1 to c = 0there is first a range of positions of the maximum for which the whole process of desorption is slower than sorption. Continuing to move the position of the maximum towards c = 0 there is evidently a further range of positions for which the desorption and sorption curves intersect, the point of intersection occurring at successively larger values of $D_0 t/l^2$ as the position of the maximum moves towards c = 0. There is some intermediate position of the maximum for which the desorption curve crosses the sorption curve at the origin only and this is the limiting case between sorption and desorption curves which intersect for t > 0 and those which do not.

For this set of curves having $D/D_0 = 2.5$, c = 1, it is found that the limiting position of the maximum for which intersection of the sorption and desorption curves occurs at $D_0 t/l^2 = 0$ is about c = 0.26. When the maximum occurs at higher values of c than this, desorption is slower than sorption right from $D_0 t/l^2 = 0$, but when the maximum lies in the range 0 < c < 0.26 the desorption curve is first above the sorption curve but crosses it later so that the final stages of desorption are again slower than those of sorption.

Still confining attention to the general form of variable diffusion coefficient expressed by (12.65), it is to be expected that the critical position of the maximum for which the sorption and desorption curves have equal gradients in the neighbourhood of t = 0 when plotted against $(D_0 t/l^2)^{\frac{1}{2}}$ will vary as the value of D at c = 1 is caused to vary, taking the maximum value of D to remain constant and the condition $D/D_0 = 1$,

c = 0, to be satisfied in all cases. This expectation is confirmed by the results presented graphically in Fig. 12.23 where the critical position of the maximum is plotted as a function of the value of D/D_0 at c = 1.0. The critical position is seen to move towards c = 0 as the value of D at c = 1 is increased.

The points at each end of the curve of Fig. 12.23 were arrived at by general reasoning and the intermediate points by calculation. Thus considering first a D-c curve for which the value of D/D_0 at c = 1 is very

close to 4.7, which is the value of the maximum D/D_0 for this family of curves, it is clear that, in general, for a D-c curve of this type the diffusion coefficient is effectively increasing over the whole range of concentration, and sorption will be quicker than desorption throughout. This is true for all positions of the maximum except when it is so near to c = 0 that



F10. 12.23. Critical position of the maximum of D/D_0 as a function of D/D_0 at c = 1.0.

the diffusion coefficient is effectively constant over the whole range of concentration, in which case the sorption- and desorption-time curves coincide throughout and c = 0 is therefore the limiting position of the maximum when $D/D_0 = 4.7$ at c = 1.

By an extension of this argument the critical position of the maximum can be determined when $D/D_0 = 0$ at c = 1. It was seen above that the sorption-time curve obtained when D is a certain function of c is the same as the desorption-time curve when D is the same function of (1-c)and vice versa. It follows immediately that if the initial rates of sorption and desorption are equal when D is a certain function of c, they will also be equal when D is the same function of (1-c), i.e. if the critical position of the maximum value of D is $c = c_m$ in the first case, it will be $c = 1-c_m$ in the second case. Now if D is a function of (1-c) is such that D is very small when c = 1, the corresponding function of (1-c) is such that the value of D at 1-c = 1 is relatively very close to the maximum value of D. This function approximates to the type just considered above and the critical position of the maximum value of D is at (1-c) = 0 and therefore at c = 1 for the original D-c curve. For any D-c curve of the general family under discussion, the relative behaviour of the sorption- and desorption-time curves can be deduced from Fig. 12.23 if the value of D/D_0 at c = 1 and the position of the maximum are known. Four regions are to be distinguished, in two of



Fig. 12.24. Sorption and desorption curves. $D_2 t/l^2$

which the sorption- and desorption-time curves intersect at some time, t > 0, and in the other two they do not intersect when t > 0. When the value of D/D_0 at c = 1 exceeds unity, the initial rate of desorption is more rapid than that of sorption if the curves intersect, and vice versa when $D/D_0 < 1.0$ at c = 1. The critical position of the maximum no doubt
depends on the magnitude of the maximum value of D, and also for a given maximum value it will depend to some extent on the detailed shape of the diffusion coefficient-concentration curve. These aspects of the problem have not yet been investigated.





Fig. 12.25. Sorption and desorption curves.

The relative rates of sorption and desorption have also been examined for diffusion coefficients which are discontinuous functions of concentration [10]. If the sorption and desorption curves of Figs. 7.1d and 7.2dwere plotted on one diagram they would be found to intersect markedly. A particular example is shown in Fig. 12.24 for the diffusion coefficient shown in the inset. These curves are for a diffusion coefficient which is infinite over an intermediate range of concentration and it is easy to see the condition necessary in this case for intersection. Referring again to Figs. 7.1 and 7.2 and using that nomenclature, we see that the height of the initial vertical part of the sorption curve of Fig. 7.1 d is lC_X , and that of the corresponding part of the desorption curve (Fig. 7.2 d) is $l(C_1 - C_T)$. Hence, provided D is greater at high than at low concentrations, intersection occurs if $C_1 - C_T$ exceeds C_X , so that

$$C_{\rm Y} < \frac{1}{2}(C_1 - a), \tag{12.70}$$

where a is the concentration range over which D is infinite. Thus the limiting case is when this range is symmetrically situated with respect to the whole concentration range 0 to C_1 . If the infinite region is mainly in the upper half of the concentration range, desorption is slower than sorption throughout, but if it is mostly in the lower half the sorption and desorption curves intersect. Clearly, the point of intersection occurs earlier the smaller D_2 is compared with D_1 in Fig. 7.1 d.

Fig. 12.25 shows sorption and desorption curves for the diffusion coefficient shown in the inset. These curves were calculated by the numerical methods described in Chapters IX and X. Although the value of D in the middle concentration range of the inset of Fig. 12.25 is still relatively high, the intersection is much less marked in Fig. 12.25 than in Fig. 12.24 and becomes even less pronounced if the largest value of D is decreased further.

12.41. Effect of the initial concentration on the rate of sorption

It might be expected that the initial rate of sorption by a sheet having a finite, uniform concentration of diffusing substance in it initially would be greater than the corresponding rate for zero initial concentration if the operative diffusion coefficient is small at low concentrations. Such an effect has been observed experimentally, for example, by King [11] for the uptake of methyl alcohol by wool. The effect should be most

marked when the diffusion coefficient is zero at low concentrations as in Fig. 7.6*a*. A convenient measure of initial rate of sorption is the initial gradient of the sorption curve when plotted against (time)¹ as in Fig. 7.7, i.e. d(M)

$$\frac{d}{dT^{\frac{1}{2}}}\left(\frac{M_l}{lC_1}\right), \quad \text{where } T = D_1 t/l^2. \tag{12.71}$$

The nomenclature is that of Chapter VII and Figs. 7.6 and 7.7 in it. The initial rate so calculated is shown in Fig. 12.26 as a function of C_{2} ,

the initial uniform concentration in the sheet [10]. The different curves refer to different values of C_X , the concentration at which D changes discontinuously. In all cases, the initial rate of sorption decreases as the initial regain is increased. This, then, is a further characteristic feature of a purely concentration-dependent system, and in systems which show qualitatively different behaviour some factor other than concentration-dependence must be sought as the cause.



FIG. 12.26. Effect of initial uptake on initial rate of sorption.

12.5. Diffusion-controlled evaporation

Some evaporative processes are diffusion controlled in the sense that the rate of evaporation depends largely on the rate at which solvent or mixture is supplied to the evaporating surface by internal diffusion. An important consideration is the effect of the proportion of solvent vapour, or the relative humidity, in the atmosphere into which the evaporation takes place. Instances have been reported [12], when evaporation takes place through an organic membrane or a polymer film, in which the rate observed in practice is increased by increasing the relative humidity at the evaporating surface. This behaviour has been attributed to the effect of a diffusion coefficient which is low at low solvent concentrations, the argument being that by maintaining some vapour in the outside atmosphere the concentration range over which diffusion within the sheet is difficult is removed. It has been shown theoretically [12], by evaluating solutions of the diffusion equation for appropriate diffusion coefficients and boundary conditions, that such behaviour is not to be expected in a purely concentration-dependent system. Both the steady-state evaporation through a membrane and the loss of vapour from a sheet containing solvent have been examined.



FIG. 12.27. Concentration distributions in steady state.

12.51. Steady-state evaporation through a membrane

We saw in § 11.61 that if we have a membrane of thickness l separating a region of high from one of low vapour pressure, then the rate of evaporation through the membrane in the steady state is F, where

$$F = (1/l) \int_{C_1}^{C_0} D \, dC. \tag{12.72}$$

Here C_0 and C_1 are the concentrations just within the surfaces of the membranes on the high- and low-pressure sides respectively. The argument leading to (12.72) is true whether D is constant or not. In par-

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ment leading to (12.72) is true whether *D* is constant of not. In particular it is true when *D* is a function of concentration, and provided *D* is never negative in the range from C_0 to C_1 , the integral in (12.72) must always increase or remain constant as the range of concentration is increased. Thus, as Park in [12] has pointed out, if the high concentration remains fixed, the rate of evaporation, *F*, can never increase as a result of increasing the lower concentration C_1 , i.e. the rate of evaporation is greatest into an atmosphere completely free of solvent vapour. Where the experimental facts genuinely differ from this, some alternative explanation must be found [12].

Further insight into the effect of changing the vapour pressure on the low-pressure side is given by Fig. 12.27. Calculated distributions of concentration through the membrane are shown for a case in which Dis an exponential function of concentration such that D increases by fiftyfold from C = 0 to $C = C_0$. The concentration, C_0 , on the highpressure side is the same for each curve, but in one case $C_1 = 0$ and in the other $C_1 = \frac{1}{2}C_0$. The curves show how the concentration distribution adjusts itself so that the rate of flow is greater when $C_1 = 0$, even though the region of low diffusion coefficient is then included. Clearly, a low diffusion coefficient is compensated by a high concentration gradient.

12.52. Evaporation from films and filaments

It is not possible to express the rate of loss of vapour from a film containing solvent in terms of a simple expression such as (12.72) and so it is less easy to examine the effect of introducing vapour into the outside atmosphere. However, some illustrative examples have been worked numerically [12] for the first diffusion coefficient shown in Fig. 12.28. This is an experimental curve relating to the diffusion of acetone in cellulose acetate. The concentration distributions through a sheet initially containing solvent at a uniform concentration have been calculated for this diffusion coefficient and two different boundary conditions:

- (i) The surface of the sheet is assumed to reach equilibrium with the outside atmosphere instantaneously when evaporation commences, i.e. if the atmosphere is free of vapour the concentration at the surface falls immediately to zero; if the vapour pressure in the atmosphere is p, the surface of the sheet immediately reaches the concentration which is in equilibrium with p.
- (ii) A condition expressing the rate of evaporation from the surface is assumed. This is taken to be

$$D_s \partial C / \partial x = \alpha (C_s - C_0), \qquad (12.73)$$

where C_s is the actual concentration in the surface of the sheet

at any time and C_0 the concentration which would be in equilibrium with the vapour pressure remote from the surface. The diffusion coefficient D_s is the value corresponding to the concentration C_s .

Fig. 12.29 shows the calculated variation of concentration with distance through the sheet at two different times for the condition (i), that of vigorous surface evaporation. For each time, curves are shown for







the cases in which (α) the surface concentration falls to zero instantaneously, (b) it falls to one-tenth of its initial value instantaneously. We see that there is little difference between the two curves at either time. In particular the total solvent content of the sheet at any time, represented by the area under the appropriate curve of Fig. 12.29, is much the same whether the surface concentration falls to zero or to one-tenth of its initial value, i.e. whether the concentration over which D is small is removed or not. In so far as there is a slight difference, the rate of loss of solvent by the sheet is greater in the vapour-free atmosphere. As in the steady state, the rate of evaporation is not increased by introducing vapour into the atmosphere.

The reason for this is clear from these calculations as it was in the steady state. When the diffusion coefficient has a small value at the surface the concentration gradient is correspondingly large so that the rate of loss of vapour, given by $D \partial C / \partial x$ at the surface, does not alter appreciably. This compensating effect is most obvious when the diffusion coefficient is zero over a range of low concentrations as in the second diffusion coefficient shown in Fig. 12.28. This is a hypothetical coefficient chosen to exaggerate the effect. The concentration-distance curve for this coefficient is sketched in the inset of Fig. 12.29 from general reasoning. The surface gradient is infinite over the concentration range for which D is zero (in this case for concentrations less than 0.10) so that the product can have a non-zero value. A finite gradient cannot develop for concentrations less than 0.10, since this would imply that solvent had been removed from a region of zero diffusion coefficient under the action of a finite gradient, which is not possible. For such a diffusion coefficient the rate of evaporation is precisely the same for all surface concentrations between zero and 0.1.

The same general conclusion holds for the surface condition (12.73), i.e. the rate of loss from the sheet is always increased by decreasing the external vapour pressure.

Many films and fibres show evidence of a surface skin having properties different from those of the underlying layer or core. In this section we examine the effect of such a skin on diffusion behaviour. The results presented were obtained as part of an attempt to understand some of the peculiar features which are sometimes observed when solvents diffuse into and out of polymer substances [7]. We shall restrict ourselves to cases in which the skin and the core are

each homogeneous and the boundary between the two is sharply defined. In the skin the diffusion coefficient is assumed to be either constant or a discontinuous function of concentration, and beneath the skin to be everywhere infinite at all concentrations.

(i) The simplest case is one in which D is constant in the skin, and the medium is semi-infinite. The solution has been given in Chapter III, equation (3.57), which becomes

$$\frac{M_l}{2lC_0} = \left(\frac{Dt}{l^2}\right)^{\frac{1}{2}} \left\{\frac{1}{\pi^{\frac{1}{2}}} + 2\sum_{1}^{\infty} \operatorname{ierfc}\frac{nl}{(Dt)^{\frac{1}{2}}}\right\}, \quad (12.74)$$

when $D_2 = \infty$. Here M_t is the total amount of diffusing substance which enters the composite medium in time t if the surface is maintained at a constant concentration C_0 . When $M_t/2lC_0$ is plotted as a function of $(Dt/l^2)^{\dagger}$ the curve is linear for small times and its gradient later increases steadily as t increases. When plotted as a function of Dt/l^2 the curve is parabolic at first and then becomes linear, the gradient of the linear part being determined by the constant rate of flow across the outer surface in the final steady state. Both the curves shown in Fig. 12.30 are noticeably different from the corresponding ones for a semi-infinite homogeneous sheet when M_t is proportional to t^{\dagger} for all times.

(ii) We consider next a finite sheet having on each surface a skin in which D is a discontinuous function of concentration, C, of the type shown in Fig. 12.31a. The general shape of the sorption-time curve for this case is easily deduced from the concentration-distance curve for the same diffusion coefficient and a homogeneous sheet. Solutions have been given in Chapter VII, Figs. 7.6 and 7.7; the sorption-time curve is parabolic for small times and the concentration-distance curve is characterized by a sharp front which advances according to the square root of time (Fig. 12.31 b). It is clear that until this sharp front has penetrated to the inner boundary of the skin the sorption-time curve is the same as for a homogeneous sheet having the properties of the skin throughout. After this the concentration on the outer surface of the sheet remains at C_0 and that on the inner surface of the skin at C_X till the uniform concentration throughout the region of infinite diffusion coefficient has reached the value C_X . During this time there is approximately a steadystate flow through the skin so that the rate of sorption by the whole sheet is constant and the sorption-time curve is linear. When the whole sheet beneath the skin has reached a concentration C_X there is a gradual decrease in rate of sorption as the final equilibrium concentration C_0 is approached throughout the sheet.







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FIG. 12.31. Sorption and desorption curves for sheet with skin.

The details of the calculation for this case are as follows. For sorption we require solutions of the usual equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2},\tag{12.75}$$

where in the region 0 < x < l, D is defined by

$$D = 0, \qquad 0 < C < C_{X}, \tag{12.76}$$

$$D = D_{\rm I}, \qquad C_{\rm X} < C < C_0, \tag{12.77}$$

and in the region l < x < l+a, D is infinite. The solutions are subject to the conditions

$$C = C_0, \quad x = 0, \quad t > 0,$$
 (12.78)

$$C = 0, \quad 0 < x < l + a, \quad t = 0.$$
 (12.79)

For small times the concentration-distance curve falls discontinuously from $C = C_X$ to C = 0, and until this vertical part of the curve reaches x = l at, say, time $t = t_0$, the medium is effectively semi-infinite and the solution is

$$C = C_0 + A \operatorname{erf} \frac{x}{2\sqrt{D_1 t}},$$
 (12.80)

where

$$A \operatorname{erf} k/(2D_1^{\dagger}) = C_X - C_0, \qquad (12.81)$$

and the constant k is given by

$$\frac{C_X - C_0}{\operatorname{erf}(k/2D_1^{\frac{1}{2}})} + \frac{\pi^{\frac{1}{2}}ke^{k^{\frac{3}{4}}D_1}}{2D_1^{\frac{1}{2}}}C_X = 0.$$
(12.82)

After $t = t_0$ the concentration at x = l remains at $C = C_X$ till an amount aC_X has crossed x = l. During this time the usual solution, § 4.31, equation (4.16), for a sheet whose surface concentrations are fixed and in which the initial concentration distribution is f(x), given by substi-



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From (12.83) it is easily deduced that the amount M_0 crossing unit area at x = 0 from time $t = t_0$ onwards is given by

$$\frac{-lM_0}{D_1} = \langle C_X - C_0 \rangle (t - t_0) + 2 \sum_{n=1}^{\infty} \frac{l^2}{D_1 n^2} [\exp\{-D_1 n^2 \pi^2 (t - t_0)/l^2\} - 1] \times \\ \times \left\{ C_X \cos n\pi - C_0 + \frac{n\pi}{l} \int_0^l f(x) \sin \frac{n\pi x}{l} \, dx \right\}. \quad (12.84)$$

The amount, M_l , crossing unit area at x = l in the same time is given by

$$-\frac{l}{D_{1}}M_{l} = (C_{X} - C_{0})(t - t_{0}) - \frac{2\sum_{n=1}^{\infty} (-1)^{n} \frac{l^{2}}{D_{1}n^{2}} [\exp\{-D_{1}n^{2}\pi^{2}(t - t_{0})/l^{2}\} - 1] \times \times \left\{ C_{X} \cos n\pi - C_{0} + \frac{n\pi}{l} \int_{0}^{1} f(x) \sin \frac{n\pi x}{l} \, dx \right\}.$$
 (12.85)

The equation (12.84) expresses the total amount absorbed by the composite sheet from time t_0 onwards and these solutions apply till $M_l = aC_X$ as calculated from (12.85). For much of this time there will be approximately a steady-state flow across the region 0 < x < l.

After the concentration throughout the region l < x < l+a has reached C_X , the boundary condition on x = l is

$$-D_1 \,\partial C/\partial x = a \,\partial C/\partial t, \qquad (12.86)$$

and the solution is conveniently continued by numerical methods described in Chapter X using for (12.86) the finite-difference form

$$\frac{\partial C}{\partial x} = \frac{C_{s-2} - 4C_{s-1} + 3C_s}{2\delta x},\tag{12.87}$$

where the range 0 < x < l is divided into equal steps δx , and C_{s+p} is the value of C at $x = l + p \, \delta x$.

For desorption we require solutions of equation (12.75) for the same diffusion coefficient but subject to the conditions

$$C = 0, \quad x = 0, \quad t > 0,$$
 (12.88)

$$C = C_0, \quad 0 < x < l + a, \quad t = 0.$$
 (12.89)

In this case the concentration-distance curve rises discontinuously at x = 0 from C = 0 to $C = C_X$, and in the early stages, when the concentration at x = l is not appreciably different from C_0 to the required

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accuracy, the solution is simply that for a semi-infinite sheet having a surface concentration C_X , i.e.



$$C - C_X = (C_0 - C_X) \operatorname{erf} \frac{x}{2(D_1 t)^{\frac{1}{2}}}.$$
 (12.90)

FIG. 12.32. Sorption and desorption curves for sheet with skin.

At later times the condition (12.86) again applies and the solution can be continued numerically as for sorption. A typical sorption-time curve is shown in Fig. 12.31 for $C_X = \frac{2}{3}C_0$ and a skin which forms one-fifth of the half-thickness of the sheet. The corresponding curve for desorption is also shown in Fig. 12.31.

The investigations into the cause of intersecting sorption- and desorption-time curves discussed in § 12.4 (iv) suggest that a diffusion coefficient in the skin of the form shown in Fig. 12.32 a might be interesting. The concentration-distance curve for this diffusion coefficient has a sharp front as in Fig. 12.32 b, and the required mathematical solutions up to the time at which this front reaches the inner surface of the skin have already been presented in § 7.24, together with a numerical procedure for extending them to later times (Chapter X). Desorption can be treated by the same equations and methods. Fig. 12.32 shows calculated sorption- and desorption-time curves for the diffusion coefficient of Fig. 12.32a and a skin one-fifth of the half-thickness of the sheet as before. Here we see that the curves intersect but the linear part has almost disappeared from the sorption curve. We can now see that this

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must always be so, for, as we have already noted, intersection of sorption and desorption curves only occurs when the region of high diffusion coefficient is in the lower half of the concentration range, which means that the diffusion coefficient is small or zero only at very low concentrations. But it is clear from what we have said and from Fig. 12.32bthat for relatively thin skins the amount absorbed by the sheet when the sorption-time curve ceases to be linear is roughly proportional to the height of the sharp front in the concentration-distance curve, i.e. to the concentration range over which D is small or zero. It follows that, in general, when the sorption-time curve calculated for the model we have chosen has a long linear portion, desorption will be everywhere slower than sorption; conversely if the sorption and desorption curves intersect markedly no appreciable linear part will be observed in the sorption curve.



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Numbers on curves are values of D_b/D_a .

12.61. Composite cylinder

The effect of a skin on the uptake of dye by a cylindrical fibre has been studied [13]. The solutions obtained relate to a circular cylinder of infinite length and radius a immersed in a solution. Dye molecules diffuse into the cylinder and are deposited in capillaries of the cylinder. The concentration of the dye in the solution is always uniform, while the cylinder is initially free of dye. The cylinder has a core of radius b,

in which the diffusion coefficient is D_b and for b < r < a the diffusion coefficient is D_a . In any element of the cylinder the amount of dye, S,



F10. 12.34. Sorption curves for a composite cylinder, $b = \frac{9}{10}a$. Numbers on curves are values of D_b/D_a .

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deposited in the capillaries and immobilized is related to C, the amount free to diffuse, by the relationship (12.91)

$$S = RC^{\ddagger},$$

where R is a constant which, in this example, is chosen so that in the final equilibrium state 90 per cent. of the dye initially in the solution has entered the fibre. When the ratio of the volume of solution to that of the fibre is 25:1, R = 70.8. If we denote by M_i the amount of dye in the cylinder after time t, and M_{∞} the corresponding amount after infinite time, Fig. 12.33 shows M_t/M_{∞} as a function of $\log_{10}(D_b t/a^2)$ for $b = \frac{9}{10}a$. The several curves correspond to different values of D_b/D_a . The effect of changing the ratio D_b/D_a is to displace the sorption curve parallel to





the time axis, and this is accompanied by a slight change in the shape of the curves. Thus, when $M_t/M_{\infty} = 0.5$, in Fig. 12.33, the abscissae of points on the curves for $D_b/D_a = 2$, 10, and 30 differ from the corresponding abscissa for $D_a = D_b$ by the amounts 0.30, 1.00, 1.45 respectively, i.e. by approximately $\log_{10} 2$, $\log_{10} 10$, $\log_{10} 30$. When $M_t/M_{\infty} = 0.8$, the abscissae differences are 0.18, 0.78, 1.18 respectively. Thus the

sorption curve for this composite cylinder almost coincides with the corresponding curve for a homogeneous cylinder having a diffusion coefficient D_a throughout. The final stages proceed more rapidly in the composite cylinder, however, as is to be expected because of the greater diffusion coefficient in the core. For a thicker skin there is less difference in the shapes of the curves for composite and homogeneous cylinders [13]. In Fig. 12.34 some of the uptake curves are replotted against $(D_b t/a^2)^{\frac{1}{2}}$ to show that the presence of a skin does not necessarily produce a point

of inflexion in the uptake curve plotted against the square root of time, as it does in the problems discussed in § 12.6. Fig. 12.35 shows the overall concentration (S+C) in a composite cylinder as a function of the radial coordinate at three different times. There is a rapid fall in concentration within the skin and a discontinuity in concentration gradient at the boundary between the skin and the core where the diffusion coefficient changes discontinuously.

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XIII

SIMULTANEOUS DIFFUSION OF HEAT AND MOISTURE

13.1. Introduction

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THE problem to be discussed in this chapter is that of the diffusion of one substance through the pores of a solid body which may absorb and immobilize some of the diffusing substance with the evolution or absorption of heat. This heat will itself diffuse through the medium and will affect the extent to which the solid can absorb the diffusing substance. We thus have two processes, the transfer of moisture and the transfer of heat, which are coupled together, and we cannot in general consider one process without considering the other simultaneously. For convenience we shall refer to diffusion through pores, but the theory will apply to alternative systems provided only that some of the diffusing substance is immobilized and that heat is given out in the process. Thus the case of a dissolved substance diffusing through a gel would be included. Equations of the same form would also be obtained, neglecting thermal effects, for the diffusion of two substances through a porous solid, each capable of replacing the other in absorption by the solid.

13.2. Uptake of water by a textile fibre

A simple illustration of the coupling between the transfer of heat and that of moisture is afforded by the uptake of moisture by a single textile fibre. Water penetrates the fibre by diffusion and for a wool fibre a diffusion coefficient of about 10^{-7} cm.²/sec. can be taken as representative. The time for a single fibre to reach say 80 per cent. of its final uptake of moisture depends not only on the diffusion coefficient but also on the diameter of the fibre—the thinner the fibre the more quickly it absorbs. Now the average diameter of a fibre is so small (rather less than 10^{-3} cm.) that for a diffusion coefficient of 10^{-7} cm.²/sec. we expect 80 per cent. absorption to be reached in about 2 seconds. King and Cassie [1] attempted to demonstrate this conclusion experimentally by measuring the rate of sorption of water vapour by a small mass of wool (0.25 g.) suspended by a sensitive spring-balance in an evacuated chamber into which water vapour was introduced at 23.5 mm. pressure. By suspending the wool in an evacuated chamber King and Cassie eliminated 304

diffusion through any surrounding atmosphere and they expected to measure directly a rate of uptake governed solely by diffusion within the fibres. In view of the small diameter of the fibre we expect this uptake to be a matter of only a few seconds. This does not appear to be at first sight supported by the uptake curve they observed, which reached 80 per cent. only after an hour or so.

We must remember, however, that when water vapour is absorbed by wool a large amount of heat is evolved which produces a considerable increase in temperature. King and Cassie showed that when this temperature rise is taken into account the relatively low rate of sorption can be reconciled with the statement that an individual fibre reaches equilibrium with its surroundings effectively instantaneously. Thus the uptake of moisture depends on the vapour pressure and also on temperature; the uptake is greater the higher the vapour pressure but is decreased by a rise in temperature. In the experiment we have described, the uptake would have been more than 30 per cent. if the temperature had remained constant. Because the temperature rose to over 65° C., however, the uptake immediately acquired was much less than 30 per cent. A temporary equilibrium is reached, in which the uptake is in equilibrium with the external vapour pressure at the modified temperature produced by the heat evolved as the vapour is absorbed. King and Cassie [1] calculated this temporary equilibrium uptake to be $2\cdot 3$ per cent. and the temperature 80° C. Subsequently heat is lost and as cooling proceeds the uptake of moisture increases. The uptake curve observed by King and Cassie was thus essentially a cooling curve. The uptake and temperature curves calculated in this way agree well with the corresponding experimental curves.

This experiment in a vacuum may seem artificial, but it illustrates that the immediate reaction of a mass of fibres when presented with a new atmosphere is to modify that atmosphere to be in equilibrium with itself at the expense of only a slight change in its own moisture content.

13.3 Two possible equilibrium conditions

We consider now an example quoted by Cassie [2] having a more direct bearing on the problem in which we are interested. Suppose a sheet of wool fibres conditioned to 45 per cent. R.H. at 20° C., so that its moisture uptake is 10 per cent., is suddenly placed in a stream of air at 65 per cent. R.H. and the same temperature. The wool and air can come to equilibrium in two very different ways:

- 1. By an increase in the uptake of the wool until it is in equilibrium with 65 per cent. R.H. The regain needed is 14 per cent.; or
- 2. By an increase in the temperature of the wool and air till the new vapour pressure represents only 45 per cent. R.H., the uptake of the wool remaining essentially unchanged at 10 per cent. It is easy to calculate from vapour pressure tables that this will be so if the temperature rises to 25° C.

Of these two possible equilibrium conditions the first, involving a considerable change in moisture uptake, can only be achieved after a large volume of air has passed through the wool. The second, involving a temperature rise, is easily attained almost immediately because of the large heat of sorption. Enough heat is produced by a relatively small increase in moisture uptake to raise the temperature of the wool to 26° C. $(\frac{1}{4} \text{ per cent. will do it if the heat capacity of the air is neglected}).$ For this reason the first equilibrium set up is the one in which the temperature rises but the regain is essentially unchanged. This is only a pseudoequilibrium, however, because if we continue to blow air at 20° C. over the wool the final temperature must be 20° C. and the final regain 14 per cent. Here we have the essential feature of the propagation of humidity and temperature changes in textiles or similar materials, namely the existence of two equilibrium states-a temporary one set up quickly and involving no change in uptake, and a permanent one set up relatively slowly and involving a change in moisture content.

13.4. Propagation of two disturbances

Clearly, therefore, when the air stream first passes through, a front, separating the original and pseudo-equilibrium conditions, moves through the textile with the speed of the air flow if we neglect the heat capacity of the textile. Thus a fast disturbance representing change of temperature and moisture in the air without change of regain, is followed by a much slower disturbance bringing a change of regain.

Furthermore, the same general behaviour is to be expected when the

transfer of heat and moisture occurs by diffusion rather than as a result of aerodynamic flow of air.

Mathematical equations describing the diffusion phenomena in detail have been set up and from them it is possible to calculate how concentration, temperature, and total moisture uptake vary with time and distance through the medium till final equilibrium is attained. Henry [3, 4] first gave the theory for diffusion of humid air into a textile package and Cassie [5] later gave the corresponding theory for air forced through the textile, neglecting diffusion effects entirely. Since then Daniels [6] has taken into account diffusion of heat and moisture in an air stream forced through the textile. We now give Henry's treatment of the diffusion problem.



FIG. 13.1. Element of textile package.

13.5. Equations for diffusion of heat and moisture

13.51. Equilibrium equation

Fig. 13.1 shows diagrammatically an element of a textile package occupied partly by fibres and partly by air spaces. This is much oversimplified but serves to fix ideas. We have said that a fibre can always be considered as in equilibrium with its immediate surroundings. We shall further assume linear dependence on both temperature and moisture content and write /12 11

$$M = \text{constant} + \sigma C - \omega T, \tag{13.1}$$

where C is the concentration of water vapour in the air spaces expressed in g./cm.³, M is the amount of moisture absorbed by unit mass of fibre, σ and ω are constants. We shall consider the equilibrium uptake of moisture by a fibre to be related to water vapour concentration and temperature T by the linear relation (13.1). This is a necessary assumption if the theory is to proceed; clearly in practice it is only an approximation which is reasonable over small ranges of humidity and temperature. 13.52. Vapour diffusion equation Consider an element of a textile package. We can derive two equations, one expressing the rate of change of concentration and the other the rate of change of temperature.

The rate of change of concentration is governed by

- (a) Diffusion of vapour through the air spaces and through the fibres, both these being proportional to the concentration gradient in the usual way. Diffusion through the pores will in many cases be greater than through the fibres, but even if this is not so we can represent both processes by one term if we make the assumption that the vapour in the fibre is always in equilibrium with that in the air in the immediate neighbourhood and the absorption isotherm is linear as in (13.1).
- (b) The absorption or desorption of moisture by the fibres from the air spaces.

Thus we can say,

Net amount of vapour entering element by diffusion

(13.2)= increase in moisture in air+increase in moisture in fibres.

If a fraction v of the total volume of the package is occupied by air and 1-v by fibre of density ρ_s then, expressing (13.2) mathematically, the equation governing the movement of vapour can be written

$$vg D_{A} \frac{\partial^{2} C}{\partial x^{2}} = v \frac{\partial C}{\partial t} + (1 - v) \rho_{s} \frac{\partial M}{\partial t}, \qquad (13.3)$$

where C and M have been defined and D_A is the diffusion coefficient for moisture in air. The factor, g, allows for the fact that the diffusion is not along straight air channels but through a matrix of intertwined fibres and any diffusion along the fibres themselves can also be allowed for in this factor. It is a factor which can be measured by permeability measurements under steady-state conditions.

13.53. Heat diffusion equation

The rate at which the temperature of the element changes is determined by

(a) Conduction of heat through air and fibres.

- (b) The heat evolved when moisture is absorbed by fibres.

Thus

Increase in heat content of fibres = net amount of heat entering by conduction+heat evolved (13.4)as fibres absorb moisture,

and this is expressed mathematically by the equation

$$\alpha \rho \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial x^2} + q \rho \frac{\partial M}{\partial t}, \qquad (13.5)$$

where α is the specific heat of the fibres, K the overall heat conductivity of the package, ρ the density of the package, expressed as mass of fibre per unit overall volume, and q is the heat evolved when 1 g. of water vapour is absorbed by the fibres. In writing (13.5) the reasonable assumption has been made that the heat content of the air is negligible compared with that of the fibres.

One vital point to be noticed is that both (13.3) and (13.5), that is the vapour equation and the temperature equation, involve M, the amount of moisture in the fibres. It is at once obvious that the two processes, the transfer of moisture and the transfer of heat, are coupled together in this way and that we cannot in general consider one process without considering the other simultaneously.

13.54. Assumptions underlying the mathematical theory

It is worth while to enumerate some of the assumptions on which the theoretical treatment is based. The main ones are:

- (a) The linear dependence of M on C and T to which reference has already been made.
- (b) The quantities D_A , K, α , ρ are assumed constant and independent of moisture concentration and temperature.
- (c) The heat of sorption q is assumed independent of regain though in practice it is not so.
- (d) Hysteresis of sorption is neglected, that is the equilibrium equation
 (13.1) is assumed to hold whether the fibre is gaining or losing moisture.
- (e) The relative volumes occupied by fibre and air are assumed not to change as diffusion proceeds, i.e. v is assumed constant. In actual fact, as the fibres sorb moisture they swell and occupy progressively more space, and the air correspondingly less. This is thought to be unimportant except for very dense packages.
 (f) No account has been taken of the influence of capillarity in the air spaces. This will be appreciable only at very high humidities or in water.

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(g) The fibres have been assumed to reach equilibrium with their immediate surroundings instantaneously. There is some evidence that relatively slow changes of fibre structure may occur as the moisture is taken up, and that while most of the uptake is effectively instantaneous there may be a slow drift of moisture content persisting for some time. The information on this at the moment is too sparse for it to be taken into account even if the mathematics permitted.

13.6. Solution of the equations

Using Henry's nomenclature the equations to be solved can be written

$$D''\frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial t} = \gamma \frac{\partial M}{\partial t}, \qquad (13.6)$$

$$\mathscr{D}''\frac{\partial^2 T}{\partial x^2} - \frac{\partial T}{\partial t} = -\epsilon \frac{\partial M}{\partial t}, \qquad (13.7)$$

$$\partial M/\partial C = \sigma; \quad \partial M/\partial T = \omega,$$
 (13.8)

where

$$D'' = g D_A;$$
 $\mathscr{D}'' = K/(\alpha \rho);$ $\gamma = (1-v)/(v \rho_B);$ $\epsilon = q/\alpha.$ (13.9)

Eliminating M, we get

$$D''\frac{\partial^2 C}{\partial x^2} - (1 + \gamma \sigma)\frac{\partial C}{\partial t} + \gamma \omega \frac{\partial T}{\partial t} = 0, \qquad (13.10)$$

$$\mathscr{D}''\frac{\partial^2 T}{\partial x^2} - (1 + \epsilon \omega)\frac{\partial T}{\partial t} + \epsilon \sigma \frac{\partial C}{\partial t} = 0, \qquad (13.11)$$

which can be written more simply in the forms

$$D\frac{\partial^2 C}{\partial x^2} - \frac{\partial}{\partial t}(C - \lambda t) = 0, \qquad (13.12)$$

$$\mathscr{D}\frac{\partial^2 T}{\partial x^2} - \frac{\partial}{\partial t}(T - \nu C) = 0, \qquad (13.13)$$

where the significance of D, \mathcal{D} , λ , and ν is immediately obvious. These equations are now in a form analogous in some respects to those representing two coupled vibrations, and they may be treated in the usual manner, provided λ and ν are assumed constant, by the introduction of 'normal coordinates', which are linear combinations of C and T, of the form rC + sT. With proper choice of the ratio r/s, the equations (13.12) and (13.13), expressed in terms of the new coordinates, give rise to two simple diffusion equations, each containing only one of the normal coordinates. The quantities represented by the latter consequently diffuse according to the usual law, and independently of each other, just as the normal modes of vibration of coupled mechanical systems, once started, continue without mutual interference. In order to find the normal coordinates, we multiply (13.12) by r/D and (13.13) by s/\mathcal{D} , and add, obtaining

$$\frac{\partial^2}{\partial x^2}(rC+sT) - \frac{\partial}{\partial t} \left\{ \left(\frac{r}{D} - \frac{s\nu}{\mathscr{D}} \right) C + \left(\frac{s}{\mathscr{D}} - \frac{r\lambda}{D} \right) T \right\} = 0.$$
(13.14)

If this is to be expressible as a simple diffusion equation for rC + sT we must have rID_sul@ ol (r) ID

$$\frac{r_{I}v - sv_{I}v}{r} = \frac{s_{I}v - r_{A}v}{s},$$

$$\frac{1}{D} - \frac{s}{r}\frac{v}{\mathscr{D}} = \frac{1}{\mathscr{D}} - \frac{r}{s}\frac{\lambda}{D} = \mu^{2} \text{ say.}$$
(13.15)

i.e.

This is a quadratic in r/s and gives the two values of r/s required to form the two normal coordinates. Also, μ^2 will have two values, corresponding to the roots of r/s. Equation (13.14) can now be written

$$\frac{\partial^2}{\partial x^2}(rC+sT) - \frac{\partial}{\partial t}\mu^2(rC+sT) = 0, \qquad (13.16)$$

which is a simple diffusion equation for rC + sT with diffusion coefficient $1/\mu^2$.

We can now determine the normal coordinates and their diffusion coefficients. Elimination of r/s between the equations (13,15) gives

$$\left(\mu^2 - \frac{1}{D}\right) \left(\mu^2 - \frac{1}{\mathscr{D}}\right) = \frac{\lambda\nu}{D\mathscr{D}},\qquad(13.17)$$

the roots of which are

$$\mu^{2} = \frac{D + \mathscr{D} \pm \sqrt{\{(\mathscr{D} - D)^{2} + 4\lambda\nu D\mathscr{D}\}}}{2D\mathscr{D}}.$$
 (13.18)

13.61. Diffusion rates

If we write $1/\mu_1^2 = D_1$ and $1/\mu_2^2 = D_2$ in order to preserve the representation of a diffusion coefficient by the letter D, and if we put $D/\mathscr{D}=u$, then we have from (13.18)

$$\frac{D_1}{D} = \frac{2}{u+1+\sqrt{\{(1-u)^2+4u\lambda\nu\}}},$$
(13.19)

$$\frac{D_2}{D} = \frac{2}{u+1-\sqrt{\{(1-u)^2+4u\lambda\nu\}}}.$$
(13.20)

Fig. 13.2 shows a nomogram, reproduced from Henry's paper [4] for solving these equations. If a straight line be placed so as to cut the two straight scales at the appropriate values for u and λv , then the points at which it cuts the circular scale give D_1/D and D_2/D respectively. To

find D_1/\mathscr{D} and D_2/\mathscr{D} , 1/u must be used in place of u. Usually it is convenient to express D_1 in terms of D and D_2 in terms of \mathscr{D} .



FIG. 13.2. Nomogram for D_1/D and D_2/D in terms of u and λ_{ν} .

If $\lambda \nu$ is small compared with $(\mathcal{D}-D)^2/(4D\mathcal{D})$, i.e. if either the coupling between the two diffusion processes is weak or D and \mathcal{D} are of widely different magnitudes, the roots become

$$\mu_{1}^{2} = \frac{1}{D} + \frac{\lambda \nu}{\mathscr{D} - D} \bigg\}, \qquad (13.21)$$
$$\mu_{2}^{2} = \frac{1}{\mathscr{D}} - \frac{\lambda \nu}{\mathscr{D} - D} \bigg\},$$

approximately. Thus as the coupling becomes weaker μ_1^2 tends towards 1/D, and μ_2^2 tends towards $1/\mathcal{D}$, so that we may speak of $\pm \mu_1$ as the variance and $\pm \mu_2$ as the thermal roots, then show here coupling exists

vapour roots, and $\pm \mu_2$ as the thermal roots, though when coupling exists all roots are concerned with both diffusion processes to a greater or lesser extent.

13.62. Expressions for concentration and temperature changes Proceeding from (13.17) or (13.18) we see that $\mu_1^2 + \mu_2^2 = 1/D + 1/\mathscr{D},$

that is $\mathscr{D}(1-\mu_1^2 D) = -D(1-\mu_2^2 \mathcal{D}).$ (13.22)

Using (13.15) and (13.22) we find that

$$\frac{s_1}{r_1} = \frac{1 - \mu_1^2 D}{\nu} \frac{\mathscr{D}}{D} = -\frac{1 - \mu_2^2 \mathscr{D}}{\nu} \\ \frac{r_2}{s_2} = \frac{1 - \mu_2^2 \mathscr{D}}{\lambda} \frac{D}{\mathscr{D}} = -\frac{1 - \mu_1^2 D}{\lambda} \\ \end{cases}.$$
(13.23)

Hence if we choose r_1 and s_2 to be equal to unity, the normal coordinates are determined, and the solution of the differential equations (13.6), (13.7), (13.8) can be written

$$\Delta C - \frac{1 - \mu_2^2 \mathscr{D}}{\nu} \Delta T = \psi_1(x, y, z, t), \qquad (13.24)$$

$$\Delta T = \frac{1 - \mu_1^2 D}{\lambda} \Delta C = \psi_2(x, y, z, t), \qquad (13.25)$$

where ΔC and ΔT are the deviations of C and T from some given values (e.g. the initial), and the ψ 's are solutions of ordinary diffusion equations with diffusion coefficients equal to $1/\mu_1^2$ and $1/\mu_2^2$ respectively, and subject to appropriate boundary and initial conditions. Solving for C and Twe get

$$\Delta C = \phi_1(x, y, z, t) + \frac{1 - \mu_2^2 \mathscr{D}}{\nu} \phi_2(x, y, z, t), \qquad (13.26)$$

$$\Delta T = \phi_2(x, y, z, t) + \frac{1 - \mu_1^2 D}{\lambda} \phi_1(x, y, z, t), \qquad (13.27)$$

where

$$\phi_1(x, y, z, t) = \frac{1 - \mu_2^2 D}{D(\mu_1^2 - \mu_2^2)} \psi_1(x, y, z, t), \qquad (13.28)$$

$$\phi_2(x, y, z, t) = \frac{1 - \mu_1^2 \mathscr{D}}{\mathscr{D}(\mu_2^2 - \mu_1^2)} \psi_2(x, y, z, t).$$
(13.29)

The ϕ 's, being proportional to the ψ 's, are also solutions of the ordinary diffusion equation with diffusion coefficients equal to $1/\mu_1^2$ and $1/\mu_2^2$ respectively, and with boundary and initial conditions which give the required conditions for C and T.

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The physical interpretation of these equations derived by Henry is that each diffusion 'wave' of vapour is accompanied by a temperature 'wave' proceeding at the same rate, whose magnitude is proportional to that of the vapour diffusion wave, the relation between the two depending only upon the properties of the materials. Similarly, the main temperature 'wave' is accompanied by a subsidiary vapour diffusion wave. Even if only one of the external conditions, say the vapour concentration, alters, there will nevertheless be the complete

set of two vapour 'waves' and two temperature 'waves', though the latter may be small if the coupling is weak.

Henry points out that similar reasoning to that just given still holds if equations (13.12) and (13.13) have on their right-hand sides, instead of zero, any functions of the independent variables x, y, z, and t. Such equations would correspond to the case where either the diffusing substance or heat, or both, are being set free or absorbed in a manner additional to and independent of the diffusion processes, and independent of C and T. There might, for example, be a chemical reaction causing both the diffusing substance and heat to be evolved throughout the medium. In such cases the solution to the problem of the simultaneous transfer of heat and vapour reduces to the sum of solutions for the ordinary diffusion of the 'normal coordinates' with appropriate rates of evolution throughout the medium of the quantities they represent.

13.63. Solutions for sudden changes of external conditions

The above equations enable the solution of the coupled diffusion problem to be obtained in terms of the solution for the ordinary diffusion problem with the same boundary conditions. Suppose a specimen of any shape is in equilibrium with its surroundings and that at time t = 0the concentration C and temperature T of the diffusing substance are suddenly altered to $C+\Delta_0 C$ and $T+\Delta_0 T$ respectively at the boundary, and maintained constant. Let the solution to the *simple* diffusion problem, assuming diffusion constants $D_1 = 1/\mu_1^2$ and $D_2 = 1/\mu_2^2$, be

$$\Delta C = \Delta_0 C f_1(x, y, z, t), \qquad (13.30)$$

$$\Delta T = \Delta_0 T f_2(x, y, z, t). \tag{13.31}$$

The specimen eventually reaches equilibrium with the new conditions so that f_1 and f_2 must increase from 0 to 1 as t increases from 0 to infinity. The form of these functions depends on the shape of the specimen and typical solutions have been given in earlier chapters for plane sheets, cylinders, and spheres, for example. Clearly f_1 and f_2 , multiplied by suitable constants depending upon the initial conditions at the boundary,

are the functions ϕ_1 and ϕ_2 in equations (13.26) and (13.27). Thus, remembering that the system must eventually come to equilibrium with $\Delta C = \Delta_0 C$ and $\Delta T = \Delta_0 T$, and that f_1 and f_2 are then both unity, we find

$$\Delta C = \frac{1}{D(\mu_1^2 - \mu_2^2)} \left[\{ (1 - \mu_2^2 D) \Delta_0 C - \lambda \Delta_0 T \} f_1 - \{ (1 - \mu_1^2 D) \Delta_0 C - \lambda \Delta_0 T \} f_2 \right],$$
(13.32)

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$$\Delta T = \frac{1}{\mathscr{D}(\mu_1^2 - \mu_2^2)} \left[\{ (1 - \mu_2^2 \mathscr{D}) \Delta_0 T - \nu \Delta_0 C \} f_1 - \{ (1 - \mu_1^2 \mathscr{D}) \Delta_0 T - \nu \Delta_0 C \} f_2 \right].$$
(13.33)

An alternative form of these equations, put forward by Henry [3] is

$$\Delta C = \Delta_0 C f_1 - \frac{(1 - \mu_1^2 D) \Delta_0 C - \lambda \Delta_0 T}{D(\mu_1^2 - \mu_2^2)} (f_2 - f_1), \qquad (13.34)$$

$$\Delta T = \Delta_0 T f_2 - \frac{(1 - \mu_2^2 \mathscr{D}) \Delta_0 T - \nu \Delta_0 C}{\mathscr{D}(\mu_1^2 - \mu_2^2)} (f_2 - f_1).$$
(13.35)

The first term on the right-hand side of each equation represents the 'wave' which would result if there were no coupling between the diffusion processes and which may be referred to as the 'permanent wave'. The second term represents the result of the coupling and may be called the 'temporary wave' since it starts at zero, increases to a maximum, and then diminishes to zero again.

In many cases it is required to know the rate at which M, the amount of diffusing substance absorbed, varies. To determine this we substitute

$$\Delta M = \sigma \Delta C - \omega \Delta T \tag{13.36}$$

in (13.34) and (13.35), and after some rearrangement we obtain

$$\Delta M = \Delta_0 M f_1 + \left\{ \left(\mu_1^2 - \frac{1}{D} - \frac{\epsilon \omega}{\mathscr{D}''} \right) \Delta_0 M + \left(\frac{1}{\mathscr{D}''} - \frac{1}{D''} \right) \omega \Delta_0 T \right\} \left(\frac{f_2 - f_1}{\mu_1^2 - \mu_2^2} \right),$$
(13.37)

where from (13.10) and (13.12)

$$D'' = D(1 + \gamma \sigma), \qquad (13.38)$$

and from (13.11) and (13.13)

$$\mathscr{D}'' = \mathscr{D}(1 + \epsilon \omega).$$
 (13.39)

If it is desired to include both the amount absorbed and the amount in the pores, and M' is the total amount of diffusing substance contained in unit mass of solid, then from (13.36) and the definition of γ in (13.9) we obtain **۱** ۱

$$\Delta M' = \left(1 + \frac{1}{\gamma \sigma}\right) \Delta M + \frac{1}{\gamma \sigma} \Delta T, \qquad (13.40)$$

which may be evaluated using (13.35) and (13.37). If $\gamma\sigma$ is large, i.e. if much more diffusing substance is absorbed by the solid than is contained in the pores, M' is nearly equal to M and (13.40) is not needed. Henry points out that this is so for baled cotton, for example, for which $\gamma\sigma$ may be as much as 7,000. In this case also, since the terms in the expression $(\mu_1^2 - 1/D - \epsilon \omega / \mathscr{D}'')$ occurring in (13.37) nearly cancel if $\epsilon \omega$ is



fairly large compared with unity, e.g. for cotton it is about 10 or 30, (13.37) may be written approximately

$$\Delta M = \Delta_0 M f_1 + \left\{ -\frac{u^2}{(1+u^2)(1+\epsilon\omega)+u} \Delta_0 M + \frac{1/\mathscr{D}'' - 1/D''}{\mu_1^2 - \mu_2^2} \omega \Delta_0 T \right\} (f_2 - f_1), \quad (13.41)$$

where u is written for D/\mathscr{D} . Here $\omega \Delta_0 T$ is the total change in the equilibrium value of M which would be produced by the change in temperature $\Delta_0 T$, if C remained constant. Henry [3] has given numerical values of the various constants involved in the above equations for the case of baled cotton at densities 0.2, 0.4, 0.6 g./c.c. and has written (13.40) in numerical form for each density.

13.64. Change in external humidity only

Henry [4] has explored further the case in which no change is made in the external temperature, only the external humidity being changed. Then we can put $\Delta_0 T = 0$ in equation (13.32) and by substituting $1/D_1$ and $1/D_2$ for μ_1^2 and μ_2^2 respectively and then rearranging we obtain for the ratio of the change in C at any instant to the equilibrium value of the change, $\Delta C = D_1(D_2 - D)f_1 - D_2(D_2 - D)f_2$

$$\frac{\Delta C}{\Delta_0 C} = \frac{D_1 (D_2 - D) f_1 - D_2 (D_1 - D) f_2}{D(D_2 - D_1)}.$$
(13.42)

This can be written very simply as

$$\Delta C/\Delta_0 C = (1-p)f_1 + pf_2, \qquad (13.43)$$

where

$$p = \frac{D_2(D - D_1)}{D(D_2 - D_1)}.$$
(13.44)

Thus p is a dimensionless quantity that can be expressed in terms of the ratios D_1/D and D_2/D . We have already seen in equations (13.19) and (13.20) that these ratios can be calculated directly from $u = D/\mathcal{D}$ and λv , and so p can also be obtained from u and λv . The necessary relationship is

$$(u - 1)^2$$

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$$(2p-1)^2 = \frac{(u-1)^2}{(u-1)^2 + 4u\nu\lambda}.$$
 (13.45)

Henry's nomogram [4] for calculating p in terms of u and λv is reproduced in Fig. 13.3. Since the right-hand side of (13.45) is unaltered if 1/u is substituted for u, the scale for u from 1 to ∞ enables all possible values of u to be dealt with. It also follows from this symmetry that the same numerical value for p can be used to handle the problem in which the external temperature is changed instead of the humidity.



FIG. 13.3. Nomogram for p in terms of u and λv .



FIG. 13.4. Nomogram for n in terms of u and λv or $1/(1 + \epsilon \omega)$.

DIFFUSION OF HEAT AND MOISTURE

Putting $\Delta_0 T = 0$ in (13.41), we get

$$\frac{\Delta M}{\Delta_0 M} = f_1 - \frac{u^2 (f_2 - f_1)}{(1 + u)^2 (1 + \epsilon \omega) + u} = (1 + n) f_1 - n f_2, \qquad (13.46)$$

where

$$n = \frac{u^2}{(1+u)^2(1+\epsilon\omega)+u}.$$
 (13.47)

Henry's nomogram for calculating n in terms of u and $1/(1+\epsilon\omega)$ is reproduced in Fig. 13.4. Under the conditions for which (13.41) and (13.46) apply we have

$$1 + \epsilon \omega = 1/(1 - \lambda \nu), \qquad (13.48)$$

approximately.

Henry has given a table of values of p and n and also of the diffusion coefficients D, \mathcal{D} , D_1 , D_2 for cotton packages of two densities and three relative humidities and temperatures. For the experimental data on which his calculations are based his original paper [4] should be consulted. The two densities are 0.2 and 0.5 g./cm.³ at temperatures 20° , 50° , and 80° C., and the relative humidities are 20, 65, and 90 per cent. The results are shown in Table 13.1 reproduced from Henry's paper [4], the significance of the figures being clear from the labelled cells. Figures for 80° C. and 90 per cent. R.H. are omitted because under these conditions the vapour pressure would be a considerable fraction of atmospheric pressure and fluid flow would make an appreciable contribution to the process. From this table and equations (13.43), (13.46), it is a simple matter to calculate how concentration and total moisture content vary for a package of known size and shape. When dealing with total moisture content, f_1 and f_2 are, of course, functions only of time. As an example, suppose the package is in the form of a large flat sheet then we have (§ 4.32)

$$f_1 = 1 - \frac{8}{\pi^2} (e^{-m} + \frac{1}{9}e^{-9m} + \frac{1}{25}e^{-25m} + \dots), \qquad (13.49)$$

where $m = \pi^2 D_1 t/l^2$, *l* being the thickness of the sheet. The function f_2 is the same with D_1 replaced by D_2 .

The following points about the solutions are of particular interest. (i) In Table 13.1 it is seen that, as the temperature rises, the moisture diffusion coefficient D, which is at first much smaller than the thermal diffusion coefficient \mathcal{D} , eventually becomes much larger. Furthermore, the diffusion coefficient D_1 for the slower normal function is always less than either D or \mathcal{D} but never by a factor of less than $\frac{1}{2}$. On the other hand, D_2 is always much greater than D or \mathcal{D} . The figures for n show that the secondary wave is of very small amplitude, as judged by the total moisture content, at low temperatures, but becomes appreciable at high temperatures. The figures for p show that in the case of an external thermal disturbance only, the secondary wave may be important even at room temperatures.

(ii) Since both f_1 and f_2 always change from 0 to 1 we see from (13.35) that the change in temperature associated with an external change of humidity only ($\Delta_0 T = 0$) is a transient one, which increases from zero to a maximum and disappears again. This transient temperature has been observed by Cassie and Baxter [7].

(iii) If the initial disturbance is one of temperature only there is a corresponding transient change in moisture content.

(iv) The effect of size or shape is all included in the function f and so conversion from one package to another is relatively simple. In particular t and l always appear as t/l^2 in (13.49), for example, and we have the usual dependence of the time scale on the square of the linear dimensions, familiar in simple diffusion problems.

(v) For comparisons of calculated and experimental values the papers of Cassie and Baxter [7] and of Daniels [6] should be consulted. The former describes a pure diffusion experiment, the latter a flow-underpressure experiment with diffusion as a complicating feature. It is not to be expected that the theoretical treatment of a subject as complicated as this can reproduce all the features accurately and quantitatively. Its value lies in clarifying the mechanism by which heat and moisture are transferred, in making possible rough estimates of time scales under given conditions, and in particular, showing how the times for a given package can be estimated from measurements on a standard package.

13.7. Surface temperature changes accompanying the sorption of vapours

A much simpler problem but one of practical interest is to calculate the temperature change which accompanies the sorption of vapour by a solid, in cases where the temperature rises due to the heat of con-

densation given up at the surface of the solid and the heat of mixing can be neglected.

We consider a plane sheet suspended in a vapour maintained at constant pressure. The sheet is taken to be so thin that effectively all the vapour enters through the plane faces and a negligible amount through the edges. Uptake of vapour therefore occurs by uni-directional diffusion through the sheet and the amount taken up is assumed proportional to the square root of time. The heat of mixing is taken to be a negligible



fraction of the heat of sorption which thus becomes simply the heat of vaporization. This assumption carries the implication that during sorption heat is evolved only at the two surfaces of the sheet. Values of heat conductivity, specific heat, and density of the sheet are taken to be constant, independent of temperature and vapour content. The calculated results are based in the first place on the assumption that heat is lost from the surfaces by radiation only, according to Stefan's law. For small temperature differences, however, both radiation and convection losses proceed at rates directly proportional to the temperature difference between the surface and its surroundings, and so convection losses can be allowed for by adjusting the radiation constant.

13.71. Mathematical equations

Taking θ to be the temperature difference between an element of the sheet and the vapour in which the sheet is suspended, θ_0 the temperature of this vapour assumed constant, x the space coordinate perpendicular to the surface of the sheet (the surfaces being at x = 0 and x = l), and t the time during which uptake of vapour has occurred, the equation governing the conduction of heat through the sheet is

$$\frac{\partial\theta}{\partial t} = \frac{K}{\rho\alpha} \frac{\partial^2\theta}{\partial x^2}.$$
(13.50)

Here K is heat conductivity, ρ density, and α specific heat of the substance of the sheet, all expressed in e.g.s. units. At each surface heat is continuously evolved, as vapour is taken up, at a rate given by $\frac{1}{2}\rho lL dR/dt$, where R is the regain at time t, i.e. mass of vapour taken up per unit initial mass of sheet, and L the heat of vaporization. Some of this heat is lost by radiation from the surface at a rate which for small temperature differences is given by $k\theta$, where $k = 4\sigma_0 \theta_0^3$ and σ_0 is Stefan's constant. The remainder of the heat enters the sheet by conduction at a rate given by $-K \partial \theta / \partial x$. The equation expressing conservation of heat at the surface x = 0 is therefore

$$\frac{1}{2}\rho lL\frac{dR}{dt} - k\theta + K\frac{\partial\theta}{\partial x} = 0, \qquad x = 0.$$
(13.51)

There is a corresponding condition for the surface x = l, but for purposes of calculation it is preferable to consider only half the sheet and to use the condition $\partial \theta / \partial x = 0$, $x = \frac{1}{2}l$, (13.52)

because the uptake of vapour and the heat flow are symmetrical about the central plane of the sheet. We need therefore to evaluate solutions of (13.50) with the boundary conditions (13.51) and (13.52) and the initial condition

$$\theta = 0, \quad 0 < x < \frac{1}{2}l, \quad t = 0.$$
 (13.53)

We consider the regain, R, at time t to be given by

$$R = B(t/l^2)^{\frac{1}{2}}, \qquad (13.54)$$

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where B is a constant for a given experiment. It follows from equation (4.20), for example, that

$$B = 4C_0(D/\pi)^{\frac{1}{2}},\tag{13.55}$$

where C_0 is the equilibrium regain attained theoretically after infinite time, and D an average diffusion coefficient for the concentration range 0 to C_0 of vapour. The constant B is thus dependent on the experiment considered, i.e. on the system, the temperature and the vapour pressure, but is independent of the thickness of the sheet.

On introducing the non-dimensional variables

$$\phi = \left(\frac{K\alpha}{\rho}\right)^{\frac{1}{2}} \frac{\theta}{BL}, \quad \tau = \frac{Kt}{\rho\alpha l^{\frac{3}{2}}}, \quad X = \frac{x}{\overline{l}}, \quad (13.56)$$

and substituting for R in (13.51) from (13.54), equations (13.50), (13.51), (13.52), (13.53) become $\partial \phi = \partial^2 \phi$

$$\frac{\partial \phi}{\partial r} = \frac{\partial^2 \phi}{\partial X^2},\tag{13.57}$$

$$\frac{1}{4\tau^{\frac{1}{2}}} - \frac{kl}{K}\phi + \frac{\partial\phi}{\partial X} = 0, \qquad X = 0, \qquad \tau > 0, \qquad (13.58)$$

$$\partial \phi / \partial X = 0, \qquad X = \frac{1}{2}, \qquad \tau > 0,$$
 (13.59)

$$\phi = 0, \quad 0 < X < 1, \quad \tau = 0.$$
 (13.60)

When expressed in terms of the new variables ϕ , X, and τ , the problem therefore contains only a single non-dimensional parameter kl/K, which we denote for convenience by h. A number of solutions of equation (13.57) satisfying (13.58), (13.59), (13.60) have been evaluated for different values of h, using the step-by-step method of integration described in § 10.5. The calculated surface temperatures are shown graphically in Fig. 13.5, and together with the two special cases for $K = \infty$ and K = 0 they constitute the solution of this problem for all values of the physical properties involved. For convenience of scale in Fig. 13.5, $(kl\alpha/\rho)^{\dagger}(\theta/BL)$ is plotted against $(kt/l\rho\alpha)^{\dagger}$. These variables are respectively $h^{\dagger}\phi$ and $(h\tau)^{\dagger}$ and hence are readily deduced from ϕ and τ for a given h.

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13.72. Special cases of zero and infinite conductivity

While the case of zero heat conductivity may be of little practical significance it is nevertheless a useful limiting solution from the mathematical point of view. When K = 0, no heat penetrates the sheet and we are concerned only with equation (13.51) which becomes

$$\frac{1}{2}\rho Ll\,dR/dt = k\theta. \tag{13.61}$$

For the particular case of R given by (13.54), integration of (13.61) leads immediately to Bl_{0}

$$\theta = \frac{Bl\rho}{4kt^{\frac{1}{4}}}.\tag{13.62}$$

When K is infinite the temperature is always uniform throughout the sheet and some of the heat evolved at the surface is lost by radiation while the rest raises the temperature of the whole sheet. This is expressed by the equation $\frac{dR}{dt} = \frac{d\theta}{dt}$ (12.62)

$$\frac{dH}{dt}\rho lL = 2k\theta + l\rho\alpha \frac{d\theta}{dt}, \qquad (13.63)$$

which becomes

$$\frac{d\theta}{dt} + \frac{2k}{l\rho\alpha}\theta - \frac{BL}{2l\alpha t^{\frac{1}{2}}} = 0 \qquad (13.64)$$

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on substituting for R from (13.54). The solution of (13.64) is

$$\theta = \frac{BL}{l\alpha} \exp\left(-\frac{2kt}{l\rho\alpha}\right) \int_{0}^{t} \frac{1}{t_{1}^{4}} \exp\left(\frac{2kt_{1}}{l\rho\alpha}\right) dt_{1}.$$
 (13.65)

When expressed in terms of the variables $h^{\dagger}\phi$ and $h\tau$ used in Fig. 13.5, equation (13.65) becomes

$$h^{\frac{1}{2}}\phi = e^{-2h\tau} \int_{0}^{t} e^{2h\tau_{1}} d(h^{\frac{1}{2}}\tau_{1}^{\frac{1}{2}}).$$
 (13.66)

Tabulated values of the right-hand side of (13.66) are available [8] for values of $(h\tau)^{\frac{1}{2}}$ in the range $0 < 2h\tau < 100$. The solution (13.66) is shown as the curve marked $K = \infty$ in Fig. 13.5.

13.73. Calculated results. General solution in non-dimensional variables

In Fig. 13.5, $h^{\dagger}\phi$ is plotted against $(h\tau)^{\dagger}$ for different values of h = kl/K. Since both variables and the parameter h are non-dimensional, the variation of surface temperature with time can be deduced from this figure for any system (subject to the basic assumptions) by inserting appropriate values of the physical constants involved.

The following general points are of interest.

(a) For any finite conductivity the surface temperature rises discontinuously at t = 0 to some finite value and immediately afterwards begins to fall.

(b) For the smaller values of h, i.e. larger conductivities, the surface temperature passes first through a minimum and later through a maximum before falling eventually to the temperature of the surroundings. The initial fall in temperature occurs while the sheet is behaving semi-infinitely with respect to heat flow. The temperature rises when an appreciable amount of the heat entering the sheet through its second surface reaches the surface under consideration. The later maximum in surface temperature occurs when heat is removed from the surface by conduction and radiation (and possibly convection) as quickly as it is given up by the vapour entering the sheet. It is to be remembered that the rate of uptake of vapour and hence the rate of supply of heat to the surface steadily decreases, being proportional to $1/\sqrt{t}$.

It is to be expected that the smaller the heat conductivity of the sheet the longer the time that elapses before the heat from one surface reaches the other and hence the later the minimum temperature occurs.
(c) For h > 1 no minimum or maximum temperatures occur but the surface temperature falls continuously for t > 0, so that theoretically the highest temperature is achieved instantaneously at zero time.

(d) When the conductivity is infinite, the surface temperature rises dcontinuously from that of the surroundings up to a maximum and then falls. For zero conductivity the surface temperature is theoretically infinite at t = 0 and then falls steadily.

(e) To within the accuracy of plotting, the maximum temperature can be deduced from the curve for $K = \infty$ even if the conductivity is finite, provided kl/K < 0.2 approximately.

(f) For a given sheet the temperature change in degrees is proportional to the heat of vaporization, L, and also to the constant B. We have seen in equations (13.54) and (13.55) that B is the gradient of the linear plot of regain against $(t/l^2)^{\frac{1}{2}}$, and is also proportional to the product of the equilibrium regain and the square root of an average diffusion coefficient.

The following are two examples of the use of the general solution. \rightarrow

(i) Effect of thickness

As an example of the use of the curves of Fig. 13.5 we have calculated the way in which the temperature at the surface of a polymer sheet varies with time as it takes up vapour, and how this depends on thickness. The following values are taken as representative of a variety of polymers and vapours:

$$ho = 1.0, \qquad lpha = 0.35, \qquad L = 100, \qquad k = 1.6 \times 10^{-4},$$

 $K = 4.5 \times 10^{-4},$

all in e.g.s. units. The value of k comes from Stefan's constant and relates to an ambient temperature of 35° C. The value $B = 7 \cdot 10 \times 10^{-5}$ has been used. It corresponds to a system in which the equilibrium regain is 5 per cent. and the average diffusion coefficient is

$$4 \times 10^{-7}$$
 cm.²/sec.

Temperature-time curves are plotted in Fig. 13.6 for a number of thicknesses. For a sheet 0.07 cm, thick the maximum temperature change is approximately 1.4° C. at about 65 seconds. The maximum temperature is lower and occurs later, the thicker the sheet, but for a sheet as thick as 5.66 cm. the highest temperature is 0.25° C. attained at t = 0. We note incidentally that in theory for all thicknesses the surface temperature changes instantaneously by 0.25° C. at the beginning of sorption. As we have already mentioned, corresponding curves for



FIG. 13.6. Variation of surface temperature with time, shown as excess over 35° C. Numbers on curves are sheet thicknesses in cm.

lpha = 0.35, L = 100, $\rho = 1,$ $B = 7.1 \times 10^{-5},$ $k = 1.6 \times 10^{-4},$ $K = 4.5 \times 10^{-4}.$ All units are e.g.s.





other equilibrium regains in the same system can be deduced from those of Fig. 13.6 since θ is directly proportional to B and hence to C_0 .

(ii) Limiting rate of sorption for 1° C. rise in surface temperature

Dr. G. S. Park suggested that, from an experimental point of view, it is useful to know what is the fastest sorption or alternatively the greatest regain for which the rise in surface temperature does not exceed 1° C. Accordingly, in Fig. 13.7 are plotted curves which show how the limiting value of B for a 1° C. rise in temperature depends on the thickness of the sheet. The thicker the sheet the faster the sorption permissible.

The three curves of Fig. 13.7 are for different values of the emissivity constant k. The middle of the three corresponds to a surface loss purely by radiation when the temperature of the surroundings is 35° C. Changes in k may be due to differences in ambient temperature θ_0 since $k = 4\sigma_0 \theta_0^3$. Alternatively a higher value of k can correspond to some loss of heat by convection in the vapour, since both the convective term and the radiation term in the heat loss are directly proportional to temperature difference for small temperature excesses. Thus the curve on Fig. 13.7 for $k = 6.4 \times 10^{-4}$ could correspond to an experiment in which a stream of vapour is passed over the surfaces of the sheet.

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12 iterfe z	0-0313	0.0261	0.0217	0-0180	0.0149	0.0123	0.0101	0-0083	0-0068	0-0055	0.0015	0.0020	0.0000		4700-0	8700-0	0-0015	0-0012	0.0010	0-0008	0-0006	0-0015	0-0003	0-0002	0-001	0-0001																
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8 iterfo æ	0.25	0.2148	0.1841	0.1573	0.1341	0.1130	0.0965	0.0816	0.0887	0.0677	0.0484	FUTU-0	0.0336	0.0970		1020.0	0.0190	0.0158	0.0128	0-0104	0-0085	0-0069	0-0045	0.0029	0-0019	0-0011	0-0002	0.0004	0.0003	0.0002	0-001	0000					•					
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4 i ⁴ erfc z	1.0	0.8921	0-7936	0.7040	0.6227	0.5491	0.4828	0.4233	0.3699	0.3223	0.2799	0-9493	0-2090	0-1708	0.1541		0101.0	0.1120	0.0950	0.0808	0.0677	0.0568	0.0396	0-0272	0.0184	0.0122	0.0080	0.0052	0.0033	0.0021	0.0013	0-0008	0-0005	0.0003	0.0002	0-0001						
2 ierfe z	1.1284	1.0312	0-9396	0.8537	0.7732	0-6982	0-6284	0-5639	0.5043	0.4495	0-3993	0.9585	0-3110	6746.0	0.0400		JENZ-0	0.1823	0.1580	0.1364	0.1173	0.1005	0-0729	0.0521	0-0366	0.0253	0.0172	0-0115	0-0076	0.0049	0.0031	0.0020	0.0012	0.0007	0.0004	0.0002	1000-0	0.0001				
erfc <i>x</i>	1-0	0.043628	0-887537	0-832004	0-777297	0.723674	0-671373	0.620618	0.571608	0.524518	0.479500	0-436677	0.396144	0.357071	0.209100	0010000 0	0.200344	0-257899	0-229332	0-203092	0179109	0.157299	0-119795	0-089686	0.065932	0.047716	0-033895	0.023652	0.016210	0-010900	0.007210	0.004678	0.002979	0.001863	0-001143	0.000839	0.000407	0-000236	0-000134	0-000075	0-000041	0.000022
erfæ	0	0.056372	0.112463	0.167996	0.222703	0.276326	0.328627	0-379382	0.428392	0.475482	0-520500	0-563323	0-603856	0-842029	0.677201	100100-0		0.742101	0-770668	0-796908	0.820801	0.842701	0-880205	0.910314	0.934008	0.952285	0-966105	0-976348	0-983790	0-989091	0.992790	0-995322	0-997021	0-998137	0-998857	0.999311	0-999593	0-099764	0-999866	0.999925	0-9999559	0-999978
2-16-21	1-1284	1.1256	1-1172	1-1033	1-08+1	÷0800	1·0313	0-9983	0.9615	0.9215	0.8788	0.8338	0.7872	0-7395	0-6013	0.64.00	(7#0.)	0-23-20	0.5479	0.5020	0-1576	0-4161	0-3365	0-2673	0-2082	0.1589	0-1189	0-0872	0-0627	0-0442	0-0305	0-0207	0-0137	0-0080	0-0057	0-0036	0.0022	0-0013	0.0008	0.0004	0.0003	0-0001
4 7 -1 <i>26</i> -7	0	0.1126	6.22.0 1	0-3310	0-4336	0.5300	0.6188	0-6988	0.7692	0.8294	0.8788	0.9172	0-9447	0-9614	0-9878	0.000	4+0A.0	0.9520	0-9314	0-9035	0.8695	0-8302	0-7403	0-6416	0.5413	0.4450	0-3568	0.2791	0-2132	0.1591	0.1160	0.0827	0-0576	0-0393	0-0262	0-0171	6010-0	0-0068	0.0042	0-0025	0-0015	0-0008
er erfo x	0·Ľ	0.9460	0.8965	0.8509	0608-0	0.7703	0-7348	0.7015	0.6708	0-6423	0-6157	0.5909	0.5678	0.5462	0.6950	0.5060	5000.0	0.4891	0-4723	0-4565	0.4416	0.4276	0-4017	0-3785	0.3576	0.3387	0-3216	0.3060	0-2917	0.2786	0-2665	0.2554	0-2451	0-2356	0-2267	0-2185	0.2108	0-2036	0-1989	0.1905	0.1848	0-1290
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TABLE 2.1. Table of the error function and associated functions

TABLES

 $\operatorname{i}^{\operatorname{terfo}} x = \int_{x}^{\infty} \operatorname{ierfe} \xi \, d\xi = \frac{1}{4} \left\{ (1 + 2x^{*}) \operatorname{erfo} x - \frac{2}{x^{*}} x e^{-x^{*}} \right\} = \frac{1}{4} \left\{ \operatorname{erfo} x - 2x \operatorname{lerfo} x \right\}$ $2n \operatorname{i}^{\operatorname{terfo}} x = 2n \int_{x}^{\infty} 1^{n-1} \operatorname{erfc} \xi \, d\xi = \frac{1^{n-2} \operatorname{erfc} x - 2x}{n^{-2} \operatorname{erfc} x}$

lerfc $x = \int_{x}^{\infty} \operatorname{erfc} \xi \, d\xi = \frac{1}{\pi^4} e^{-x^4} - x \operatorname{erfc} x$

TABLE 2.2

Table of Laplace transforms

$$\bar{v}(p) = \int_{0}^{\infty} e^{-pt} v(t) \, dt$$

We write $q = \sqrt{(p/D)}$. D, x, and h are always positive. α is unrestricted.

	$ar{v}(p)$	v(t)
1.	$\frac{1}{p}$	I
2.	$\frac{1}{p^{\nu+1}}, \nu > -1$	$\frac{t^{\nu}}{\Gamma(\nu+1)}$
3.	$\frac{1}{p+\alpha}$	$e^{-\alpha t}$
4.	$rac{\omega}{p^3+\omega^3}$	$\sin \omega t$
5.	$\frac{p}{p^2+\omega^2}$	coswt
6.	e^{-qx}	$rac{x}{2\sqrt{(\pi Dt^3)}}e^{-x^2/4Dt}$.
7.	$\frac{e^{-qx}}{q}$	$\left(\frac{D}{\pi t}\right)^{\frac{1}{2}}e^{-x^2/4Dt}$
8.	$\frac{e^{-qx}}{p}$	$\operatorname{erfc} rac{x}{2\sqrt{Dt}}$
9.	$rac{e^{-qx}}{pq}$	$2\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}e^{-x^{2}/4Dt}-x\mathrm{erfc}\frac{x}{2\sqrt{Dt}}$
10.	$rac{e^{-qx}}{p^2}$	$\left(t+rac{x^2}{2D} ight)\mathrm{erfc}rac{x}{2\sqrt{(Dt)}}\!-\!x\!\left(rac{t}{\pi D} ight)^{rac{1}{2}}e^{-x^*/4Dt}$
11.	$rac{e^{-qx}}{p^{1+rac{1}{4}n}}, n=0,1,2,$	$(4t)^{\frac{1}{2}n} i^n ext{erfc} rac{x}{2\sqrt{(Dt)}}$
12.	$rac{e^{-qx}}{q+h}$	$\left(\frac{D}{\pi l}\right)^{\frac{1}{2}}e^{-x^{*}/4Dt} - hDe^{hx+Dth^{*}} \times $
		$\times \operatorname{erfc} \left\{ \frac{x}{2\sqrt{Dt}} + h\sqrt{Dt} \right\}$
13.	e^{-ax}	$De^{hx+Dth^{2}} \operatorname{erfe} \left\{ \frac{x}{2} + h\sqrt{Dt} \right\}$



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TABLE 2.2 (contd.)

		v(t)
16.	$\frac{e^{-qx}}{\overline{q^{n+1}(q+h)}}$	$\frac{D}{(-h)^n} e^{hx+D(h^*)} \operatorname{erfc} \left\{ \frac{x}{2\sqrt{(Dt)}} + h\sqrt{(Dt)} \right\} -$
		$-\frac{D}{(-h)^n}\sum_{r=0}^{n-1} \left[-2h\sqrt{(Dt)}\right]^r \operatorname{i}^r\operatorname{erfe}\frac{x}{2\sqrt{(Dt)}}$
17.	$\frac{e^{-ax}}{(q+h)^2}$	$\left -2h\left(\frac{D^3t}{\pi}\right)^{\frac{1}{2}}e^{-x^3/4Dt}+D(1+hx+2h^2Dt)\times\right $
		$\times e^{i\pi t D t t} \operatorname{erre}\left(\frac{1}{2\sqrt{Dt}}\right)^{+} h \sqrt{Dt}$
18.	$rac{e^{-qx}}{p(q+h)^2}$	$\left \frac{1}{h^2}\operatorname{erfc}\frac{x}{2\sqrt{(Dt)}}-\frac{2}{h}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}e^{-x^4/4Dt}-\right $
		$-\frac{1}{h^{\frac{1}{2}}}\{1-hx-2h^{2}Dt\}e^{hx+Dth^{2}}\times$
		$ imes \operatorname{erfc} \left\{ \frac{x}{2\sqrt{(Dt)}} + h\sqrt{(Dt)} \right\}$
19.	$\frac{e^{-qx}}{p-a}$	$\frac{1}{2}e^{\alpha t}\left\{e^{-x\sqrt{(\alpha/D)}}\operatorname{erfe}\left[\frac{x}{2\sqrt{(Dt)}}-\sqrt{(\alpha t)}\right]+\right\}$
		$+e^{x\sqrt{(\alpha/D)}} \operatorname{erfe}\left[\frac{x}{2\sqrt{(Dt)}}+\sqrt{(\alpha t)}\right]$
20.	$rac{1}{p^{rac{1}{4}}}e^{-qx}$	$\frac{1}{\pi} \left(\frac{x}{2tD^{\frac{1}{2}}} \right)^{\frac{1}{2}} e^{-x^2/8D^{\frac{1}{2}}} K_{\frac{1}{2}} \left(\frac{x^3}{8Dt} \right)$
21.	$\frac{1}{p^{\frac{1}{2}}}K_{2\nu}(qx)$	$\frac{1}{2\sqrt{(\pi t)}}e^{-x^2/6Dt}K_{\nu}\left(\frac{x^2}{8Dt}\right)$
22.	$egin{array}{llllllllllllllllllllllllllllllllllll$	$rac{1}{2t}e^{-(x^2+x'^2)/4Dt}I_ uigg(rac{xx'}{2Dt}igg), u\geqslant 0$
23.	$K_0(qx)$	$\frac{1}{2t}e^{-x^3/4Dt}$
24.	$rac{1}{p}e^{x/p}$	$I_0[2\sqrt{xt}]$
25.	$\frac{\exp\{xp - x[(p+a)(p+b)]^{\frac{1}{2}}\}}{[(p+a)(p+b)]^{\frac{1}{2}}}$	$e^{-\frac{1}{2}(a+b)(t+x)}I_0\{\frac{1}{2}(a-b)[t(t+2x)]^{\frac{1}{2}}\}$
2 6.	$p^{rac{1}{2} u-1}K_ u(x\sqrt{p})$	$x^{-\nu}2^{\nu-1}\int_{x^{2}/4i}e^{-u}u^{\nu-1}du$
07	$\Gamma_{m} = l(m^{2} - m^{2}) l^{\mu} = \nu > 0.$	$ u x^{ u} I_{ u}(xt)/t$.



ţ.

TABLE 4.1

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Fractional uptake 0 0·1 0·2 0·3 0·4 0·5 0·6 0·7 0·8 0·9	∝ 9.0000 4.0000 2.3333 1.5000 1.0000 0.6667 0.4286 0.2500 0.1111	$\begin{array}{r} q_1 \\ 1.5708 \\ 1.6385 \\ 1.7155 \\ 1.8040 \\ 1.9071 \\ 2.0288 \\ 2.1746 \\ 2.3521 \\ 2.5704 \\ 2.8363 \\ 2.1416 \end{array}$	9: 4.7124 4.7359 4.7648 4.8014 4.8490 4.9132 5.0037 5.1386 5.3540 5.7172 6.2832	q3 7.8540 7.8681 7.8681 7.9081 7.9378 7.9787 8.0385 8.1334 8.3029 8.6587 9.4248	q_4 10.9956 11.0057 11.0183 11.0344 11.0358 11.0856 11.1296 11.2010 11.3349 11.6532 12.5664	$\begin{array}{r} q_{\rm s} \\ 14\cdot 1372 \\ 14\cdot 1451 \\ 14\cdot 1549 \\ 14\cdot 1674 \\ 14\cdot 1841 \\ 14\cdot 2075 \\ 14\cdot 2421 \\ 14\cdot 2990 \\ 14\cdot 2990 \\ 14\cdot 4080 \\ 14\cdot 6870 \\ 15\cdot 7080 \end{array}$	q_{0} $17 \cdot 278$ $17 \cdot 285$ $17 \cdot 293$ $17 \cdot 303$ $17 \cdot 317$ $17 \cdot 336$ $17 \cdot 364$ $17 \cdot 412$ $17 \cdot 503$ $17 \cdot 74$ $18 \cdot 84$
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Roots of $\tan q_n = -\alpha q_n$

TABLE 4.2

Roots of $\beta \tan \beta = L$

						β.
		8.	β_3	β_4	<u>Ps</u>	P8
	P1	^M =		0 4949	19.5664	15.7080
	0	3.1416	6-2832	9.4248	10 5670	15.7086
0.01	0.0008	3.1448	6-2848	9-4258	12.0012	15.7142
0.01	0.0330	9.173]	8-2991	9.4354	12.5743	10-1149
0.1	0.3111	9.1101	A.9148	9 4459	12-5823	15.7207
0.2	0.4328	3-2039	0.0140	0.4775	12.6060	15.7397
0.5	0.6533	3-2923	0.3010	0 5002	12-6453	15.7713
1.0	0.8603	3-4256	6.4373	9.5285	10.7993	15-8336
10	1.0789	3.6436	6.5783	9.6290	12.1220	18.0107
2.0	1.0100	4.0336	6-9096	9.8928	12.9352	10.0101
$5 \cdot 0$	1.3130	4.0000	7.9281	10-2003	13.2142	16.2094
10-0	1.4289	4-3000	7 2201	10.8871	13.9981	17.1093
100-0	1.5552	4.6658	7.7704	10.0056	14.1372	17.2788
100 V	1.5708	4.7124	7.8540	10.9990	111000	<u> </u>
~		1	l			

TABLE 5.1

Roots of $\alpha q_n J_0(q_n) + 2J_1(q_n) = 0$

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{r} \underline{q_2} \\ 5.5201 \\ 5.5599 \\ 5.6083 \\ 5.6682 \\ 5.7438 \\ 5.8411 \\ 5.9692 \\ 6.1407 \\ 6.3710 \\ 6.6694 \\ 7.0156 \end{array}$	q_3 8.6537 8.6793 8.7109 8.7508 8.8028 8.8028 8.8727 8.9709 9.1156 9.3397 9.6907 10.1735	$\begin{array}{r} q_4 \\ 11 \cdot 7915 \\ 11 \cdot 8103 \\ 11 \cdot 8337 \\ 11 \cdot 8634 \\ 11 \cdot 9026 \\ 11 \cdot 9561 \\ 12 \cdot 0334 \\ 12 \cdot 1529 \\ 12 \cdot 3543 \\ 12 \cdot 7210 \\ 13 \cdot 3237 \end{array}$	$\begin{array}{r} \hline q_{5} \\ \hline 14.9309 \\ 14.9458 \\ 14.9643 \\ 14.9879 \\ 15.0192 \\ 15.0623 \\ 15.1255 \\ 15.2255 \\ 15.2255 \\ 15.4031 \\ 15.7648 \\ 16.4706 \end{array}$	q_6 18.0711 18.0833 18.0986 18.1183 18.1443 18.1803 18.2334 18.3188 18.4754 18.8215 19.6159
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TABLE 5.2

	β1	βı	βa	β₄	β	β_6
0	0	3-8137	7.0156	10.1735	13-3237	16-4706
0.01	0.1412	3.8343	7.0170	10.1745	13.3244	16.4712
0.1	0.4417	3.8577	7.0298	10.1833	13-3312	16-4767
0.2	0.6170	3.8835	7.0440	10-1931	13-3387	16-4828
0.5	0.9408	3-9594	7.0864	10.2225	13-3611	16.5010
1.0	1.2558	4-0795	7.1558	10-2710	13-3984	16-5312
$2 \cdot 0$	1.5994	4-2910	7.2884	10.3658	13-4719	16-5910
5.0	1.9898	4.7131	7.6177	10.6223	13-6786	16.7630
10.0	2.1795	5.0332	7.9569	10.9363	13-9580	17/0099
100-0	2.3809	5.4652	8.5678	11.6747	14.7834	17-8931
æ	2.4808	5.5201	8.6537	11.7915	14.9309	18.0711
		,	-			· · · · · · · · · · · · · · · · · · ·

Roots of $\beta J_1(\beta) - L J_0(\beta) = 0$

TABLE 5.3

b/a	a_{α_1}	$a\alpha_2$	$a\alpha_8$	aa4	$a\alpha_5$
1.2	15.7014	31-4126	47-1217	62-8302	78-5385
1.5	6-2702	12.5598	18.8451	25.1294	31-4133
$2 \cdot 0$	3.1230	6.2734	9.4182	12.5614	15.7040
$2 \cdot 5$	2.0732	4.1773	6.2754	8.3717	10.4672
3.0	1.5485	3.1291	4.7038	6.2767	7.8487
3.5	1.2339	2.5002	3.7608	5.0196	6.2776
4.0	1.0244	2.0809	3.1322	4.1816	5.2301

Roots of $J_0(a\alpha_n)Y_0(b\alpha_n)-J_0(b\alpha_n)Y_0(a\alpha_n)$

TABLE 6.1

Roots of $\tan q_n = \frac{3q_n}{3 + \alpha q_n^2}$

Fractional uptake	α	<i>q</i> 1	7 2	q_3	<i>q</i> 4	95	
0	æ	3.1416	6.2832	9-4248	12.5664	15-7080	18.8496
0.1	9.0000	3.2410	6-3353	9.4599	12.5928	15.7292	18-8671
0.2	4.0000	3.3485	6-3979	9.5029	12.6254	15.7554	18.8891
0.3	$2 \cdot 3333$	3.4650	6.4736	9.5567	12.6668	15.7888	18.9172
0-4	1.5000	3.5909	6-5665	9.6255	12.7205	15-8326	18.9541
0.5	1.0000	3.7264	6.6814	9.7156	12-7928	15.8924	19.0048
0.6	0.6667	3.8711	6-8246	9-8369	12.8940	15.9779	19.0784
0.7	0.4286	4.0236	7.0019	10.0039	13.0424	16-1082	19-1932
0.8	0.2500	4.1811	7.2169	10.2355	13-2689	16.3211	19.3898
0.8	0.1111	4-3395	7.4645	10.5437	13-6133	16-6831	19.7564
1.0	0	4.4934	7.7253	10-9041	14.0662	17.2208	20.3713

TABLE 6.2

L	β1	β2	β_3	β₄	βs	β
0	0	4.4934	7.7253	10.9041	14-0662	17.2208
0.01	0-1730	4-4956	7.7265	10-9050	14-0669	17-2213
0-1	0.5423	4-5157	7.7382	10-9133	14.0733	17.2266
0.2	0.7593	4.5379	7.7511	10.9225	14.0804	17.2324
0.5	1.1656	4.6042	7-7899	10.9499	14-1017	17-2498
1.0	1.5708	4.7124	7.8540	10.9956	14.1372	17.2788
2.0	2.0288	4.9132	7-9787	11.0856	14.2075	17-3364
5.0	2.5704	5·3 540	8-3029	I1-3349	14.4080	17.5034
10.0	$2 \cdot 8363$	5.7172	8.6587	11.6532	14.6870	17.7481
100.0	3.1102	6.2204	9-3309	12.4414	15.5522	18-6633
\$	3.1416	6.2832	9.4248	12.5664	15.7080	18-8496

Roots of $\beta_n \cot \beta_n + L - 1 = 0$

TABLE 8.1

Values of M_l/M_∞ for $\mu a^2/D = 0.01$

· · · · · · · · · · · · · · · · · · ·]			
	Plane	e sheet	Cyli	inder	Sp	here
$Dt/(R+1)a^3$	10	100	10	100	10	100
0.005	0.024	0.009	0.043	0.012	0.057	0.013
0.01	0.034	0.013	0.058	0.017	0.073	0.018
0.02	0.048	0.021	0.074	0-026	0.086	0.027
0.04	0.067	0.036	0.088	0.043	0.093	0.046
0.06	0.079	0.051	0.093	0.060	0.096	0.064
0.08	0.086	0.065	0.096	0.077	0.098	0.081
0.10	0.091	0.079	0.099	0.094	0.100	0.099
0-15	0.099	0.114	0.104	0.133	0-105	0.140
0.2	0-104	0.147	0-108	0.172	0.109	0.180
0.3	0-114	0.210	0.118	0-243	0.119	0.254
0.4	0.123	0.268	0.128	0.308	0.129	0.322
0.5	0.133	0.322	0.137	0.368	0.138	0.383
1.0	0.178	0.537	0.183	0.597	0.184	0.616
1.5	0.220	0.683	0.226	0.743	0.227	0.761
2.0	0.261	0-782	0.267	0.836	0.269	0.851
2-5	0.299	0.850	0.306	0.895	0.307	0.907
5.0	0.463	0.977	0.471	0.989	0.473	166.0
7.5	0.588	0.996	0.597	0.999	0.599	0.999
10	0.685	0.999	0.693	1.000	0.695	1-000
15	0.815	1.000	0.822		0.823	• •
20	0.891		0.896		0.898	••
40	0.987	• •	0.988		0-989	••
60	0.998	••	0-999		0-999	* 1
80	1.000	••	1.000		1.000	

TABLE 8.2

Value	s of	$M_{\rm c}$	$[M_{\infty}]$	for	μa^2	D		0.1	_
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P		lane sh	eet	·	Cylinde	r		Sphere	
$Dt/(R+1)a^2$	1	10	100	1	10	100	1	10	100
0.005	0.057	0.025	0.017	0.108	0.044	0.029	0.155	0.059	0.037
0.01	0.080	0.035	0-032	0.149	0.060	0.054	0.210	0.076	0.068
0.02	0.113	0.052	0.062	0.205	0.081	0.101	0.279	0-095	0.127
0.04	0.160	0.076	0.116	0.277	0.106	0.188	0.361	0.117	0.232
0.06	0.197	0.095	0.166	0.327	0.125	0.265	0.409	0.136	0.324
0.08	0.227	0.112	0.211	0.365	0.143	0.333	0.441	0.153	0.404
0-10	0.254	0.128	0.253	0.395	0.159	0.394	0.463	0.171	0.474
0.15	0.310	0.164	0.343	0.445	0-200	0.519	0.494	0.212	0.613
0.2	0.354	0.198	0.418	0.476	0.238	0.612	0.508	0.252	0.712
0.3	0.418	0.261	0.536	0.507	0.309	0.748	0.522	0.325	0.838
0.4	0.459	0.320	0.626	0.524	0.373	0.832	0.532	0.391	0.907
0.2	0-488	0.374	0.696	0.535	0.432	0.887	0.542	0.451	0.946
1.0	0.559	0.585	0.889	0.579	0.652	0.983	0-585	0.672	0-996
1.5	0.601	0.724	0.959	0.619	0-786	0.997	0.624	0.804	1.000
$2 \cdot 0$	0.638	0.816	0.985	0.655	0.868	1.000	0-660	0.883	• •
2.5	0.671	0.877	0.994	0.687	0.919	••	0.692	0.930	• •
5.0	0.797	0.983	1.000	0.809	0.993	i	0.813	0-995	
7.5	0.875	0.998	••	0.884	0.999		0.886	1.000	
01	0.923	1.000		0.929	1.000	• • •	0.931	1	• •
15	0.971	• •	••	0.974		••	0.974		••
20	0.989	•••	• •	0.990			0.990	••	••
40	1.000		••	1.000			1.000		

TABLE 8.3

Values of $M_{\rm l}/M_{\infty}$ for $\mu a^2/D$ == 1.0

	Plane sheet				Cylinde	r	Sphere		
$Dt/(R+1)n^2$	1	10	100	1	10	100	1	10	100
0.005	0.057	0.028	0.045	0.109	0.051	0.085	0-155	0.070	0.120
0.01	0.081	0.045	0.081	0.151	0.079	0.151	0.211	0.105	0.212
0.02	0.115	0.075	0.136	0.208	0.129	0.250	0.283	0.166	0.346
0.04	0.164	0.131	0.210	0.285	0.217	0.378	0.371	0.273	0.510
0.06	0.203	0.181	0.264	0.341	0.295	0.465	0.429	0.366	0.613
0.08	0.237	0.226	0.309	0.385	0.363	0.531	0.471	0.445	0.687
0.10	0.267	0.268	0.348	0.423	0.423	0.587	0.504	0.514	0.743
0.15	0.334	0.358	0.430	0.495	0.547	0.692	0.564	0.648	0.840
0.2	0.390	0.432	0.497	0.549	0.638	0.767	0.608	0.743	0.899
0.3	0.481	0.549	0.607	0-630	0.768	0.866	0.676	0.860	0.959
0.4	0.553	0.637	0.691	0.691	0.848	0-923	0.732	0.922	0.983
0.5	0.613	0.707	0.758	0.741	0.898	0.955	0.777	0-956	0.993
1.0	0.804	0.895	0.927	0-891	0.986	0.997	0.912	0.997	1.000
1.5	0.900	0.962	0.978	0.954	0.998	1.000	0.965	1.000	·
2.0	0.948	0.986	0.994	0-980	1.000		0-986		
2.5	0.973	0.993	0-998	0.992			0-995		
5.0	0.999	1.000	1.000	1.000			1.000		
7.5	1.000	•••		• •	• •		۰.		••



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TABLE 8.4

	Plane sheet	Cylinder	Sphere
$Dt/(R+1)a^2$	1	1	1
0.005	0.059	0.112	0.160
0.01	0.085	0.159	0-224
0.02	0-126	0.230	0.316
0.04	0.190	0.336	0.448
0.06	0.242	0.420	0.546
0.08	0.288	0.489	0.623
0.10	0.329	0-547	0.686
0.15	0.414	0.660	0.796
0.2	0.484	0.740	0.865
0.3	0.595	0.845	0.939
0-4	0-680	0.906	0.972
0.5	0.746	0.943	0.987
1.0	0.920	0.995	000.1
1.5	0.975	1.000	
2.0	0-992		
2.5	0.998	••	
5.0	1.000		

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Values of $M_{\rm i}/M_{\infty}$ for $\mu a^2/D=10$

TABLE 9.1

0·2 0.40.6 0.0 0.81.0 1.21.41.6 1.8 2.0 $2 \cdot 2$ ø $2 \cdot 4$ y. -2.0-998 - 995] -1000-1.9 -993 -996 --- 999 -1000-1.8 - 994 -998-989 -999;-1.7 - 984 -990-996--- 998 -1000-1.6 -976 -984 -992-996 -- 9999 -1000-1.5 - 966 -976 -985-992 -- 997 -999 -1000 -1.4 -952 -964 -976- 985 -- 993 -997 - 999 -1.3 -934]-948 -- 962 -975-986-994-998-1000 -- 942 -1.2-910 - 925- 958 -974-986 -995-999-1.1 -880 -896 -914 -933 -953 -972 -987- 996 -1000-1.0 - 843 - 858 -876 -896 -920-945- 969 -987-997-1000-1000-0.6-826-872- **79**7| -810-845--- 901 -- 938 -963- 986 -- 998 -999-742-751-0.8 -765-781-804-834-870-984-- 997 -912 -962-1000--0.7 -678<u>]</u> -682-690-700-717-741 -774-928- 996 -817-869-975-1000-0.6 - 604 - 602 **---6**02 -605-612-626 -647-- 678 -721-785- 866 -946 -993-494-494-0.2 -520 - 511-504-497 -498 -501-528-662-615-697--831 -0.4- 429 -397-412--- \$81 -366-354-348-334- 329 - 329 --- 336 -353-- 398 -0.3 - 329 -306-282-259-237-214-191-127-169-148-107-89-76-0.5-223-196 -117-138-109-- 79 - 50 -2039 129 9 7099 -112 -0.1 143 -81- 50 -1878 17620924027214 46 111 0.0 0 $\mathbf{32}$ 64 97 129161 193 225256288320349 380 325 353 +0.1 112 143 174 205235265295 382411 438 466 +0.5223250278305 $\mathbf{332}$ 359 385 411 486 462487 511 535 +0.3329 352 374397 420465 442487 508 530552572 **59**3 ± 0.4 429462 481 499 517 535 607 445 553570 589624642+0.5520531648555 668 582598 611 624 640 654668 684 +0.6604 608 614 622 631 640 650 672 684 896 709 720 661 +0.7713 678 677 678-681686 691 698, 706723732740761 +0.8742736 740737733 733 784 745 750757764771 779 787, +0.8797 758781 778776775777779 782792798 804 +1.0812 831 823 809 **810** 843 816 810 809 813 817 820 825 +1.1 880 868 858 889 849 844 837 836 835 837 839 841 845 +1.2**9**10 899 886 878 871865 861 859, 857 859 858 859 862 +1.3879 934 922911 901 894 888 888 878 876 876 878 877 +1.4952931 **92**1 913 906 901 897 941 894 892 891 890 891 +1.5966 947 938 930 924917 956 913 909 906 905 903 903 +1.6976 968 959 951 943 937 931 926 922 919] 917 915 915 + 1.7 984 977 969 962 **9**55 948 943 938 933, 930 928924 924+1.8 958 989 984 977 971 964 953 948 948 940 937 934 933 +1.9 993 989 972 966 983 978 961956 952 949 946 943 941 +2.0 995992 988; 983 978 973 968 964 959 956 952 950 948

Numerical values of the function $1,000\psi(y,g)$



TABLE 9.2

. 0	-2.4	-2.2	-2.0	-1.8	-1.6	-1.4	-1.2	-1.0	1-0.8	-0.6	-0.4	-0.2	-0.00
Vs										ļ			
0.0	0	0	0	0	0	0	0	1 0	1-0				
0.1	78	81	84	87	ด้า	93	0A		100	1 105	107	110	
0.2	182	185	189	193	198	200	204	907	910	014	107	010	112
0.3	330	325	323	322	821	322	399	201	994	214 00L	217	220	223
0.4	600	520	497	479	486	457	440	449	490	040	320	028 490	329
0.5	877	775	709	860	624	800	580	581	551	400 KA1	400	43U 607	429
0.6	995	960	898	833	778	737	704	678	865	890	004 004	027	020 dua
0.7	1000	997	981	944	896	851	811	777	750	000	020	014 400	004
0.8		1000	998	987	962	928	891	857	897	800	700	092 750	0/8
0-9			1000	998	989	970	944	015	804	980	000	108	742
1.0		Í		1000	998	089	074	959	0.00	000	000	040	197
1.1					1000	996	089	078	050	020	010	902	044
1.2				1		999	998	088	077	061	910	099	000
1.3			i			1000	908	005	087	077	940	920 040	310
1.4		' I				1000	900	008	001	0977 098	804	949 Aoc	904
1.5		. !		- 1	[1000	990	607	900	9(7 00A	900 077	922
1.6	i	[1000	000	008	900	9/1	900
1.7				[ĺ			1000	1000	009	892	900	870
1.8		- 1	1		ļ				1000	000	990	980	000
1-9			ł							1000	000	394	909 909
2.0		İ				[1000	1000	997	002 992
	I		<u> </u>				[l			1000	220	880

Numerical values of the function $1,000c(y_s,g)$

0	+0.2	+0.4	+0.6	+0-8	+1.0	+1.2	+1.4	+1.6	+1.8	+2.0	+2.2	+2.4
¥8					i				1			
0.0	0	0	0	0	0	0	0	0	0	-0	0	<u> </u>
0.1	115	117	120	122	124	126	128	130	132	134	136	138
0.5	226	228	231	233	236	238	240	242	244	246	248	250
0.3	830	331	833	384	335	336	338	339	840	341	342	344
0-4	427	428	425	424	424	423	423	422	422	422	422	422
0.2	516	512	508	505	502	499	497	495	494	492	491	489
0.6	595	588	582	576	571	567	563	559	556	553	650	548
0.7	666	656	647	639	632	626	620	615	610	606	602	599
0:8	728	715	704	694	685	677	670	664	658	653	648	644
0.8	781	766	754	742	782	723	715	707	700	694	688	683
1.0	826	811	797	784	773	763	754	745	738	731	724	718
1.1	863	848	833	820	809	798	788	779	771	763	766	749
1.2	896	879	865	851	839	828	818	808	800	792	784	777
1.3	919	905	891	878	866	855	844	835	825	817	809	802
1.4	939	926	913	900	889	878	867	857	848	840	832	824
1.5	955	943	931	919	910	897	887	877	868	860	852	844
1.6	967	956	946	935	925	914	904	895	886	878	870	862
1.7	976	987	958	948	938	929	919	910	902	893	885	878
1.8	983	976	986	959	950	941	932	924	915	903	900	892
1.9	988	982	975	968	960	952	944	935	928	920	912	905
2.0	992	987	981	975	968	961	953	945	938	929	923	916

•

and the second
TABLE 9.3

Concentration gradients $-(dC/dy_a)/(C_1-C_2)$ against $y_a = x/\{2\sqrt{D_a t}\}$

b =	ratio of	the diffusion	coefficient at conce	ntration C_1	to	that a	t C	2
-----	----------	---------------	----------------------	----------------	----	--------	-----	---

y _a	$b = 1^*$	b = 0.8806	b = 0.7228	b = 0.5506	b = 0.3270	b = 0.1407
2.8				0.001	0.002	0.003
2.6	0.001	0.001	0.001	0.002	0.004	0.006
2.4	0.002	0.002	0.003	0.005	0.007	0.011
2.2	0.005	0.005	0.007	0.009	0.013	0.017
$\overline{2 \cdot 0}$	0.010	0.012	0.015	0.018	0.023	0.028
1.8	0.022	0.024	0.028	0.032	0.039	0-043
1.6	0.044	0.047	0.050	0.055	0.062	0-066
1.4	0.079	0-083	0.086	0.089	0.092	0.095
1.2	0.134	0.136	0.135	0.134	0.134	0.132
1.0	0-208	0-207	0.200	0.195	0.188	0-179
0.8	0-298	0.292	0.280	0.268	0.250	0.233
0.6	0.394	0.384	0.367	0-348	0.321	0.296
0.4	0.481	0.468	0.452	0-430	0.398	0.365
0.2	0.542	0.533	0.522	0-504	0-474	0.439
0.0	0.564	0.561	0-560	0-555	0-539	0.513
0.2	0.542	0.547	0.558	0-569	0.579	0.578
-0.4	0.481	0.491	0-511	0.535	0.577	0.621
-0.6	0.394	0.406	0.423	0.455	0.514	0.607
-0.8	0.298	0-308	0-319	0.339	0.388	0.479
1.0	0.208	0.212	0.215	0.221	0.232	0.226
	0-134	0.135	0.130	0.125	0.108	0.049
-1·4	0.079	0.077	0.071	0.061	0.039	0.002
-1·6	0.044	0.040	0.035	0.027	0.011	••
1.8	0.022	0.019	0.015	0.010	0.003	•••
-2.0	0.010	0.008	0.006	0.003	••	••
$-2 \cdot 2$	0.005	0.003	0.002	0.001	••	
-2.4	0.002	••				••
-2.6	0.001					· · ·
-2.8		• •	· · ·	•••	••	

• The data for b = 1 represent the Gaussian curve corresponding to ideal diffusion.



TABLE 9.4

Relative concentrations (C-C_2)/(C_1-C_2) against $y_a = x/(2\sqrt{(D_a t)})$

b	_	ratio of	diffusion	coefficient	at concentrati	on C	V_1 to	that at	С,
---	---	----------	-----------	-------------	----------------	------	----------	---------	----

y _a	b = 1	b = 0.8806	b = 0.7228	b = 0.5506	b - 0- 3 270	b = 0.1407
2.6	• •				0.001	0.001
2.4) .		0.001	0.002	6-003
2-2		0.001	0.001	0.003	0.004	0.006
$2 \cdot 0$	0.002	0.003	0.004	0.005	0.007	0.010
1.8	0.005	0.006	0.008	0.010	0-013	0.017
1.6	0.012	0.013	0.015	0.019	0.024	0.028
1-4	0.024	0.026	0.029	0.033	0.039	0.044
$1 \cdot 2$	0.045	0.048	0.051	0.055	0.061	0.068
1.0	0.079	0.082	0.084	0-088	0-093	0.099
0.8	0-129	0-131	0.132	0.134	0.137	0-139
0.6	0.198	0-199	0.197	0.195	0.194	0.192
0.4	0.286	0.284	0.279	0-273	0.266	0.258
0-2	0.389	0.385	0.376	0.367	0.353	0-339
0.0	0.500	0.495	0.485	0.473	0.455	0-434
-0.5	0.611	0.606	0.597	0.586	0.567	0.543
0-4	0.714	0.710	0.705	0.697	0.683	0.664
— 0-6	0-802	0.800	0.799	0.797	0.793	0.785
−0·8	0-871	0-872	0.873	0.876	0.884	0-898
-1.0	0-921	0.923	0.927	0.933	0.946	0.970
-1.2	0.955	0.958	0.961	0-967	0.980	0.995
—1 ∙ 4	0-976	0.979	0.981	0-986	0.994	0.999
1 ∙₿	0.988	0-990	0-992	0.995	0.998	1.000
I ·8	0.995	0- 996	0.997	0.998	1.000	1.000
-2.0	0.998	0.999	0.999	1.000	1.000	1.000
-2.2	1.000	1.000	1.000	1.000	1.000	1.000

TABLE 10.1

Section of computation sheet for Schmidt method

Values of c are tabulated

T	x 1.0	0.875	0.750	0.625	0.500	0-375	0.250	0.125	0
9/256	1-0	0.637	0-346	0.157	0.059	0.018	0.005	0.001	0
11/256	1.0	0.673	0.397	0.203	0.088	0.032	0.010	0.003	0.001
13/256	0.1	0.699	0.438	0.243	0.118	0.049	0.017	0.006	0.003
15/258	1.0	0.719	0.471	0.278	0.146	0.068	0.027	0.010	0-006
17/256	1.0	0.736	0-499	0.308	0.173	0.087	0.039	0.016	0.010
19/256	1.0	0.750	0.522	0.336	0-198	0.106	0.051	0.025	0.016
21/256	1.0	0.761	0.543	0.360	0.221	0.124	0.066	0.033	0.025
23/256	1.0	0.772	0.560	0-382	0.242	0-143	0.079	0-046	0.033
25/256	1.0	0.780	0.577	0.401	0.263	0-161	0.094	0.056	0.046
27/256	1.0	0.788	0.590	0.420	0.281	0.179	0.108	0.070	0.056
29/256	1.0	0.795	0.604	0.436	0.300	0.194	0.124	0.082	0.070
	(1.0)	(0.793)	(0-600)	(0-432)	(0-295)	(0-193)	(0.124)	(0.084)	(0.071)

L

TABLE 10.2

Section of computation sheet for Crank-Nicolson method

							· •	(I	
T	1.0	0-875	0.750	0.625	0.500	0.375	0.250	0-125	0
9/256 13/256 17/256 21/256 25/256 29/256	1·0 1·0 1·0 1·0 1·0 1·0 (1·0)	0.637 0.695 0.731 0.757 0.776 0.792 (0.793)	0-346 0-432 0-492 0-536 0-570 0-598 (0-600)	0.157 0.238 0.302 0.353 0.395 0.430 (0.432)	0.059 0.116 0.169 0.216 0.258 0.294 (0.295)	0.018 0.050 0.086 0.123 0.158 0.193 (0.193)	0.005 0.019 0.040 0.066 0.094 0.124 (0.124)	0.001 0.007 0.019 0.037 0.059 0.085 (0.084)	0 0-004 0-013 0-028 0-048 0-072 (0-071)

Values of c are tabulated

TABLE 10.3

Section of computation sheet for $D = e^{2 \cdot 803c}$

Values of s are tabulated

						·			
X	1.0	0.875	0.750	0.625	0.500	0.375	0.220	0.125	0
0.1724 0.1740 0.1756 0.1756 0.1772 0.1788 0.1804 0.1804	1·0 1·0 1·0 1·0 1·0 1·0 1·0 (1·0)	0·767 0·774 0·780 0·785 0·790 0·794 (0·911)	0-546 0-556 0-566 0-576 0-585 0-593 (0-802)	0-340 0-355 0-369 0-382 0-394 0-405 (0-667)	0.176 0.190 0.203 0.216 0.229 0.242 (0.502)	0.065 0.075 0.085 0.095 0.106 0.116 (0.310)	0.016 0.020 0.025 0.030 0.036 0.042 (0.139)	0.003 0.004 0.005 0.007 0.009 0.011 (0.041)	0 0.001 0.002 0.003 0.004 0.005 (0.019)
	1 ' '		·	<u> </u>					

Values of c are shown in brackets for T = 0.1804



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TABLE 13.1

Diffusion coefficients and amplitudes

The figures in each cell of the top half are for diffusion coefficients, the arrangement being as shown in the cell for 80° C. and 90% R.H. The unit is 10^{-5} cm.³/sec. The significance of the figures in the bottom half is shown in the corresponding cell.

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	87	14 3	õ	6	Ó	-
20° C.	50° C.	80° C.	20° C.	50° C.	80° C.	The farmer





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