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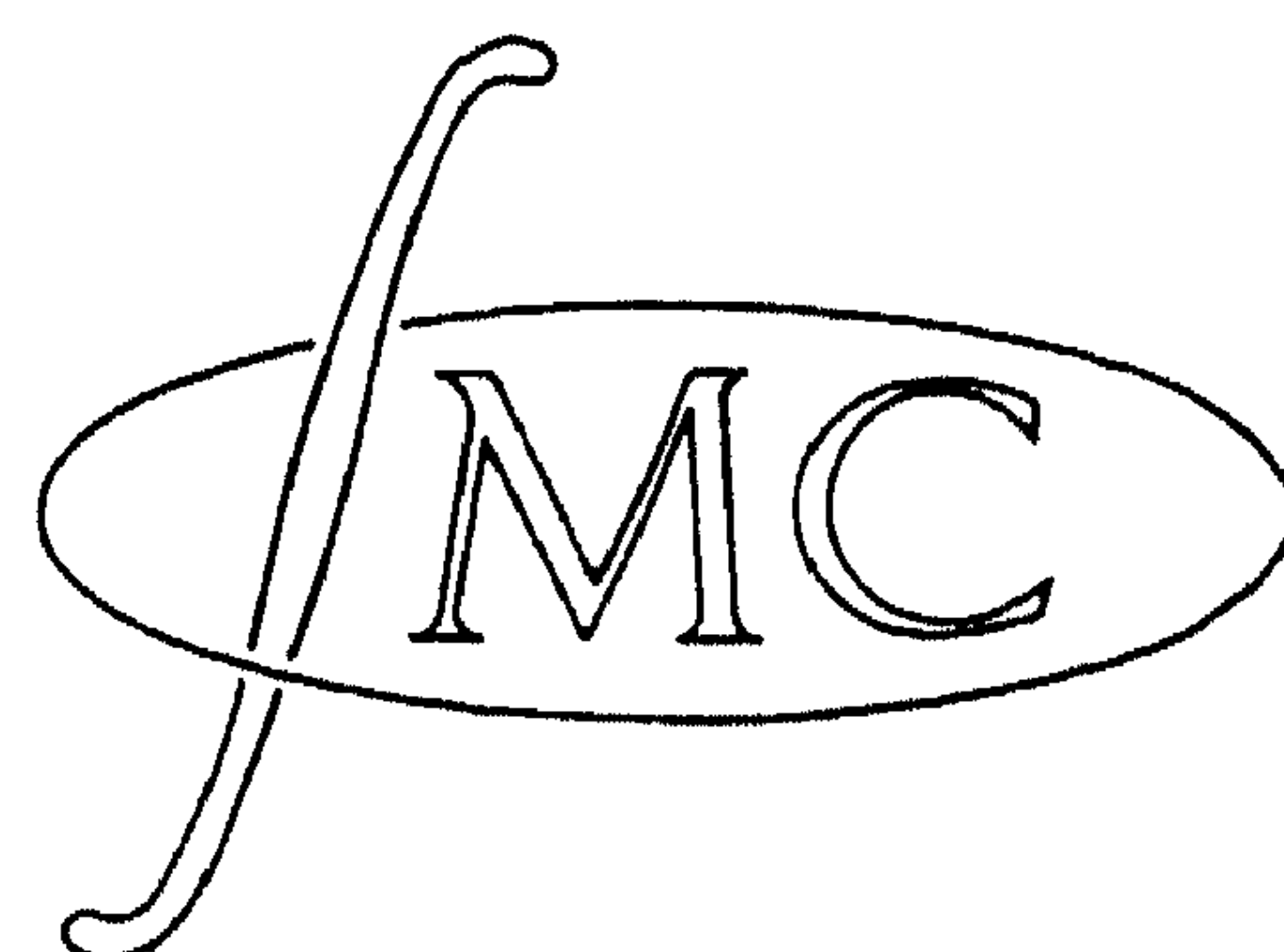
AFDELING TOEGEPASTE WISKUNDE

Technical Note TN 37

Diffusion in layered media

by

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October 1964

Printed at the Mathematical Centre at Amsterdam, 49, 2nd Boerhaavestraat.
The Netherlands.

The Mathematical Centre, founded the 11th of February 1946, is a non-profit institution aiming at the promotion of pure mathematics and its applications, and is sponsored by the Netherlands Government through the Netherlands Organization for Pure Scientific Research (Z.W.O.) and the Central National Council for Applied Scientific Research in the Netherlands (T.N.O.), by the Municipality of Amsterdam and by several industries.

§ 1. Introduction,

In this technical note we investigate the diffusion of material into a medium, consisting of two layers with different diffusion coefficients.

Assuming the concentration of the material outside the two layers to be constant, we consider consecutively the following three cases:

- i) Both layers are bounded by parallel planes; the first one has finite thickness, while the second one extends to infinity, (see fig.1).
- ii) Both layers are bounded by parallel planes and both have finite thickness, (see fig.2).
- iii) The layers are outer shell and inner core of a sphere and they are separated by a spherical surface concentric with the surface of the sphere, (see fig.3).

Formulae are derived for the total amount of absorbed material as a function of time with the dimensions and the diffusion coefficients of the layers as parameters.

These formulae could be used e.g. to determine the diffusion coefficients from measurements of the total amount of absorbed material, when the experimental setup is such that constant concentration of the material at the boundary of the first layer can be assumed.

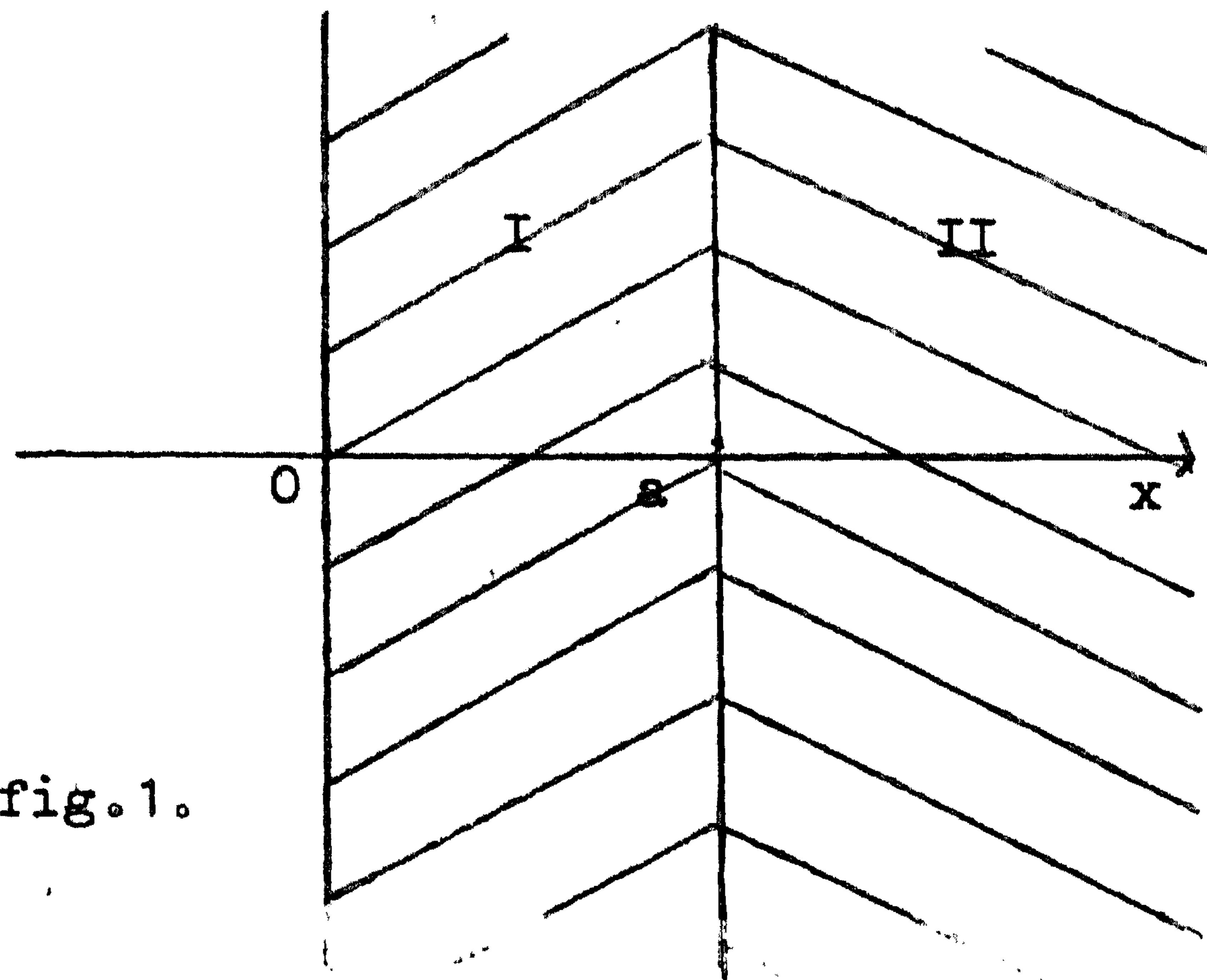
§ 2. Diffusion in a medium consisting of one layer of finite thickness and another layer extending to infinity.

Consider a medium which can absorb material from a neighbouring reservoir. We suppose that the medium consists of two layers, which are bounded by parallel planes. Introducing the coordinate x the first layer (I) lies in the region $0 < x < a$ and the second layer (II) in the region $x > a$ (see figure 1).

In the region $x \leq 0$ a substance is present, which can penetrate by diffusion into the regions I and II.

In this section the total amount of material absorbed in the regions I and II

fig.1.



is determined as a function of the time t with the parameters a , D_1 and D_2 , where D_1 and D_2 are the diffusion coefficients for the layers I respectively II. Assuming that the diffusion process starts at the time $t=0$ and denoting the concentrations of the absorbed material in the layers I and II by respectively $C_1(x,t)$ and $C_2(x,t)$, we describe the process by the well-known diffusion equation; i.e. C_1 and C_2 satisfy the partial differential equations

$$D_1 \frac{\partial^2 C_1}{\partial x^2} = \frac{\partial C_1}{\partial t} \quad \text{for} \quad 0 < x < a, \quad \text{and} \quad 0 < t, \quad (2.1)$$

and

$$D_2 \frac{\partial^2 C_2}{\partial x^2} = \frac{\partial C_2}{\partial t} \quad \text{for} \quad a < x, \quad \text{and} \quad 0 < t, \quad (2.2)$$

with the initial conditions

$$C_1(x,t) = 0 \quad \text{for} \quad 0 < x \leq a \quad \text{and} \quad t = 0, \quad (2.3)$$

and

$$C_2(x,t) = 0 \quad \text{for} \quad a \leq x \quad \text{and} \quad t = 0. \quad (2.4)$$

We assume that the total amount of material absorbed in I and II in some finite time interval is small in comparison with the amount present in the region $x < 0$ and that the concentration of this material changes only slightly in $x \leq 0$ as the diffusion process continues. Therefore it is allowed to take this concentration equal to a constant for $x \leq 0$. Putting this constant equal to 1, we get the boundary condition

$$C_1(x,t) = 1 \quad \text{for} \quad x = 0 \quad \text{and} \quad 0 \leq t. \quad (2.5)$$

The boundary conditions at the contact surface $x=a$ are obtained by considering the continuity of the concentration itself and the continuity of the amount of material passing the plane $x=a$. This yields the conditions

$$C_1(x,t) = C_2(x,t) \quad \text{for} \quad x = a \quad \text{and} \quad 0 \leq t, \quad (2.6)$$

and

$$D_1 \frac{\partial C_1}{\partial x} = D_2 \frac{\partial C_2}{\partial x} \quad \text{for} \quad x = a \quad \text{and} \quad 0 \leq t. \quad (2.7)$$

The boundary condition at $x=\infty$ needs a little discussion. It is known that the diffusion equation describes a diffusion process in such a way, that the velocity of diffusion can be said to be infinite. The concentrations have non-vanishing values for all finite values of x and all positive values of t . Even at infinity the diffusion process is going on for all positive values of t , although the concentrations are infinitely small. Therefore we may put as the boundary condition at $x=\infty$

$$C_2(x,t) = 0 \quad \text{for} \quad x = \infty \quad \text{and} \quad 0 < t < \infty. \quad (2.8)$$

An alternative boundary condition, leading to exactly the same results, would be the condition reflecting the vanishing of transport of

absorbed material at infinity; this leads to

$$\frac{\partial C_2}{\partial x}(x,t) = 0 \quad \text{for } x = \infty \quad \text{and } 0 < t. \quad (2.9)$$

This would be the natural boundary condition to pose if we consider the second infinitely thick layer as the limit of a series of layers of finite thickness, a case treated in the following section. In that case the choice of a boundary condition of type (2.9) is obligatory. We now proceed to the calculation of the total amount of material absorbed in the time t and which is given by

$$M(t) = - \int_0^t D_1 \frac{\partial C_1}{\partial x}(0,\tau) d\tau. \quad (2.10)$$

This function $M(t)$ will be determined by aid of the Laplace transformation, defined by

$$\bar{C}_{1,2}(x,p) = \int_0^\infty e^{-pt} C_{1,2}(x,t) dt, \quad (2.11)$$

with $\text{Re } p > 0$.

Applying (2.11) to the equations (2.1) and (2.2) and using (2.3) and (2.4) we obtain the ordinary differential equations

$$D_1 \frac{\partial^2 \bar{C}_1}{\partial x^2} - p\bar{C}_1 = 0 \quad \text{and} \quad D_2 \frac{\partial^2 \bar{C}_2}{\partial x^2} - p\bar{C}_2 = 0, \quad (2.12)$$

with the boundary conditions

$$\begin{aligned} \bar{C}_1(0,p) &= \frac{1}{p}, \\ \bar{C}_1(a,p) &= \bar{C}_2(a,p), \end{aligned} \quad (2.13)$$

$$D_1 \frac{\partial \bar{C}_1}{\partial x}(a,p) = D_2 \frac{\partial \bar{C}_2}{\partial x}(a,p),$$

$$\text{and} \quad \bar{C}_2(\infty,p) = 0 \quad \text{or} \quad \frac{\partial \bar{C}_2}{\partial x}(\infty,p) = 0.$$

When we put

$$\frac{p}{D_1} = q_1^2 \quad \text{and} \quad \frac{p}{D_2} = q_2^2, \quad (2.14)$$

the general solution of (2.12) may in view of further calculations most conveniently be written as

$$\begin{aligned} \bar{C}_1(x, p) &= A_1 \operatorname{ch} q_1(a-x) + B_1 \operatorname{sh} q_1(a-x), \\ \bar{C}_2(x, p) &= A_2 \exp[q_2 x] + B_2 \exp[-q_2 x]. \end{aligned} \quad (2.15)$$

The coefficients A_1 , A_2 , B_1 and B_2 in (2.15) can be found from the transformed boundary conditions (2.13). After some simple calculations we find

$$\bar{C}_1(x, p) = \frac{1}{p} \cdot \frac{\operatorname{ch} q_1(a-x) + \delta \operatorname{sh} q_1(a-x)}{\operatorname{ch} q_1 a + \delta \operatorname{sh} q_1 a}, \quad (2.16)$$

and

$$\bar{C}_2(x, p) = \frac{1}{p} \cdot \frac{\exp[-q_2(x-a)]}{\operatorname{ch} q_1 a + \delta \operatorname{sh} q_1 a},$$

with

$$\delta = \sqrt{\frac{D_2}{D_1}}. \quad (2.17)$$

It is clear that the boundary conditions (2.8) and (2.9) lead to the same result for \bar{C}_2 and are therefore evidently equivalent. Using (2.16) we obtain for the Laplace-transform of $M(t)$

$$\bar{M}(p) = \frac{1}{pq_1} \cdot \frac{\operatorname{sh} q_1 a + \delta \operatorname{ch} q_1 a}{\operatorname{ch} q_1 a + \delta \operatorname{sh} q_1 a}. \quad (2.18)$$

In order to obtain an expansion for $M(t)$ which can be used for small values of the time t , we expand $\bar{M}(p)$ in the following way

$$\begin{aligned}
\bar{M}(p) &= \frac{1}{pq_1} \cdot \frac{(1 + \delta) \exp[q_1 a] - (1 - \delta) \exp[-q_1 a]}{(1 + \delta) \exp[q_1 a] + (1 - \delta) \exp[-q_1 a]} = \\
&= \frac{1}{pq_1} \cdot \frac{1 - \varepsilon \exp[-2q_1 a]}{1 + \varepsilon \exp[-2q_1 a]} = \\
&= \frac{1}{pq_1} \cdot \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \varepsilon^n \exp[-2nq_1 a] \right\},
\end{aligned} \tag{2.19}$$

where

$$\varepsilon = \frac{1 - \delta}{1 + \delta}. \tag{2.20}$$

We now transform (2.19) inversely term by term and retaining only the first two terms we finally get the result (see lit.1)

$$M(t) \approx 2 \sqrt{\frac{D_1 t}{\pi}} \left[1 - 2 \varepsilon \left(\exp \left[-\frac{a^2}{D_1 t} \right] - a \sqrt{\frac{\pi}{D_1 t}} \operatorname{Erfc} \frac{a}{\sqrt{D_1 t}} \right) \right]. \tag{2.21}$$

Formula (2.21) can effectively be used, when the second term is small as compared with the first one that is for

$$t \ll \frac{a^2}{D_1}, \tag{2.22}$$

(see further the examples given in the last section).

For these values of t the complement of the error function may be expanded as follows (see lit.2)

$$\operatorname{Erfc} \frac{a}{\sqrt{D_1 t}} = \frac{\exp \left[-\frac{a^2}{D_1 t} \right]}{a \sqrt{\frac{\pi}{D_1 t}}} \left\{ 1 - \frac{D_1 t}{2a^2} + \frac{3D_1^2 t^2}{4a^4} \dots \right\}. \tag{2.23}$$

Substitution of (2.23) into (2.21) leads finally to the simpler formula

$$M(t) \approx 2 \sqrt{\frac{D_1 t}{\pi}} \left(1 - \frac{\epsilon D_1 t}{a^2} \exp \left[-\frac{a^2}{D_1 t} \right] \right). \quad (2.24)$$

To obtain an expansion, useful for large values of t , an expansion of $\bar{M}(p)$, valid for small values of $p \neq 0$, is appropriate and this leads to

$$\bar{M}(p) = \sqrt{D_2} p^{-\frac{3}{2}} + a(1 - \delta^2) p^{-1} + \dots \quad (2.25)$$

Transforming again inversely term by term, we obtain the result

$$M(t) \approx 2 \sqrt{\frac{D_2 t}{\pi}} + a(1 - \delta^2). \quad (2.26)$$

This expression too can be used whenever the first term is large as compared with the second term.

§ 3. Diffusion in a medium consisting of two finite layers.

In this section we consider the case that both layers have a finite thickness. The first one (I) lies in the region $0 < x < a$ and the second one (II) in the region $a < x < b$ (see figure 2).

The differential equations for the concentrations $C_1(x,t)$ and $C_2(x,t)$ are again the diffusion equations (2.1) and (2.2). Also the initial conditions are the same as for the problem treated in the former section, namely equations (2.3) and (2.4).

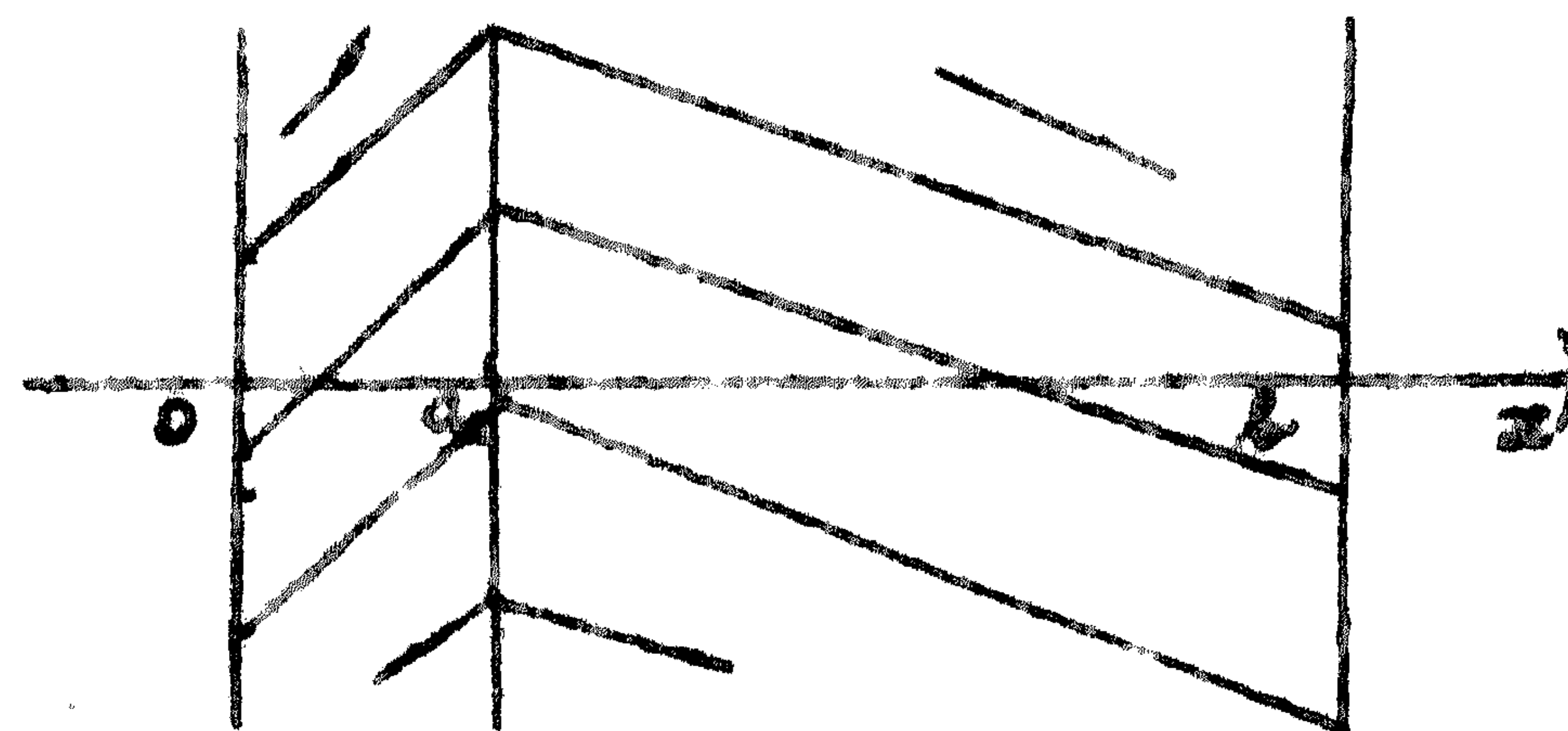


fig.2

The boundary conditions, based on the same assumptions as in the former section, are

$$\begin{aligned} C_1(x,t) &= 1 && \text{for } x=0 \text{ and } 0 < t, \\ C_1(x,t) &= C_2(x,t) && \text{for } x=a \text{ and } 0 < t, \end{aligned} \quad (3.1)$$

$$D_1 \frac{\partial C_1}{\partial x} = D_2 \frac{\partial C_2}{\partial x} \quad \text{for } x=a \text{ and } 0 < t,$$

$$\text{and} \quad \frac{\partial C_2}{\partial x} = 0 \quad \text{for } x=b \text{ and } 0 < t.$$

The last condition is the same as condition (2.9) and stems from the assumption that there will be no transport of absorbed material through the plane $x=b$. In contrast to the case where the second layer extends to infinity the concentration at $x=b$ increases and finally at $t=\infty$ it will be 1.

Using again the Laplace transformation and accounting for the conditions (3.1) we obtain for the Laplace transform of the concentrations $C_1(x,t)$ and $C_2(x,t)$ the expressions.

$$\bar{C}_1(x,p) = A_1 \operatorname{ch} q_1(a-x) + B_1 \operatorname{sh} q_1(a-x) \quad (3.2)$$

and

$$\overline{C}_2(x,p) = A_2 \operatorname{ch} q_2(x-a) + B_2 \operatorname{sh} q_2(x-a), \quad (3.3)$$

with

$$A_1 = A_2 = \frac{\operatorname{ch} q_2(b-a)}{p\Delta_1},$$

$$B_1 = \frac{\delta \operatorname{sh} q_2(b-a)}{p\Delta_1} \quad \text{and} \quad B_2 = -\frac{\operatorname{sh} q_2(b-a)}{p\Delta_1},$$

where q_1 , q_2 and δ are given by (2.14) and (2.17) whereas

$$\Delta_1 = \operatorname{ch} q_2(b-a) \operatorname{ch} q_1 a + \delta \operatorname{sh} q_2(b-a) \operatorname{sh} q_1 a. \quad (3.4)$$

From (2.10) and (3.2) we obtain the Laplace transform of the function $M(t)$, viz.

$$\overline{M}(p) = \frac{1}{pq_1 \Delta_1} \{ \operatorname{sh} q_1 a \operatorname{ch} q_2(b-a) + \delta \operatorname{ch} q_1 a \operatorname{sh} q_2(b-a) \}. \quad (3.5)$$

Expanding $\overline{M}(p)$ into a series analogous to eq. (2.19), we obtain

$$\begin{aligned} \overline{M}(p) &= \frac{1}{pq_1} \cdot \frac{\exp[q_1 a] \cdot \{1 + \delta \operatorname{th} q_2(b-a)\} + \exp[-q_1 a] \cdot \{1 - \delta \operatorname{th} q_2(b-a)\}}{\exp[q_1 a] \{1 + \delta \operatorname{th} q_2(b-a)\} + \exp[-q_1 a] \{1 - \delta \operatorname{th} q_2(b-a)\}} = \\ &= \frac{1}{pq_1} \cdot \frac{1 - \xi \exp[-2q_1 a]}{1 + \xi \exp[-2q_1 a]} = \frac{1}{pq_1} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \xi^n \exp[-2nq_1 a] \right] = \\ &= \frac{1}{pq_1} (1 - 2\xi e^{-2q_1 a} + 2\xi^2 e^{-4q_1 a} \dots). \end{aligned} \quad (3.6)$$

where ξ is given by

$$\xi = \frac{\operatorname{ch} q_2(b-a) - \delta \operatorname{sh} q_2(b-a)}{\operatorname{ch} q_2(b-a) + \delta \operatorname{sh} q_2(b-a)} = \frac{\epsilon + \exp[-2q_2(b-a)]}{1 + \epsilon \exp[-2q_2(b-a)]},$$

and ϵ is defined by (2.20).

Expanding the denominator into powers of $\epsilon \exp[-2q_2(b-a)]$ we may write ξ in the form

$$\begin{aligned}\xi &= \{\epsilon + \exp[-2q_2(b-a)]\}\{1 - \epsilon \exp[-2q_2(b-a)] \dots\} = \\ &= \epsilon + (1-\epsilon^2)\exp[-2q_2(b-a)] + 0 (\exp[-4q_2(b-a)]).\end{aligned}\quad (3.7)$$

Substituting (3.7.) into (3.6) we finally get

$$\begin{aligned}\bar{M}(p) &= \frac{1}{pq_1} [1-2\{\epsilon \exp[-2q_1a] + (1-\epsilon^2)\exp[-2q_1a-2q_2(b-a)] \\ &\quad - \epsilon^2 \exp[-4q_1a] + \dots\}].\end{aligned}\quad (3.8)$$

For the applications we have in mind, we investigate here the case that we may assume

$$\frac{a}{b-a} \delta < 1. \quad (3.9)$$

This means that we restrict ourselves to those cases where

- a) the thickness of the second layer is much larger than that of the first layer and the diffusion constant D_2 is at most of the same order of magnitude as the diffusion constant D_1 .
- b) δ is very small, which corresponds to the fact that the second layer consists of material that is much harder to penetrate than the material the first layer consists of. The second layer may then be of equal thickness as the first one or even slightly thinner.

From (3.8) we see that the term containing the thickness of the second layer $b-a$, is small in comparison with the other terms in case (3.9) is valid, unless ϵ is approximately zero (When $\epsilon=0$, then $\delta=1$ and therefore $D_1=D_2$ as well as $q_1=q_2$. We are then essentially considering only one layer of thickness b).

Assuming nonzero value of ϵ , the effect of the finiteness of the second layer on the solution, as compared with the solution given in the former section, can be seen from transforming inversely term by term the expression

$$\bar{M}(p) = \frac{1}{pq_1} \left[1-2\{\epsilon \exp[-2q_1a] + (1-\epsilon^2)\exp[-2q_2(b-a)]\} \right],$$

which leads to (lit.1)

$$M(t) \approx 2 \sqrt{\frac{D_1 t}{\pi}} - 4 \epsilon \sqrt{\frac{D_1 t}{\pi}} \left(\exp\left[-\frac{a^2}{D_1 t}\right] - a \sqrt{\frac{\pi}{D_1 t}} \operatorname{Erfc} \frac{a}{\sqrt{D_1 t}} \right) - 4(1-\epsilon^2) \sqrt{\frac{D_2 t}{\pi}} \left(\exp\left[-\frac{(b-a)^2}{D_2 t}\right] - (b-a) \sqrt{\frac{\pi}{D_2 t}} \operatorname{Erfc} \frac{b-a}{\sqrt{D_2 t}} \right). \quad (3.10)$$

This result should be compared with the result (2.21). Assuming (3.9) to be valid, in which case the third term in (3.10) is negligible, the result (2.21) of the former section, eventually in the form (2.24), can well be used for the values of t indicated by (2.22) also in the case that the thickness of the second layer is not infinite but much larger than that of the first one ($b \gg a$), or in the case that the finite second layer is much harder to penetrate than the first one ($D_2 \ll D_1$). This is in accordance with what we should expect physically. For large values of t the problem is essentially different from the problem treated in the former section. There the second layer can absorb an unlimited amount of material, which fact is reflected in the first term of (2.24), which can become arbitrarily large with increasing t . Here however the absorption capacity is limited by the finite thickness of the layer. It is remarked, that $M(t)$ denotes the amount of material absorbed per unit area in time t . Therefore $M(t)$ can be at most b , in which case the layers I and II are totally filled with absorbed material. This of course under the assumption that the maximum concentration is 1 in both layers.

When we try to make an expansion of $\bar{M}(p)$ valid for small values of p , similar to the expansion given in (2.25), we obtain

$$\bar{M}(p) \approx \frac{b}{p} + \text{const} + \dots$$

From this formula we can only conclude that $M(t)$ approaches asymptotically the value b for $t \rightarrow \infty$. In order to obtain more information about the behaviour of $M(t)$ for large values of t , it is more appropriate to use the inversion formula for the Laplace transformation, namely

$$M(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} e^{pt} \overline{M(p)} dp. \quad (3.11)$$

This integral may be evaluated by closing the path of integration by a large semicircle which lies at the left hand side of this path and which does not pass through the singularities of the integrand. It is easily seen from (3.5) that this extension of the path of integration does not yield a contribution to the integral and according to Cauchy's theorem its value is the sum of the residues in the poles of the integrand.

In addition to $p=0$ simple poles are found from $\Delta 1 = 0$, which leads to the following equation for the location of the poles:

$$\delta \operatorname{th} q_2(b-a) \operatorname{th} q_1 a + 1 = 0 \quad (3.12)$$

Because (3.12) is a rather complicated transcendental equation for the location of the poles, its roots will only be approximated under the physical assumption (3.9).

Putting

$$p = - \frac{D_2}{(b-a)^2} \sigma^2, \quad (3.13)$$

equation (3.12) becomes

$$\delta \operatorname{tg} \sigma \operatorname{tg} \left(\frac{\delta a \sigma}{b-a} \right) = 1,$$

and we obtain for not too large values of σ the approximate equation

$$\operatorname{tg} \sigma = \frac{b-a}{\delta^2 a \sigma}. \quad (3.14)$$

On account of (3.9) the right hand side of (3.14) is large unless δ has a large value. In that case (3.9) is valid only on account of the fact that the second layer has much larger thickness than the first layer. Physically a large value of δ means that the second layer is less hard to penetrate than the first layer.

We shall only consider those cases in which the right hand side of (3.14) is large and we get the approximate solutions

$$\sigma_k \approx (2k+1) \frac{\pi}{2} \left(1 - \frac{\delta^2 a}{b-a}\right) \quad (k=0,1,2,\dots). \quad (3.15)$$

The use of these approximate solutions is restricted by the fact that we must have

$$\frac{\delta a \sigma}{b-a} < 1 \quad (3.16)$$

and so (3.15) is only valid for moderate values of the integer k . We are dealing with simple poles and the residues of these poles are found by substituting the values of p corresponding with (3.15) into

$$\frac{2D_1}{p} \cdot \frac{\text{ch} q_2(b-a) \text{sh} q_1 a + \delta \text{sh} q_2(b-a) \text{ch} q_1 a}{\frac{d\Delta_1}{dq_1}} \cdot \exp[pt] \quad (3.17)$$

Using (3.13) this expression can be written as

$$\frac{2D_1}{p} \cdot \frac{\cos \sigma \sin \frac{\delta a \sigma}{b-a} + \delta \sin \sigma \cos \frac{\delta a \sigma}{b-a}}{b \cos \sigma \sin \frac{\delta a \sigma}{b-a} + (a\delta + \frac{b-a}{\delta}) \sin \sigma \cos \frac{\sigma a \delta}{b-a}} \cdot \exp\left[-\frac{D_2 \sigma^2 t}{(b-a)^2}\right],$$

and we obtain respectively for $k=0$ and $k=1$ the residues:

$$R_0 = -\frac{8}{\pi^2} [b - (1-\delta^2)a] \exp\left[-\frac{D_2 \pi^2 t}{4(b-a)^2}\right],$$

$$R_1 = -\frac{8}{9\pi^2} [b - (1-\delta^2)a] \exp\left[-\frac{9D_2 \pi^2 t}{4(b-a)^2}\right].$$

Taking only into account the residue at $p=0$ and the residues R_0 and R_1 we obtain for $M(t)$ the approximation

$$M(t) \approx b - \frac{8}{\pi^2} [b - (1-\delta^2)a] \exp\left[-\frac{D_2 \pi^2 t}{4(b-a)^2}\right] - \frac{8}{9\pi^2} [b - (1-\delta^2)a] \exp\left[-\frac{9D_2 \pi^2 t}{4(b-a)^2}\right] \quad (3.18)$$

This result is appropriate for values of t with

$$t > \frac{4(b-a)^2}{D_2 \pi^2} . \quad (3.19)$$

In this case the second term is small in comparison with b (see further the examples given in the last section). The first term, resulting from the pole $p=0$, gives to $M(t)$ a contribution equal to b and this term represents the stationary state.

§ 4. Diffusion in a layered sphere.

Let us now consider a sphere with radius b . Denoting by r the distance from a point to the centre of the sphere and assuming rotational symmetry we distinguish again two regions. The outer shell (I) lies in the region $c < r < b$ and the inner core II in the region $0 \leq r < c$ (see fig. 3).

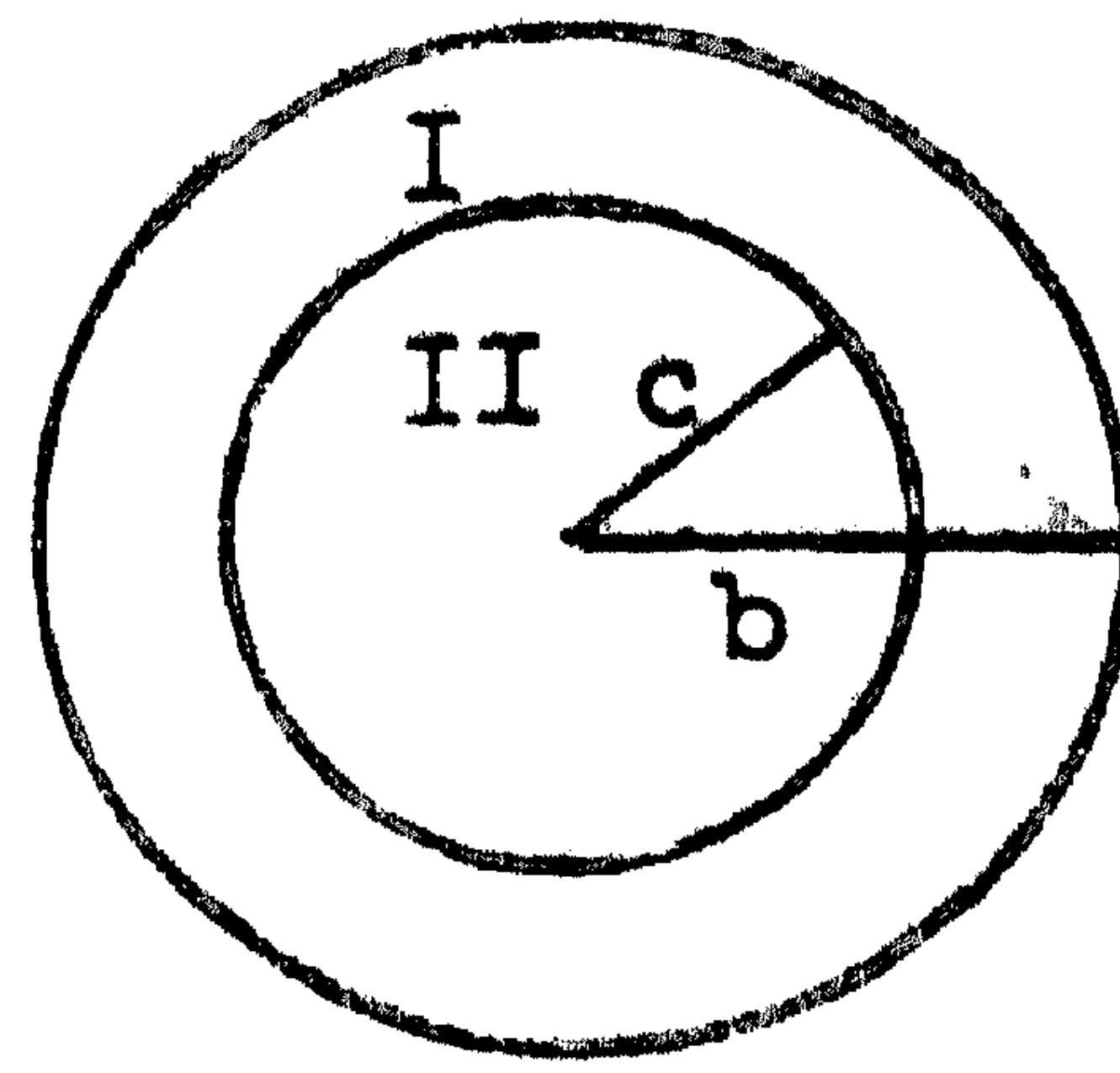


Fig. 3

In region I, with diffusion constant D_1 , the concentration of the material to be absorbed

from the region $r \geq b$ is denoted by $C_1(r, t)$. In region II, with diffusion constant D_2 , the concentration is denoted by $C_2(r, t)$. Using the coordinates r and t , the equations corresponding with (2.1) and (2.2) now become

$$\text{in region I :} \quad D_1 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) C_1(r, t) = \frac{\partial C_1}{\partial t}(r, t), \quad (4.1)$$

$$\text{in region II:} \quad D_2 \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) C_2(r, t) = \frac{\partial C_2}{\partial t}(r, t). \quad (4.2)$$

The initial and boundary conditions are posed on assumptions similar to those used in the former sections. The boundary conditions are

$$\begin{aligned} C_1(b, t) &= 1 && \text{for } 0 \leq t, \\ C_1(c, t) &= C_2(c, t) && \text{for } 0 < t, \\ D_1 \frac{\partial C_1}{\partial r}(c, t) &= D_2 \frac{\partial C_2}{\partial r}(c, t) && \text{for } 0 < t, \\ C_2(0, t) &\text{ is finite } && \text{for } 0 \leq t. \end{aligned} \quad (4.3)$$

The initial conditions are

$$\begin{aligned} C_1(r, 0) &= 0 && \text{for } c \leq r < b, \\ \text{and} \quad C_2(r, 0) &= 0 && \text{for } 0 \leq r \leq c. \end{aligned} \quad (4.4)$$

If we put

$$\begin{aligned} E_1(r,t) &= r C_1(r,t), \\ \text{and} \quad E_2(r,t) &= r C_2(r,t), \end{aligned} \quad (4.5)$$

the differential equations (4.1) and (4.2) become

$$D_1 \frac{\partial^2}{\partial r^2} E_1 = \frac{\partial}{\partial t} E_1 \quad \text{and} \quad D_2 \frac{\partial^2}{\partial r^2} E_2 = \frac{\partial}{\partial t} E_2, \quad (4.6)$$

with the initial conditions

$$\begin{aligned} E_1(r,0) &= 0 & \text{for } c \leq r < b, \\ \text{and} \quad E_2(r,0) &= 0 & \text{for } 0 \leq r \leq c. \end{aligned} \quad (4.7)$$

and the boundary conditions

$$\begin{aligned} E_1(b,t) &= b & \text{for } 0 \leq t, \\ E_1(c,t) &= E_2(c,t) & \text{for } 0 < t, \end{aligned} \quad (4.8)$$

$$D_1 \left\{ r \frac{\partial E_1}{\partial r} - E_1 \right\} = D_2 \left\{ r \frac{\partial E_1}{\partial r} - E_2 \right\} \quad \text{for } r = c \text{ and } 0 < t,$$

$$E_2(0,t) = 0 \quad \text{for } 0 \leq t.$$

Laplace transformation of (4.6), using (4.7) and the substitution (2.14), leads to

$$\frac{\partial^2 \bar{E}_1}{\partial r^2}(r,p) = q_1^2 \bar{E}_1(r,p) \quad \text{and} \quad \frac{\partial^2 \bar{E}_2}{\partial r^2}(r,p) = q_2^2 \bar{E}_2(r,p) \quad (4.9)$$

with the boundary conditions

$$\bar{E}_1(b,p) = \frac{b}{p},$$

$$\bar{E}_1(c,p) = \bar{E}_2(c,p), \quad (4.10)$$

$$c \frac{\partial \bar{E}_1}{\partial r}(c,p) - \bar{E}_1(c,p) = \delta^2 \left\{ c \frac{\partial \bar{E}_2}{\partial r}(c,p) - \bar{E}_2(c,p) \right\},$$

$$\bar{E}_2(0,p) = 0.$$

The total amount of material absorbed by the sphere in time t is

$$M(t) = 4\pi b^2 \int_0^t D_1 \frac{\partial C_1}{\partial r} (b, \tau) d\tau. \quad (4.11)$$

Hence the Laplace transform of $M(t)$ is

$$\bar{M}(p) = 4\pi \frac{D_1}{p} \left[b \frac{\partial \bar{E}_1}{\partial r} (b, p) - \bar{E}_1(b, p) \right]. \quad (4.12)$$

As in the foregoing sections the general solution of the equations (4.9) is given by

$$\begin{aligned} \bar{E}_1(r, p) &= A_1 \operatorname{ch} q_1(r-c) + B_1 \operatorname{sh} q_1(r-c), \\ \bar{E}_2(r, p) &= A_2 \operatorname{ch} q_2(c-r) + B_2 \operatorname{sh} q_2(c-r). \end{aligned} \quad (4.13)$$

and

By aid of (4.10) we can find the coefficients A_1 , B_1 , A_2 and B_2 . This yields for $\bar{E}_1(r, p)$ the expression

$$\begin{aligned} \bar{E}_1(r, p) &= \frac{b}{p\Delta_2} \{ cq_1 \operatorname{sh} q_2 c \operatorname{ch} q_1(r-c) + (1-\delta^2) \operatorname{sh} q_2 c \operatorname{sh} q_1(r-c) + \\ &\quad + cq_1 \delta \operatorname{ch} q_2 c \operatorname{sh} q_1(r-c) \}, \end{aligned} \quad (4.14)$$

with

$$\Delta_2 = cq_1 \operatorname{sh} q_2 c + (1-\delta^2) \operatorname{sh} q_2 c \operatorname{sh} q_1 a + cq_1 \delta \operatorname{sh} q_1 a \operatorname{ch} q_2 c, \quad (4.15)$$

and $a = b-c$.

Substituting (4.14) in (4.12) we obtain

$$\begin{aligned} \bar{M}(p) &= \frac{4\pi b D_1}{p^2 \Delta_2} \left[\{ (bcq_1^2 - 1 + \delta^2) \operatorname{sh} q_2 c - cq_1 \delta \operatorname{ch} q_2 c \} \operatorname{sh} q_1 a + \right. \\ &\quad \left. + \{ (aq_1 - bq_1 \delta^2) \operatorname{sh} q_2 c + bcq_1^2 \delta \operatorname{ch} q_2 c \} \operatorname{ch} q_1 a \right]. \end{aligned} \quad (4.16)$$

An expansion of $\bar{M}(p)$ similar to the expansion given in (2.19) and (3.8) could be given. However, because in the applications we have in mind the radius b is usually extremely small, the resulting expansion

of $M(t)$ is in most cases only useful for a comparatively short time interval following the start of the diffusion process. We therefore only calculate an expansion of $M(t)$, useful for large values of t . For reasons similar to those given in connection with the corresponding problem in the former section we apply the method of residues. The pole $p=0$ again gives the state of saturation, i.e. $M(t) = \frac{4}{3} \pi b^3$. The residues in the other poles are found in a way, completely similar to that in section 3. We therefore cut the lengthy but rather trivial calculations short. Having in mind applications where the inner core is the main bulk of the sphere's material and consists of harder material than the outer shell, so that δ is smaller than 1, we assume

$$\frac{a}{c} \ll 1 \quad \text{and} \quad \delta < 1. \quad (4.17)$$

The location of the first pole, to be obtained from $\Delta_2 = 0$, is solved by approximation. In

$$cq_1 \operatorname{th} q_2 c \operatorname{ch} q_1 a + (1-\delta^2) \operatorname{th} q_2 c \operatorname{sh} q_1 a + cq_1 \delta \operatorname{sh} q_1 a = 0 \quad (4.18)$$

we put, similarly as in (3.13)

$$p = -\frac{D_2}{c^2} \sigma^2. \quad (4.19)$$

Due to (4.17) equation (4.18) may be reduced to

$$\operatorname{tg} \sigma \left\{ \delta \sigma + (1-\delta^2) \frac{\delta a \sigma}{c} \right\} = -\frac{\delta^3 a \sigma^2}{c}. \quad (4.20)$$

or

$$\operatorname{tg} \sigma = -\frac{\delta^2 a \sigma}{c}$$

so that

$$\sigma = \pi \left(1 - \frac{\delta^2 a}{c} \right). \quad (4.21)$$

Using (4.16) and switching from hyperbolic functions of q_1 and q_2 to goniometric functions of σ by means of (4.19) we find for the residue in $\sigma = \pi(1 - \frac{\delta^2 a}{c})$

$$- \frac{8c^3}{\pi} \left(1 + \frac{\delta^2 a}{c}\right) \exp \left[- \frac{D_2 \pi^2 t}{c^2} \right]. \quad (4.22)$$

The total amount of material absorbed in time t is therefore approximately given by

$$M(t) \approx \frac{4}{3} \pi b^3 - \frac{8c^3}{\pi} \left(1 + \frac{\delta^2 a}{c}\right) \exp \left[- \frac{D_2 \pi^2 t}{c^2} \right]. \quad (4.23)$$

This result may be used for values of t such that the second term is small in comparison with the first one, i.e. for

$$t \gg \frac{c^2}{D_2 \pi^2}, \quad (4.24)$$

(see further the examples in section 5).

§ 5. Application and discussion of the result.

As has already been remarked in the introduction, the formulae, derived for the function $M(t)$, may be used for the determination of the diffusion-constants D_1 and D_2 , when the total amount of absorbed material can be measured.

The theory of sections 2 and 3 can be applied if we consider e.g. sea-water containing radioactive material which is absorbed by a sand-mud layer at the bottom of the sea. The theory of section 4 may be used, if we investigate e.g. a suspension of mud particles with a hard core, which absorb radioactive material, present in the suspension.

The amount of absorbed radioactive material may be determined by aid of Geiger-Müller counters.

If (2.24) or (3.10) are valid, then the direction of the tangent of the $(M(t), \sqrt{t})$ diagram for small values of t gives a value for $2 \sqrt{\frac{D_1}{\pi}}$, and therefore a value for D_1 . Noting that for positive ϵ ($\delta < 1$)

$$\log \left\{ \frac{2 \sqrt{\frac{D_1 t}{\pi}} - M(t)}{\frac{D_1 t}{\frac{a^2}{2}}} \right\} = - \frac{a^2}{D_1 t} + \log \epsilon,$$

$\log \epsilon$ can be determined by the point of intersection of the tangent of the $(\log \{...\}, \frac{1}{t})$ diagram, at small values of t , with the $\log \{...\}$ -axis. From the values for ϵ and D_1 we can calculate D_2 .

If (2.26) is valid, the direction of the tangent of the $(M(t), \sqrt{t})$ diagram for large values of t gives a value for D_2 . The point of intersection of the tangent with the $M(t)$ -axis gives a value for $a(1-\delta^2) = a(1-\frac{D_2}{D_1})$, so that with the found value of D_2 the value of

D_1 can be determined.

If (3.18) or (4.23) is valid, D_1 and D_2 can be calculated in an analogous way from a $(\log \{b-M(t)\}, t)$ resp. $(\log \{\frac{4}{3} \pi b^3 - M(t)\}, t)$ diagram. To illustrate the effect of conditions like (2.22), (3.19) and (4.24) on the applicability of the obtained results we indicate for 3 examples

the time intervals for which the use of the formulae is justified. These examples are the following

- A: $a = 10^{-5}$ cm, $b = 10^{-3}$ cm, $D_1 = 10^{-6}$ cm²/sec, $D_2 = 10^{-10}$ cm²/sec.
 B: $a = 10^{-3}$ cm, $b = 10^{-1}$ cm, $D_1 = 10^{-6}$ cm²/sec, $D_2 = 10^{-10}$ cm²/sec.
 C: $a = 1$ cm, $b = 100$ cm, $D_1 = 10^{-6}$ cm²/sec, $D_2 = 10^{-5}$ cm²/sec.

The ranges for which the formulae (2.24), (2.26), (3.10), (3.18) and (4.23) are applicable are given in the following table

	A	B	C
(2.24)	$t \leq 5 \cdot 10^{-5}$ sec	$t \leq \frac{1}{2}$ sec	$t \leq 6$ days
(2.26)	$t \geq 1\frac{1}{2}$ minute	$t \geq 12$ days	$t \geq 30$ years
(3.10)	as (2.24)	as (2.24)	as (2.24)
(3.18)	$t \geq 2$ hours	$t \geq 3$ years	$t \geq 30$ years
(4.23)	$t \geq \frac{1}{2}$ hour	$t \geq 7$ years	.

We see that for an ~~experimenter~~ in case A only formulae (2.26), (3.18) and (4.23) are of importance. In case B only (2.26), and in case C only (2.24) and (3.10) are of any use.

In praxis of course, one must assume validity for a certain time interval and in principle one must check the assumed validity afterwards with the calculated diffusion coefficients. Fortunately the diagrams are approximately straight lines in the time intervals where application is allowed, so that these intervals are easily recognized in the diagrams. Altogether the use of the formulae is rather restricted.

We finally want to point out two major further restrictions on the applicability of the theory, that are of physical nature. In the first place the boundary condition that the concentration of the material that is absorbed is constant on the surface of the absorbing medium, is rather often not in agreement with the actual situation. In the second place the diffusion coefficients need not be constant even for rather homogeneous layers.

Literature.

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