DETERMINATION OF THE DIMENSIONS OF CAPILLARIES IN POROUS MATERIAL BY DIFFUSION

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Starting from the exact solution of FICK's equation, the theoretical time dependence of the conductivity of an electrolyte diffusing into a capillary was determined. In capillaries of unknown cross-section and length the changes in time of the conductivity can be measured. By comparing the theoretical and measured conductivities, a method is given for determining the dimensions of the capillary.

FICK's differential equations for diffusion are nowadays considered as classical laws, despite the fact that this description proved to be only approximative in modern irreversible thermodynamics. The physical problems arising in connection with these equations are of steadily increasing importance, as their mathematical background has been well elaborated.

There are different experimental ways of investigating porous material [1]; of these, the method based on diffusion is especially important. Therefore the discussion of problems of diffusion based on exact solution and fitted to the experimental conditions is of great importance from the point of view of applications. Let us consider first the problem of diffusion.

Putting a prism of quadratical cross-section with open end faces, filled with a solvent of an electrolyte, into a vessel filled with an electrolyte of concentration c_0 and diffusion constant D, at this moment $t=0$ the electrolyte begins to diffuse into the interior of the prism trough the open end faces, and after a sufficiently long time the differences in concentration will be balanced. If the volume of the vessel is great enough compared with that of the prism then, after reaching the equilibrium, the concentration will be c_0 everywhere.

For considering first the well-known question [2] concerning the changes in electrolyte concentration in the interior of the prism as a function of time and place, let us take a system of coordinates according to Fig. 1 and solve FICK's equation

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) \qquad (1)$$

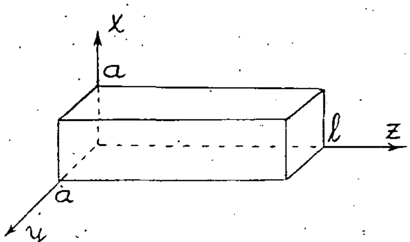

Fig. 1

with suitable conditions. We have to find a solution $c(x, y, z, t)$ with prescribed initial and boundary conditions. The initial condition is that at $t=0$ the concentration is $c=0$ in the interior of the prism and $c=c_0$ at its end faces $z=0$ and $z=l$. The boundary conditions are as follows: the concentration at the end faces $z=0$ and $z=l$ is always $c=c_0$, and at the side faces let it be always given by

$$\left(\frac{\partial c}{\partial y}\right)_{y=0,\,a} = 0, \quad \left(\frac{\partial c}{\partial x}\right)_{x=0,\,a} = 0. \tag{2}$$

These conditions, however, do not express the requirement that at $t=\infty$, $c=c_0$ everywhere. To satisfy the latter, let us consider the function

$$\vartheta = \frac{c_0 - c}{c_0} \tag{3}$$

instead of c. It is easy to see that ϑ satisfies the same differential equation as c, and the values of ϑ will be $\vartheta=1$ for $c=0$ and $\vartheta=0$ for $c=c_0$. Let ϑ be determined in the product form $T(t)X(x)Y(y)Z(z)$; in this case the differential equation will be separable. Denoting by α the separation constant, the part of the equation containing the time, and its solution will be

$$\frac{dT}{dt} = \alpha DT, \quad T(t) = e^{\alpha Dt}, \tag{4}$$

respectively. The condition $\vartheta=0$ prescibed for $t=\infty$ will be fulfilled if $\alpha<0$, therefore let be $\alpha = -k^2$. Using the decomposition $k^2 = k_x^2 + k_y^2 + k_z^2$ the equations

$$\frac{d^2X}{dx^2} = -k_x^2 X, \quad \frac{d^2Y}{dy^2} = -k_y^2 Y, \quad \frac{d^2Z}{dz^2} = -k_z^2 Z \tag{5}$$

will be obtained. The solution of the third of these equations, satisfying the boundary conditions $Z(0)=Z(l)=0$, is

$$B_m \sin k_z z, \; k_z = \frac{m\pi}{l}, \quad m = 0, 1, 2, \ldots \tag{6}$$

with every B_m. The B_m-s are to be determined so as to satisfy the initial condition $\vartheta=0$ for the values $0<z<l$:

$$\sum_m B_m \sin \frac{m\pi}{l} z = 1. \tag{7}$$

From this we obtain: $B_m=0$ for even m, and $B_m = \dfrac{4}{m\pi}$ for odd m. Thus with $m = 2n+1$ the solution will be

$$Z(z) = \sum_{n=0}^{\infty} \frac{4}{2n+1} \sin \pi \frac{2n+1}{l} z. \tag{8}$$

Similarly, with the boundary conditions (2) in mind

$$X = 1, \quad Y = 1 \tag{9}$$

can be obtained. Returning to c, the function

$$c = c_0\left(1 - \sum_{n=0}^{\infty} \frac{4}{(2n+1)\pi} e^{-\left(\frac{2n+1}{l}\right)^2 Dt} \sin\frac{2n+1}{l}\pi z\right) \tag{10}$$

satisfies all conditions prescribed.

Let us consider Eq. (10) valid for tubes of the same cross-section q everywhere. Let two vessels of great volume, permitting to measure the conductivity, be connected by such a tube. Let us calculate with a conductivity σ, written in the form

$$\sigma = \sigma_0 \frac{c}{c_0}, \tag{11}$$

where σ_0 is the conductivity of the electrolyte of concentration c_0. At $t=0$ there is no electrolyte in the tube, therefore in this moment $\sigma=0$. To determine the function $\sigma(t)$ let the tube be divided into discs of thickness dz; than the tube can be considered as consisting of resistances in series. The total resistance R of the tube of length l will be

$$R = \int_0^l \frac{1}{\sigma}\frac{dz}{q} \tag{12}$$

i.e. using Eqs. (10) and (11)

$$R = \frac{c_0}{\sigma_0 q}\int_0^l \frac{dz}{c(z,t)} \equiv R(l,t). \tag{13}$$

If we begin to measure at a time t_0, for which

$$D\left(\frac{\pi}{l}\right)^2 t_0 \geqq 1 \tag{14}$$

than the second term of the sum in Eq. (10) will be three orders of magnitude less than the first term, thus it can be neglected. The rest can be written as

$$R(l,t) = \frac{1}{\sigma_0 q}\int_0^l \frac{dz}{1 - \frac{4}{\pi} e^{-\left(\frac{\pi}{l}\right)^2 Dt} \sin\frac{\pi}{l} z}. \tag{15}$$

With the notation

$$A = \frac{4}{\pi} e^{-\left(\frac{\pi}{l}\right)^2 Dt},$$

after integrating, we obtain the result

$$R(l,t) = \frac{4l}{\pi\sigma_0 q}\frac{1}{\sqrt{1-A^2}} \operatorname{arc\,tg}\frac{\sqrt{1-A^2}}{1-A}. \tag{16}$$

From this, for $t=\infty$, the natural value

$$R(l,\infty) = \frac{l}{\sigma_0 q} \tag{17}$$

can be obtained. The inverse of Eqs. (15) and (16) gives the conductivity.

The resistance expressed by Eq. (16) is an intricated function of time, therefore it cannot be directly used in applications, especially for studying porous materials. The quantity defined by

$$\sigma_r(t) \equiv \frac{\sigma(l, t)}{\sigma(l, \infty)} \tag{18}$$

depends on time through A, but it is independent of q. Let us introduce a new variable with the definition

$$\tau = \left(\frac{\pi}{l}\right)^2 Dt. \tag{19}$$

Some values of the function $\sigma_r(\tau)$ are listed in Table I. Finding in Table I a given value of σ_r' (e.g. about 0,8) and reading the corresponding τ', let us determine the point $\sigma_r = \sigma_r'$ of the measured σ_r curve and read the corresponding time t'. If we know the diffusion constant D of the electrolyte, l can be calculated from Eq. (19). From this, using Eq. (17), q can be obtained.

Table I

τ	σ_r	τ	σ_r
1.000	0.5795	1.709	0.8051
1.034	0.5928	1.781	0.8201
1.070	0.6094	1.858	0.8339
1.107	0.6256	1.942	0.8479
1.146	0.6416	2.033	0.8615
1.186	0.6574	2.132	0.8752
1.227	0.6731	2.244	0.8887
1.271	0.6883	2.369	0.9021
1.316	0.7037	2.512	0.9156
1.364	0.7191	2.679	0.9283
1.414	0.7338	2.880	0.9419
1.467	0.7485	3,131	0.9551
1.522	0.7630	3.468	0.9680
1.581	0.7776	3.978	0.9810
1.643	0.7918	5.077	0.9938

References

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[2] *Frank, Ph., R. v. Mises:* Die Differential- und Integralgleichungen der Mechanik und Physik, II. Teil, Vieweg, Braunschweig, (1961).

ОПРЕДЕЛЕНИЕ РАЗМЕРОВ КАПИЛЛЯРОВ В ПОРИСТЫХ МАТЕРИАЛАХ ДИФФУЗИОННЫМ МЕТОДОМ

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Исходя из решения уравнения диффузии Фика, мы определили временную зависимость проводимости электролита диффундирущего в узкий капилляр. В капилляре неизвестного поперечного сечения и длины временное изменение проводимости измеримо. Сравнивая теоретическую и измеряемую проводимости мы задали метод для определения размеров капилляра.