

EXPERIMENTAL METHODS OF STUDYING THE DIFFUSION OF RADIOACTIVE GASES IN SOLIDS.

IV. A MULTIFILM FORM OF THE PERMEABILITY METHOD

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A method is described for conducting the experiment in the multifilm form of the permeability method. The phenomenological theory and the data-processing methods are considered. Expressions are derived for the concentration profile on the basis of radioactive decay and accumulation. The method has been tested on the diffusion of radon and tritium-labeled water in irradiated low-density polyethylene. It is found that the diffusion of radon in unirradiated low-density polyethylene follows the usual diffusion mechanism. On irradiation, a concentration dependence of the diffusion coefficient is found, which becomes more pronounced with dose. In the case of water-vapor diffusion, there is a marked concentration dependence of the diffusion coefficient, and boundary conditions of the third kind apply at the exit surface of the membrane. In this system, it is incorrect to represent the specimen as a stack of membranes.

The permeability method involves examining the diffusion of the gas through a thin specimen [1]. During the experiment, one monitors the processes in the gas phase at the entrance or exit to the membrane. However, in some cases it is necessary to examine the concentration distribution over the thickness, as when there is a concentration dependence of the diffusion coefficient, or diffusion in a compound medium or unsymmetrical membrane. The small thicknesses of membranes do not allow one to use a method such as longitudinal sectioning or removing layers. Therefore, the specimen is produced as a stack of extremely thin films. After the experiment, the stack is removed and the amount of material in each film is measured. One usually [2] examines the steady-state distribution over the thickness, while the amount of absorbed material is determined by weighing. Unfortunately, gravimetric methods are of low sensitivity. It may be expected that this method can be improved by using tagged atoms, since radiochemical methods are of high sensitivity and enable one to monitor the diffusion directly on the solid.

Here we consider radiochemical methods in the multifilm form of the permeability method. The method has been applied to the diffusion of a radioactive inert gas (radon, ^{222}Rn) and the vapor of tritium-labeled water in irradiated low-density polyethylene.

THEORY

Classical Diffusion. In the permeability method one examines the concentration distribution over the thickness of planar membrane (curve 2 in Fig. 1A), which is described by the following equation [1]:

$$C(x, t) = \frac{C_0 x}{H} + \frac{2C_0}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi x}{H} \exp\{-n^2 B t\} = C_0 \left[\operatorname{erfc} \frac{x}{2\sqrt{Dt}} \sum_{n=1}^{\infty} \left(\operatorname{erfc} \frac{2nH+x}{2\sqrt{Dt}} - \operatorname{erfc} \frac{2nH-x}{2\sqrt{Dt}} \right) \right], \quad (1)$$

where C_0 is the concentration at the input side of the membrane ($x = H$), x is coordinate, t is time, H is membrane thickness, $B = \pi^2 D/H^2$, and D is diffusion coefficient.

The series on the left in (1) converges rapidly for large times, while that on the right converges rapidly for small ones.

In deriving (1) it has been assumed that D is independent of time, concentration, and coordinate, and also that the membrane at the initial instant is free from the gas and that boundary conditions of the first kind apply at the surface.

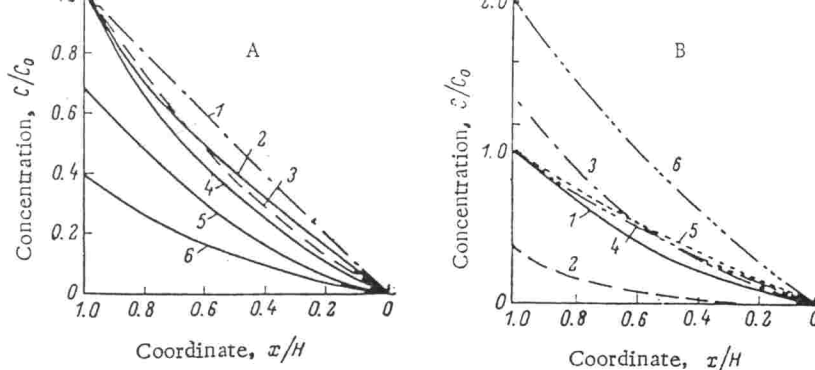


Fig. 1. Concentration diffusions for a diffusing radioactive isotope and decay products: A) distribution of the radioactive-gas concentration over the thickness ($D = 10^{-8}$ cm²/sec, $H = 0.1$ cm): 1) $\lambda = 0$, $t = 5 \times 10^5$ sec (steady state); 2) $\lambda = 0$ ($t = \theta = 1.667 \times 10^5$ sec); 3) $\lambda = 2.1 \times 10^{-6}$ sec⁻¹, $t = 5 \times 10^5$ sec (steady state); 4) $\lambda = 2.1 \times 10^{-6}$ sec⁻¹, $t = 5 \times 10^5$ sec (allowance for decay in the source); 5) $\lambda = 2.1 \times 10^{-6}$ sec⁻¹, $t = \theta = 1.667 \times 10^5$ sec; 6) $\lambda = 2.1 \times 10^{-6}$ sec⁻¹, $t = 1.667 \times 10^5$ sec (allowance for decay in reservoir). Here $\theta = H^2/6$ is the diffusion delay. B) Distributions of the diffusing isotope and immobile decay products (the comparatively short-lived isotope diffuses, while the long-lived daughter isotope is immobile), $D_p = 10^{-8}$ cm²/sec, $D_d = 0$, $\lambda_p = 2.1 \times 10^{-6}$ sec⁻¹, $\lambda_d \rightarrow \infty$, $H = 0.1$ cm: 1) $t = \theta = 1.667 \times 10^5$ sec, mobile phase; 2) $t = \theta = 1.667 \times 10^5$ sec, immobile phase; 3) $t = \theta = 1.667 \times 10^5$ sec, sum of the mobile and immobile phases; 4) $t = 5 \times 10^5$ sec, steady state, mobile phase; 5) $t = 5 \times 10^5$ sec, steady state, immobile phase; 6) $t = 5 \times 10^5$ sec, steady state, sum of the mobile and immobile phases.

In the steady state at $t \rightarrow \infty$, one has a rectilinear concentration distribution $C(x, t)$ ($C_0 = x/H$, curve 1 of Fig. 1A).

The results from the multifilm form of the permeability method are processed by techniques analogous to the method of removing layers, i.e., either in differential form, where one measures the amount of the substance in each layer, or in integral form, where one measures the amount of material in the specimen remaining after removing layer i . The latter technique is usually employed when working with fairly hard radiation.

The mean concentration of the material in layer $h_i = x_{i+1} - x_i$ (differential form) is

$$\bar{C}_i = \int_{x_i}^{x_{i+1}} C(x, t) \frac{dx}{x_{i+1} - x_i} = \frac{C_0}{x_{i+1} - x_i} \left[\frac{x_{i+1}^2 - x_i^2}{2H} + \frac{2C_0H}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \left(\cos \frac{n\pi x_{i+1}}{H} - \cos \frac{n\pi x_i}{H} \right) \exp\{-n^2 Bt\} \right] = \frac{C_0}{x_{i+1} - x_i} \left[\frac{x_{i+1}^2 - x_i^2}{2H_1} - \frac{4C_0H}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \sin \frac{n\pi(x_{i+1} + x_i)}{2H} \sin \frac{n\pi(x_{i+1} - x_i)}{2H} \exp\{-n^2 Bt\} \right]. \quad (2)$$

The following is the amount of gas in the layer from $x = x_i$ to $x = H$ (integral form):

$$m_i = \frac{C_0}{H - x_i} \left(\left[\frac{H^2 - x_i^2}{2H} + \frac{2C_0H}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \left\{ (-1)^n - \cos \frac{n\pi x_i}{H} \right\} \exp\{-n^2 Bt\} \right] \right). \quad (3)$$

It is clear that

$$\sum_{i=1}^n (x_{i+1} - x_i) \bar{C}_i = m_i. \quad (4)$$

Diffusion in the Presence of Radioactive Decay. The use of radioactive indicators with comparatively short half-lives requires some modification of the phenomenological theory to

allow for radioactive decay. Similar equations are encountered in diffusion accompanied by a first-order chemical reaction, diffusion in the presence of traps with constant retention, etc.

On the basis of the decomposition (or chemical reaction of first order), we rewrite the equation for Fick's second law as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \lambda C, \quad (5)$$

where λ is the radioactive-decay constant (rate constant of reaction, trapping probability, etc.). Then the following is the concentration distribution over the thickness:

$$\begin{aligned} C(x, t) &= \frac{C_0 x}{H} + \frac{2C_0 \lambda}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n \sin \frac{n\pi x}{H}}{n [n^2 B + \lambda]} [1 - \exp\{-(n^2 B + \lambda)t\}] + \frac{2C_0}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi x}{H} \exp\{-(n^2 B + \lambda)t\} = \\ &= \frac{C_0 \operatorname{sh} \sqrt{\lambda_1 D} (H-x)}{\operatorname{sh} \sqrt{\lambda_1 D} \cdot H} - \frac{2C_0 \pi}{H^2} \sum_{n=1}^{\infty} \frac{(-1)^n \cdot n}{n^2 B + \lambda} \sin \frac{n\pi x}{H} \exp\{-(n^2 B + \lambda)t\}. \end{aligned} \quad (6)$$

Figure 1A shows the distribution of the concentration over the thickness and its variation with time in the presence of radioactive decay; in that case, one does not have a rectangular distribution in the steady state. The steady-state distribution is attained the more rapidly the larger λ . The decay in the source has a particularly marked effect on the form of the curves.

Diffusion in the Presence of Decay and Accumulation. We now consider the presence of successive decay chains. This situation occurs, for example, in examining the permeability to radon. When the diffusion is accompanied by the accumulation of radioactive decay products, the concentration distribution over the thickness will have two parts: a mobile one (due to radon) and an immobile one (radioactive decay products).

Let $A_1 \xrightarrow{\lambda_1} A_2 \xrightarrow{\lambda_2}$, where $\lambda_1 \gg \lambda_2$, $D_1 \gg D_2$; then

$$C_{A_2} = e^{-\lambda_2 t} \int_0^t \lambda_1 C_{A_1} e^{\lambda_2 t} dt, \quad (7)$$

and if $\lambda_2 \rightarrow 0$, then the number of practically immobile daughter-isotope atoms is

$$\begin{aligned} C_A &= C_{A_1}^0 \lambda_1 \left[\frac{x}{H} t + 0.6366 (1 + \lambda_1 t) \sum_{n=1}^{\infty} \frac{(-1)^n \sin \frac{n\pi x}{H}}{n (n^2 B + \lambda_1)} - 0.6366 \lambda_1 \sum_{n=1}^{\infty} \frac{(-1)^n \sin \frac{n\pi x}{H}}{n [n^2 B + \lambda_1]^2} + \right. \\ &\left. + 0.6366 \lambda_1 \sum_{n=1}^{\infty} \frac{(-1)^n \sin \frac{n\pi x}{H} \exp\{-(n^2 B + \lambda_1)t\}}{(n^2 B + \lambda_1)^2} - 0.6366 \sum_{n=1}^{\infty} \frac{(-1)^n \sin \frac{n\pi x}{H} \exp\{-(n^2 B + \lambda_1)t\}}{n (n^2 B + \lambda_1)} \right]. \end{aligned} \quad (8)$$

The following is the number of mobile parent atoms for $t \rightarrow \infty$:

$$C_{A_1} = C_{A_1}^0 \left(\frac{x}{H} + 0.6366 \lambda_1 \sum_{n=1}^{\infty} \frac{(-1)^n \sin \frac{n\pi x}{H}}{n [n^2 B + \lambda_1]} \right). \quad (9)$$

Figure 1B shows the concentration distribution over the thickness for the mobile and immobile species. It is clear that the decay and accumulation distort the form of the curves. Model calculations from these expressions allow one to choose the working conditions (diffusion time, temperature, and specimen thickness) to be such that the decay and accumulation can be neglected.

EXPERIMENTAL METHOD AND DATA PROCESSING

We used low-density polyethylene with a melting point of 116-120° and a density of 0.915 g/cm³. Films of thickness 80-100 μm were made by pressing the molten material. Irradiation to a dose of 1 MGy was performed in air with the γ rays of ⁶⁰Co with an RKHM- γ -20 apparatus at a dose rate of 0.03 MGy/h.

The membrane was simulated as a stack of thin films in contact in a thermostatic diffusion cell. The membrane was outgassed before the experiment and brought to a given temperature before the gas was admitted to the source vessel. The ^{222}Rn source was provided by ^{226}Ra adsorbed on zeolite, the HTO source was a solution of a salt of appropriate concentration to provide the working partial pressure. The receiver was continuously flushed with a vigorous stream of air. At the end of the diffusion experiment, the cell was cooled rapidly to stop the diffusion, the gas was removed from the source vessel, and the stack was transferred to counting apparatus. The film temperature was that of liquid nitrogen during the measurement. Usually, the first film on the input side was discarded and did not participate in the measurement.

When radon is used, one can measure directly either the α activity of the radon or the γ activity of the decay products.

If an α detector is employed, one measures the activity of each film. Note that the film thickness h must be chosen in accordance with the theory applicable to thick α -ray sources:

$$h = \frac{2R\alpha}{e} = 0.75R\alpha,$$

where $R\alpha$ is the α -ray range in polyethylene. The total number of α particles emerging from the upper surface is [3]

$$N_1 = \int_0^h \frac{1}{2} \left(1 - \frac{x}{R\alpha}\right) n_\alpha C(x) dx, \quad (10)$$

where n_α is the total number of α -particle emitted and $C(x)$ is the concentration distribution over the thickness of a layer of thickness h arising from diffusion. The number of α particles emerging from the lower surface of the film is

$$N_2 = \int_0^h \frac{1}{2} \left(1 - \frac{h-x}{R\alpha}\right) n_\alpha C(x) dx. \quad (11)$$

In principle, the activity may be measured either on one side or simultaneously from both sides with two counters. When the count is performed from one side, one can relate the count rate to the activity in accordance with (10) and (11) if one knows $C(x)$, which is the object of the investigation. However, the position is substantially simplified if the measurement is made simultaneously from the two sides.

The total number of α particles emerging from both sides is

$$N = N_1 + N_2 = \int_0^h \frac{1}{2} n_\alpha \left(2 - \frac{h}{R\alpha}\right) C(x) dx = n_\alpha \left(1 - \frac{h}{2R\alpha}\right). \quad (12)$$

It follows from (12) that the total yield of α particles is independent of the depth distribution of the activity, being solely determined by the total activity of the film and the ratio of thickness to the α -particle range.

For each film we measured the count rate on both sides, and from (12) we found n_α , which was normalized to the film thickness. The diffusion coefficient was calculated from the C_1-x relationship.

The measurements on the γ activity of the decay products were made after the attainment of radioactive equilibrium between the radon and the products (at 3 h after the end of the diffusion experiment). The measurements were made by the differential and integral techniques. In the latter case, we initially measured the total activity of the stack, and then the residual activity after removing layer 1. The diffusion coefficient was calculated from $\Xi_1(x)$; the β activity of tritium was measured on a MARK-2 liquid-scintillation counter. A disadvantage of this method is that the polymer swells in toluene, which leads to the release of water and thus to drift in the count rate during the measurement. Therefore, the activity is usually measured by autoradiography. For this purpose the membrane is laid out on a photographic plate with a nuclear emulsion and covered with another such plate. The

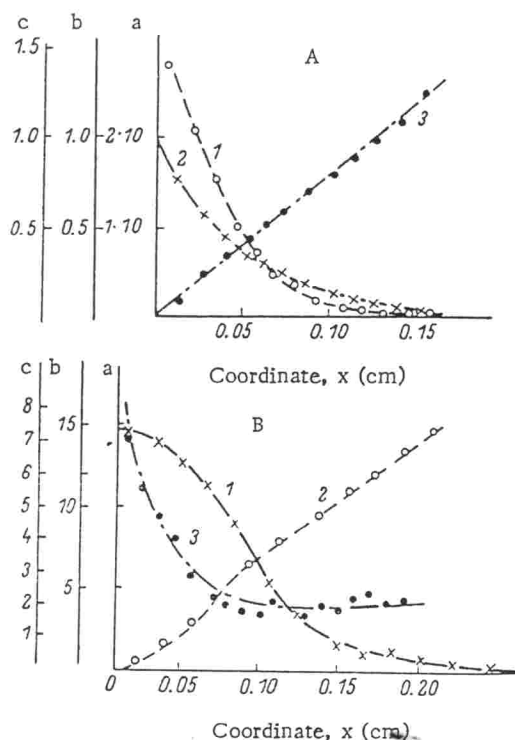


Fig. 2. Concentration distribution for radon in low-density polyethylene: A) ordinates: a) concentration C (count/sec · cm); b) integral concentration distribution M (arbitrary units); c) integral concentration distribution on functional scale F ; B), ordinates: a) integral concentration distribution on functional scale F ; b) concentration C (count/sec · cm) $\times 10^{-4}$; c) diffusion coefficient $D \times 10^7$ cm²/sec; A) unirradiated polyethylene ($t = 50^\circ\text{C}$, diffusion time 1.08×10^4 sec); 1) concentration distribution; 2) integral concentration distribution; 3) integral concentration distribution on functional scale; B) polyethylene irradiated to a dose of 1 MGy ($T = 80^\circ\text{C}$, diffusion time 1.8×10^3 sec): 1) concentration distribution; 2) integral concentration distribution constructed on functional scale; 3) coordinate dependence of diffusion coefficient.

autoradiograms after exposure and development are photometered. The data give $\bar{C}_1 - x$, and at the same time one monitors the homogeneity of the diffusion over the surface and volume.

Data processing from the formulas for membranes of finite dimensions represents a serious problem. To facilitate the calculations, we can use the fact that the term with the sum on the right part of (1) can be neglected for small diffusion times. We thus approach diffusion in a semi-infinite medium (this situation is readily approached experimentally by increasing the total thickness of the membrane). Then the concentration distribution [4] takes the form

$$C(x, t) = C_0 \operatorname{erfc}(z/\sqrt{D}), \quad (13)$$

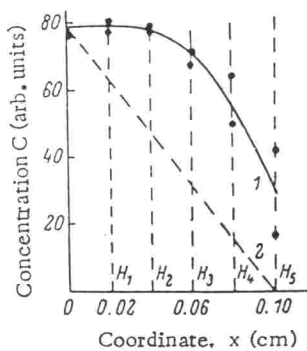


Fig. 3. Concentration distribution for water vapor in irradiated low-density polyethylene (dose 1 MGy, $T = 20^\circ\text{C}$, steady-state diffusion): 1) expected concentration distribution without allowance for concentration dependence of diffusion coefficient; 2) observed water-vapor distribution curve.

where $z = x/2\sqrt{t}$; $\text{erfc}(v) = 1 - \frac{2}{\sqrt{\pi}} \int_v^\infty e^{-u^2} du$.

The amount of diffusing gas (or a quantity proportional to m_i such as the count rate) is described by

$$m_i = \int_{x_i}^{\infty} C(x, t) dx = m_0 i \text{erfc}(z/\sqrt{D}), \quad (14)$$

where $m_0 = 2C_0\sqrt{Dt}$; $i \text{erfc}(v) = \int_v^\infty \text{erfc} u du = \frac{1}{\sqrt{\pi}} e^{-v^2} - v \text{erfc} v$; $v = \frac{z}{\sqrt{D}} = \frac{x}{\sqrt{2Dt}}$.

If $x_1 = 0$, then $m_1 = m_0/\sqrt{\pi}$; the function of [14] normalized to the value of m_1 is

$$m_H = \frac{m_i}{m_1} = \sqrt{\pi} i \text{erfc}(z/\sqrt{D}). \quad (15)$$

We used rectilinear plots to calculate the diffusion coefficient, for which purpose we introduce the function F inverse to $i \text{erfc}$, when

$$F\left(\frac{m_H}{\sqrt{\pi}}\right) = \frac{z_i}{\sqrt{D}} = \frac{1}{2\sqrt{Dt}} x. \quad (16)$$

By least-squares fitting to the linear relationship of (16) it is easy to calculate D and the error of this from the observed values of $N_i/N_1 = m_H$ and z_i ; the method can be used with the deviations of the observed points from the straight line to determine the applicability limits of the mathematical model. The diffusion coefficient is given by

$$D = \frac{1}{4t \tan^2 \alpha}, \quad (17)$$

where t is diffusion time and α is the slope of the straight line.

The correctness of the model can also be judged from the closeness of the correlation coefficient to one.

In the differential form, the planes $x = x_i$ and $x = x_{i+1}$ are used in measuring the mean concentration \bar{C}_i :

$$\bar{C}_i = \int_{x_i}^{x_{i+1}} C(x, t) \frac{dx}{x_{i+1} - x_i} = \frac{m_0}{x_{i+1} - x_i} \left[\text{ierfc}\left(\frac{z_i}{\sqrt{D}}\right) - \text{ierfc}\left(\frac{z_{i+1}}{\sqrt{D}}\right) \right] \quad (18)$$

and

$$\sum_{i=1}^n (x_{i+1} - x_i) \bar{C}_i = m_i,$$

if the summation is carried through to the layer where the concentration $\bar{C}_n = 0$.

In that case one can also use the straight-line diagrams. A disadvantage of the linearization method is the difference in distributions for the random error in the forward and reciprocal functions. Practical computer calculations have shown that it is desirable on using the inverse function to perform a qualitative check on the model and get approximations for the constants, while the final values for the latter are calculated by nonlinear least-squares fitting of the theoretical curve.

These processing algorithms have been implemented in the BEDIF program.* This program processes results obtained by the differential and integral methods to calculate C_0 , the error of this, and the correlation coefficient. If necessary, the program splits up a compound diffusion process into elementary components, i.e., it derives a diffusion-coefficient spectrum.

RESULTS

Figure 2A shows typical observed $C(x)$ and $m(x)$ curves (curves 1 and 2 respectively), which were recorded in the diffusion of radon into unirradiated low-density polyethylene. The total specimen thickness and the diffusion time were chosen such as to guarantee obedience to the boundary conditions for a semi-infinite medium. Curve 3 gives the same data constructed on a linearized scale. The concentration profiles become highly rectilinear (the correlation coefficient $r = 0.99$, which confirms the classical-diffusion hypothesis). Then $D = (3.3 \pm 0.4) \cdot 10^{-7} \text{ cm}^2/\text{sec}$ at 50° .

Above a dose of 0.1 MGy, the concentration profile becomes distorted, and at 1 MGy the radon distribution takes a form characteristic of the case of concentration dependence of the diffusion coefficient [2] (curve 1 of Fig. 2B). In that case, the diffusion coefficient increases with the concentration. This can be represented formally as a coordinate dependence of the diffusion coefficient (curve 3). When one constructs $m(x)$ on a linearized scale, the rectilinear part persists (curve 2) for large x (small C), which gives the diffusion coefficient as $D(0) = (2.7 \pm 0.5) \cdot 10^{-7} \text{ cm}^2/\text{sec}$ at 80°C .

In operating with inert gases (here radon), there are no effects associated with overcoming the boundary between the solid and the gas. The concentration distribution always indicated that boundary conditions of the first kind apply. Therefore, it is correct to represent a compact specimen as a stack of thin films in that case. Additional evidence for this is agreement over the diffusion coefficients calculated from the concentration distribution and from direct measurements of the rate of passage of gas through the stack as a function of time. For irradiated low-density polyethylene, the data were processed on the basis of the concentration dependence of the diffusion coefficient. Also, the results were in good agreement within the error of measurement with those obtained on a solid membrane equal in thickness to the thickness of the stack. The method can therefore be recommended for simulating diffusion in layered media and unsymmetrical membranes.

On the other hand, boundary conditions of the third kind were observed in the diffusion of water vapor. Figure 3 shows that the HTO distribution in the steady state is not represented by a straight line, which indicates a marked concentration dependence of the diffusion coefficient, and the concentration is not zero at the exit surface, which demonstrates the presence of a semi-permeable wall. No success was obtained in attempts to reduce the concentration at the exit surface by means of a strong current of dry air or inert gas, or by reducing the pressure to 0.133 Pa. Relationships of the type shown in Fig. 3 indicate that it is not correct to simulate the specimen with a stack of membranes for the diffusion of water vapor, and there is also doubt as to the reliability of the results obtained on the diffusion of water in the ordinary form of the permeability method. In any case, the results should be processed for such systems on the basis of boundary conditions of the third kind. More reliable results on the diffusion would be obtained by using longitudinal sectioning.

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