EXPERIMENTAL METHODS FOR THE STUDY OF THE DIFFUSION OF RADIOACTIVE GASES IN SOLIDS.

VI. INVESTIGATION OF THE TOPOLOGICAL PECULIARITIES OF THE DIFFUSION PROCESS

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An autoradiographic variant of the permeability method based on the simultaneous use of a radiochemical modification of the gas-permeability method and autoradiography was used to analyze complex diffusion processes in solids. The topological peculiarities of the diffusion of radon in polypropylene with a macrospherulite structure were studied. The existence of pronounced spatial and temporal nonuniformity of the diffusion process was observed. The spectra of the dimensionless diffusion times were calculated for two diffusion times. It was established that all of the spectra have a complex continuous structure that is associated with the existence in the sample of a set of diffusion pathways that are characterized by different sorption capacities and a sinuosity factor. Some methodical difficulties that arise when the autoradiographic variant of the permeability method is used for the analysis of diffusion processes in complex media are discussed.

It is well known that the gas-permeability method is extremely sensitive to the presence of macrodefects in the membrane. For example, a pronounced increase in the permeability of the films for spherulite diameters greater than 100 μm was observed during a study of the effect of the morphological structure of the polymer on the rate of diffusion of various gases in polypropylene [1]. A detailed analysis of the results showed that relaxation of the stresses during preparation of the membrane leads to the development of microcavities and cracks on the boundaries of the spherulites. They are initially internal but gradually become through passages, giving rise to an increase in the flow of gas through the membrane. The existence of several diffusion pathways in the sample leads to distortion of the form of the kinetic curves and hinders calculation of the diffusion parameters. It therefore seems of interest to develop methods to ascertain anomalies of this sort and to create algorithms for their qualitative interpretation.

This paper is devoted to the combined use of a radiochemical variant of the permeability method and autoradiography (ARG) for the analysis of complex diffusion processes in solids. The method was worked out in the case of the diffusion of radon in polypropylene with a macrospherulite structure.

All of the experiments were carried out with the same isotactic polypropylene membrane. The sample was prepared by hot pressing. For this, the polymer was maintained for 30 min at 250°C and $5 \cdot 10^{-6}$ Pa with subsequent thermal crystallization at 145°C for 8 h. By photographing the membrane in polarized light we established that the structure of the film is represented by individual large spherulites (with diameters of up to 400 μm) distributed among spherulites with diameters of 20–30 μm.

The diffusion characteristics were determined by the isostatic variant of the permeability method. During the experiment we recorded the dependence of the flow of radon through the membrane on the time, during which we observed anomalous behavior of the "breakthrough" curves. 1. The diffusion process reaches the steady state considerably more rapidly than one might have expected from the results of a preliminary study of the permeability of radon through polypropylene with a different thermal past history. 2. The curves are not rectified satisfactorily on a linearized scale. 3. The coefficients of diffusion calculated at the "special" points do not coincide with one another. For example, $D_{\tau_{br}} = 1.5 \cdot 10^{7}$ cm²/sec,

$D_{\tau_{tr}} = 1.2 \cdot 10^{-7}$ cm^2/sec, $D_{\tau_{1/2}} = 1.0 \cdot 10^{-7}$ cm^2/sec, and $D_\theta = 8.9 \cdot 10^{-8}$ cm^2/sec, i.e., the coefficient of diffusion decreases systematically as the flow approaches the steady state. Let us note that even the lowest value of the coefficient still considerably exceeds the corresponding value for microspherulite polypropylene ($D = 0.9 \cdot 10^{-8}$ cm^2/sec).

The data obtained constitute evidence for the existence of several diffusion pathways in the membrane. However, attempts to use the nonlinear method of least squares to break down the complex kinetic curve into individual components were unsuccessful. The spectrum of the coefficients of diffusion evidently has a complex continuous structure, for the resolution of which one should use special methods.

To solve this problem we used an autoradiographic variant of the permeability method. In carrying out experiments on this method the diffusion process was stopped at a certain time, and the membrane was removed and clamped between two photoplates. After exposure and development, the plates were subjected to photometric evaluation. The data were obtained for two diffusion times: $t_1 = 160$ sec, which corresponded approximately to $\tau_{1/2}$, i.e., the time required for the flow to reach the value $Q_t = 0.5Q_\infty$, and $t_2 = 220$ sec, i.e., somewhat greater than lag time θ (flow $Q_t = 0.7Q_\infty$). In this research we used a photoemulsion that was sensitive only to α radiation. The slit width of the photometer was 10 μm. Since the path of α particles in polypropylene $R_\alpha \approx 35$ μm, whereas the membrane thickness $H = 100$ μm, the distribution of an impurity in a section at the center of the membrane is inaccessible for recording on photoplates. The autoradiograms therefore contain information only regarding a part of the spatial distribution of the impurity. Nevertheless, autoradiographic data make it possible to obtain information regarding the principal topological peculiarities of the diffusion process.

Even visual examination of the autoradiograms with a microscope demonstrates the irregular character of the distribution of α tracks at both the point of entry and the point of exit from the sample. The principal peculiarity is the formation of accumulations of tracks, including ordered ones of the "star" type. To ascertain the reasons for the development of density irregularities we matched the autoradiograms and photographs of the same section of the polymeric film in polarized light. First and foremost we found that the density irregularities encompass areas that considerably exceed the size of the spherulites. The development of such large deviations is possibly associated with the presence of a temperature gradient on the surface of the membrane, which arises during pressing; the latter in turn leads to the development of regions with different densities and, consequently, with different degrees of crystallinity. Fluctuations in the thickness of the membrane also possibly play a definite role. As a rule, accumulations of the "star" type develop on the entry side of the membrane and mainly on the boundaries of the spherulites. The existence of such accumulations shows that the polymer contains sites that are extremely active with respect to the sorption of gas. There may be many such sites, so that the "stars" in turn form accumulations. The accumulations of stars are situated on the boundaries of the spherulites. It is possible that such stars are inclusions of radon in the microbubbles that are present in the polymer. The accumulations of radon do not pass through the film, so that one does not encounter them on the side from which the gas exits, or, if one does encounter them, they do not have a characteristic darkened center.

The set of photometric evaluation curves makes it possible to construct topological density maps. With this in mind, we selected a 600 by 600 μm section on the autoradiogram located approximately in the middle of the membrane, broke it down into 900 identical squares, and determined the average density in each square. We used this procedure to obtain four matrixes of values (for two diffusion times), which were subsequently used to calculate the diffusion parameters. The results are presented in Fig. 1 in the form of isolines that pass through identical densities. It follows from Fig. 1 that the entire area of the membrane is encompassed by sorption and diffusion processes. The density distribution has nonuniform character: Both large regional and numerous local anomalies are present. Insofar as one can judge, the regional anomalies reflect the topological peculiarities of the structure of the membrane. The irregularities of the relief are expressed to the maximum degree on the entry side of the membrane in the case of t_1 and to the minimum degree on the exit side of the membrane in the case of t_2. The principal features of the regional perturbations are retained in all of the autoradiograms; however, they become smoother during diffusion, thereby confirming the existence of pronounced lateral diffusion. It is possible that a virtually uniform distribution of the concentration on the exit surface of the membrane will be reached in the steady state.
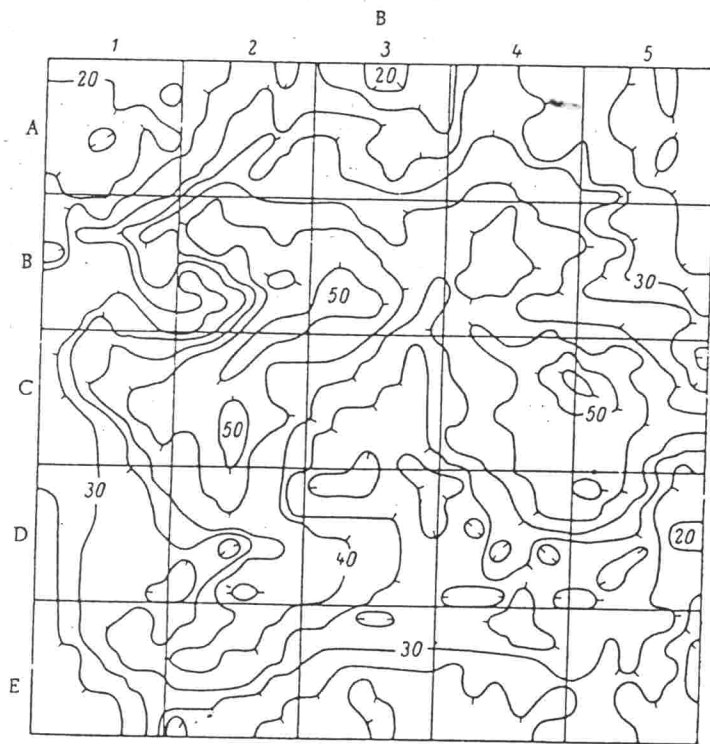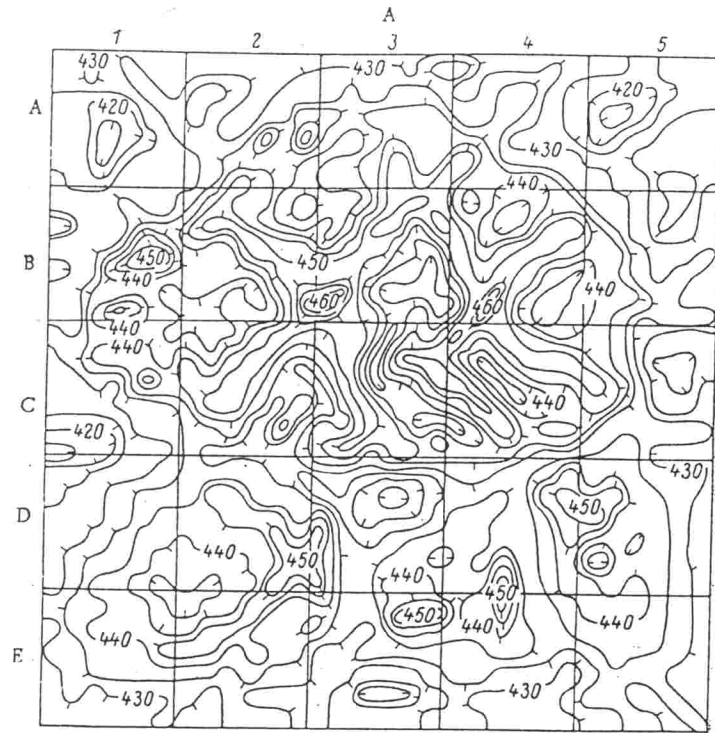
112

Fig. 1. Results of photometric evaluation of the auto-
radiogram (radon in polypropylene with a macrospheru-
lite structure): A) entry side of the membrane, t_1 =
160 sec; B) exit side of the membrane, t_1 = 160 sec;
C) entry side of the membrane, t_2 = 220 sec; D) exit
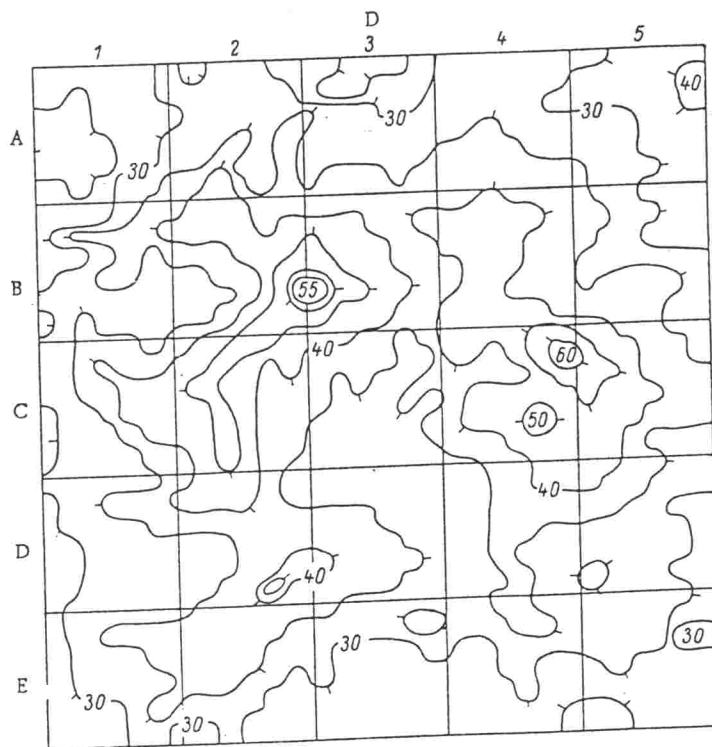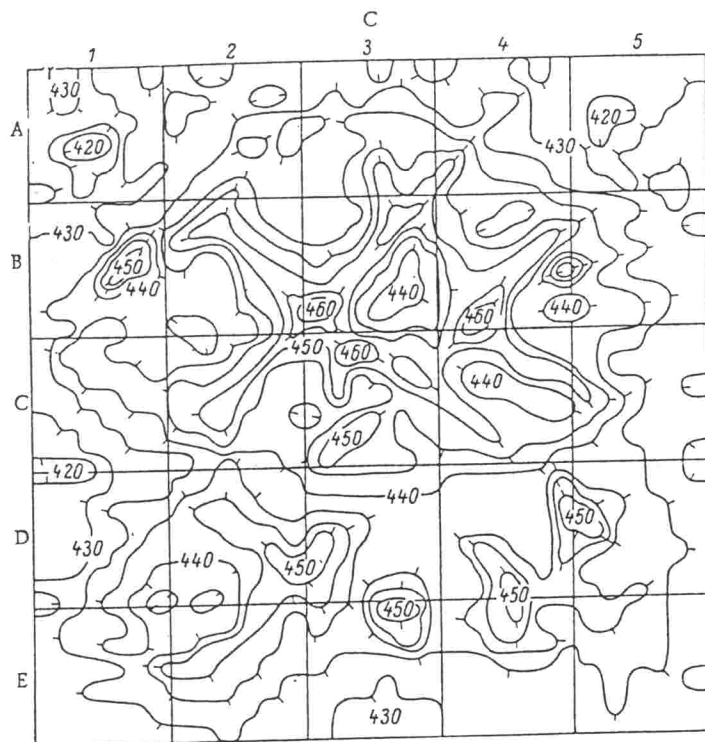side of the membrane, t_2 = 220 sec. (Continued on next
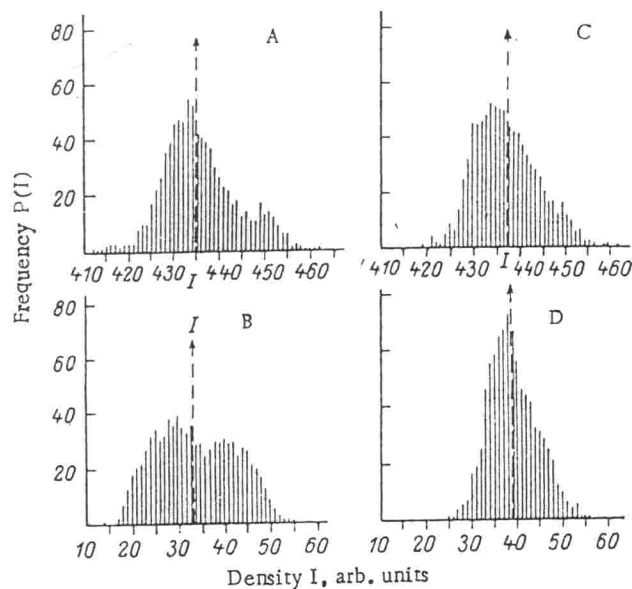page.)

113

Fig. 1 (continued)

Fig. 2. Sampling of the results of photometric evaluation of the autoradiogram: A) entry side of the membrane, t_1 = 160 sec; B) exit side of the membrane, t_1 = 160 sec; C) entry side of the membrane, t_2 = 220 sec; D) exit side of the membrane, t_2 = 220 sec.

Certain information regarding the topological peculiarities of diffusion can be obtained from the distribution density of the degree of density. The corresponding distributions of the frequencies for samples of the results of scanning are presented in Fig. 2. The initial, central, and principal statistical moments of the distribution density calculated by the standard method [2] are presented in Table 1. The results make it possible to compare the distributions of the combined results of scanning with such well-known distributions as the Gaussian [for which normalized asymmetry $\beta_1 = (\mu_3^2/\mu_2^3) = 0$, normalized excess $\beta_2 = (\mu_4/\mu_2^2) = 3$, where μ_3 is the third central moment or the distribution asymmetry, μ_4 is the fourth central moment or the steepness in the mode, and μ_2 is the dispersion] and uniform ($\beta_1 = 0$, $\beta_2 = 1.8$) distributions. It follows from Table 1 that the distribution function for all of the densities has asymmetrical character, particularly on the entry side of the membrane. In the course of diffusion distribution I on the exit surface of the membrane undergoes conversion from the form characteristic for the uniform distribution to a form that is closer to the Gaussian distribution (although the right-hand asymmetry is still retained, and the peaks are more planar than they should be in the purely normalized distribution). The presence of anomalously large densities is appreciable in all cases.

Density data for the entry and exit surfaces of the membrane make it possible to calculate the spectrum of the dimensionless diffusion times $u = Dt/l^2$ (1), where D is the coefficient of diffusion, t is the diffusion time, and l is the length of the diffusion tube of the flow (to a first approximation it can be assumed that l=H, where H is the thickness of the membrane).

In the determination of spectrum u for each i-th part of the membrane we calculated the normalized density

$$F_i = \frac{I_{ex}(y_i, z_i)}{I_{en}(y_i, z_i)},$$ (2)*

where $I_{ex}(y_i, z_i)$ and $I_{en}(y_i, z_i)$ are the densities at mutually opposite points of the membrane.

We then sought the solution, relative to C(x, u), of the integral equation

$$F(u) = \frac{\int_{H-R}^{H} C(x, u) K(x, H-x)\, dx}{\int_{0}^{E} C(x, u) K(H-x, x)\, dx},$$ (3)

*Equation (1) does not appear in the original Russian — Consultants Bureau.

TABLE 1. Statistical Moments of the Distribution Functions of the Frequencies for the Density and the Dimensionless Diffusion Time

Exptl. conditions	Mathematical expectation	Dispersion	Principal moments	
	μ_0'	μ_2	β_1	β_2
	Density			
Diffusion time $t_1 = 160$ sec				
Entry side of membrane	$4.49 \cdot 10^2$	$6.95 \cdot 10^1$	0.194	2.97
Exit side of membrane	$3.68 \cdot 10^2$	$7.43 \cdot 10^1$	0.016	2.06
Diffusion time $t_2 = 220$ sec				
Entry side of membrane	$4.49 \cdot 10^2$	$5.02 \cdot 10^1$	0.153	2.84
Exit side of membrane	$2.79 \cdot 10^2$	$2.83 \cdot 10^1$	0.107	2.74
	Dimensionless diffusion time			
Diffusion time $t_1 = 160$ sec	2.04	$1.62 \cdot 10^{-3}$	0.65	3.11
Diffusion time $t_2 = 220$ sec	1.96	$9.14 \cdot 10^{-4}$	1.63	5.31

where C(x, u) is the distribution of the concentration of radon throughout the thickness of the membrane

$$C(x, u) = C_0 \left(1 - \frac{x}{H} - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi x}{H} \exp(-n^2\pi^2 u) \right), \qquad (4)$$

K(x, H−x) is the core of the primary Fredholm equation (the apparatus function),

$$k = \frac{1}{2} \left(1 - \frac{x}{R_\alpha} \right), \qquad (5)$$

and $R_\alpha \simeq 35$ μm is the path of the α particles of radon in polypropylene. The u parameter was calculated directly from C(x, u).

Topological diffusion maps are presented in Fig. 3. It is apparent that distribution u along the surface of the membrane has markedly nonuniform character, particularly for short diffusion times. The principal features of the relief are similar for all of the diffusion times, although during the process the amplitudes of the perturbations decrease, and the loca anomalies vanish. A comparison with the density maps (Fig. 1) reveals substantial difference in the character of the relief. Only one region (squares B2, C3, and C2) shows up clearly in both figures. The anomaly in square C4 noted in Fig. 1 is virtually absent in Fig. 3, while the anomaly in square D2 is diminished significantly. One's attention is directed to the strong perturbation in squares D3, E3, and E4 on the map of distribution u, in which the maximum height of the relief is reached. This perturbation was not present on the autoradio grams.

The combined results of sampling of parameter u are presented in Fig. 4, while the sta- tistical moments are presented in Table 1. It is apparent that the spectra have continuous character and right-hand asymmetry (particularly for long diffusion times); not one of the spectra can be described by a Gaussian or uniform distribution. Let us note that the P(u) spectrum is subject to statistical fluctuations to a greater degree than the I spectrum.

It is interesting to compare the data for the autoradiographic variant of the permeabil- ity method with the data obtained from kinetic breakthrough curves. It follows from Fig. 4 that the calculations with respect to the early times (for example, τ_{br}) give an estimate of the upper boundary of the spectrum that is probably associated with diffusion along the macr defects. Calculations of u with respect to long diffusion times give a better reflection of the character of the spectrum, since low values of the coefficients of diffusion are involved in the examination. The u value determined from $\tau_{1/2}$ proves to be closest to both the mathe- matical description and to the mode of distribution. This once again confirms the well-know principle that the calculations should be made from the medium of the distribution (it is known that $\tau_{1/2}$ is the median of the distribution that describes the breakthrough curve). Let us note that even the last "special" point — lag time θ (the mathematical expectation of the breakthrough curve) — does not give a reliable estimate of the lower boundary of the spectrum.
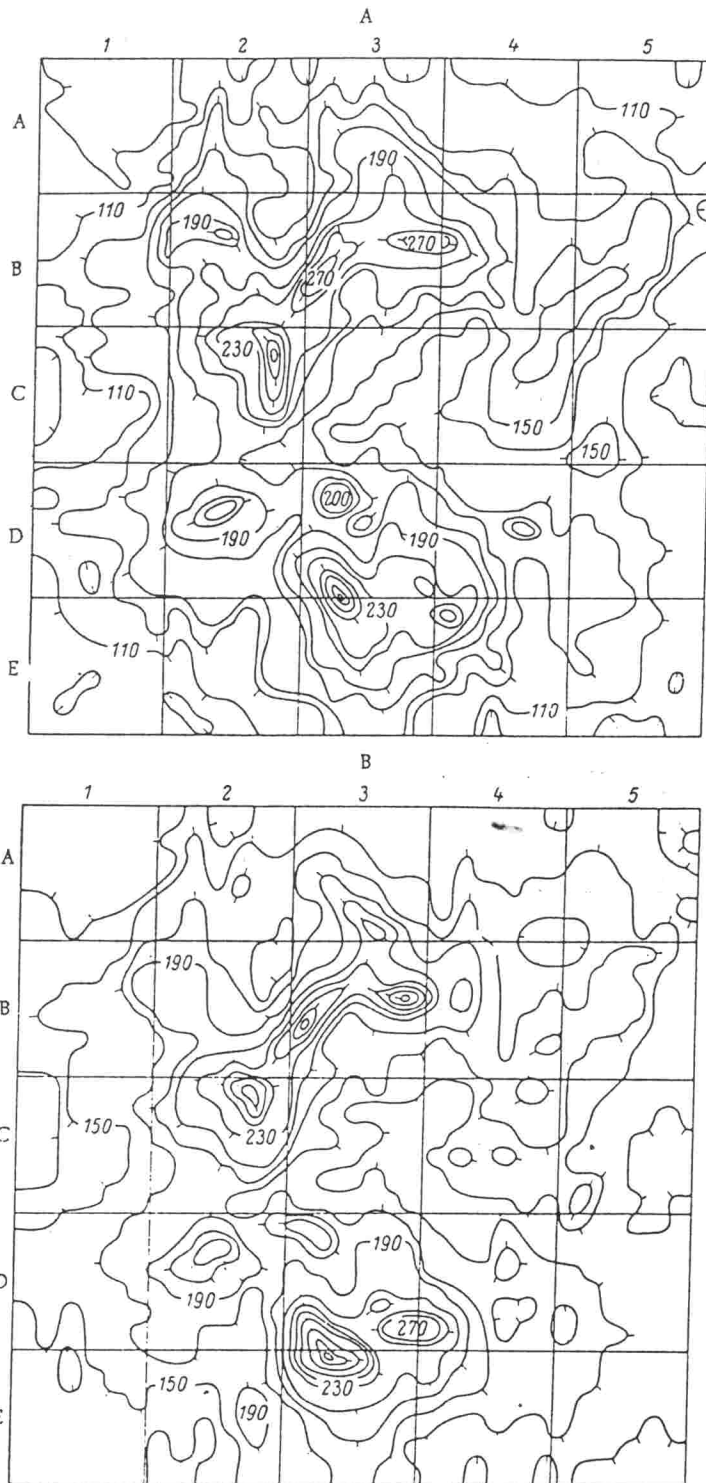
Fig. 3. Distribution of the dimensionless diffusion times along the surface of the membrane: A) diffusion time $t_1 = 160$ sec; B) diffusion time $t_2 = 220$ sec.
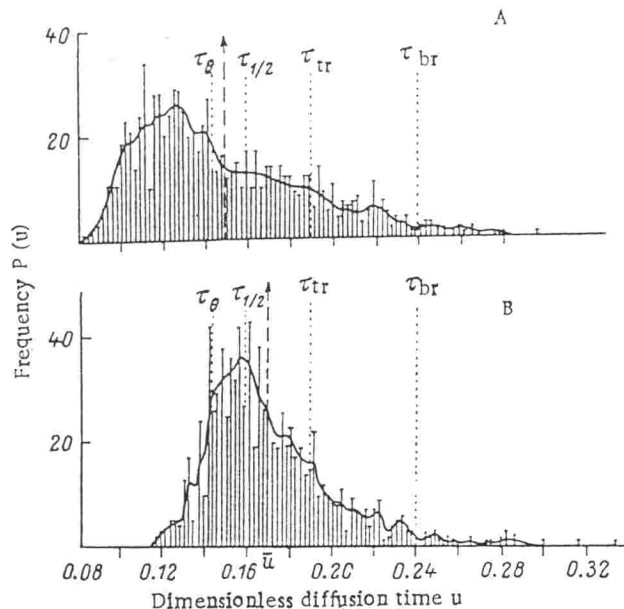
Fig. 4. Frequency distribution function for the dimensionless diffusion time: A) diffusion time $t_1 = 160$ sec; B) diffusion time $t_2 = 220$ sec.

The chief advantage of the autoradiographic variant of the permeability method is the possibility of the separate determination of the spectrum of the solubility constants $[P(K_s)]$ and the spectrum of the coefficients of diffusion $[P(D)]$. In fact, the density distribution on the entry side of the membrane $[P(I_{en})]$ for short times (and in the case of small R_α values for virtually all times) reflects the $P(K_s)$ spectrum. In the course of diffusion the $P(D)$ spectrum is superimposed on the $P(K_s)$ spectrum. The spectrum on the exit side of the membrane $[P(I_{ex})]$ is associated with the $P(K_sD)$ spectrum. We find the $P(D)$ spectrum by calculating the spectrum of the normalized densities $[P(F)]$. Unfortunately, the application of this simple scheme $I_{ex}/I_{en} \rightarrow C \rightarrow u \rightarrow D$ is fraught with considerable difficulties in the investigation of such complex media as polypropylene with a macrospherulite structure. Let us examine some peculiarities of the autoradiographic variant of the permeability method that hinder the interpretation of the experimental results.

First Stage: $F \rightarrow u$ Transition. The optimum selection of the diffusion times, the primary treatment of the two-dimensional information, and demarcation of the forward and lateral diffusion are important in this stage. 1. It is well known that in autoradiography the image is diffuse due to the final breakthrough value. As a result, the $P(F)$ spectrum proves to be an inadequate true distribution of the concentration. To regenerate the actual form of the distribution one should carry out reduction to the apparatus function using the two-dimensional Fredholm equation. In our case path $R_\alpha = 35$ μm, the image was made distinct by means of 20 by 20 μm squares, and the effect of the point source was extended to only two squares, in connection with which this sort of distortion could be disregarded. However, the errors due to this factor may become significant in work with stronger emitters. 2. The pronounced lateral diffusion observed in the present research leads to distortion of the $P(u)$ spectrum: the $F = I_{ex}/I_{en}$ ratio may both decrease and increase, depending on the region of the profile of the membrane in which deviation of the diffusion flow from a rectilinear path occurs. Because of this effect, the appearance of F values that exceed the limiting value of F for the steady state (and, consequently, $u = \infty$) is possible. Microvacancies that accumulate radioactive gas may have a particularly strong effect. The development of vacancies in the vicinity of the entry surface leads to a sharp decrease in F, whereas such development in the vicinity of the exit surface leads to a decrease in F (in the latter case it may be erroneously concluded that the steady state is reached in this section). 3. The correct selection of the diffusion times is of greatest importance in the study of diffusion in complex media. In the present research the results were obtained for only two times; this makes it impossible to sufficiently reliably describe the evolution of the diffusion process with time. In fact, the shortest diffusion time should be selected in such a way that the im-

purity has traveled a distance that is sufficient for its reliable recording on the exit surface of the membrane. From this point of view, the selection of time t_1 was correct — the entire surface of the membrane was encompassed by diffusion. However, in connection with the fact that the $P(u)$ spectrum proved to be very broad, some of the u values fell in an unstable region in the vicinity of the steady state. In this region the fluctuations in u considerably exceed the fluctuations in $F(u)$, and the upper boundary of the $P(u)$ spectrum is fraught with large errors.

Second Stage: u → D Transition. At first glance, this problem is simply solved: if one assumes the condition $l = H$, only D is unknown in expression (1). The following characteristics of the spectrum of the local coefficients of diffusion were obtained using this formal approach: for time t_1, $D_{min} = 5.2 \cdot 10^{-8}$ cm^2/sec, $\overline{D} = 9.4 \cdot 10^{-8}$ cm^2/sec, and $D_{max} = 1.9 \cdot 10^{-7}$ cm^2/sec; for time t_2, $D_{min} = 5.3 \cdot 10^{-8}$ cm^2/sec, $\overline{D} = 7.8 \cdot 10^{-8}$ cm^2/sec, and $D_{max} = 1.5 \cdot 10^{-7}$ cm^2/sec, or, after averaging, $D_{min} = 5.2 \cdot 10^{-8}$ cm^2/sec, $\overline{D} = 8.6 \cdot 10^{-8}$ cm^2/sec, and $D_{max} = 1.7 \cdot 10^{-7}$ cm^2/sec. A comparison with the results obtained from the breakthrough curve ($D_{\tau br} = 1.5 \cdot 10^{-7}$ cm^2/sec and $D_0 = 9.0 \cdot 10^{-8}$ cm^2/sec) shows that from kinetic data one can obtain an accurate estimate of the upper boundary of the spectrum and the average value of the coefficients of diffusion; however, the lower boundary of the spectrum has virtually no effect on the form of the breakthrough curve. The existence of low coefficients of diffusion can therefore be revealed only by means of the autoradiographic variant of the permeability method.

In work with complex media the u → D transition is an incorrectly posed problem, in the solution of which serious problems arise. 1. Even when the condition $l = H$ is satisfied, for the calculation of the local coefficients of diffusion one must know the local thicknesses of the membrane. It is virtually impossible to make such H_i measurements (in our case 900 H_i values must be determined on a section with an area of $3.6 \cdot 10^{-3}$ cm^2). Therefore, even when one knows the average thickness of the membrane $(\overline{H})$, calculated from data for various points of the membrane that are sufficiently remote from one another, its error (in our case $\delta = 4\%$), and distribution function $P(H)$, there is still a certain inaccuracy in the transition to $P(D)$. 2. The condition $l = H$ is not satisfied in the case of diffusion in a complex medium of the dispersion type: In connection with the presence of impermeable crystallites and spherulites with semipermeable centers the rectilinear character of the flow tubes is disrupted, and the migration pathway increases. Then $l = \xi H$, where $\xi > 1$ is the sinuosity factor, which is unknown. The u → D transition is therefore impossible. The local coefficients of diffusion can be determined only for a certain part of the $P(u)$ spectrum. Our preliminary calculations of the autocorrelation and intercorrelation functions for the density at the entry and exit surfaces of the membrane made it possible to isolate sections for which a substantial correlation between $I_{en}(y_i, z_i)$ and $I_{ex}(y_i, z_i)$ is observed. The condition $l = H$ is valid for these sections, and the local coefficients of diffusion can be estimated. In particular, it has been demonstrated by this method that through diffusion that is not disrupted by spherulites occurs in the C3 and E3 squares (Fig. 3). Since the maximum u values are reached precisely for these regions, they are evidently through macrodefects that are responsible for the increase in the permeability of polypropylene when the size of the spherulites increases. 3. In the present research we observed that not all of the impurity that is recorded on the entry side of the membrane participates in the diffusion process. In fact, a comparison of the u maps for two diffusion times (Fig. 4, maps a and b) shows that a significant part of the local flows at time t_1 has already attained the steady state. However, this conclusion contradicts the $F(u)$ values for the same coordinates, which were always lower than F_{st}. This contradiction can be explained only by assuming that a certain amount of the impurity adsorbed on the entry surface of the membrane does not participate in diffusion. The observed effects can be produced by sections of the sample that have anomalously high sorption capacities, gas bubbles, or radioactive products of radon decay.

Thus in the modern state of the methodical provision of the autoradiographic variant of the permeability method one can obtain quantitative information regarding the topological peculiarities of dissolving and diffusion processes only in those relatively simple systems in which lateral diffusion is completely suppressed and the length of the flow tube corresponds approximately to the thickness of the membrane. For the analysis of complex diffusion processes one must realize further development of the theoretical foundations of the method; for example, one must invoke methods for analytical continuation of the concentration fields.

However, the results obtained in this research show that the proposed method makes it possible to obtain information regarding transfer processes that is inaccessible by tradi-

tional variants of the permeability method. Thus we were able to demonstrate the complex character of dissolving and diffusion processes, ascertain the role of spherulites, estimate the form of the spectrum of the coefficients of diffusion and prove the continuous character of its structure, detect the existence on the entry surface of the membrane of stationary states of the impurity, establish the existence of pronounced lateral diffusion, which is evidently associated with envelopment of the dense centers of the spherulites by the diffusion current, ascertain the presence of through channels, microbubbles, etc. It therefore seems possible to us even at this stage to recommend the autoradiographic variant of the permeability method for the analysis of complex diffusion anomalies.

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POSSIBILITY OF THE PREDICTION OF THE BEHAVIOR OF

PLUTONIUM IN THE MARINE ENVIRONMENT FROM DATA ON

THE EMISSION OF ITS NATURAL RADIOACTIVITY

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The disposal of low-activity liquid wastes in coastal sea waters that is currently the practice in a number of countries [1] and the global radioactive fallout of products of tests of nuclear arms [2] have been the principal reasons that microamounts of transuranium elements have been included in the composition of the marine environment. The burial of containers filled with consolidated radioactive wastes in the deep-sea regions of the ocean that is being realized in conformity with the London convention also poses the potential danger of contamination of the marine environment by these elements [3]. The need for a detailed study of the behavior of transuranium elements in the marinum environment becomes apparent from a consideration of the material set forth above. The urgency of this problem is explained not only by the high radiotoxicity of plutonium and transpultonium elements and the long half-lives of a number of their isotopes but also above all by the fact that transuranium elements are in a certain sense "new" elements for the marine environment that, in contrast to most other elements, do not have stable isotopes, the behavior of which is well known.

One of the principal difficulties associated with practical studies of the physicochemical behavior of transuranium elements in the marine environment (waters, suspensions, deposits, and marine organisms) involves the extremely low specific activity of substances in the marine environment [4]. For this reason we are as yet unable to fully utilize for the study of the forms of existence in the marine environment of plutonium and transplutonium elements the entire complex of methods (ultrafiltration, extraction, ion exchange, electromigration, centrifugation, etc.) that is ordinarily used in investigations of the physicochemical state of microamounts of elements in solutions [5].

However, it should be noted that even if we were able to obtain information regarding the behavior of transuranium elements in the marine environment by means of the indicated complex of methods, these data still could not be regarded as a sufficient basis for the long-range prediction of the behavior of plutonium and transuranium elements in the seas and oceans. The reasoning behind this is the fact that the incorporation of plutonium and transplutonium elements in the marine environment has taken place over a period of time that is not comparable with the time of existence of the seas and oceans and (to a lesser extent) with the times of the occurrence in them of deep-sea sedimentation and diagenesis of the deep-sea oceanic deposits. Thus a direct study of the physicochemical state of plutonium and