EXPERIMENTAL METHODS FOR STUDYING THE DIFFUSION OF RADIOACTIVE GASES IN SOLIDS. VII. SORPTION METHOD

I. N. Bekman

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The details of the use of a sorption method in the study of the diffusion of gases and vapors labeled with radioactive tracers in solids have been considered. Three variants of diffusion systems, which permit the determination of the diffusion coefficient and the solubility constant of gases both from the increase in the amount of diffusate in the sample and from the decrease in its amount in the reservoir, have been tested. Different ways of conducting the experiment have been discussed. A universal method for taking into account the processes of the absorption and scattering of radiation in the material of the sample has been proposed. The experimental results were treated with the aid of a specially developed program package, which is realized on computers of the BÉSM-6 type. Various mathematical models of the diffusion of gases in solids have been analyzed. Solutions of the diffusion equations under the boundary conditions of the sorption method for the cases of diffusion with trapping, dissociative diffusion, and diffusion in a plate containing spherical inclusions have been obtained. The method has been tested in the example case of the diffusion of a radiative inert gas, viz., radon-222, in low-density polyethylene.

The sorption method based on the study of the migration of an impurity from the surrounding atmosphere into a solid is one of the main methods of gas diffusion. It makes it possible to simultaneously determine the diffusion coefficient and the solubility constant. During an experiment, either the decrease in the concentration of the diffusate in the gaseous phase or the increase in its amount in the sample is detected. The sorption method has a number of advantages over the permeability method. For example, the consolidation of the membrane, which is so important in the study of the permeability, is not a problem for sorption. The study of diffusion in samples of any geometry, including powders, is possible in the sorption method. The absence of a pressure drop permits work with brittle and elastic materials and even with melts. In addition, the individual defects in the membrane, which are capable of completely altering the permeability kinetics, have practically no influence on the sorption kinetics. Thus, it becomes possible to study diffusion in very thin films with a low diffusion coefficient.

In the present work we shall describe systems and methods for conducting an experiment and treating the results, which can be used in the study of diffusion processes by the radiochemical variant of the sorption method. The proposed methods have been applied to the determination of the diffusion parameters of radon (^{222}Rn) in low-density polyethylene.

We prepared and tested three systems for determining the diffusion coefficient and the solubility constant of radioactive gases by the sorption method.

Variant 1 (Fig. 1A). The apparatus consisted of a glass "chain," in which samples in the form of tablets or films were placed in the individual intercommunicating cells. The lowest cell contained zeolite. After evacuation the cell was filled with a radioactive gas (e.g., radon). After the zeolite was cooled to the temperature of liquid nitrogen, all the radon was transferred to it. The cells were evacuated again to remove the carrier gas (helium). Then the zeolite was heated, and an even distribution of the diffusate among all the cells was achieved. After the ampul with the zeolite was preliminarily removed, the chain was separated into individual ampuls. This method makes it possible to achieve a high specific activity of the gas at a total pressure of 1.33 Pa. The low pressure of the residual gas

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makes it possible to heat the ampuls to high temperatures without fear of their bursting. The ampuls were placed in a thermostat, and diffusion annealing was carried out. Periodically one of the ampuls was removed and opened, and the total amount of diffusate in the sample was determined.

Variant 2 (Fig. 1B). This system was developed for studying the kinetics of the absorption of tritium by metals,* but it was also used for the determination of the diffusion parameters of radon in polymers. The device provided for the heating of the samples up to a temperature of 1000°C in an inert atmosphere or a vacuum with an assigned specific activity of the diffusate and the collection of samples after definite time intervals without breaking the hermetic seal of the system. The system consists of a quartz test tube, which is connected to the remaining system through a water-cooled ground-glass joint. The test tube contains the samples and a sample push rod. The heating is effected by an external resistance furnace. The samples are collected through a sluice valve. Radon is admitted from an ampul with zeolite, on which the radon was adsorbed. The evacuation of the system is effected by a zeolite pump to a residual pressure of 0.13 Pa.

Before the beginning of an experiment, several identical samples of the polymer were placed in the water-cooled section. The entire system was evacuated and heated at the required temperature for several hours. Then the radon was admitted, and the samples were pushed into the heating zone by the magnetic push rod. The samples were removed from the heating zone after definite time intervals and dumped into the sluice valve. The valve was turned, and the sample was taken out.

Variant 3 (Fig. 1C). A shortcoming of the methods described above is the discrete nature of the measurements, the points on the kinetic curve being obtained with different samples. In variant 3 the sorption process was monitored by the continuous measurement of the rate of decrease in the activity of the diffusate in the gaseous phase. The system consisted of a quartz test tube, a branch from which was located in the well of a scintillation counter. The activity of the gaseous phase was continuously recorded with the aid of an electronic potentiometer. A shortcoming of this method is the need for large amounts of the polymer. In addition, it is applicable only for isotopes with sufficiently hard radiation.

The diffusion coefficient and the solubility constant can be calculated from the results obtained in variants 1 and 2 by two methods: either from the distribution of the concentration of the diffusate across the thickness of the sample or from the dependence of the amount of the impurity in the solid phase on the time. The longitudinal-section method was not considered in this case. The method for determining the amount of the impurity in the sample depends on the mobility of the impurity in the material at room temperature and on the type of isotope used.

In the case of a mobile diffusate (for example, tritium in polyethylene), the work was carried out according to variant 2, the hot sample being dropped into the desorption cell, which was heated to a temperature above the melting point of the sample, through the sluice valve. The carrier gas carried along the radioactive diffusate released to an internal-admission counter, where its activity and, therefore, the amount of gas entering the polymer during the sorption experiment, were measured.

If the diffusing substance is relatively immobile and is labeled with an isotope with sufficiently hard radiation for its self-attenuation to be negligible, the quantity of the impurity in the sample is easily obtained by direct measurement of the activity of the sample. The diffusion parameters of radon were determined by just such a method. The γ radiation of the active sample was measured after the attainment of radioactive equilibrium. The temperature of the sample did not exceed 0°C over the course of all the manipulations.

In the cases considered until now, equations which are applicable in the ordinary variants of the sorption method were used for treating the results of the experiments. For example, in the case of a plate of thickness H initially free of the diffusate, when the boundary conditions of the first kind are fulfilled (diffusion from a constant source), the amount of substance which has entered the sample at the time t is described by the equation [1]

*A. P. Brovko participated in the development of the design and its assembly.

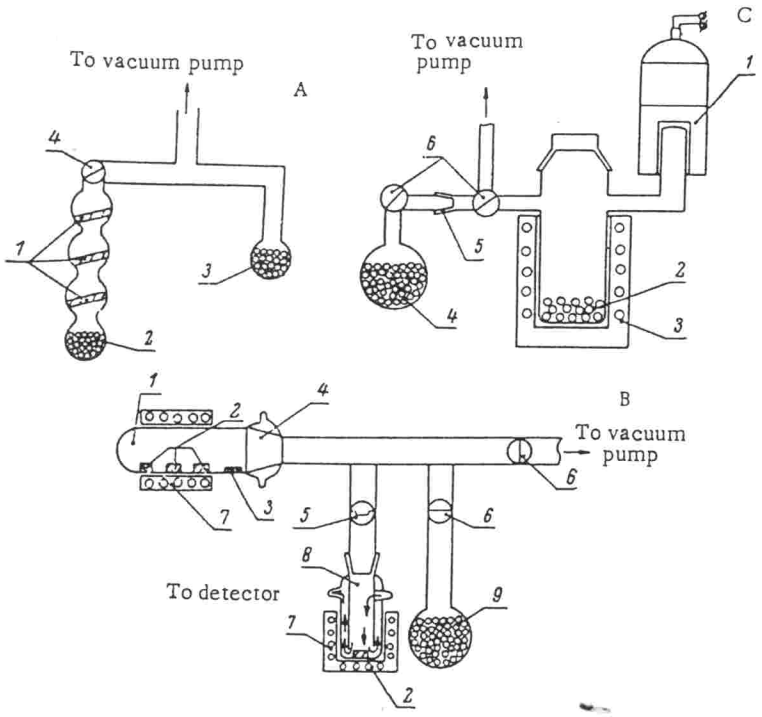

Fig. 1. Systems for radiochemical variants of the sorption method. A) Device for introducing a radioactive gas into powders and films: 1) sample; 2) zeolite; 3) zeolite with ^{226}Ra adsorbed on it; 4) vacuum valve. B) System for collecting samples without breaking the hermetic seal of the system: 1) sorption cell; 2) sample; 3) magnetic push rod; 4) water-cooled ground-glass joint; 5) sluice valve; 6) valve; 7) resistance furnace; 8) desorption cell; 9) zeolite with ^{226}Ra adsorbed on it. C) System for continuous recording of the kinetics of the absorption of gases: 1) scintillation detector; 2) sample; 3) resistance furnace; 4) source of radioactive gas; 5) ground-glass joint; 6) vacuum valves.

$$\gamma_t = \frac{M_t}{M_\infty} = 4\left(\frac{Dt}{H^2}\right)^{1/2}\left\{\frac{1}{\sqrt{\pi}} + 2\sum_{n=1}^{\infty}(-1)^n \operatorname{ierfc}\frac{nH}{2\sqrt{Dt}}\right\} = 1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left\{-\frac{(2m+1)^2\pi^2 Dt}{H^2}\right\}, \quad (1)$$

where $M_\infty = C_0SH = K_SPH$ is the amount of the substance in the sample at the conclusion of the sorption process, D is the diffusion coefficient, C_0 is the concentration of the gas at the entrance surface of the sample, S is the surface area of the plate, K_S is the solubility constant of the gas in the material of the sample, and P is the partial pressure of the diffusate vapor in the reservoir.

We note that the series on the left-hand side of Eq. (1) rapidly converge at small times and that those on the right-hand side rapidly converge at long times.

The flux of the diffusate into the plate is

$$Q(t) = \frac{8DC_0S}{H}\sum_{m=0}^{\infty}\exp\left\{-\frac{(2m+1)^2\pi^2 Dt}{H^2}\right\}. \quad (2)$$

If the isotope has sufficiently soft radiation (for example, ^{14}C), it becomes necessary to take into account the complex radiation absorption, scattering, and reflection processes. The approximate equations used in this case were presented in [2, 3]. We developed a method for taking into account the radiation-attenuation processes based on the solution of a Fredholm-type integral equation of the first kind. In fact, the counting rate measured from an isotope in the sample is

$$I_t/I_\infty = \int_0^R f(x)\,\psi(x, t)\,dx, \tag{3}$$

where $R \leqslant H$ is the free path of the radiation in the substance, f(x) is a function which takes into account the absorption and scattering of the radiation in the material of the sample, and $\psi(x,t)$ is a function which can be determined by solving the diffusion equation. In the present case,

$$\psi(x, t) = 1 - \frac{4}{\pi}\sum_{m=0}^{\infty}\frac{1}{2m+1}\exp\left\{-\frac{(2m+1)^2\pi^2 Dt}{H^2}\right\}\sin\frac{(2m+1)\pi}{H}x. \tag{4}$$

for β and soft γ radiation

$$f^{\beta}(x) = \int_{\mu x}^{\infty}\frac{e^y}{y}dy = E_i(-\mu x) = E_1(\mu x), \tag{5}$$

where E_i is an integral exponential function, and μ is the attenuation factor of the radiation in the substance.

For α radiation

$$f^{\alpha}(x) = \frac{1}{2}\left(1 - \frac{x}{R_\alpha}\right), \tag{6}$$

where R_α is the free path of the α radiation in the substance, and $x \leqslant R_\alpha$.

In principle, if R_α and μ were determined from independent experiments, the diffusion coefficient can be found from (3) with consideration of (4) and (5) by the ordinary least-squares method. However, expression (5) is applicable only for the thickness $\mu x < 0.3R_\beta$. It does not take into account the complex processes of scattering and reflection of the radiation, and, finally, it is difficult to use in work with a mixture of isotopes. Therefore, f(x) should be determined experimentally. For this purpose, a thin film of the same polymer (its thickness was selected so that the self-attenuation would be negligible) was held in the sorption system together with the tablets. The film was saturated uniformly with the diffusate. After measurement of the counting rate on an end-plate counter, the film was covered by another similar film, which did not contain the diffusate, and the counting rate was measured again. The layers of the absorber were piled up until the thickness of the working sample was achieved. The function obtained $I(\Delta)$, where Δ is the thickness of the layer of the absorber, is equivalent to the function f(x). Using the function $f_{ex}(x)$ and the measured values of M_t (in the form of I_t, where I_t is the counting rate from the diffusate in the sample) and solving integral equations (3) with respect to $\Psi(x, t)$ according to the program described in [4], we find the concentration profile, from which the diffusion coefficient can easily be calculated.

The proposed method has a universal character and can be used for isotopes with any type of decay, for mixtures of isotopes, and for isotopes having several types of radiation. The method does not introduce any approximations. The complex scattering and reflection processes, which have scarcely been studied, are taken into account automatically.

In the case of variant 3, in which the sorption kinetics are monitored according to the decrease in the pressure in a closed vessel of restricted volume, the variation of the amount of the substance with the time is described by the equation [5]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty}\frac{2\beta(1+\beta)}{1+\beta+\beta^2 q_n^2}\exp\left\{-\frac{Dq_n^2 t}{H}\right\}, \tag{7}$$

where $\beta = V_1/K_S V_2$, V_1 is the volume of the reservoir, V_2 is the volume of the sample, and q_n is a nonzero positive root of the equation $\tan q_n = -\beta q_n$.

For the statistical treatment of the results of the experiments on the study of the diffusion of radioactive gases by the sorption method we used a program package including: a system for the preliminary treatment of the results of the diffusion experiments (screening of thick layers, smoothing, consideration of the instrumental errors, introduction of corrections for the absorption of the radiation, etc.), a system for preliminary evaluation of the values of the diffusion parameters (use of approximate equations, method of moments, lineariza-

tion method), a system for treatment of the results according to the nonlinear variant of the least-squares method (calculation of the diffusion parameters in the framework of the "classical" model of diffusion, determination of the errors in the parameters and the confidence integrals for the curves), and a system for discrimination and selection of a mathematical model of diffusion (classical diffusion, diffusion in the presence of a chemical reaction, diffusion with trapping, dissociative diffusion, diffusion in dispersion media, diffusion under boundary conditions of the third kind, etc.).

The program package was written in the universal FORTRAN language and realized on a computer of the BÉSM-6 type. The smoothing of the results was carried out by the cubic spline regularization method, and the instrumental errors were considered according to the method in [6]. Approximate equations based on linearization of the initial or final portions of the kintic curve were used for the preliminary evaluation of the diffusion coefficient.

For the purpose of facilitating the process of treating the results of the experiments for studying diffusion phenomena, we developed special types of graph paper, which make it possible to make complex relationships between the quantities investigated linear [7]. The functional scale was calculated from Eq. (1). The dependence of $F(u) = M_t/M_\infty$, where $u = t/H^2$, on t constructed in these coordinates (Fig. 2) is described by the straight line

$$u = \frac{D}{H^2}(t - t_0), \tag{8}$$

where t_0 is the x intersect, which reflects the time of the beginning of diffusion and can be used to determine the response time of the instrumentation. From the slope of the straight line we find the diffusion coefficient

$$D = H^2 \operatorname{tg} \alpha. \tag{9}$$

The proposed method for representing diffusion data in the form of a linear dependence is simple and graphic, permits the use of the linear variant of the least-squares method, and makes it possible to monitor the adequacy of the model used from the value of the correlation coefficient.

Since the treatment of the results according to the linear least-squares method can lead to displaced estimates of the parameters, the final calculation of the diffusion coefficients and its errors was calculated by the nonlinear variant of the least-squares method. The adequacy of the model was tested according to the χ^2 criterion.

The treatment of the results was begun with the testing of the classical mechanism of diffusion. In this case, if the hypothesis of classical diffusion did not work out, a search for another phenomenological model was carried out. Let us consider some of them.

1. Diffusion + First-Order Chemical Reaction. If the diffusate interacts with the material of the sample in an irreversible first-order chemical reaction (or undergoes radioactive decay), the differential equation for Fick's second law has the form

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - kC, \tag{10}$$

where k is the rate constant of the chemical reaction (constant decay).

In this case, the amount of the substance absorbed by the plate up to the time t is

$$M_t = \frac{8DC_0S}{H}\sum_{m=0}^{\infty}\frac{\{u + (k+u)\,kt - u\exp[-(k+u)\,t]\}}{(k+u)^2}, \tag{11}$$

where $u = \pi^2 D(2m+1)^2/H^2$. The corresponding equations for other geometries can be found in [8].

2. Boundary Conditions of the Third Kind. Boundary conditions of the third kind reflect the fact that the exchange of concentrations between the surface layer of the sample and the surrounding medium occurs with a certain finite rate. In this case, the boundary condition has the form

$$D\frac{\partial C}{\partial N} = k_s(C_0 - C_s), \tag{12}$$

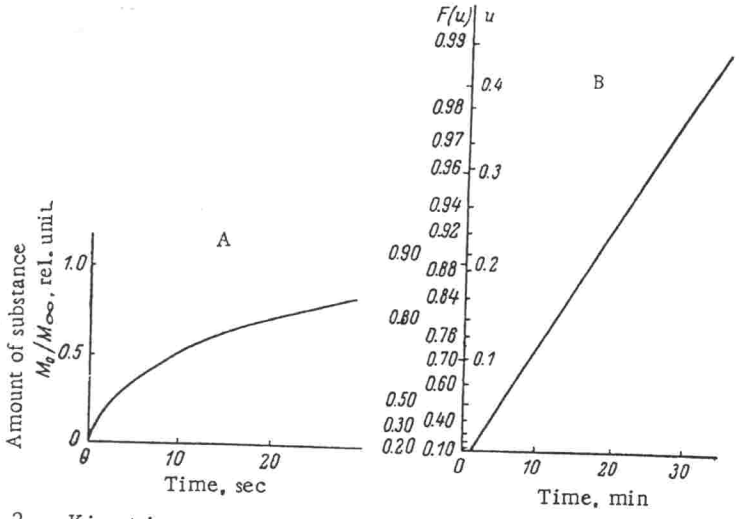

Fig. 2. Kinetic curve in the sorption method. A) Ordinary scale; B) functional scale.

where $\partial C/\partial N$ is the concentration gradient at a certain point on the surface, C_S is the con centration on the surface at the point where $\partial C/\partial N$ is taken, and k_S is the rate constant. Then the amount of substance absorbed by the plate up to the time t is

$$M_t = C_0 \sum_{n=0}^{\infty} g\left[\frac{1-\exp(-ut)}{u}\right], \quad (1$$

where $g = 4SD\mu_n/H^2 \cdot (\mu_n - \sin\mu_n \cdot \cos\mu_n)$, $u = \mu_n^2 D/H^2$, and μ_n denotes the positive roots of t equation

$$\operatorname{ctg}\mu_n = \frac{\mu_n^2 - B_i}{2\mu_n B_i}, \text{ where } B_i = \frac{k_S}{D}H. \quad (1$$

When boundary conditions of the third kind and a first-order chemical reaction are pre simultaneously,

$$M_t = C_0 \sum_{n=0}^{\infty} g\left\{\frac{u + (k+u)\,kt - u\exp[-(k+u)\,t]}{(k+u)^2}\right\}. \quad (1.$$

3. Diffusion with Trapping. In a number of cases, there arises a need to take into account special properties of the diffusion medium, which are manifested in its interaction with the diffusing substance. The appearance of such an interaction is attributed to the presence in the solid of traps, which capture the diffusing atoms and prevent their diffusio for a certain time. If the probabilities of the capture and release of an atom by a trap ar not dependent on the time, if the traps are evenly distributed in space, and if the concentr tion of the impurity is much lower than the concentration of the defects, the corresponding system of differential equations may be written in the form [9]

$$\begin{cases} \dfrac{\partial C(x,\,t)}{\partial t} = D\dfrac{\partial^2 C(x,\,t)}{\partial x^2} - k_1 C(x,\,t) + k_2 m(x,\,t), \\ \dfrac{\partial m(x,\,t)}{\partial t} = k_1 C(x,\,t) - k_2 m(x,\,t), \end{cases} \quad (16$$

where C(x, t) and m(x, t) are the concentrations of the mobile and trapped atoms, respectivel D is the diffusion coefficient, k_1 is the probability of the capture of a diffusing atom by a trap, and k_2 is the probability of its release. Solving system (16), for the amount of the substance we obtain

$$M_t = (C_0 + m_0)\,HS + \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2 A}\{[C_0(\alpha_1 - k_1 - k_2) - m_0\alpha_2]\,e^{-\alpha_1 t} - [C_0(\alpha_2 - k_1 - k_2) - m_0\alpha_1]\,e^{-\alpha_2 t}\}, \quad (17)$$

where C_0 and $m_0 = (k_1/k_2)C_0$ are the concentrations of the impurity in the mobile and immobile forms on the surface of the sample; $\alpha_1 = 1/2(k_1 + k_2 + D\omega^2) - A$, $\alpha_2 = 1/2(k_1 + k_2 + D\omega^2) + A$, $A = \sqrt{k_1 k_2 + 1/4(k_1 - k_2 + D\omega^2)}$, $\omega = (2m+1)\pi/H$.

4. Parallel Diffusion. If the kinetic plot of γ_t constructed in the linearized scale deviates significantly from the linear dependence, an attempt is made to decompose the complex diffusion process into elementary components, i.e., to find the spectrum of diffusion coefficients. In this case, it is assumed that diffusion takes place simultaneously along several independent channels, each of which is characterized by its own diffusion coefficient. In this case, the total diffusion flux may be represented in the form

$$J = \sum_{i=1}^{n} p_i J_i(D_i), \tag{18}$$

where J_i is the flux characterized by the diffusion coefficient D_i, and p_i is the contributio of this partial flux to the total diffusion process.

5. Dissociative Diffusion. In the case of dissociative diffusion [10], it is assumed that the migration process takes place along two interrelated channels, for example, along vacancies and interstitial sites, along defects with two charge states, through the bulk of the solid and along its microdefects, etc. A similar situation arises when there are two types of diffusion paths, each of which is characterized by its own diffusion coefficients. Processes of mutual exchange of the impurity atoms, which are formally described by the kinetics of a reversible first-order chemical reaction, occur between the two paths. The system of differential equations for dissociative diffusion has the form

$$\begin{cases} \dfrac{\partial C_1}{\partial t} = D_1 \dfrac{\partial^2 C_1}{\partial x^2} - k_1 C_1 + k_2 C_2, \\ \dfrac{\partial C_2}{\partial t} = D_2 \dfrac{\partial^2 C_2}{\partial x^2} + k_1 C_2 - k_2 C_1. \end{cases} \tag{19}$$

where C_1 and C_2 are the concentrations of the impurity in states 1 and 2, respectively, k_1 the rate constant of the transition process from state 1 to state 2, k_2 is the rate constan of the reverse process, and D_1 and D_2 are the diffusion coefficients for mechanisms 1 and 2 respectively.

We obtained a solution of system (19) for the amount of the impurity in a flat plate:

$$M_t = (C_{10} + C_{20})\, HS + S \sum_{m=0}^{\infty} \frac{2}{\omega} \{(A_1 + A_3)\, e^{-\alpha_1 t} + (A_2 + A_4)\, e^{-\alpha_2 t}\}. \tag{2}$$

Here

$$A_1 + A_3 = \frac{(\psi_1 + \psi_2)(-a_1 + k_1 + k_2) + (\psi_1 D_2 + \psi_2 D_1)\omega^2}{2A};$$

$$A_2 + A_4 = \frac{(\psi_1 + \psi_2)(a_2 - k_1 - k_2) - (\psi_1 D_2 + \psi_2 D_1)\omega^2}{2A};$$

$$a_1 = \frac{1}{2}[(D_1 + D_2)\omega^2 + k_1 + k_2] - A;$$

$$a_1 = \frac{1}{2}[(D_1 + D_2)\omega^2 + k_1 + k_2] + A;$$

$$A = \frac{1}{2}\sqrt{(D_1 + D_2)^2\omega^4 + 2(D_1 - D_2)(k_1 - k_2)\omega^2 + (k_1 + k_2)^2};$$

$$\psi_1 + \psi_2 = \frac{4}{H\omega}\left[-\frac{(C_{10}D_1 + C_{20}D_2)(k_1 + k_2)}{D_1 k_2 + D_2 k_1}\right] - \frac{4\omega(k_1 C_{10} - k_2 C_{20})(D_2 - D_1)}{(z^2 + \omega^2) H (D_1 k_2 + D_2 k_1)};$$

where

$$\psi_1 D_2 + \psi_2 D_1 = \frac{4}{H\omega}\left[-\frac{(C_{10}D_1 + C_{20}D_2)(D_2 k_2 + D_1 k_1)}{D_1 k_2 + D_2 k_1}\right] - \frac{4\omega(k_1 C_{10} - k_2 C_{20})(D_2^2 - D_1^2)}{(z^2 + \omega^2) H (D_1 k_2 + D_2 k_1};$$

$$\omega = \frac{(2m+1)\pi}{H}; \quad C_{10} = K_{S1} \cdot P; \quad C_{20} = K_{S2} \cdot P,$$

Here K_{S1} and K_{S2} are the solubility constants of the gas in phases 1 and 2, respectively; $\sqrt{k_1/D_1 + k_2/D_2}$. When there is local equilibrium ($k_1 C_{10} = k_2 C_{20}$)

$$A_1 = -\frac{2C_{10}}{(2m+1)\pi} \cdot \frac{-a_1 + D_2\omega^2 + k_1 + k_2}{A}; \quad A_2 = -\frac{2C_{10}}{(2m+1)\pi} \cdot \frac{a_2 - D_2\omega^2 - k_1 - k_2}{A};$$

$$A_3 = -\frac{2C_{10}}{(2m+1)\pi} \cdot \frac{k_1}{k_2} \frac{-a_1 + D_1\omega^2 + k_1 + k_2}{A};$$

$$A_4 = -\frac{2C_{10}}{(2m+1)\pi} \cdot \frac{k_1}{k_2} \frac{a_2 - D_1\omega^2 - k_1 - k_2}{A}.$$

6. Diffusion in Media of the Dispersion Type. If the defect sites are capable of forming their own phase, which is characterized by a concrete geometric shape and its own diffusion coefficient and solubility constant, the mathematical machinery for diffusion in media of the dispersion type [11, 12] should be used to describe the processes of migration in these media. Let the sample be a plate of thickness $H = 2l$, in which inclusions of spherical shape and radius r_0 are randomly distributed. Then the system of the corresponding differential equations has the form

$$\begin{cases} \dfrac{\partial C_1}{\partial t} = D_1 \dfrac{\partial^2 C}{\partial x^2} - 4\pi r_0^2 \rho_{in} \cdot D_2 \left(\dfrac{\partial C_2}{\partial r}\right)_{r=r_0}, \\ \dfrac{\partial C_2}{\partial t} = \dfrac{D_2}{r^2} \dfrac{\partial}{\partial r}\left(r^2 \dfrac{\partial C_2}{\partial r}\right), \end{cases} \tag{21}$$

where D_1 and D_2 are the diffusion coefficients in the dispersion medium and the dispersed phase (the inclusions), respectively, C_1 and C_2 are the distributions of the concentration in phases 1 and 2, $\rho_{in} = N/V$ is the density of the inclusions, N is the number of inclusions, and V is the volume of the sample.

Here it is assumed that the dispersion medium is an ultradilute suspension of spheres in the plate. The inclusions are assumed to be considerably smaller than the thickness of the sample, the "sinks" operate independently of one another, the local equilibrium is established instantaneously, and the diffusion within an inclusion has spherical symmetry. We shall solve system (21) under the following conditions: initial conditions — $C_1(x, 0) = C_{10}$, $C_2(r, 0) = C_{10}$; boundary conditions for the sample (the plate) — $C_1(l, t) = C_1^{\infty} = K_{S1}P$, $\partial C_1/\partial t(0, t) = 0$; boundary conditions for an inclusion (a sphere) — $C_2(r_0, t) = kC_1(x, r_0, t)$; $\partial C_2(0, t)/\partial t = 0$. The amount of the substance absorbed by such a plate up to the time t is

$$\gamma_t = \frac{M_t}{M_\infty} = \frac{\sum\limits_{m=0}^{\infty}\sum\limits_{n=1}^{\infty} \dfrac{\mu_m [1 - \exp(-\alpha \xi_{nm}^2 B_1 t)]}{\xi_{nm}^4 \left[\dfrac{\alpha}{\beta} + 1 + \operatorname{ctg}^2 \xi_{nm} - \left(1 - \dfrac{\mu_m^2}{\beta}\right)\dfrac{1}{\xi_{nm}^2}\right]}}{\sum\limits_{m=0}^{\infty}\sum\limits_{n=1}^{\infty} \dfrac{\mu_m^2}{\xi_{nm}^4 \left[\dfrac{\alpha}{\beta} + 1 + \operatorname{ctg}^2 \xi_{nm} - \left(1 - \dfrac{\mu_m^2}{\beta}\right)\dfrac{1}{\xi_{nm}^2}\right]}}, \tag{22}$$

where ξ_{nm} denotes the roots of the equation

$$\alpha \xi_{nm}^2 + \beta(1 - \xi_{nm} \operatorname{ctg} \xi_{nm}) = \mu_m^2; \quad \mu_m = \frac{2m-1}{2}\pi; \quad m = 0, 1, 2, 3... \tag{23}$$

$\alpha = D_2 l^2/D_1 r_0^2$, $\beta = (\delta/r_0)(D_2/D_1) l^2 k = 3\alpha k \varepsilon_2$, k is the distribution coefficient of the impurity between the dispersion medium and the inclusions, ε_2 is the volume fraction of the inclusions, $\delta = 4\pi r_0^2 \rho_{in}$, and $B = l^2/D_1$.

The proposed methods were used to study the diffusion of a radioactive inert gas, viz., radon, in low-density polyethylene tablets (the degree of crystallinity was 57%). It was found that in the case of the system under consideration, the diffusion process is described sufficiently well in the framework of the model of classical diffusion. The value of the diffusion coefficient is $D = (9.5 \pm 0.8) \cdot 10^{-8}$ cm^2/sec and the value of the solubility constant is $K_S = 0.60 \pm 0.1$ cm^3/cm^3·atm. These values are in good agreement with the results obtained by the permeability method [13].

LITERATURE CITED

1. J. Crank and G. S. Park, Diffusion in Polymers, Academic Press, London—New York (1968), p. 3.
2. C. R. Rhee and J. D. Ferry, J. Appl. Polym. Sci., 21, 733 (1977).
3. C. L. Rayner, L. Thomassen, and L. J. Ronse, Trans. Am. Soc. Met., 30, 313 (1962).
4. M. V. Aref'eva, in: Numerical Analysis in FORTRAN. Methods and Algorithms [in Russian], MGU, Moscow (1978), p. 3.
5. A. H. Wilson, Philos. Mag., 39, 48 (1948).
6. I. N. Bekman and A. A. Shvyryaev, Vestn. Mosk. Gos. Univ., Ser. 2, Khim., 22, No. 5 (1981).
7. A. A. Shvyryaev and I. N. Bekman, Vestn. Mosk. Gos. Univ., Ser. 2, Khim., 22, No. 5, 517 (1981).
8. P. V. Danckwerts, Trans. Faraday Soc., 46, No. 4, 300 (1950).
9. H. Gans, Z. Naturforsch, 20a, 1298 (1965).
10. F. Maesen and G. A. Brenkman, J. Electrochem. Soc., 102, 229 (1955).