METHODS OF EXAMINING RADIOACTIVE-GAS DIFFUSION IN SOLIDS.

V. AN AUTORADIOGRAPHIC FORM OF THE PERMEABILITY METHOD

I. N. Bekman

UDC 539.217.5:778.33:546.296:7678.742.3

A new technique is described for determining the diffusion parameters of radioactive gases in solids, which uses the gas permeability method along with autoradiography. The technique is intended for examining the topological features of the diffusion and for determining the spectrum of the local diffusion coefficients. An apparatus has been developed and the appropriate mathematical techniques have been devised, and the method of performing the experiment has been checked out. The autoradiographic form of the permeability method has been used to determine diffusion coefficients for a radioactive inert gas (radon) in polypropylene. The results are in good agreement with those from traditional methods.

Autoradiography is used to determine diffusion coefficients and to obtain information on the distribution of trace components over surfaces or volumes. Unfortunately, there are considerable difficulties in using this method with gas diffusion, on account of the high mobility of a gaseous impurity.

Here we describe a technique for using the radiochemical form of the permeability method in conjunction with autoradiography to determine the diffusion parameters of gases in solids. The autoradiographic form of the permeability method has been developed for the diffusion of radon ^{222}Rn in polypropylene.

The material was isotactic polypropylene containing less than 1% of the atactic fraction. The polymer was provided in the form of granules, which were converted to film by pressing in a press mold with controlled heating. For this purpose the polypropylene was heated to 200°C and a pressure of 10^7 Pa was applied, after which the specimen was cooled rapidly. The operations were performed with a single membrane of thickness 110 μm. Photographs in polarized light showed that the specimen had a small-spherulite texture with a mean spherulite diameter of 10 μm.

The experiments on the autoradiographic form of the permeability method were performed with three different techniques.

A. The membrane was placed in the diffusion cell and the usual experiment in the permeability method was performed. At a certain instant the diffusion was halted by cooling the cell rapidly to liquid-nitrogen temperature, and the membrane was removed and clamped between two photographic plates. The exposure was performed at −50°C. It had previously been shown that the impurity did not migrate under these conditions. The photographic plates were photometered after exposure and development. Similar experiments were performed with various times until the steady state of diffusion was attained.

In principle, this technique gives all the information required to derive the complete spatial distribution of the impurity over the thickness of the specimen, but it is laborious and its use is promising only in the analysis of complicated diffusion anomalies. Also, there is the possibility of some loss of the gas in the manipulations with the membrane.

B. To prevent gas loss during the exposure, one can use a diffusion cell as shown in Fig. 1. Here the photographic plate is in constant contact with the membrane. The diffusion and exposure processes begin together when the cell is filled with radioactive gas.

This form is applicable only if the radiation from the gas volume does not reach the material or does not influence it. It can be used in operation with soft β^- emitters (^{14}C, ^3H, etc.) or α emitters, and then the

Translated from Radiokhimiya, Vol. 23, No. 5, pp. 760-766, September-October, 1981. Original article submitted June 28, 1980.

0038-576X/81/2305-0614$07.50

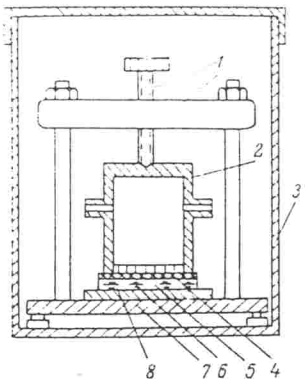

Fig. 1

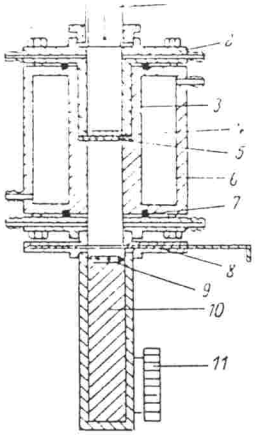

Fig. 2

Fig. 1. Device for combined use of gas permeability and autoradiography: 1) clamping device; 2) diffusion cell; 3) thermostatic body; 4) porous ceramic; 5) photographic plate with nuclear emulsion; 6) corrugated rubber inset; 7) metal plate; 8) polymer membrane.

Fig. 2. Apparatus for the autoradiographic form of the permeability method: 1) radiation counter; 2) upper section of diffusion cell (gas space); 3) lower section of diffusion cell (receiver); 4) porous ceramic substrate; 5) membrane; 6) thermostatic volume; 7) teflon seal; 8) cassette; 9) photographic plate with nuclear emulsion; 10) vertical-lift shaft; 11) lift raising system.

thickness of the membrane should exceed the range of the radiation in the material. We used type A-2 emulsion to record the radon, which is sensitive to the α rays from the radon but largely insensitive to the γ and β^- emissions from the decay products. The diffusion and exposure occur simultaneously, so the method has a strong integrating effect, which hinders calculation of the diffusion coefficient. The technique is simple and can be recommended for qualitative monitoring of the homogeneity of the diffusion.

C. The apparatus shown in Fig. 2 enables one to avoid most of the above disadvantages. Here the diffusion cell is separated from the chamber containing the photographic plate. The cell is fitted with a radiation counter for monitoring the activity at the entrance to the membrane. The membrane is supported by a porous ceramic plate on the gas-space side. This provides close and uniform contact between the photographic plate and the membrane.

During the diffusion the receiver is flushed with a strong flow of air (here the photographic plate attached to a vertical-lift shaft is withdrawn into the cassette). The gas is introduced into the gas space at the start and the usual diffusion experiment is performed. Then the cassette is opened, the shaft is raised, and the photographic plate is brought into contact with the membrane. From this instant the diffusion and exposure are combined. After the end of the exposure the shaft is withdrawn and the cassette is closed and removed for reloading. In this form, the thickness of the membrane is chosen such that the time required to reach the steady state is one day. The specific activity of the radon provided an exposure time of 1 hr. Under these conditions the integrating action was small, and it was possible to record several frames representing the development of the diffusion process for a particular part of the membrane during the experiment.

With the use of a thin membrane ($H = 110\ \mu m$), the diffusion was halted by cooling the cell to $-40°C$, and the exposure was performed in the cold (the gas space remained filled with the radioactive gas, which prevented loss from the membrane). Then the photographic plate was removed, the temperature was raised to the initial value, and the diffusion experiment was continued.

In technique C, as in the previous one, one can use only isotopes with soft radiations. The advantage of the technique is that it is dynamic. It is possible to record a complete film of the development of the diffusion in the solid with optimum choice of membrane thickness and gas specific activity.

We now consider briefly the phenomenological theory of the autoradiographic form for the permeability method. We consider a layer dx in the membrane, whose emission dI in either direction is

$$dI = C(x, t)\, AK(x, H - x)\, dx, \tag{1}$$

where C(x, t) is the distribution of the impurity concentration over the thickness of the membrane, A is a quantity proportional to the number of particles radiated by a given volume of the layer of radioactive materia in unit time, and K(x, H−x) is a function that corrects for the absorption and back-scattering of the radiation by the membrane material. The plate blackening density at the entrance side of the membrane is

$$I_{en} = \int_0^H AC(x, t)\, K_1(x, H - x)\, dx, \tag{2a}$$

and at the exit side of the membrane is

$$I_{ex} = \int_0^H AC(x, t)\, K_2(H - x, x)\, dx, \tag{2b}$$

If α or β^- radiations are used and for H > R

$$I_{en} = \int_0^R AC(x, t)\, K_1(x, H - x)\, dx, \tag{3a}$$

$$I_{ex} = \int_{H-R}^H AC(x, t)\, K_2(H - x, x)\, dx. \tag{3b}$$

The following formula describes the concentration of the diffusing component over the thickness of the membrane under the traditional boundary conditions of the permeability method:

$$C(x, t) = C_0\left[1 - \frac{x}{H} - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin\frac{n\pi x}{H}\exp\{-n^2Bt\}\right], \tag{4}$$

where C_0 is the concentration at the entrance side, x is coordinate, H is membrane thickness, $B = \pi^2 D/H^2$, and D is diffusion coefficient.

To calculate the diffusion coefficient we first have to convert from the measured blackening density to the concentration profile C(x, t); from the mathematical viewpoint, equations (2) and (3) are integral Fredholm equations of the first kind. One measures I_{en} (or I_{ex}) and knowing K_1 (or K_2) one finds C(x, t). Such problems are of the class of inverse incorrectly formulated ones in mathematical physics, so a solution can be obtained only by the use of regularization methods. From the physical viewpoint, the kernel of (3), K(x, H−x), reflects the dose produced at the photographic plate by the radiation from an infinitely thin unbounded layer of active material lying at depth x parallel to the surface of the membrane. Various expressions apply for K(x, H−x) in accordance with the form of the radiation. In parricular, for β^- and soft γ rays [1], the attenuation is in accordance with $1/r^2$ and $e^{-\mu r}$ laws, and

$$K_1^{\gamma} = \int_{-\mu x}^{\infty}\frac{e^{-y}}{y}\,dy = -E_i(-\mu x) = E_1(\mu x), \tag{5a}$$

$$K_2^{\gamma} = \int_{\mu(H-x)}^{\infty}\frac{e^{-y}}{y}\,dy, \tag{5b}$$

where E_i is the integral-exponential function and μ is the attenuation coefficient for the radiation in matter.

For α rays [2]

$$K_1^{\alpha} = \frac{1}{2}\left(1 - \frac{x}{R_{\alpha}}\right), \tag{6a}$$

$$K_2^{\alpha} = \frac{1}{2}\left(1 - \frac{H}{R_{\alpha}} + \frac{x}{R_{\alpha}}\right), \tag{6b}$$

where R_{α} is the range of the α rays in matter and $x \leq R_{\alpha}$.

To demonstrate the features of the method we calculated I_{en} and I_{ex} in relation to diffusion time. The calculations were performed for ^{14}C (E = 0.158 MeV, μ = 350 cm^{-1}, and R_{max} = 300 μm). The thickness of the layer of material between the membrane and the photographic plate was Δ = 10 μm, while the thickness of the

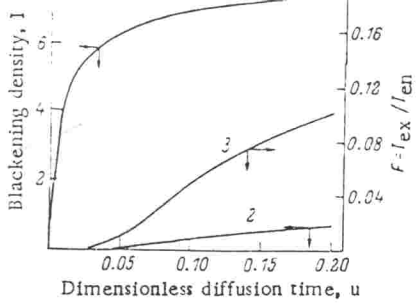

Fig. 3. Dependence of blackening density on dimensionless diffusion time: 1) density at entrance surface; 2) density at exit surface; 3) ratio of density at exit surface to density at entrance surface (^{14}C, E = 0.158 MeV, μ = 350 cm^{-1}, R_{max} = 300 μm, thickness of layer between membrane and photographic plate Δ = 10 μm).

membrane was H = 100 μm, and B = 1. Figure 3 shows that $I_{en}(u)$ and $I_{ex}(u)$ are parabolic and attain a constant value in the steady diffusion state. The $F = I_{ex}/I_{en}$ dependence is S-shaped. In practice, the use of I_{en} (or I_{ex}) alone encounters serious difficulties, since it becomes necessary to determine the absolute specific activity of the gas and it is necessary to calibrate the blackening function in activity units.

The distribution of the blackening density at the entrance surface of the membrane can be used to calculate the diffusion-coefficient spectrum (more precisely, to calculate values for the dimensionless diffusion time, i.e., the parameter $u = (D/H^2)(t)$. In fact, the spread in I_{ex} in a sense reflects the development of the diffusion in a particular part of the membrane. However, this approach can be used only if the inhomogeneity in the blackening is related solely to inhomogeneity in the diffusion. If there is a spectrum of solubility constants K_S, then the blackening density is $I_{ex} \sim K_S D$, and to calculate the spectrum of D one should use simultaneously the values of I_{en} and I_{ex} on mutually opposite points on the surfaces of the membrane. An additional advantage of this technique is that it is not necessary to calibrate in terms of absolute activity, i.e., to determine the parameter A in (1).

To facilitate the calculation of parameter u we have tabulated the functions $F(u) = I_{ex}/I_{en}$ for various values of μx (Fig. 4a) and R_α (Fig. 4b). Figure 4 shows that there is a range in F(u) that is optimal from the viewpoint of the determination of u. This range is dependent on the combination of H, t, and μ (or R_α). If the range is large (H is small or μ is small), the main contribution to the blackening of both photographic plates comes from C_0, and it is practically impossible to determine D. If the range is short (H > 2R), the radiation from the central part of the membrane does not reach the photographic plate and the information on the concentration distribution in this part of the membrane becomes inaccessible. As a result, the accuracy in calculating D falls. If the range is very short and the diffusion times are small, we have $F(u) \to 0$, and it is also impossible to calculate D. If the times are large (u large), the steady state is approached, and the system becomes unstable, since minor fluctuations in F(u) lead to large deviations in u. It is impracticable to determine D at all in the steady state, since then the concentration distribution is independent of D and is determined soley by the difference in the concentrations at the entrance and exit surfaces of the membrane. Therefore, under each set of particular conditions there is a definite range in time giving reliable determination of the diffusion parameters. In this connection it is desirable to have several autoradiographs recorded from one part of the specimen but with different diffusion times.

This set of data is necessary also when it is difficult to determine the attenuation coefficient or range of the radiation in matter. The method of processing the results that does not require knowledge of μ (or R_α) is based on the fact that one can restrict oneself to the first term of the series in (4) for comparatively large diffusion times (but still far from the steady state). Then:

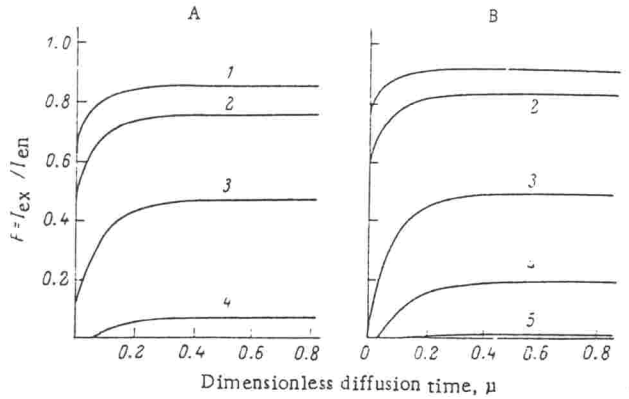

Fig. 4. Theoretical curves for $F(u) = I_{ex}/I_{en}$ in relation to dimensionless diffusion time $u = Dt/H^2$: A) β^- radiation: 1) $\mu = 10^{-4}$; 2) 10^{-3}; 3) 10^{-1}; 4) 1 cm^{-1}; B) α radiation: 1) $R_\alpha = 500$; 2) 250; 3) 100; 4) 50; 5) 5 μm.

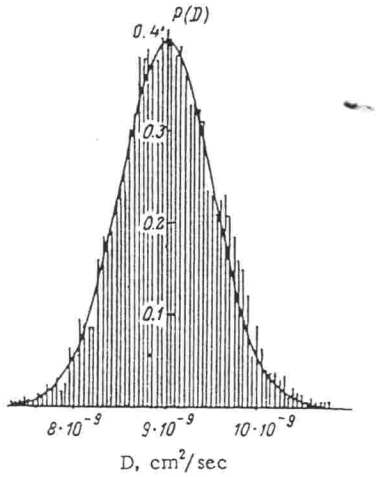

Fig. 5. Distribution of the sample of diffusion coefficients for radon in polypropylene.

$$F(u) = \frac{I_{ex}}{I_{en}} = \frac{\int_0^H C_0\left(1-\frac{x}{H}\right) AK(H-x, x)\,dx - \frac{2}{\pi}\exp(-Bt)\int_0^H A\sin\frac{\pi x}{H}K(H-x, x)\,dx}{\int_0^H C_0\left(1-\frac{x}{H}\right) AK(x, H-x)\,dx - \frac{2}{\pi}\exp(-Bt)\int_0^H A\sin\frac{\pi x}{H}K(x, H-x)\,dx} = \frac{1-k\exp(-Bt)}{1+k\exp(-Bt)}, \quad (7)$$

$$k = \frac{\frac{2}{\pi}\int_0^H \sin\frac{\pi x}{H}K(H-x, x)\,Adx}{\frac{2}{\pi}\int_0^H \left(1-\frac{x}{H}\right)AK(H-x, x)\,dx} = -\frac{\frac{2}{\pi}\int_0^H A\sin\frac{\pi x}{H}K(x, H-x)\,dx}{\frac{2}{\pi}\int_0^H \left(1-\frac{x}{H}\right)AK(x, H-x)\,dx}. \quad (8)$$

After transformation we have

$$\ln\frac{I_{en}-I_{ex}}{I_{en}+I_{ex}} = \ln k - Bt. \quad (9)$$

Parameter k collects all the quantities related to absorption of the radiation by the specimen material. The slope B in (9) is dependent only on the diffusion factors. A plot of $\ln(I_{en}-I_{ex}/I_{en}+I_{ex})$ against t gives D from the inclination of the straight line to the abscissa.

Preliminary experiments were performed by the traditional form of the permeability method, and we examined the diffusion of radon through a polypropylene membrane of thickness $H=110\ \mu m$. The kinetic break-through curves were processed by the standard method using least squares. There was good agreement between the experimental results and theoretical relationships; no anomalies indicating the presence of several diffusion coefficients were observed. The diffusion coefficient was $D=(11.5\pm0.5)\cdot10^{-9}\ cm^2/sec$.

On operating with autoradiographic technique A, the diffusion experiment was interrupted at time $t=\tau_{1/2}$, and the membrane was removed and gripped between two photographic plates. F_{exp} was calculated from the photometry data for the entrance and exit surfaces, and the previously calculated F_{th} was used to derive the set of u. Figure 5 collects the results. The distribution of the sample fits closely to a normal distribution (the basic moments of the observed distribution are $\beta_1=0.01$; $\beta_2=2.98$, whereas the corresponding values for a Gaussian distribution are $\beta_1=0$; $\beta_2=3$). The mean diffusion coefficient given by the autoradiographic data was $D=(9\pm1)\cdot10^{-9}\ cm^2/sec$.

In operating with technique C, we obtained results for six diffusion times. The data were processed via (9). Then $D=(7.5\pm0.5)\cdot10^{-9}\ cm^2/sec$.

Therefore, the diffusion coefficients derived from two techniques in the autoradiographic form of the diffusion method are in agreement with one another within the errors of experiment and also with the data from the traditional form of the permeability method (although they are somewhat less for the autoradiographic technique).

The distribution of the α tracks over the surface of the membrane was reasonably uniform. Only for small diffusion times was there a certain inhomogeneity on the autoradiogram recorded at the exit surface. For large times, the entrance surface showed isolated ordered clumps of star type, which are evidently related to the deposition of the decay products of radon (active deposit).

LITERATURE CITED

1. B. P. Golubev, Dosimetry and Protection from Ionizing Radiations [in Russian], Atomizdat, Moscow (1976), p. 412.
2. V. I. Ivanov, Ionizing-Radiation Dosimetry [in Russian], Atomizdat, Moscow (1964), p. 250.