EXPERIMENTAL STUDIES OF RADIOACTIVE GAS DIFFUSION IN SOLIDS. I. APPARATUS ASSEMBLY FOR RADIOCHEMICAL VERSIONS OF THE PENETRANCE METHOD

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An apparatus assembly for integral and differential radiochemical versions of the penetrance method was developed and tested. Diffusional parameters (penetrability, solubility, and diffusion constants) for radon in low-density polyethylene were determined.

Extensive studies of foreign atom migration in solids became possible only when quantitative methods for determining diffusional parameters using radioisotopes as tracers were developed. However, tracer methods are still employed sparingly for studying sorption, diffusion, and penetrance of gases. Meanwhile, several factors contributed to the development of radiochemical versions of the well-known methods:

1. Diffusional parameters of elements lacking stable isotopes, e.g., radon, cannot be measured by traditional methods;

2. use of radioisotopes greatly enhances the sensitivity of the methods and facilitates their automation;

3. use of spectroscopic type of detectors permits determination of diffusional parameters of several gases simultaneously. This provides scope for studying gradual and counterdiffusion of various substances;

4. detectors are indifferent to the composition of the surrounding medium. Work is permissible in vacuum, inert atmosphere, usual atmospheric conditions, and even agressive media;

5. use of autoradiographic recording techniques makes it possible to directly control the progress of diffusion in the solid phase.

The peculiarities of radioisotopes (penetrating radiation, growth and decay processes, etc.) demand modification of both the apparatus assembly and the phenomenological theory underlying the method. Thanks to its simplicity and easy applicability, the penetrance method occupies a leading place among other methods of study of gas diffusion in solids. The method permits concurrent determination of diffusion, penetrability, and solubility constants. For performing the experiment, a cell partitioned into two chambers, viz., reservoir and receiver, by a membrane of the test substance is generally used. The gas is led into the reservoir and the process of its transfer to the receiver is studied. In the integral version of the penetrance method the temporal change in gas volume in the receiver is recorded, while in the differential version the temporal change in the rate of gas flow through the membrane is recorded.

Radiochemical apparatus assemblies are known [1] where an ionizing radiation detector built into the receiver monitors gas activity in the specimen. This version necessitates special experiments to study the laws of radiation attenuation in the membrane material. Therefore, apparatus assemblies based on the determination of the quantity of the substance passed through the specimen has gained wide popularity. The monitoring is done by transferring samples collected from the receiver periodically to an external counter. An example of such an apparatus assembly [2] is the one designed for monitoring water permeability of polymer films using water labelled with tritium. Periodic sampling is detrimental to reproducibility of results and does not permit study of fast diffusional processes. The experiment is arduous and not amenable to automation.

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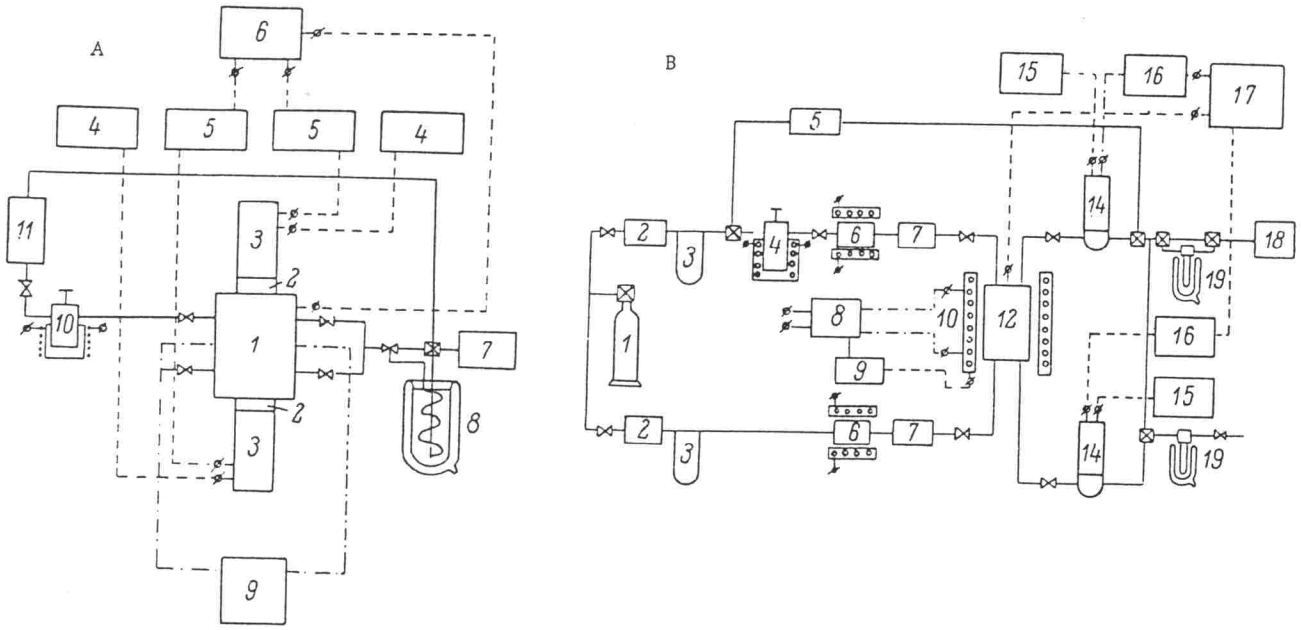

Fig. 1. Block diagram of apparatus assembly for radiochemical penetrance method. A) Integral version: 1) diffusion cell; 2) radioactive radiation detector; 3) photomultiplier; 4) high-voltage detector power pack; 5) counting-rate meter; 6) multipoint electronic potentiometer; 7) preevacuation pump; 8) zeolite collector in Dewar flask containing liquid nitrogen; 9) thermostat; 10) pressing device with heater; and 11) circulation pump. B) Differential version: 1) carrier gas cylinder; 2) carrier gas flow stabilizing system; 3) rheometer; 4) pressing device with heater; 5) circulation pump; 6) carrier gas purifying system; 7) drier; 8) heater power source; 9) temperature control panel; 10) heater; 11) regulating thermocouple; 12) diffusion cell; 13) control thermocouple [missing in the diagram — Publisher]; 14) flow detector; 15) high-voltage detector power pack; 16) counting-rate meter; 17) multipoint electronic potentiometer; 18) pre-evacuation pump; 19) zeolite collector in Dewar flask containing nitrogen.

The aim of this work is to create an automatic versatile apparatus assembly for the radiochemical versions of the penetrance method. The methods proposed are applicable for determining the parameters of randon diffusion in low-density polyethylene.

Apparatus Assembly. The assembly consists of a diffusion cell, a recording system, a system for admitting the radioactive gas, a carrier gas purifying system, a temperature measuring and regulating system, and a system for absorbing the radioactive gas after completion of the experiment (Fig. 1). The apparatus assembly permits continuous automatic recording of gas activity on both sides of the membrane or in the membrane itself as well as of specimen temperature during the experiment. The design provides for change of detectors for different types of radiations.

Integral Version. The diffusion cell (Fig. 2A shows a version having scintillation detectors) consists of two sections for gripping the specimen and two sections for fixing the detectors. The former have gas entry and exit holes and knife seals. One of the sections is integral with the thermostating space and has a thermocouple socket. The specimen supported by the mesh occurs at the center of the thermostating space. The section is sealed by the film material or by using inserts. The radioactive radiation detectors isolated from the cell by a thin aluminum foil, the light pipes, and the photomultipliers are located in the detector-fixing sections. The detectors are cooled by running water. The functional temperature range is 0-150°C.

Differential Version. The diffusion cell consists of two parts which, on contraction, seals the membrane. The sylphon permits one to seal the specimen upon attainment of the desired temperature and complete degassing. The diffusion cell is fixed to the heater with the aid of a flange. The temperature is measured by a built-in thermocouple placed in the nearest vicinity of the membrane. During the experiment the carrier gas flows over the membrane and draws the diffused gas into an external flow-type detector. The functional temperature range is 20-800°C.

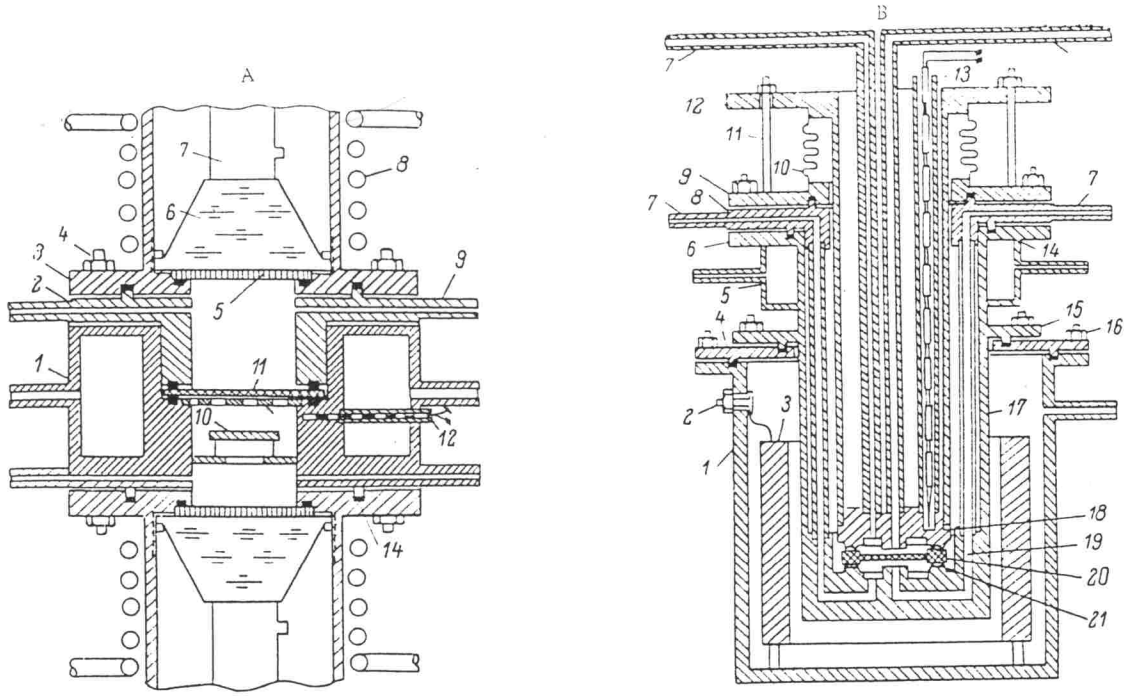

Fig. 2. Design of diffusion cells. A) Integral version: 1) cell section integral with thermostating space; 2) second section of diffusion cell; 3) section for fixing detectors; 4) bolts which seals the section on tightening; 5) scintillation detector; 6) light pipe; 7) photomultiplier; 8) water cooling of detector; 9) gas pipe; 10) shields preventing direct entry of radiation from the gas in the reservoir to the detector in the receiver; 11) membrane made of the test substance; 12) thermocouple; 13) supporting mesh; and 14) knife seal. B) Differential version: 1) oven shell; 2) current lead; 3) heater; 4) oven cover; 5) water-cooled jacket; 6, 8, 10, 14-16) coupling flanges; 17) shell integral with diffusion-cell section; 18) second diffusion-cell section; 19) specimen; 20) knife seal; 9) bolt; 11) nuts for sealing the membrane by tightening; 12) sylphon; 7) gas pipe; and 13) thermocouple.

The apparatus assembly developed by us is fully automated and permits use of isotopes having different types of radiations, including short-lived, and complex decay characteristics. The pressures on both sides of the membrane being the same, it is possible to use membrane made of brittle and elastic materials. Use of two detectors (in the reservoir and receiver) greatly widens the scope of the method:

1. Facilitates calculation of penetrability constant.
2. Permits one to regulate decay and growth of radioisotopes.
3. Makes it possible to eliminate the temperature dependence of penetrability constant in a wide temperature range relying on a single specimen.
4. Use of data recorded by the detector in the receiver or the reservoir or by both detectors is permitted for processing the results.

It is expected that the proposed apparatus assemblies will find use in the study of diffusion of radioactive gases and vapors in metallic, vitreous, and polymer membranes.

Experimental Procedure and Processing of Results. The specimen was degassed before the experiment. To do this, the reservoir and the receiver were evacuated concurrently and the membrane was held at a temperature slightly higher than the experimental. After degassing the temperature was lowered to the desired level. During this period the apparatus assembly recorded the background activity in both chambers. Thereafter with the aid of a vacuum or circulation pump the test gas was transferred to the reservoir and the increase in the counting rate was recorded in the closed receiver (integral version) or in the flow-type detector (differential version).

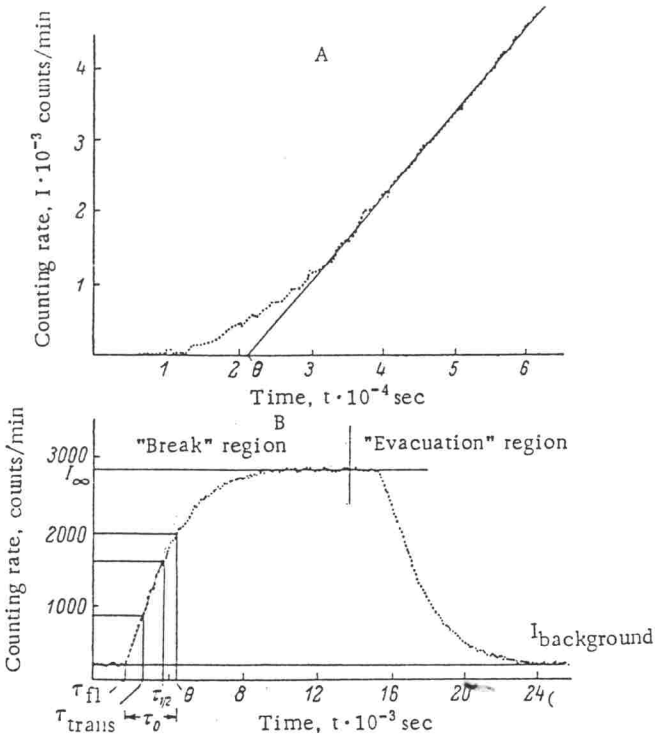

Fig. 3. Typical plots of radon diffusion in low-density polyethylene. A) Integral version; B) differential version.

In the integral version the time-dependence of the counting rate (i.e., the volume of the gas passing into the receiver through the membrane surface X = H) takes the form

$$I_1 = akP\frac{S}{H}\frac{T}{T_0}p_0\left[t - \frac{H^2}{6D} - \frac{2H^2}{\pi^2 D}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left\{-\left(\frac{n\pi}{H}\right)^2 Dt\right\}\right], \quad (1)$$

where D is the diffusion constant; H is the membrane thickness; a is the specific gas activity in the reservoir; P is the penetrability constant; S is the area of the membrane surface; T is the temperature, °K; T_0 and p_0 are the normal temperature and pressure, respectively; and k is the radiation counting coefficient of the given isotope.

For long durations the plot by Eq. (1) is a straight line from whose slope the penetrability constant can be found out as follows:

$$P = \frac{V}{p_0}\frac{T_0}{T}\frac{H}{S}\frac{1}{p}\operatorname{tg}\alpha, \quad (2)$$

where V is the reservoir volume and α is the slope of the rectilinear segment. The diffusion constant can be calculated from the segment (the so-called "time lag" θ) intercepted by the extension of the rectilinear segment on the time axis:

$$D = \frac{H^2}{6\theta}. \quad (3)$$

The solubility constant was calculated by the equation

$$K_p = \frac{P}{D}. \quad (4)$$

In the differential version of the penetrance method employed under usual boundary conditions the time dependence of the counting rate in the flow-type detector (i.e., the gas flow through the membrane) is described by the following equation:

$$I_t = \frac{DSC_0}{H}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n\exp\left\{-\frac{n^2\pi^2}{H^2}Dt\right\}\right]. \quad (5)$$

TABLE 1. Parameters of Radon Diffusion in Low-Density Polyethylene

Method	D, cm^2/sec	P, $cm^2/sec \cdot Pa$	K_p, cm^3/Pa
Integral	$(5.2\pm0.4)\cdot10^{-8}$	$(4.4\pm0.4)\cdot10^{-13}$	$(0.85\pm0.02)\cdot10^{-5}$
Differential	$(3.2\pm0.1)\cdot10^{-8}$	$(2.6\pm0.5)\cdot10^{-13}$	$(0.82\pm0.05)\cdot10^{-5}$

The plot by Eq. (5) for long durations attains the constant quantity $I_\infty = (DSC_0)/H$, from which the penetrability constant can be found as

$$P = \frac{Q_\infty H}{Sp}. \quad (6)$$

The diffusion constant can be determined from the time for attaining a flow rate half that in the stationary state (i.e., $\tau_{1/2}$ is a time at which $J_1/J_0 = 0.5$):

$$D = \frac{H^2}{7.2\tau_{1/2}}. \quad (7)$$

Study of Radon Diffusion in Polyethylene. The methods proposed were used to study the diffusion of the radioactive inert gas radon (^{222}Rn) in low-density (57% crystallinity) polyethylene films. The typical experimental plots are given in Fig. 3. The evaluations of the parameters of radon diffusion in polyethylene at the 90% significance level (temperature 18°C), made in the integral (three specimens, seven measurements) and differential (four specimens, seven measurements) methods, are given in Table 1.

The referred values agree well with the theoretical ones based on physicochemical properties of radon and with the diffusion parameters of other gases in low-density polyethylene [3].

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EXPERIMENTAL STUDIES OF RADIOACTIVE GAS DIFFUSION IN SOLIDS. II. EVALUATION OF RADIOACTIVE DECAY AND GROWTH IN THE PENETRANCE METHOD

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The phenomenological theory of the radiochemical penetrance method is discussed with due regard for radioactive decay and growth. Expressions are given for time dependence of flow, amount of substance diffused, and concentration distribution across the membrane thickness under conditions of gradual radiochemical conversions. It is shown that the time lag may diminish (on radioactive decay) or increase (due to active deposition). Equations are proposed for calculating diffusion constants of gases labelled with short-lived isotopes having complex decay characteristics (e.g., of radon) from the experimental data obtained by the penetrance method.

Processing of experimental data obtained in the radiochemical version of the penetrance method often makes it necessary to take account of complex processes of radioactive decay and

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