

Comparative Evaluation of Diffusion Coefficients for Gases and Vapors of Organic Substances through Polyethylene Membranes Determined by Absorption and Desorption Upstream Time Lag Method

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Synopsis

The diffusion coefficients for carbon dioxide and methanol vapor through a polyethylene membrane were measured by means of absorption and desorption upstream time lag methods. A volumetric vacuum apparatus was used to perform the measurements. The diffusion coefficients determined by the two methods were similar for carbon dioxide permeating through a polyethylene membrane but were different by a factor of about 2 for methanol vapor diffusing through the same membrane. The difference found in the latter case was caused by methanol sorption on the measuring cell walls. However, the diffusion coefficients for methanol determined by both methods became similar after introducing the necessary correction. The desorption upstream time lag method was found to be very useful, particularly when a penetrant is strongly absorbed on the measuring cell walls.

INTRODUCTION

The partition cell technique allows to determine diffusion coefficients by a time lag method¹ in four modes such as: absorption upstream $L^a(0)$, desorption upstream $L^d(0)$, absorption downstream $L^a(l)$, and desorption downstream $L^d(l)$.

Volumetric vacuum apparatus²⁻⁴ equipped with manostat to keep the pressure constant enables one to determine diffusion coefficients by absorption and desorption upstream time lag methods. Diffusion coefficients were determined in our previous works by the absorption upstream time lag method using the partition cell technique. A serious limitation of this method consists of penetrant sorption on the measuring cell walls that results in large errors in determining the diffusion coefficients, while the permeability coefficients are not affected. To avoid this, the measuring cells had to be made of special materials. However, even cells made of stainless steel did not allow determination of the diffusion coefficients of water vapor by this technique.

The aim of this work was to test whether the partition cell desorption upstream method can be used to determine diffusion coefficients and then to compare them with those measured by the absorption upstream method. The penetrant sorption on the measuring cell walls must not affect the determinations performed by the desorption upstream method due to constant pressure at the membrane side, where the penetrant permeating through the polymer membrane is determined quantitatively. Thus, the quantity of the sorbed gas or vapor is kept constant.

**MATHEMATICAL RELATIONS DESCRIBING DIFFUSION
THROUGH A FLAT POLYMER MEMBRANE**

Barrer⁵ gives the general equation describing the relation between the time lag and the boundary conditions of measurement and the diffusion coefficient:

$$L = \frac{1}{c_2 - c_1} \left[\frac{c_2 l^2}{6D} + \frac{c_1 l^2}{3D} - \frac{c_0 l^2}{2D} \right] \quad (1)$$

where L is time lag; c_1 is penetrant concentration at the membrane side, where a penetrant permeating through a polymer membrane is determined quantitatively; c_2 is penetrant concentration at the reverse membrane side; c_0 is penetrant concentration within the membrane; l is membrane thickness; and D is diffusion coefficient.

When $c_1 > c_2$, upstream time lag occurs; while at $c_2 > c_1$, downstream time lag is attained. For absorption upstream time lag $L^a(0)$, the boundary conditions are as follows:

$$\begin{array}{lll} c_1 = c & \text{at } x = 0 & \text{for any time } t \\ c_2 = 0 & \text{at } x = l & \text{for any time } t \\ c_0 = 0 & \text{at } 0 < x < l & \text{for } t = 0 \end{array}$$

where x is the distance from the membrane boundary.

Substituting the above values into eq. (1), we obtain

$$L^a(0) = -\frac{l^2}{3D} \quad (2)$$

For desorption upstream time lag $L^d(0)$, the boundary conditions are as follows:

$$\begin{array}{lll} c_1 = c & \text{at } x = 0 & \text{for any time } t \\ c_2 = 0 & \text{at } x = l & \text{for any time } t \\ c_0 = c & \text{at } 0 < x < l & \text{for } t = 0 \end{array}$$

Substituting these values into eq. (1)

$$L^d(0) = \frac{l^2}{6D} \quad (3)$$

Transforming eqs. (2) and (3), we get

$$D = -\frac{l^2}{3L^a(0)} \quad (4)$$

and

$$D = \frac{l^2}{6L^d(0)} \quad (5)$$

respectively. Equations (4) and (5) can then be used to calculate the diffusion coefficients in case of absorption and desorption upstream time lags, respectively.

EXPERIMENTAL

The diffusion D and permeability P coefficients were determined by means of a modified Strother-Taylor apparatus³ equipped with an electrochemical manostat and Rotaflo Teflon valves. The diagram of the apparatus is shown in Figure 1. The measuring cell (5), gas burett (8), and manostat (7) were kept at a constant temperature by means of the water thermostat to within ± 0.1 K. The measuring cells were made of stainless steel. Their active surface was 125 cm². They were connected to the apparatus with greaseless glass-metal joints.⁶ Foil disks were placed inside the cell, their thickness was measured in nine different points with an accuracy of up to $0.2 \mu\text{m}$ using an Optimetr thickness gauge of Carl Zeiss Ltd. The disks, prepared of chromatographic blotting paper, were used to protect the foil disks against any bulging.

Diffusion coefficients were determined by two methods, i.e., absorption and desorption upstream time lags using the partition cell technique.

In the absorption upstream time lag method (method 1), the measurement was performed as follows: A foil was placed within the measuring cell (5) which was then degassed to obtain vacuum of 5×10^{-4} torr. The predetermined quantity of penetrant was introduced into the system through a tap (4) keeping the taps 2 and 3, closed, whereas taps 1 and 6 were left open. The penetrant pressure was indicated by a manometer (10). The mercury level in the manostat sensor (13) was adjusted by opening a tap (9) and connecting a mercury bulb with atmosphere or vacuum through a tap (11) to contact mercury with a platinum wire. Then tap 9 was closed and 12 V dc was supplied. When the manostat was switched off automatically, the mercury level was read out, it was assumed to be zero. To compensate partly for the dead volume of the measuring cell and the tube extending to tap 2, the mercury level inside the buret (8) was raised by opening tap 12 to atmosphere. Then, tap 2 was open and a stop watch was turned on. The changes in mercury volume were observed and noted at predetermined periods of time starting from the zero level. The dead volume of the measuring cell was determined using gas of a much lower permeability than that of the vapor

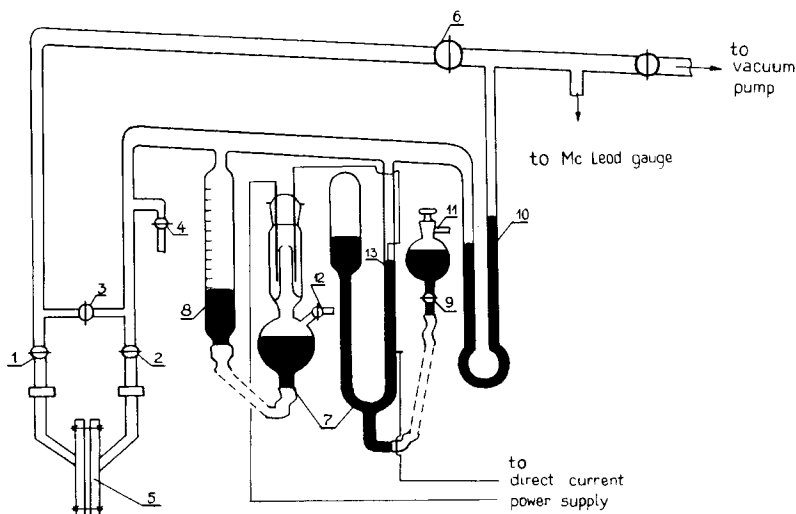


Fig. 1. Apparatus for determining the diffusion and permeability coefficients of gases and vapors through polymer membranes. For key see text.

under examination, e.g., dry air. This dead volume was then subtracted from each determined volume. The corrected volumes were plotted versus time on the graph $\Delta V = f(t)$. The directional factors of straight lines were determined from the linear part of the curves by the method of least squares. Then, the absorption upstream time lag values were calculated from eq. (4).

In the desorption upstream time lag method (method 2), the measurement was carried out as follows: A foil specimen was degassed as in the previous case. The predetermined quantity of penetrant was then introduced into the system keeping tap 6 closed, while taps 1, 2, and 3 were left open. Due to the sorption of penetrant within the membrane, the pressure decreased. The penetrant was, therefore, introduced into the system several times until constant pressure was indicated by the manometer (10). Then, following the earlier procedure, the manostat was switched on. The mercury level inside the buret (8) was observed for 2 h. If it was constant the measurement was performed by closing taps 1 and 3 and opening tap 6. Next, tap 1 was opened and a stopwatch was turned on. At that moment, some deformation of the test specimen was observed in spite of the blotting paper support due to a pressure difference. The membrane deformation occurred also in method 1, but any volume change caused by it was covered by the dead volume of the cell.

The membrane deformation resulted in a pressure drop inside the apparatus and switching on the manostat. The time of the next switching off of the manostat and the corresponding mercury level were noted, the latter being assumed as zero. This procedure allowed to determine a systematic error in the measurement of the $L^d(0)$ value (see Fig. 2). In Figure 2, curve 1 illustrates the function $\Delta V = f(t)$ under no membrane deformation, whereas curve 2 is experimental. The latter is shifted down on the ordinate axis by $\Delta V'$ in relation to

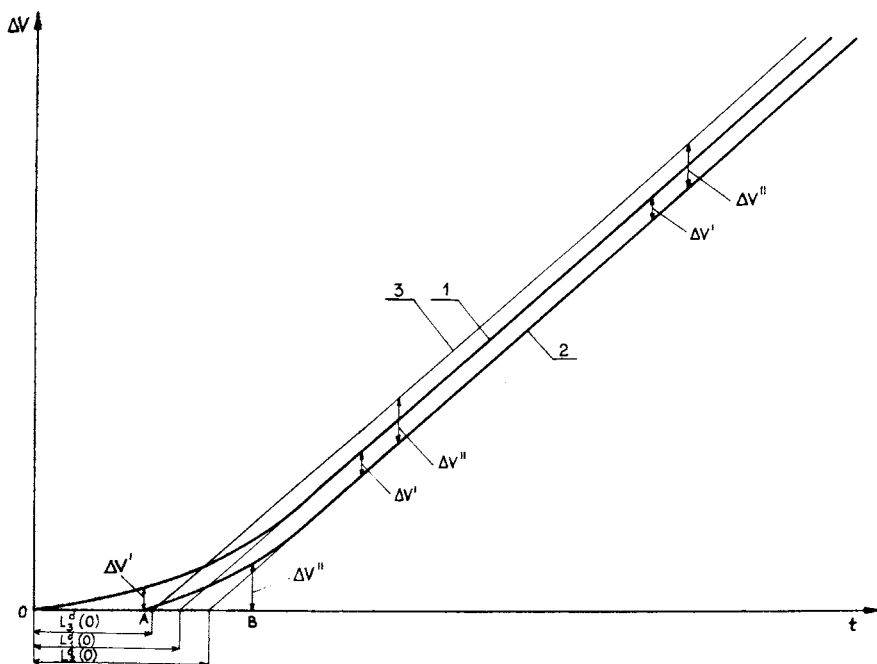


Fig. 2. Method for determining the desorption upstream time lag $L^d(0)$. For key see text.

curve 1. The intersection point of the linear extension of curve 2 with the t -axis determines the value of the desorption upstream time lag $L_2^d(0)$ which is greater than the $L_1^d(0)$ value.

To eliminate this error, the following procedure was used. The segment AB = OA was produced on the t -axis from point A, which corresponds to the switching-off point of the manostat. From the curve 2, the corresponding volume increment $\Delta V''$ was found and the auxiliary straight line 3, parallel to the rectilinear part of curve 2 and shifted up the ordinate axis by $\Delta V''$, was produced. The intersection point of the straight line 3 with the abscissa determines the second value of the time lag $L_3^d(0)$. Since $\Delta V' < \Delta V''$, curve 1 must be between curves 2 and 3. Therefore, $L_3^d(0) < L_1^d(0) < L_2^d(0)$. The arithmetic mean of $L_3^d(0)$ and $L_2^d(0)$ was assumed to be the value of $L_1^d(0)$. This value was determined with an accuracy of

$$L_1^d(0) = L_{\text{mean}}^d(0) \pm \frac{L_2^d(0) - L_3^d(0)}{2}$$

where

$$L_{\text{mean}}^d(0) = \frac{L_2^d(0) + L_3^d(0)}{2}$$

the latter being calculated from the equations of the straight lines 2 and 3 determined in turn by a method of least squares. The value of the diffusion coefficient was calculated from eq. (5).

For both methods, the permeability coefficient P was determined from eq. (6) as follows:

$$P = \frac{\Delta V l}{S \Delta t}$$

where ΔV is volume increment (cm^3), l is membrane thickness (cm), S is active membrane surface (cm^2), and t , is time (s).

CHARACTERISTICS OF POLYMER MEMBRANE AND PENETRANTS UNDER EXAMINATION

Polyethylene sheeting of density $0.917 \times 10^3 \text{ kg/m}^3$ was used for the tests. Gaseous methanol and carbon dioxide were used as penetrants. Some selected physical and chemical properties of the penetrants are presented in Table I.

TABLE I
Physical and Chemical Characteristics of Penetrants

Penetrant	Purity grade	Dehydration method	Refractive index n_D^{20}		Dipole moment D	Molecule diameter, Å ^a
			determined	reference		
Methanol	analytically pure	anhydrous CaSO ₄	1.3310	1.3290	1.69	3.76
Carbon dioxide	technically pure	SiO ₂	—	—	0,0	3.24

^a Calculated from the b constant in the van der Waals equation.

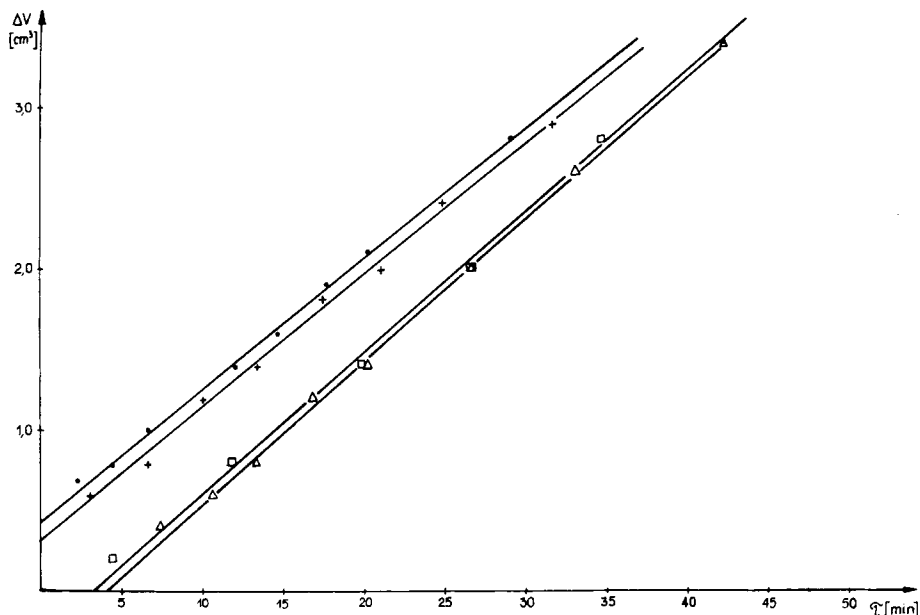


Fig. 3. Plot of ΔV vs. $f(t)$ for methanol vapor diffusing through a polyethylene membrane: (●) and (+) – determination by absorption upstream technique, (□) and (Δ) – determination by desorption upstream technique.

RESULTS AND DISCUSSION

Figure 3 and 4, respectively show the functions $\Delta V = f(t)$ for polyethylene–methanol vapor and polyethylene–carbon dioxide systems. The determined values of both diffusion and permeability coefficients are listed in Table II.

The curves $\Delta V = f(t)$ for the PE–methanol vapor and PE–carbon dioxide

TABLE II
Diffusion and Permeability Coefficients Determined by Absorption and Desorption Time Lag Methods Using the Partition Cell Technique (Foil Thickness 61.4 μm)

Ref./penetrant	Pressure torr	$L^a(0)$, s	$L^d(0)$, s	$D \times 10^8$, cm^2/s	$\bar{D} \times 10^8$, cm^2/s	$D^a(0)/D^d(0)$	$P_3 \times 10^8,^c$ [$\text{cm}_g^3 \cdot \text{cm}_f / \text{cm}_f^2 \cdot \text{s}$]	$\bar{P} \times 10^8,^c$ [$\text{cm}_g^3 \cdot \text{cm}_f / \text{cm}_f \cdot \text{s}$]
CO₂								
1	182	281		4.47			6.5	
2	182	341		3.69	4.08		6.6	6.6
3	173		175 ± 70	3.59	3.71	1.10	7.3	7.2
4	182		164 ± 29	3.83			7.1	
CH₃OH_v								
5	69.0		356 ± 26	1.76			19	20
6	77.0		296 ± 25	2.12	1.94		20	
7	75.0	935 ^a		1.34	1.14	0.59	23	23
8	75.5	1334 ^a		0.94			22	
9	75.0	402 ^b		3.13	2.35	1.21	23	23
10	75.5	792 ^b		1.57			22	

^a Without correction for methanol sorption on the measuring cell walls.

^b With correction for methanol sorption on the measuring cell walls.

^c g = gas; f = foil.

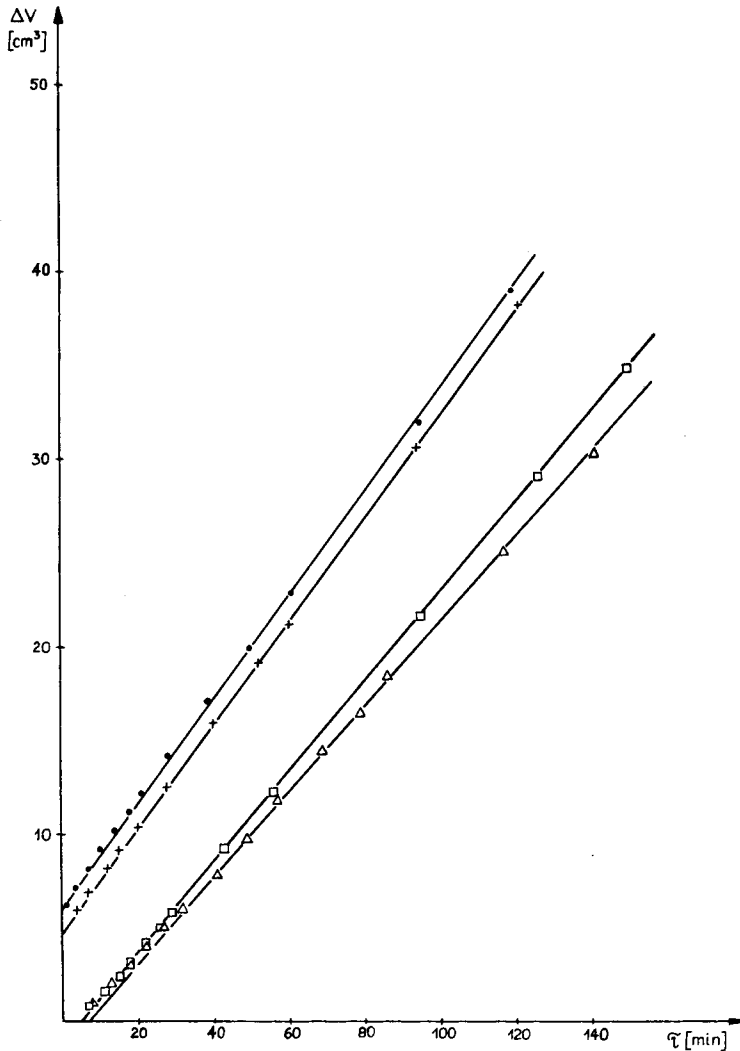


Fig. 4. Plot of ΔV vs. $f(t)$ for carbon dioxide diffusing through a polyethylene membrane: (●) and (+), determination by absorption upstream technique; (□) and (Δ), determination by desorption upstream technique.

systems have a course as expected, and therefore diffusion coefficients, D can be calculated from eqs. (4) and (5). For the PE-carbon dioxide system, diffusion coefficients determined by absorption and desorption upstream time lag methods are similar and differ only by about 10%, i.e., within the limits of error of the method.

For the PE-methanol vapor system, diffusion coefficients determined by the absorption upstream method are about two times smaller than those found by the desorption upstream method. It was experimentally found that the difference is due to the sorption of methanol vapor on the measuring cell walls. To eliminate this error, the equations of the straight lines must be corrected by the value of the methanol vapor sorption. Thus, to determine this correction, the

dead volume of the cell without test specimen and blotting paper support was measured by performing two series of determinations—one using dry air and the other with methanol vapor. The volume difference found indicates methanol sorption on the measuring cell surface. The penetrant is in contact with only one-half of the measuring cell when the partition cell technique is used. Thus, the value obtained is divided by 2 since both parts of the cell are identical. The correction was then introduced in the equations for determining the absorption upstream time lags. The corrected time lags and diffusion coefficients are shown in Table II. They differ slightly from those determined by the desorption upstream time lag method. It proves the correctness of the procedure applied.

CONCLUSIONS

(1) The volumetric vacuum apparatus described allows to determine diffusion coefficients by the desorption upstream time lag method.

(2) The desorption method enables determination in case of penetrants strongly sorptive on the measuring cell walls without any corrections.

(3) No special materials are required for the measuring cells when this method is used.

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