

A New Method of Determination of the Permeability of Vapors of Volatile Liquid Substances Through Polymer Membranes

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Synopsis

A new apparatus for the determination of vapor permeability of volatile liquid substances through polymer membranes has been described. The permeability of the vapor is calculated from the measurements of the depression rate of the liquid meniscus in a calibrated capillary tube. The conditions of the measurements by means of the described method are very close to those of the average and practical application of foils. The method is characterized by a simple design of the apparatus, easy handling, and simplicity of the determinations, so it may constitute the basis of vapor permeability determination standards. The results obtained by means of the described method were compared with those derived from the partition cell method.

INTRODUCTION

Transfer of gases and vapors through polymer membranes can be investigated by flow and sorption methods.¹ To determine the permeability of gases and vapors, only flow methods are used. These methods consist in the determination of the flow intensity under steady-state conditions. The magnitude of the flow intensity is determined by various techniques: gravimetric,^{2,3} manometric or volumetric,⁴ and instrumental, e.g., interferometric,^{5,6,7} radiographic,⁸ chromatographic,^{9,10} or nuclear magnetic resonance.¹ For each of these methods, a great variety of apparatus and measurement techniques have been developed.

In the flow methods, there is a gas or vapor of constant pressure p_1 on one side of the tested foil, while on its other side there is a pressure $p_2 < p_1$. Generally, p_2 is equal to zero, $p_2 \cong 0$ under applied vacuum.^{8,11} The permeability is determined at practically constant difference of pressure on both sides of the foil.

The methods used in scientific research for the determinations of diffusion and permeability coefficients require sophisticated apparatus and highly skilled staff. For routine tests, these methods are useless, and also the standard methods applied for the permeability determinations of dry gases¹² are not adaptable for vapors. These reasons have induced the authors to develop new methods for the determination of the vapor permeability through polymer foils which should find practical application.

EXPERIMENTAL

Description and Principle of Apparatus Operation

The permeability apparatus is shown on Figure 1. This apparatus consists of three main parts: (1) housing in which a foil is fixed, (2) calibrated capillary, and (3) manometer.

The steel housing of the apparatus consists of two parts (1 and 5). The upper part (1) of the housing, having openings 50.0 mm in diameter and sockets for perforated steel disks (2) is used to press the foil against the lower part of the housing (5). The perforated steel disks (2) prevent bulging of the foil. P.T.F.E. rings (3) ensure a good seal between a foil sample and the lower housing part. Two shallow chambers are bored 50.0 mm in diameter and capacity of approx. 25 cm³ in the lower part of the housing. These chambers are connected with the manometer legs (11) by a system of tubes. One chamber is connected with a calibrated glass capillary (13) through a valve (7), while the other chamber is connected with a connection tube (10).

Thus, the permeability apparatus has two separated parts: measuring (A) and compensating (B), isolated from one another by a monometric liquid. The capacities of both parts are the spaces surrounded by foil disks (4), manometric liquid meniscus, then a valve (7), and mercury meniscus in a tube (10), respectively. The capacities of these parts (A) and (B) are equal to each other. In the measuring part (A), a mixture of air and vapor is formed due to the evaporation of the liquid in the capillary. The capillary (13) is inserted in a thermostatic mantle keeping the temperature within $\pm 0.2^\circ\text{C}$ and equipped with a control thermometer with a 0.1° scale. The capillaries of various diameters make possible to carry out the measurements for foils of different permeabilities.

A tube (10) 50.0-mm long, with a 1-mm scale, is filled with mercury. This tube is used to compensate the capacities in the test space as well as in the compensating space after steady-state conditions have been reached. The differential manometer (11) is used to determine the partial vapor pressure Δp in the measuring part of the apparatus. This manometer is filled with mercury or other liquid in which the vapors of the substance tested do not dissolve.

The compensating chamber eliminates the influence of the atmospheric pressure changes on response of the differential manometer. There is a mixture of air and tested substance vapors in the measuring chamber. This mixture is isolated from the environment by means of a polymer foil which acts as an elastic membrane. The membrane deformations under the atmospheric pressure changes should cause compression or decompression of the mixture in the measuring part.

The application of the chambers closed by membranes and situated symmetrically in relation to the manometer eliminates the effect of the atmospheric pressure changes on the response of this manometer. Besides, the atmospheric pressure changes should cause air permeability through the foil from the chamber to the atmosphere, or vice versa. The direction of the air permeation depends on the relation between the atmospheric pressure when the measurement has been started and that at a given moment. The compensation system used by the authors also eliminates the effect of the air permeation on the response of the manometer.

The liquid evaporation from a capillary causes pressure increase in the test

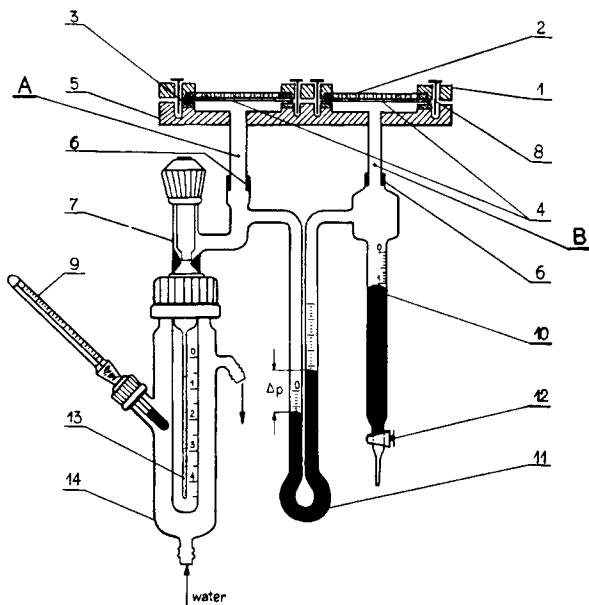


Fig. 1. Schematic diagram of the apparatus for the determination of the permeability coefficient of volatile substances penetrating through polymer foils: A, measuring part; B, compensating part; 1 and 5, steel housing of the apparatus; 2, perforated steel disks; 3, P.T.F.E. rings; 4, foil disks; 6, kovar-glass tube; 7, Rotaflo valve; 8, M6 screws; 9, thermometer; 10, calibrated glass tube; 11, differential manometer; 12, tap; 13, calibrated glass capillary; 14, thermostating capillary mantle.

chamber, which is then indicated on the manometer (11). The displacement of the mercury column causes the capacity increase of the chamber (A) and simultaneously the capacity decrease of the chamber (B). The capacity changes result in air decompression in the chamber (A) and air compression in the chamber (B). Air pressure on both sides of the manometer should be equal in order to compensate indicated manometric pressure with partial vapor pressure. Therefore, it is necessary to compensate those pressures. It is carried out by the increase of the chamber (B) capacity occurring when a definite amount of mercury is released from the calibrated tube (10) through a tap (12). The manometer tube cross section is so assembled with the tube cross section (10) that the capacity difference between the chambers (A) and (B), being the result of 1-mm displacement of the mercury column, is compensated by lowering the mercury level 1 mm in the tube (10).

The permeability, or vapor permeability coefficient, is calculated from the determined rate of vapor flow through the foil under steady-state conditions. These conditions are reached when the evaporation rate of the liquid in a capillary is equal to the vapor permeation rate through the foil. In this state, the liquid meniscus in a capillary decreases steadily, and the partial vapor pressure Δp indicated by the manometer is constant. The lowering rate of the liquid meniscus in a capillary reflects the vapor flow rate through the foil. The thermostatic capillary mantle (14) enables a change in rate of the liquid evaporation and thus to carry out the measurements at various vapor pressures.

The permeability apparatus is placed in the weathering chamber where temperature and humidity can be optionally selected. This chamber is equipped

with a fan directing a strong air jet into the outside foil surface to eliminate any additional resistances associated with vapor diffusion to the atmosphere.

Procedure

The permeability apparatus should be washed and dried before proceeding to the measurements. The capillary should be particularly well cleaned.

The measurement is conducted as follows: The manometer U-tube (11) and the tube (10) are filled with a sufficient amount of mercury. After removing the valve core (7), the capillary (11) is filled with a liquid to be tested by means of a syringe with a long needle. Then, the valve (7) is closed. To remove the vapors gathered in the test chamber (A) while filling the capillary with a liquid, air is blown through that chamber. In selected areas of the housing (5), P.T.F.E. packing rings (3), foil disks prepared for testing (4), and perforated steel disks (2) are placed, respectively. The upper housing part (1) is placed onto the lower one and screwed together by means of item (8). Water flow of required temperature through the thermostatic mantle (14) is turned on and then the valve (7) is opened. At determined periods of time, the readings of the liquid meniscus level in a capillary (h_t) and the manometer indications ($\Delta p'$) are taken. When the constant pressure ($\Delta p' = \text{const.}$) in the chamber (A) is reached, the capacities of both parts are compensated by releasing a proper amount of mercury from the tube (10). The readings of the manometer indications, being equal to the vapor pressure, are taken again. Then the readings of the liquid meniscus position in the capillary ($\Delta h = h_{t_2} - h_{t_1}$) and the manometer indications (Δp) are taken every 24 hr. At high permeabilities, those readings are taken at shorter intervals. The permeability vapor coefficient P is calculated from the equation resulting from Henry's law and the first Fickian law:

$$P = 22.414 \times 10^3 \cdot \left(\frac{d_k}{d_f}\right)^2 \cdot \frac{1 \cdot \rho}{M \cdot \Delta p} \cdot \frac{\Delta h}{\Delta t} \quad (1)$$

where P = permeability coefficient, cm^3 (S.T.P.) $\cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{mm Hg}$; d_k = diameter of the capillary tube, cm; d_f = active diameter of the foil disk, cm; ρ = density of the liquid in the capillary, g/cm^3 ; M = molecular mass of the liquid, g/mole ; l = thickness of the foil, cm; $\Delta h/\Delta t = (h_{t_2} - h_{t_1})/(t_2 - t_1)$ = depression rate of the liquid meniscus in the capillary tube in steady-state conditions, cm/sec ; and Δp = partial vapor pressure of the volatile, liquid substance in the test chamber after steady-state conditions have been reached, mmHg .

The vapor permeability P^x defined as the mass amount permeating through the unit of the foil surface in 24 hr has been calculated from the equation

$$P^x = 8.64 \times 10^4 \cdot \left(\frac{d_k}{d_f}\right)^2 \cdot \rho \cdot \frac{\Delta h}{\Delta t} \quad (2)$$

RESULTS AND DISCUSSION

The permeability measurements were carried out by means of this new apparatus at 293°K for the system of the polyester foil Estrofol T-19 and methanol vapors.

The aim of these measurements was (1) to determine the time necessary to reach the steady-state of the vapor permeation, (2) to determine the effect of

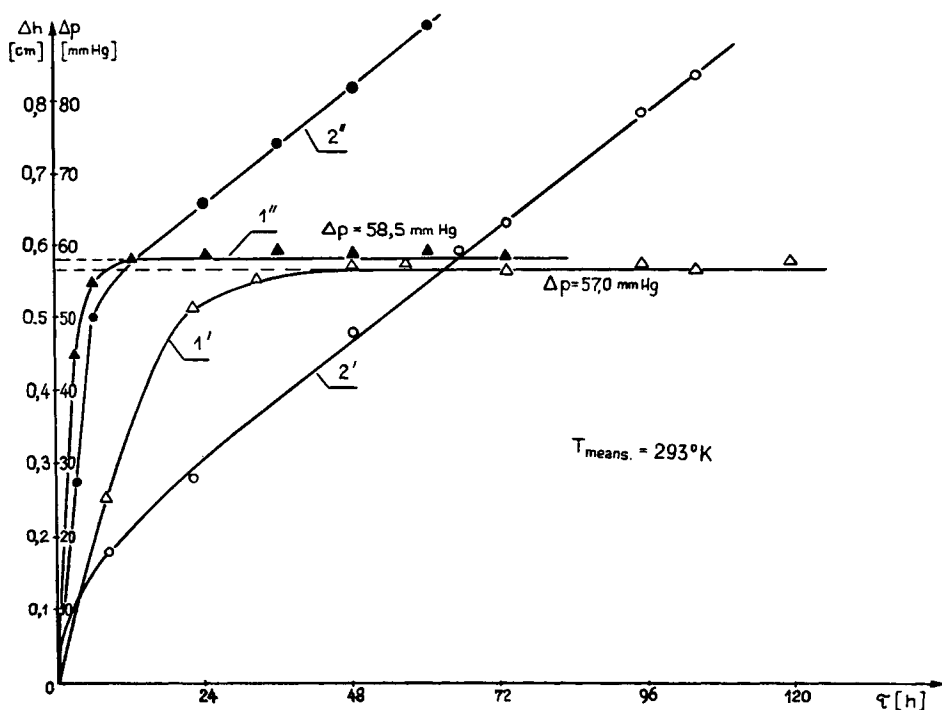


Fig. 2. Diagram of pressure changes (curves 1' and 1'') and of changes in the positions of the meniscus of the liquid in the capillary tube (curves 2' and 2'') during measurements: 1' and 2', temperature of the liquid in the capillary equal to the temperature of the measurement (293°K); 1'' and 2'', liquid on the capillary, heated to a temperature of 313°K through first 3 hr of measurement.

the foil deformation on the measurement results, (3) to find the optimum method to eliminate this effect.

Figure 2 shows the relation between the pressure changes Δp of methanol vapor and the level changes Δh of liquid methanol in the capillary as a function of time. Curve 1' shows that constant vapor pressure in the permeability apparatus will be reached after about 50 hr when the temperature of liquid methanol is permanently equal to the measurement temperature, i.e., 293°K. It is possible to shorten effectively this period of time by heating the capillary at a temperature which is 10–20° higher than the normal measurement temperature, within 2–4 hr, then cooling it to the measurement temperature. This is illustrated by curve 1'' in Figure 2. The rectilinear segments on the curves of the functions $\Delta h = f(t)$ and $\Delta p = F(t)$ prove that steady state has been reached.

In Table I, there are collected the values of the permeability coefficients P and also the permeability coefficients P^x of methanol vapors through polyester foil Estrofol T-19. These values were determined in a series of preliminary measurements. The results presented in Table I show that the values of the permeability coefficients P depend to a great degree on the protection means used against the foil deformation. The values of the permeability coefficients P determined without any protection are three times greater than those when the perforated steel disks were used.

The correctness of the calculated P values depends mainly on the determination of the real partial vapor pressure. It is possible to determine that partial

TABLE I
Results of Preliminary Measurements of Methanol Vapor Permeability Through Polyester Foil Estrofol T-19

Measure- ment no.	$T, ^\circ\text{K}$	Method of preventing foil deformation	$\Delta p,$ mm Hg	$10^{12} \times P,$ $\text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/$ $\text{cm}^2 \cdot \text{sec} \cdot \text{mm Hg}$	$P^x,$ $\text{g}/$ $\text{m}^2 \cdot 24 \text{ h}$
1	293	Perforated steel disks	57.0	47	1.5
2			56.4	39	1.4
3		Chromatographic paper	37.5	58	1.4
4		discs	36.0	65	1.6
5		No prevention	16.5	118	1.3
6			17.0	108	1.2

pressure using the apparatus described in this paper, in which the capacities of measuring and compensating parts are equal to each other. Without any protection, a distinct bulging of the foil occurs due to overpressure in the measuring part. It also causes an increase of the measuring part capacity and simultaneously a decrease of the partial pressure of air enclosed in it. Finally, the measured overpressure Δp is smaller than the partial vapor pressure of the substance examined in the test chamber. Table I shows that the values of the permeability coefficients P^x do not depend in practice on the type of the protection means used against the foil deformation. It is evident that the partial vapor pressure value is not necessary to calculate P^x from eq. (2). But, in fact, P^x is the function of the partial vapor pressure. If the diffusion in the foil satisfies the first Fickian law, then this function should be linear. The calculated P^x values do not depend on the Δp value determined at various protection means. It proves that the real partial vapor pressure is the same at constant temperature for any protection means.

The results gathered in Table I show that no protection means are required for the determination of the permeability coefficient P^x , but that the correct determinations of the permeability coefficients P needs protection against the foil deformation. It was found that the best protection was achieved by applying the perforated steel disks. This method of protection was selected to be used in further investigations.

It is worthwhile to mention that there are various methods of protection against the foil bulging. Stern¹³ has applied disks made of porous steel, while Huldy¹⁴ has used disks prepared from sintered glass G2. However, these protection means make it impossible to use a fan for decreasing the additional resistances of the vapor diffusion to the atmosphere.

In Table II, the values of the permeability coefficients P for methanol vapors through the polyester foil Estrofol T-19 at a temperature of 293°K from six measurements are presented in order to evaluate the reproducibility of the measurements. The results shown in Table II prove the good reproducibility of the method used. In general, the deviation from the mean value does not exceed $\pm 10\%$. And, also, it can be stated that the methanol vapor pressure in the measuring part is well reproducible in steady-state conditions. The difference between extreme values is 4 mmHg.

In Table III, the values are shown of the permeability coefficients for methanol and tetrachloride vapors through the P.T.F.E. foil and polyester foil Estrofol

TABLE II
Repeatability of the Results of Measurements for Polyester Foil Estrofol T-19^a

Measure- ment no.	Δp , mm Hg	$10^{12} \times P$, $\text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/$ $\text{cm}^2 \cdot \text{sec} \cdot \text{mm Hg}$	E , %
1	57.0	47	-9.3
2	56.4	39	+9.3
3	56.0	48	-11.6
4	60.0	39	+9.3
5	58.5	44	-2.3
6	57.3	42	+2.3
Avg. 43			

^aMethanol vapor system, $T = 293^\circ\text{K}$.

TABLE III
Results of Measurements of the Permeability Coefficients at a Temperature 293°K for Selected Polymer Foils and Vapor of Organic Substances

Kind of foil	Foil thick- ness, μm	Permeating substances	Described method		Partition cell method	
			Δp , mm Hg	$10^{12} \times P$, $\text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/$ $\text{cm}^2 \cdot \text{sec} \cdot \text{mm Hg}$	Δp , mm Hg	$10^{12} \times P$, $\text{cm}^3(\text{S.T.P.}) \cdot \text{cm}/$ $\text{cm}^2 \cdot \text{sec} \cdot \text{mm Hg}$
Estro- fol T-19	19	CH_3OH	56-60	43 ± 4	60.0	130 ± 10
		CCl_4	57-60	13 ± 2	60.0	700 ± 40
PTFE	20	CH_3OH	58-62	18 ± 2	60.0	130 ± 10
		CCl_4	56-60	10 ± 1	60.0	650 ± 40

T-19 determined by two different methods: the first one is referred to in this paper, and the second one is known as the partition cell method, the latter being considered mostly accurate. The methanol and tetrachloride vapors were selected for these investigations because of the following properties: (1) similar saturated vapor pressures of both substances at the measurement temperature, and (2) great difference in molecular masses and thus in vapor densities.

The results collected in Table III show that the values of the permeability coefficients P determined by the authors' method are three to six times lower for methanol and 50 to 70 times lower for tetrachloride in comparison with those found by the partition cell method. These differences, particularly great in case of tetrachloride vapors, can be explained by the existence of the diffusion resistances in an air layer surrounding the test space. The magnitude of these resistances depends on the molecular masses of diffusants and air. In the presented method, the permeation occurs through the air and the foil; hence, the greater the diffusion resistance in the foil than in the air, the better the correspondence achieved of the values determined by a new method with those derived from the partition cell method. The authors have simulated in their permeability apparatus exactly the conditions prevailing in the partition cell method in order to determine the effect of the air diffusion resistance. It was carried out by introducing to the apparatus on one side of the membrane the air and vapor mixture of total pressure equal to atmospheric pressure. On the other side of the

membrane, the permeating vapor was removed by a strong air jet. The permeability coefficient for tetrachloride vapors through polyester foil Estrofol T-19 determined under such conditions was $9.5 \times 10^{-12} \text{ cm}^3 \text{ (S.T.P.)} \cdot \text{cm/cm}^2 \cdot \text{s} \cdot \text{mm Hg}$. This value is very close to that determined by the authors' method.

The conditions at which the measurements are carried out are very close to those of the average and practical application of foils. In practice, the foils are always in contact with air and moisture. These substances can influence the foil, modifying its structure and forming the diffusion barrier affecting, subsequently, the permeation phenomenon.

The permeability apparatus for testing vapors of volatile liquid substances is characterized by a simple design, low cost, easy handling, and simplicity of making determinations.

References

1. J. Crank, and G. S. Park, *Diffusion in Polymers*, Academic Press, London and New York, 1968, pp. 1-37.
2. A. C. Newns, *J. Text. Inst.*, **41T**, 269 (1950).
3. ISO/R 1195-1970(E), Determination of the water vapour transmission rate of plastic films and thin sheets.
4. D. R. Paul, and T. Di Benedetto, *J. Polym. Sci.*, **C10**, 17 (1965).
5. S. E. Bresler, G. M. Zakharov, and S. V. Krillov, *Vysokomol. Soedin.*, **3**, 1072 (1961).
6. L. J. Gosting, *Advan. Protein Chem.*, **11**, 429 (1956).
7. C. Robinson, *Proc. Roy. Soc.*, **A204**, 339 (1950).
8. J. Crank, C. Robinson, *Proc. Roy. Soc.*, **A204**, 549 (1951).
9. D. G. Gray, and J. E. Guillet, *Macromolecules*, **6**, 223 (1973).
10. V. V. Kapanin, O. B. Lemanik, and S. A. Reitlinger, *Vysokomol. Soedin.*, **A16**, 911 (1974).
11. R. M. Barrer, and G. Skirrow, *J. Polym. Sci.*, **3**, 549 (1948).
12. ASTM D 1434-66 (1972).
13. S. A. Stern, P. J. Gareis, T. F. Sinclair, and P. J. Mohr, *J. Appl. Polym. Sci.*, **7**, 2041 (1963).
14. H. J. Huldy, *J. Appl. Polym. Sci.*, **8**, 2883 (1964).

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