

Performance of a Versatile Variable-Volume Permeability Cell. Comparison of Gas Permeability Measurements by the Variable-Volume and Variable-Pressure Methods

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I. INTRODUCTION

The accurate and rapid measurement of permeabilities of plastic films and membranes to gases is a subject of great importance to the packaging industry—especially for the packaging of food, the construction industry, and, potentially, in the separation of gases by selective permeation. Of the various methods of measuring gas permeabilities described in the literature, three have received particular attention; these three methods may be designated as the variable volume, the variable pressure, and the variable concentration methods.

According to the variable volume method, a conveniently high gas pressure is applied on one side of the membrane under investigation, and the permeated gas is allowed to expand on the opposite side against some low constant pressure, usually atmospheric. The change in the volume of the permeate is then measured as a function of time by following, for example, the displacement of a short column of liquid in a capillary. This method has been used successfully by Brubaker and Kammermeyer.¹ The variable pressure method usually requires that both sides of the membrane be initially evacuated. A constant gas pressure is then applied on one side of the membrane, and the increase in the pressure of the permeating gas is measured on the opposite side of the membrane. The variable pressure method has been employed by many investigators; for instance, Heilman et al.² have described a research apparatus for the simultaneous determination of gas permeabilities and diffusivities, while the Dow Chemical Company³ has developed a permeability cell for routine permeability measurements. Finally, according to the variable concentration method, two different gases are allowed to contact the opposite sides of the membrane and the gas composition is monitored as a function of time on either side of the membrane; the measurements are conducted under zero total pressure differential. This method has been developed by Landrock and Proctor.⁴

Of the three methods mentioned above, the first two have proved to be the more popular because they do not require costly analytical apparatus. The variable pressure method, in particular, is widely used at the present time, and has been adopted as a standard by the American Society for Testing Materials.⁵

The purpose of the present communication is to describe a simple and versatile permeability cell operating on the variable volume principle, to present typical permeability data obtained with this cell, and to compare the data with similar measurements performed with a variable pressure apparatus. The permeability cell permits the routine measurement of gas permeabilities over wider ranges of temperature and pressure differentials than was practical heretofore.

II. VARIABLE VOLUME METHOD

A. Description of Permeability Cell and Experimental Procedure

The permeability cell, shown in Figure 1, consists essentially of two Tobin bronze disks about $\frac{1}{2}$ in. thick and 6 in. in diameter. Machined depressions in each disk form a cylindrical cavity when the disks are superposed. The membrane to be tested is clamped between the two disks by means of eight equally-spaced bolts, a rubber gasket insuring a pressure-

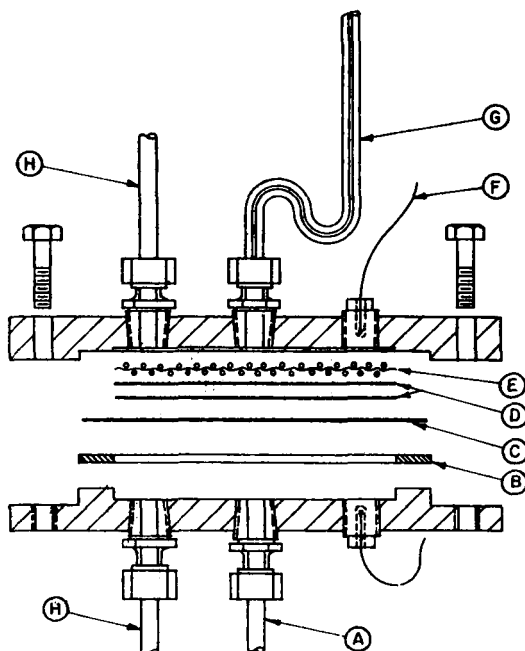


Fig. 1. Exploded view of the low-pressure permeability cell: (A) gas inlet; (B) rubber gasket, (C) membrane; (D) filter paper; (E) wire screen, (F) thermocouple; (G) glass capillary; (H) vent line.

tight fit. A 33-in.-long precision bore glass capillary is connected in a vertical position to an opening in the center of the upper disk. Suitable gas inlet and vent lines are provided on both sides of the cell.

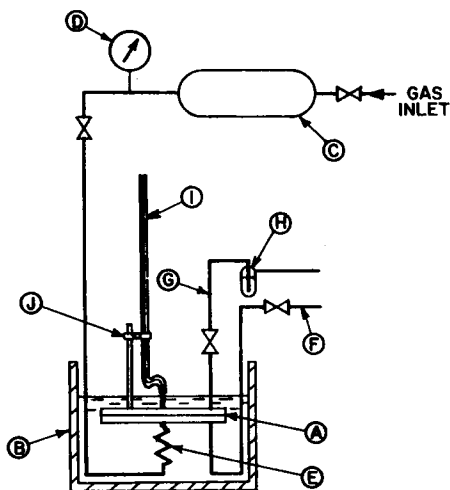


Fig. 2. Apparatus for measurement of gas permeability by the variable volume method: (A) permeability cell; (B) insulated constant-temperature bath; (C) gas supply tank; (D) pressure gauge; (E) heat exchanger; (F) vent line, (G) permeate vent line; (H) oil trap; (I) glass capillary; (J) capillary support.

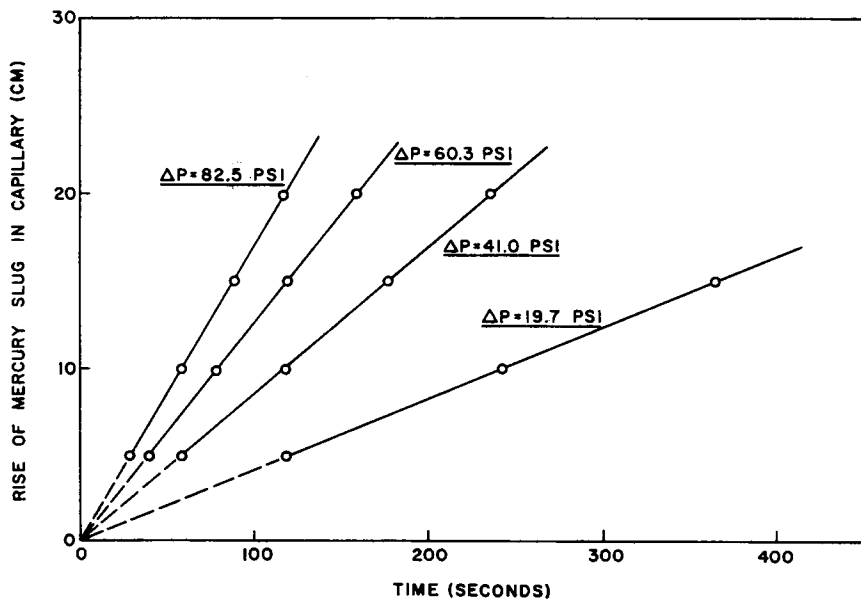


Fig. 3. Rate of permeation of helium through 1 mil-thick Alathon 15 polyethylene membrane at 0°C.

The gas is supplied at constant, overatmospheric pressure to the bottom of the cell. After permeating through the membrane, which is supported on the low-pressure side by a screen and several sheets of filter paper, the gas expands into the capillary. The latter contains a short plug of mercury, which is displaced upwards by the permeating gas; the movement of this plug offers a direct measure of the rate of permeation of the gas through the

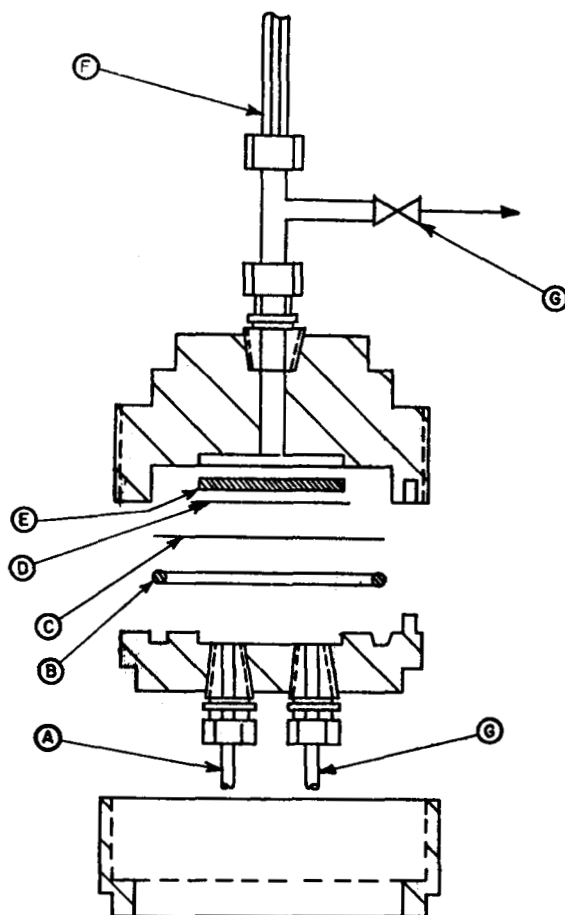


Fig. 4. Exploded view of the high-pressure permeability cell: (A) gas inlet; (B) rubber O ring; (C) membrane; (D) filter paper; (E) porous stainless steel; (F) glass capillary; (G) vent lines.

membrane. An S-shaped bend at the base of the capillary prevents the mercury from falling inside the cell. Since the mercury tends to stick in the capillary, it was found desirable to vibrate the latter during the measurements by means of an electromechanical vibrator. An even smoother displacement of the mercury plug is achieved by also coating the capillary within a thin layer of silicone oil.

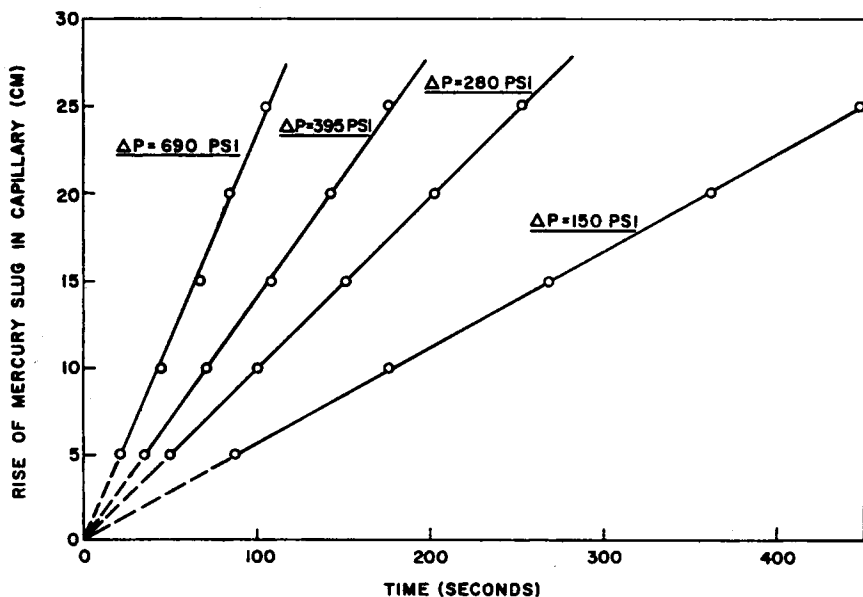


Fig. 5. Rate of permeation of helium through 1-mil-thick Alathon 15 polyethylene membrane at 0°C.

The following experimental procedure was adopted. Referring to Figure 2, the assembled cell A was immersed in a constant-temperature bath B and allowed to reach the desired temperature. Gas from the surge tank C, at a suitable constant pressure, was introduced into the high-pressure (lower) side of the cell through a copper coil E, also immersed in the bath, which served to bring the gas to the same temperature as the permeation cell. The high-pressure side of the cell was thoroughly purged with the gas through a vent line F, which was then closed, forcing the gas to permeate through the membrane into the low-pressure (upper) side of the cell. During this process the capillary I was sealed with a plug of mercury and the permeating gas was discharged to the atmosphere via a second vent line G and an oil trap H, which prevented the back-diffusion of air into the cell.

In order to measure the rate of permeation of the gas through the membrane, the vent line G on the low-pressure side of the cell was closed. The rise of the mercury plug in the capillary, caused by the expansion of the permeating gas against atmospheric pressure, was then followed with a cathetometer as a function of time. Typical measurements made at various pressure differentials across the membrane are shown in Figure 3. The time required to purge the cell and to reach steady-state permeation depended on the membrane under study; it was of the order of 30 min. for more permeable membranes such as polyethylene, and 1–3 hr. for less permeable membranes. After steady state was reached, the permeability

measurements could be completed in a period of a few minutes by proper choice of pressure and capillary diameter. Repeat runs were performed quickly by opening the upper vent line G, causing the mercury plug to drop back to the bottom of the capillary, and then closing the vent and again measuring the rate of rise of the mercury plug.

The described cell, which is now manufactured by Custom Scientific Instruments, Inc., of Kearney, New Jersey, was used for permeability measurements with pressure differentials of up to 100 psi across the membrane. Measurements under more extreme conditions were made in a different permeability cell, shown in Figure 4, which could be operated with pressure differentials as large as 1500 psi. The membrane was supported in this cell on a porous stainless steel disk with a diameter of one inch. Typical high-pressure measurements are shown in Figure 5.

B. Accuracy of Measurements

In order to compute the permeability constant, it is necessary to measure five basic variables: (1) the pressure drop across the membrane, (2) the temperature of the gas and of the membrane, (3) the volume of the permeated gas, (4) the area of the membrane, and (5) the thickness of the membrane.

These variables were determined with the following accuracy.

(1) The pressure on the inlet (high-pressure) side of the cell was measured with an open-end mercury manometer which could be read to better than 1 mm. Hg. Since the pressure on the outlet (low-pressure) side of the cell differed from atmospheric only by the length of the mercury plug in the capillary, the manometer also measured the pressure differential across the membrane. This differential was usually not less than 100 mm. Hg, and consequently the error in its determination did not exceed $\pm 1.0\%$. Higher pressures were measured with two Bourdon gauges which were calibrated with a dead-weight tester. A 60-psig gauge was read with a precision of ± 0.2 psi and a 1,000-psig gauge with a precision of ± 5 psi.

(2) The cell was immersed in a constant-temperature bath which could be maintained to within 0.05°C . of the desired temperature by means of a Fisher Scientific Company thermoregulator. The bath temperature was measured by means of a mercury thermometer with a range from -1 to $+51^\circ\text{C}$. graduated into subdivisions of 0.1°C . or one with a range from -5 to $+100^\circ\text{C}$. with subdivisions of 0.2°C . for the higher temperatures. Each of the bronze flanges constituting the two halves of the cell was provided with an iron-constantan thermocouple to insure that the cell was at uniform temperature.

(3) The volume of permeated gas was determined by measuring the displacement of a mercury plug in a Fischer-Porter precision-bore capillary. The inner diameter of the capillary was stated by the manufacturer to be within ± 0.0002 in. of the specified value over its entire length. Since the position of the plug in the capillary was measured with a Gaertner cath-

tometer reading to 0.05 mm., it is felt that the error in volume determination was negligible. (For routine measurements, the cathetometer can be replaced with a scale divided into suitable graduations.)

The length of the mercury plug could not exceed certain limits, which were determined experimentally for capillaries with an inside diameter of 0.5–1.5 mm. When the plug was longer than 10–12 mm., its rate of travel became erratic due to excessive friction, while when shorter than about 2 mm., the plug did not seal the capillary. A plug length of 2–5 mm. appeared to be satisfactory.

The section of the capillary used for volume measurements was maintained at ambient temperature by covering the constant-temperature bath with a sheet of foam plastic.

(4) The area of the membrane was assumed to be the same as that of the gasket opening. The rate of permeation of gases through the rubber gasket to the atmosphere was negligible because the ratio of gasket thickness to width was small.

(5) The thickness of the membrane was measured with an Ames thickness gauge reading to 0.0001 in. The thickness used in the computation of the permeability constant was a mean value of 15–20 random measurements. In samples of polyethylene film 6 in. in diameter the deviations from the mean were found to have a maximum spread of $\pm 10\%$. The thickness of the membrane was, consequently, the least accurate of the measured variables.

In conclusion, it may be stated that the accuracy of the reported permeability constants is of the order of $\pm 5\%$, which is comparable to that claimed by other investigators.

It is perhaps of some interest to add that a small leak in the high-pressure section of the cell cannot affect the measurements, since the pressure is maintained constant. Leaks in the low-pressure section, which are held at essentially ambient pressure, are unlikely. However, were a leak to develop in this section, it would be detected both visually (since the cell is immersed in a liquid bath) and from a sharp decrease in the rate of travel of the mercury plug in the capillary. On the other hand, a pinhole in the membrane would have just the opposite effect, causing anomalously high rates of travel of the mercury plug.

III. VARIABLE VOLUME PERMEABILITY MEASUREMENTS

It is generally accepted at present that the permeation of gases through organic membranes is a complex process which involves the adsorption of the gas at one interface of the membrane; the solution of the gas into, and diffusion through, the barrier; and, finally, its evaporation at the opposite interface. The diffusion of the gas through the membrane is usually the slowest of this sequence of phenomena, and is therefore rate-determining. If the solution of the gas in the membrane obeys Henry's law and the diffu-

sivity of the gas is concentration-independent, it is found that the rate of permeation satisfies the following simple form of Fick's law:

$$q = P A \Delta p / d \quad (1)$$

where q is the amount of gas permeating per unit time through a barrier of area A and thickness d , when the partial pressure differential across the membrane is Δp . P is the permeability constant, sometimes called simply the "permeability," which depends on the nature of both the gas and the membrane, as well as on the temperature. Equation (1) is valid only under steady-state conditions.

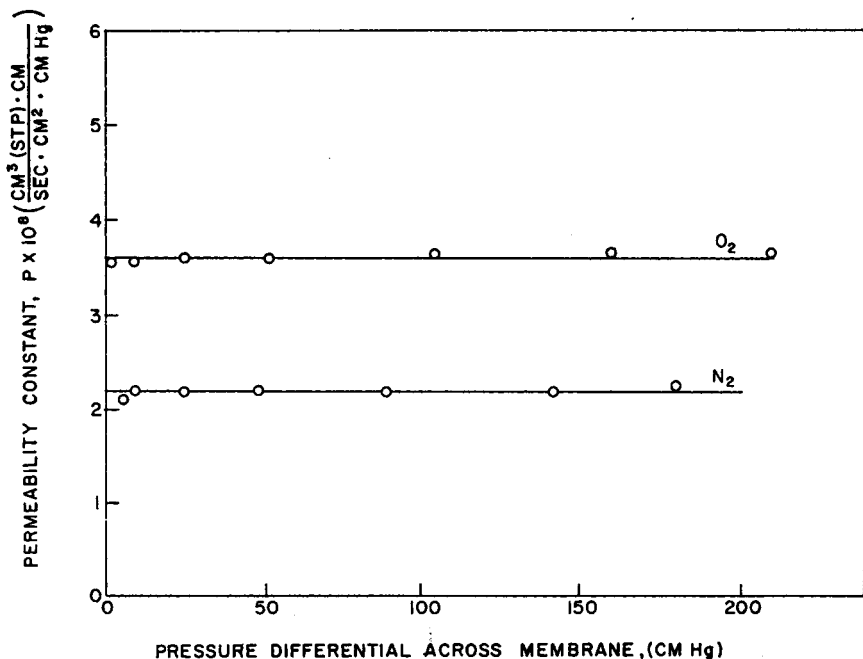


Fig. 6. Permeability of silicone rubber to oxygen and nitrogen as a function of pressure differential across the membrane.

When eq. (1) is obeyed, the permeability constant P is independent of the pressure differential of the gas across the membrane. The described permeability cells are well suited for testing this relation over a wide range of conditions. Examples are given in Figures 6 and 7, where the permeability of a silicone rubber to oxygen and nitrogen and that of Alathon 15 polyethylene to helium, respectively, are shown as a function of pressure differential. The measurements cover the range of pressure differentials from less than 2 cm. Hg to over 4100 cm. Hg (800 psi). As seen, the permeability constants are indeed independent of pressure differential under the experimental conditions. The high-pressure permeability cell can be used for measurements under pressure differentials as high as 1500 psi.

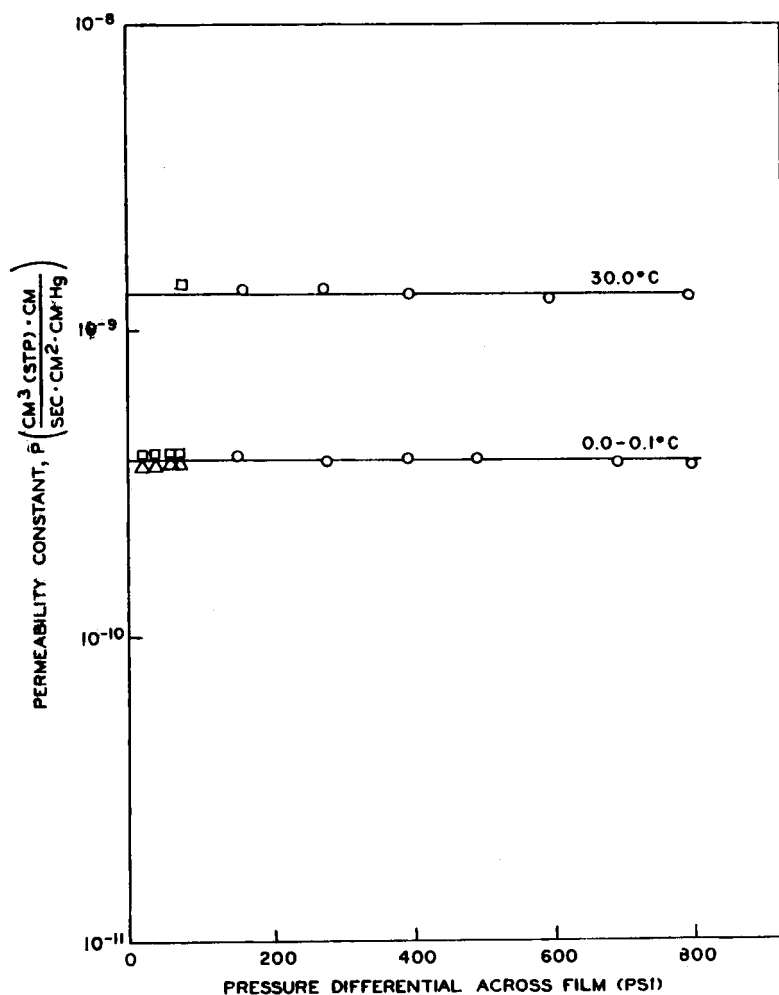


Fig. 7. Permeability of 1-mil-thick Alathon 15 polyethylene membrane to helium as a function of pressure differential: (□), (Δ) obtained with the low-pressure cell (two different samples); (O) obtained with the high-pressure cell.

The permeability constant is usually an exponential function of temperature and can be expressed by the relation

$$P = P_0 \exp \left\{ -E_p/RT \right\} \quad (2)$$

where P_0 is a constant, E_p is the activation energy of the permeation process, R is the universal gas constant, and T is the absolute temperature. The permeability cells are also well suited for determining the dependence of gas permeabilities on temperature. Examples are given in Figure 8, where the logarithm of the permeability of Alathon 15 polyethylene to carbon dioxide, hydrogen, helium, oxygen, and nitrogen is plotted vs. the reciprocal of the

absolute temperature. Equation (2) is seen to be followed in all cases. Although the data presented in Figure 8 cover only the temperature range from 0 to 50°C., the permeability cells have been used for measurements at temperatures as high as 150°C. It is of interest to note that at temperatures where the membranes undergo a phase transition, such as the glass

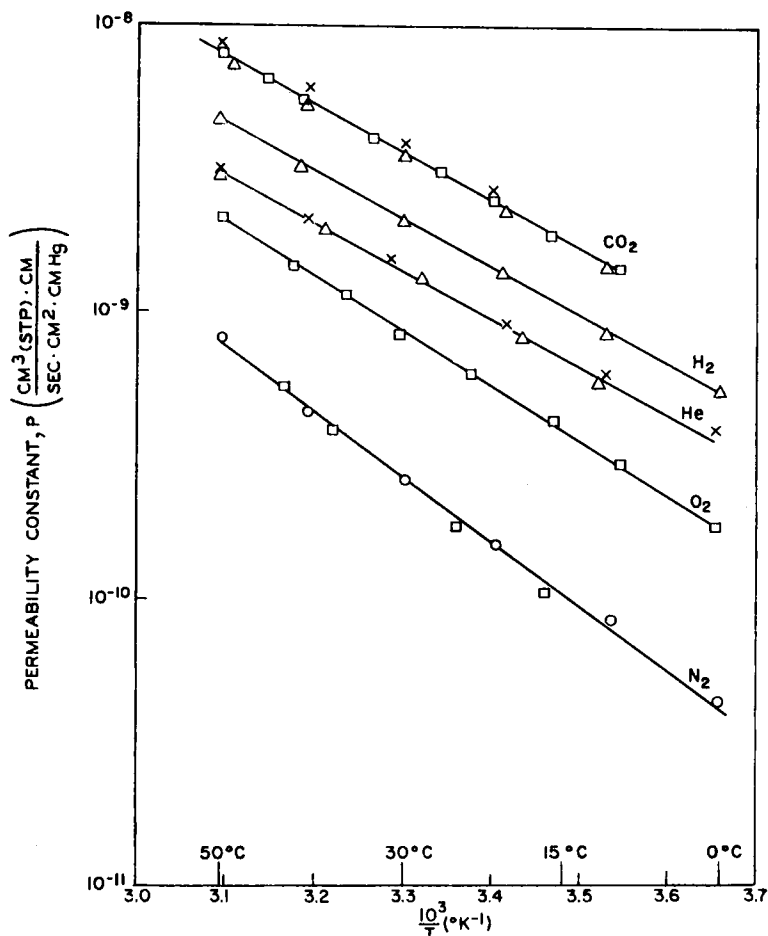


Fig. 8. Permeability of 1-mil-thick Alathon 15 polyethylene membrane to various gases as a function of temperature: (\times), (\square), (Δ), (\circ) represent four different samples of membrane.

temperature, a sharp break occurs in the plots of $\log P$ versus $1/T$; this behavior is illustrated in Figure 9 for the permeability of Tritheone B (plasticized polytrifluorochloroethylene) to methane. No breaks were observed; however, with hydrogen, indicating that the transition is dependent on the nature of the permeating gas.

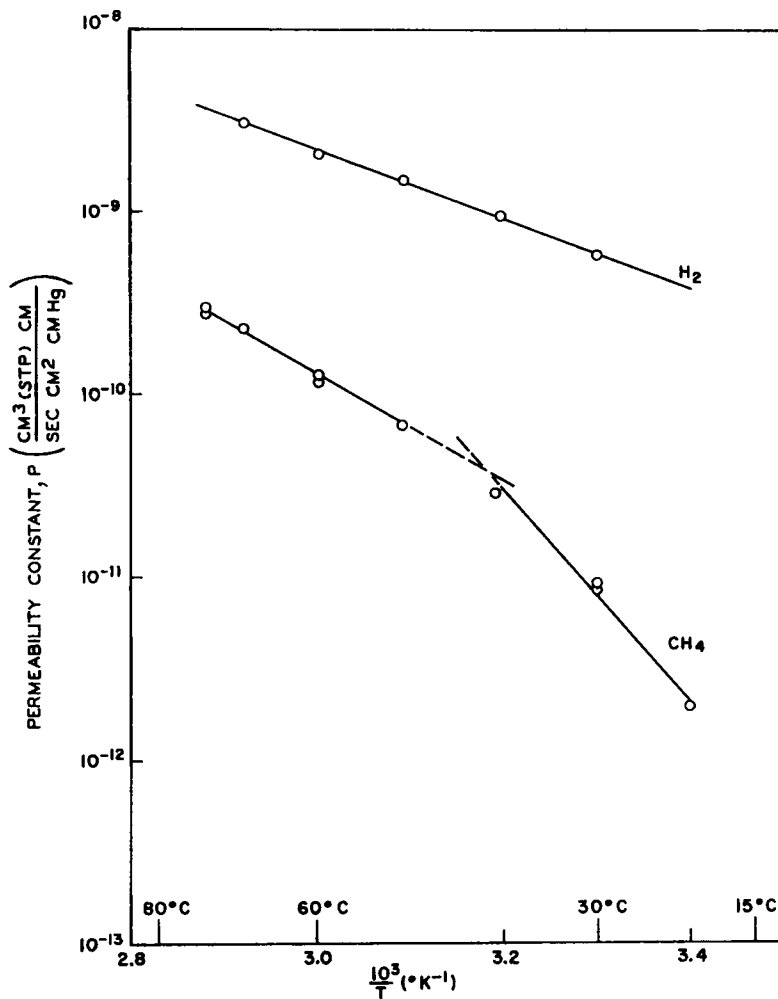


Fig. 9. Permeability of plasticized Trithene B membrane to hydrogen and methane as a function of temperature.

IV. COMPARISON OF PERMEABILITY MEASUREMENTS BY THE VARIABLE VOLUME AND VARIABLE PRESSURE METHODS

In order to compare permeability measurements obtained by the variable volume and variable pressure methods, use was made of the cell shown in Figure 4. The variable volume measurements were performed first, according to the procedure described above. The capillary was then removed, and the cell was connected to the all-glass apparatus for variable pressure measurements shown in Figure 10. The latter was similar to that used by Heilman et al.,² and, therefore, will not be further discussed. Typical data obtained with the variable pressure apparatus are shown in Figure 11; the

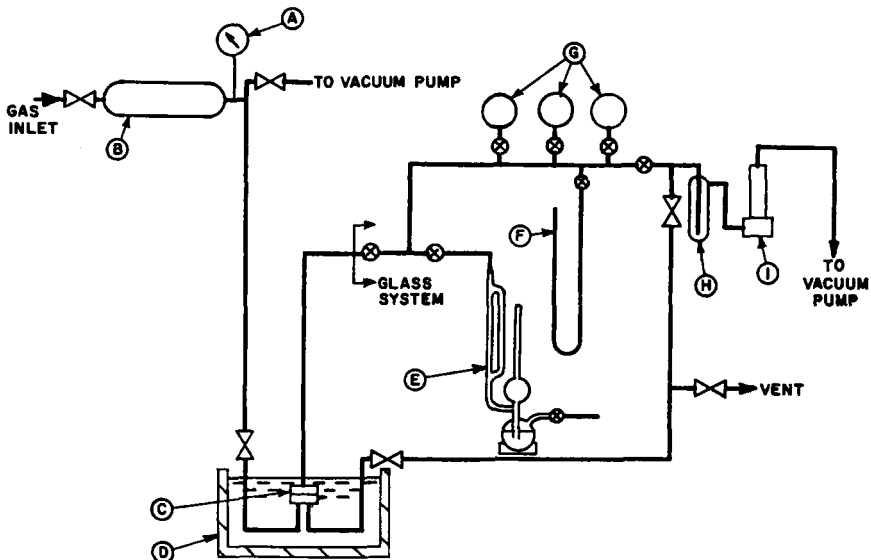


Fig. 10. Apparatus for measurement of gas permeability by the variable pressure method: (A) pressure gauge; (B) gas supply tank; (C) permeability cell; (D) insulated constant-temperature bath; (E) McLeod gauge; (F) mercury manometer; (G) auxiliary volumes; (H) liquid nitrogen-cooled trap; (I) oil diffusion pump.

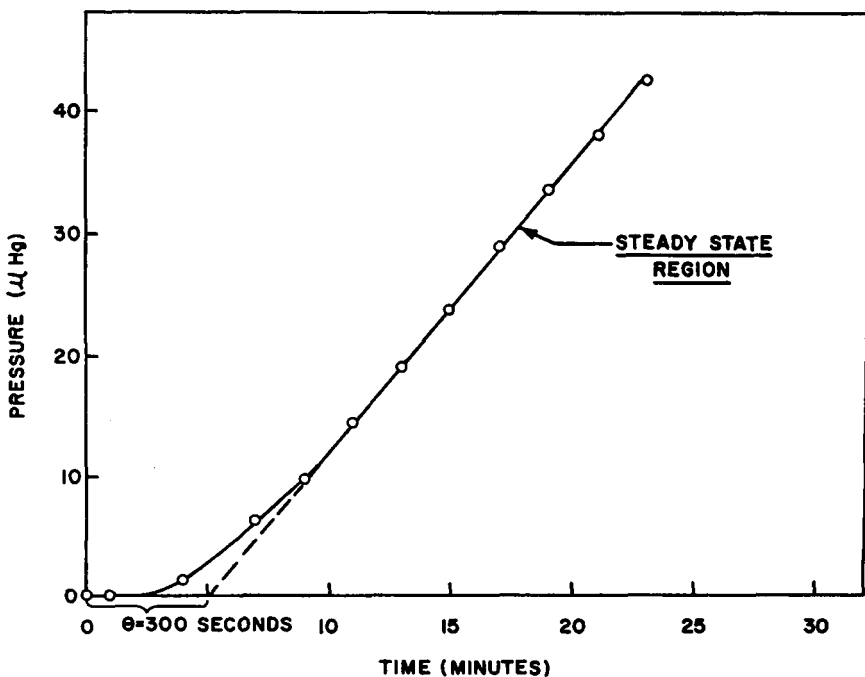


Fig. 11. Rate of permeation of carbon dioxide through 10-mil-thick Alathon 15 polyethylene membrane at 19.8°C. Data obtained by the variable pressure method.

permeability constants were calculated as usual, from the linear (or steady-state) section of the pressure-time curves

The permeability of a 0.002 in.-thick sample of Alathon 15 polyethylene to oxygen and nitrogen was measured by the two methods in the temperature range of 0–50°C., and the results are presented in Figure 12. As can

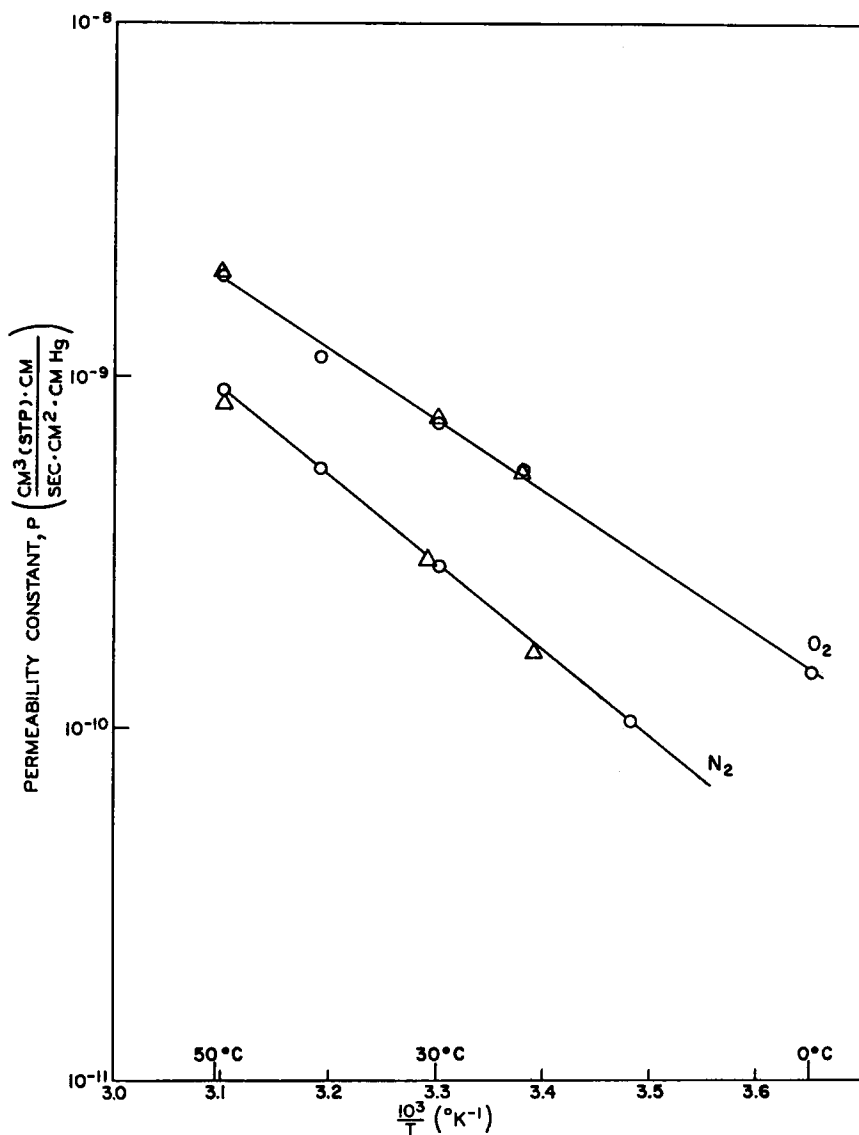


Fig. 12. Permeability of 2-mil-thick Alathon 15 polyethylene membrane to oxygen and nitrogen as a function of temperature: (Δ) data obtained by the variable volume method; (O) data obtained by the variable pressure method using the same sample of polyethylene.

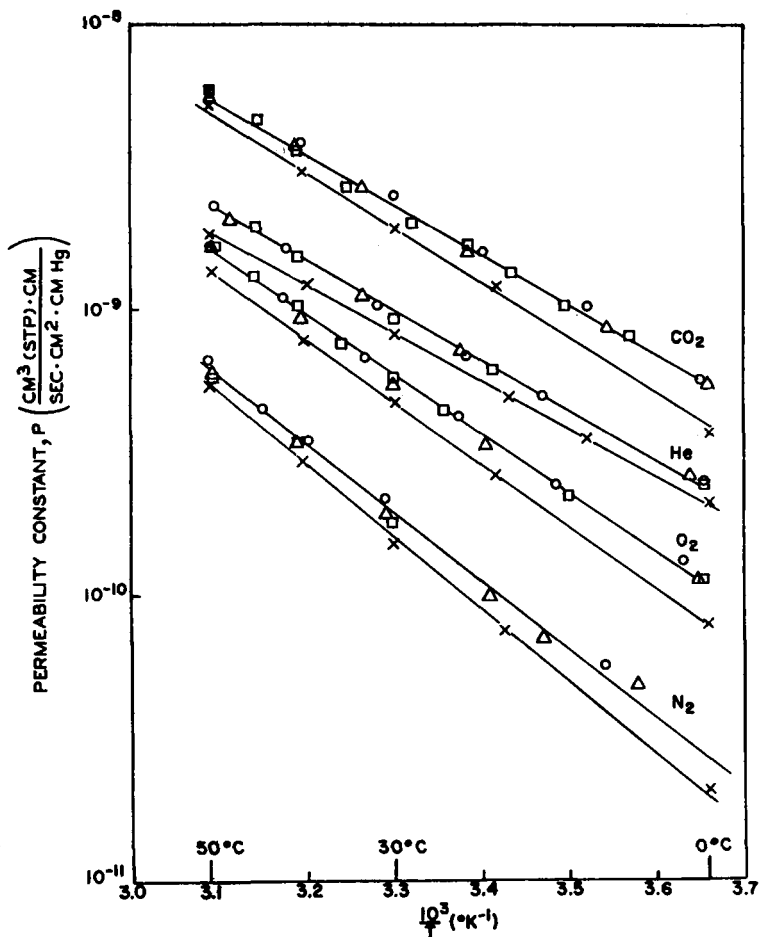


Fig. 13. Permeability of ten-mil-thick Alathon 15 polyethylene membrane to various gases as a function of temperature: (\square), (Δ), (\circ) obtained by the variable volume method (three different samples); (\times) obtained by the variable pressure method.

be seen, the measurements agree within experimental error. It is important to stress that these data were obtained with the same permeability cell, as well as with the same sample of membrane *in situ*.

Permeability measurements with different cells and different samples of membrane were also made for comparison. The permeabilities of several samples of 0.010 in.-thick Alathon 15 polyethylene to nitrogen, oxygen, helium, and carbon dioxide were determined between 0 and 50°C. by the variable volume method using the 6 in. cell shown in Figure 1, and by the variable pressure method using the 1 in. cell of Figure 4. The results are presented in Figure 13. This figure shows that the permeabilities of three samples of membrane determined by the variable volume method agree within experimental error. However, the corresponding permeability

values obtained with a fourth sample of membrane by the variable pressure method are consistently lower by 15–30%; slight differences in the slopes of the $\log P$ vs. $1/T$ curves (i.e., in the energies of activation) are also evident.

The discrepancy in the data obtained by the two methods with the thicker membranes cannot be attributed to any geometric factors, such as possible errors in the measurement of effective membrane area, because the data would then differ by some constant value independent of the permeating gas. This is clearly not the case. Furthermore, the discrepancy is larger than would be expected from differences in the structure of the membrane sample used. One possible explanation is that the variable pressure measurements were not made under true steady-state conditions, although permeabilities were calculated from apparently linear sections of the pressure–time curves.

V. CONCLUSIONS

A versatile permeability cell of the variable volume type has been described. The cell permits accurate and rapid permeability measurements to be made over wide ranges of temperature and pressure. These measurements can be performed by relatively unskilled personnel, since they do not require the use of vacuum techniques. Experimental difficulties which may arise during routine measurements, such as leaks in the apparatus and pinholes in the membrane being tested are easy to detect and identify. Also, the problem of plasticizer removal, which may result in spurious permeability measurements, is obviated by the use of this method. A permeability cell for similar measurements under very high pressure differentials has also been described.

Permeability data obtained by the variable volume method with thin membranes, of the order of 0.002 in., were found to agree within experimental error with comparable values determined by the variable pressure method. In the case of thicker membranes, of about 0.010 in., permeabilities determined by the former method were 15–30% higher.

These results indicate that a detailed comparative study of the methods used to measure permeabilities would be highly desirable. Such a study will lead to a more meaningful interpretation of permeability data reported by various investigators and, in addition, may help in formulating standardized procedures for industry.

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Synopsis

An improved cell which permits the measurement of permeabilities of membranes to gases over a wide range of temperatures and gas pressures is described. The measurements are made by the variable volume method, under constant pressure differential across the membrane. The cell lends itself particularly well to routine tests, because it does not require calibration or the use of vacuum techniques. The performance of the cell is discussed, and typical experimental results are presented. A modified permeability cell of the same type for high-pressure studies is also described. Measurements with this apparatus show that the rate of gas permeation obeys, in some cases, a single form of Fick's law, even under pressure differentials across the membrane as high as 800 psi (54 atm.). The paper also compares permeability data obtained by the variable volume and the variable pressure methods. The permeability of 0.002 in.-thick Alathon 15 polyethylene to oxygen and nitrogen was determined between 0 and 50°C. by the two methods, using the same sample of membrane *in situ*, and the measurements were found to agree within experimental error. Permeabilities of 0.010 in.-thick samples of Alathon 15 polyethylene to nitrogen, oxygen, helium, and carbon dioxide obtained in the same temperature range by the variable volume method were 15–30% higher than the corresponding data determined by the variable pressure method. This discrepancy could be due to the fact that the variable pressure measurements with the thicker membranes may not have been made under true steady-state conditions, although permeabilities were determined from apparently linear sections of permeated gas pressure *vs.* time curves. A critical re-examination of the methods used to determine permeability constants is suggested.

Résumé

On décrit une cellule perfectionnée qui permet de mesurer la perméabilité des membranes aux gaz dans de larges domaines de températures et de pressions. Les mesures sont faites par la méthode du volume variable sous une pression différentielle constante des deux côtés de la membrane. La cellule se prête particulièrement bien aux tests de routine car elle ne requiert pas de calibrage ni l'emploi des techniques du vide. On discute les performances de la cellule et on décrit des résultats expérimentaux typiques. On décrit également une cellule de perméabilité modifiée du même type pour des études à des pressions élevées. Les mesures faites avec cet appareil révèlent que la vitesse de perméation des gaz obéit, dans certains cas, à une forme simple de la loi de Fick, même lorsque la pression différentielle des deux côtés de la membrane est aussi élevée que 800 psi (54 atmosphères). L'article compare également les résultats de perméabilité obtenus par la méthode du volume variable et par celle de la pression variable. La perméabilité à l'oxygène et à l'azote du polyéthylène Alathon 15 de 0.002 pouces d'épaisseur a été déterminée par les deux méthodes entre 0°C et 50°C en employant le même échantillon de membrane *in situ*; les mesures ainsi obtenues concordaient dans la limite de l'erreur expérimentale. Les perméabilités à l'azote et à l'oxygène, à l'hélium et à l'anhydride carbonique d'échantillons de 0.010 pouces d'épaisseur de polyéthylène Alathon, obtenues dans le même domaine de température par la méthode au volume variable étaient de 15 à 30% plus élevées que les données correspondantes déterminées par la méthode des pressions variables. Cette divergence pourrait être due au fait que les mesures à pression variable faites au moyen de membranes plus épaisses n'ont pas été réalisées dans des conditions suffisantes de stationnarité, quoique les perméabilités ont été déterminées à partir de sections apparemment droites des courbes pression du gaz/temps. On suggère un réexamen critique des méthodes utilisées pour la détermination des constantes de perméabilité.

Zusammenfassung

Eine verbesserte Zelle, welche die Messung der Permeabilität von Membranen für Gase über einen weiten Temperatur- und Gasdruckbereich gestattet, wird beschrieben.

Die Messungen werden nach der Methode der Volumsänderung bei konstantem Druckdifferential über die Membrane durchgeführt. Die Zelle eignet sich besonders gut für Routinetests, da sie keine Kalibrierung und keine Verwendung von Vakuummethoden erfordert. Die Wirkungsweise der Zelle wird diskutiert und typische Versuchsergebnisse werden angegeben. Eine für Hochdruckuntersuchungen modifizierte Permeabilitätszelle des gleichen Typs wird ebenfalls beschrieben. Messungen mit diesem Apparat zeigen, dass die Geschwindigkeit der Gaspermeation in einigen Fällen auch bei Druckdifferentials über die Membrane bis hinauf zu 800 psi (54 Atmosphären) einer einfachen Form des Fickschen Gesetzes gehorchen. Weiters werden nach der Volumsänderungs- und nach der Druckänderungsmethode erhaltene Permeabilitätsdaten verglichen. Die Permeabilität eines 0,002"-dicken Alathon-15-Polyäthylens für Sauerstoff und Stickstoff wurde nach beiden Methoden zwischen 0° und 50°C unter Benützung der gleichen Membranprobe *in situ* bestimmt und die Messungen stimmten innerhalb der Versuchsfehler überein. Die nach der Volumsänderungsmethode an 0,010"-dicken Proben von Alathon-15-Polyäthylen bestimmte Permeabilität für Stickstoff, Sauerstoff, Helium und Kohlendioxyd war um 15% bis 30% höher als die entsprechenden, im gleichen Temperaturbereich nach der Druckänderungsmethode erhaltenen Werte. Diese Diskrepanz könnte darauf zurückzuführen sein, dass die Druckänderungsmessungen bei den dickeren Membranen möglicherweise nicht unter wirklich stationären Bedingungen durchgeführt wurden, wenn auch die Permeabilität aus offenbar linearen Abschnitten der Kurven Gasdruckpermeation gegen Zeit bestimmt wurde. Eine kritische Überprüfung der Methoden zur Bestimmung von Permeabilitätskonstanten wird angeregt.

Received August 28, 1962