Isobaric Measurement of Gas
Permeability of Polymers

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Synopsis

The principles and design of a gas permeability measuring instrument based on thermal conductivity measurement are described. Since the thermal conductivity of a gas mixture is dependent upon the partial pressure fraction rather than absolute partial pressure of sample gas, and the permeation rate of reference and sample gases through polymer films differ considerably, a pressure-equalizing device is necessary for the accurate measurement of gas permeability. The three types of measurements—integral, differential (flow method), and decay rate measurements—can be used with the instrument. The results of permeability constants and diffusion constants obtained with the methods showed good agreement with the conventional vacuum-type method. With proper selection of methods, the instrument can measure the gas flux through the range of 10^{-10} to 10^{-3} cm^3 (STP)/cm^2 sec cm Hg. Some advantages of the methods are discussed.

INTRODUCTION

The sensitivity of gas flux measurement, in general, depends on the ratio of the area of the membrane to the receiving volume in which the total amount of the permeant gas transported through the membrane is measured, and also the sensitivity of the detecting device itself, including the capability of amplifying the signal from the detector. The use of thermal conductivity measurements can be considered to be favorable in both terms.

Although the use of thermal conductivity measurements in analyzing the composition of a gas mixture is widely used in gas chromatography, relatively few attempts have been made to measure gas permeability of polymer films by the principle. A permeability apparatus which utilizes thermal conductivity measurement was reported by Lyssy et al.[1,2]; however, the method has not been developed beyond obtaining the magnitude of permeability of gases, and no attempt was made to obtain diffusion constants of gases in polymers. This may be due to the basic design of the instrument in which no attempt was made to minimize the pressure change caused by the difference of permeation rates of sample and reference gases. This

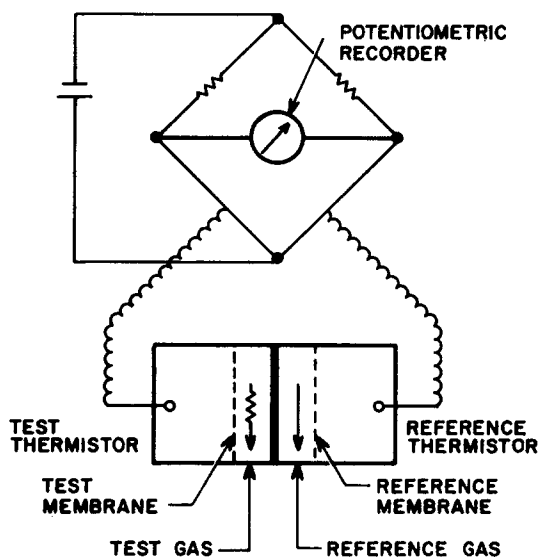* Present address: Fagersta Brucks AB, Fagersta, Sweden.

Fig. 1. Schematic representation of basic components used in the differential measurement of thermal conductivity.

is an inherent difficulty in any permeability measurement in which the amount of a gas is measured in the presence of a second gas, unless the sensor is absolutely independent of the total pressure, or some special devices to minimize the effect are included in the instrument.

One of the authors (Rosengren) has recently constructed a unique instrument which has very high overall sensitivity utilizing the principle of the thermal conductivity of gas mixtures. The new instrument* has features of minimized pressure change, high sensitivity, quick and easy sample mounting, and minimized necessary degassing of samples before the measurement. The principle of the measurement and results obtained are presented in this paper.

BASIC CONSIDERATION FOR THE DESIGN OF THE INSTRUMENT

Thermal Conductivity Measurement

In an ideal case, the heat conductivity of a mixture of two gases can be written as

$$\lambda_{mix} = X_1\lambda_1 + X_2\lambda_2 \tag{1}$$

where X_1 and X_2 are the mole fractions of gases 1 and 2, respectively.

Accordingly, the change of thermal conductivity, $\Delta\lambda$, of a gas mixture due to the second gas can be given by

$$\Delta\lambda = \lambda_1 - \lambda_{mix} = (1 - X_1)\lambda_1 - X_2\lambda_2 = X_2(\lambda_1 - \lambda_2). \tag{2}$$

If X_2 is small, even in nonideal cases, $\Delta\lambda$ is linear with X_2 and can be generally expressed as

$$\Delta\lambda = aX_2 \tag{3}$$

where a is a constant, but it may differ from $(\lambda_1 - \lambda_2)$ depending on interaction of the two gases. A linear dependence of thermal conductivity on the concentration of the second gas shown by eq. (3) is always found in the range where the concentration is small, e.g., less than 1 vol-%.[3,4]

Small differences in the thermal conductivity of gas mixtures can be sensitively detected quantitatively by the heat dissipation from two directly heated Thermistors arranged in a Wheatstone bridge circuit, one in the pure reference gas and one in the gas mixture (see Fig. 1). The sensitivity of the measurement depends on the difference of the thermal conductivity of two gases or, to be more exact, on the proportionality constant a in eq. (3). Therefore, a reference gas, whose thermal conductivity greatly differs from that of the sample gas, is preferred for sensitive and accurate measurements; for this reason, hydrogen or helium is used as the reference gas in the instrument.

Because of the fact that a very small Thermistor can be placed in the receiving volume without further extension, the total receiving volume per membrane surface can be easily reduced. The instrument used in this study has only a 0.65-ml receiving volume with a 5-cm² membrane surface, which gives a surface-to-volume ratio of 7.7 cm²/ml. (Most permeability apparatus that use pressure-volume measurement under vacuum have a surface-to-volume ratio of 0.1–0.2 cm²/ml.)

With the use of very stable Thermistors and bridge, the signal due to the small difference in thermal conductivity of the gas mixture in the receiving volume can be amplified with dependable accuracy.

Besides the sensitivity of measurement, the use of thermal conductivity measurement may have the following advantageous features:

1. The method does not depend on the total pressure difference across the membrane. Consequently, an unsupported membrane in vertical position can be used, which simplifies the procedure of mounting and changing the membrane to a great extent.

2. The interference of gases and vapors—which are sorbed in the sample membrane and come out during the permeability measurement—with flux measurement can be virtually eliminated by placing another sample specimen in the reference Thermistor cavity. The reference membrane evolves the gases and vapors at a nearly equal rate with the test specimen in the Thermistor cavity and cancels the effect of the sorbed gases and vapors in the final output of the bridge circuit. Therefore, for moderately fast membranes, practically no degassing process is necessary, which eliminates a considerable portion of the time necessary for the overall measurement of permeability. This feature may be considered particularly advantageous over other methods. For instance, the prolonged degassing of the sample

(often several times longer than the actual time necessary for permeability measurement) is required for permeability measurements by vacuum methods, and this severe degassing process may often cause the change of polymer property due to loss of relatively volatile components such as plasticizer.

3. The electric signal from the bridge is continuous and also linear with the concentration of the sample gas in the Thermistor cavity (within the region where eq. (3) is valid). These two factors make the use of an automatic recorder very useful, especially in the measurement of extremely fast or very slow permeations.

Pressure-Equalizing Device and Estimate of Errors

When permeability of gas A (sample gas) is measured by a thermal conductivity change of gas B (reference gas) due to a small amount of gas A being introduced into gas B, the measurement will be started at time zero when one side of the membrane is abruptly changed to gas A and will follow the increase of gas A on the other side of the membrane.

Under these conditions, the reference gas in the Thermistor cavity also permeates through the membrane in an opposite direction to the sample gas flux. These two gases permeate at quite different rates, and this leads to the creation of differential pressure across the membrane.

Since the change of pressure causes erroneous Thermistor output current, it is necessary to provide a special device which will equalize the pressure without changing the volume.

For this purpose, a very small (0.19–0.20 mm inner diameter) stainless steel capillary tube of 1-m length is connected to the Thermistor cavity at the opposite side of the membrane, and the other end of the capillary is purged by a reference gas stream by means of a small T joint (see Fig. 2).

Considering the very small cross-sectional area and the length of the capillary tube, it may be reasonably assumed that the mixing of sample gas takes place only in the Thermistor cavity. This is also experimentally confirmed by the concentration buildup curve of the calibration process, in which a known amount of gas mixture is allowed to diffuse into the Thermistor cavity.

On the other hand, if any pressure difference is created across the capillary tube, the gas flows through the tube. The flow rate for H_2 was found to be 0.025 mm^3/sec. mm H_2O. By this means, the pressure in the Thermistor cavity can be maintained within ± 0.02 mm Hg (measured by a differential pressure gauge). Whether the gas will flow in or flow out through the capillary depends on the difference in permeation rates of two gases.

Let us consider the case where a receiving volume, V, in which the reference gas is contained at atmospheric pressure, is separated by a membrane from the sample gas at the same pressure. The sample gas permeates into the volume at rate R_1, and the reference gas permeates out at rate R_2. The ratio of $R_2/R_1 = k$ is equal to the permeability ratio of the membrane at the given temperature.

Case 1. Flow of Sample Gas Through the Capillary

$k \geq 1$. If $k > 1$, the net loss of gases due to the permeation is $(R_2 - R_1)t$ in time t. However, in this case, the corresponding volume of the reference gas is simultaneously supplied through the capillary, and consequently a steady flow of the reference gas is maintained into the Thermistor cavity. Therefore, in this case, the concentration of the sample gas in the Thermistor cavity is $R_1 t/V$, and no correction is necessary. Since H_2 and He generally permeate faster than many other gases in most polymers, this ideal situation is expected to hold for most of the measurements if either of these gases is used as the reference gas.

If $k = 1$, no flow due to the difference of permeation rates of sample and reference gases occurs, and no correction is necessary.

$k < 1$. If, on the other hand $k < 1$, $(R_1 - R_2)t$ will accumulate in the Thermistor cavity. However, owing to the flow through the capillary tube, the corresponding volume of gas will flow out from the Thermistor cavity. In this case, the concentration of sample gas in the Thermistor cavity can be estimated as follows.

As R_1 and R_2 are expressed by cc(STP)/sec, the total volume of gas flowing out through the capillary at the condition of measurement is $(R_1 - R_2)f$, where f is the factor to correct the difference of temperature and pressure from the standard state. Then, the amount of sample gas in this volume flow is given by $(R_1 - R_2)fc$, where c is the concentration of the sample gas.

The change of concentration in the Thermistor cavity can be given by

$$V \frac{dc}{dt} = R_1 - (R_1 - R_2)fc. \tag{4}$$

With the boundary condition $c = 0$ at $t = 0$, eq. (4) can be solved as

$$c = \frac{1}{f(1 - k)} \left(1 - e^{-\frac{f(1 - k)R_1 t}{V}} \right). \tag{5}$$

For small $R_1 t$, eq. (5) can be expanded as

$$c = \frac{R_1 t}{V} - \frac{1}{2} \frac{f(1 - k)(R_1 t)^2}{V^2} + \cdots \tag{6}$$

which is smaller than the ideal case of $R_1 t/V$ and the relative error due to the convectional loss of the sample gas is

$$\frac{1}{2} \frac{f(1 - k)R_1 t}{V}.$$

From the above considerations, it is clear that if $k \geq 1$, no error due to flow of sample gas is introduced. Only when $k < 1$ is a slightly smaller value obtained owing to the loss of sample gas by the flow. However, even in this case, the maximum error (when $k = 0$) of the concentration is $fR_1 t/2V$. Since the measurement is carried out with only low concentrations of the sample gas, i.e., less than 1% ($fR_1 t/V < 1\%$), the error due to this factor

will never exceed 0.5%. Therefore, if the reference gas permeates slower than a sample gas, the resulting permeability would be slightly lower than the true value. The smaller the concentration of sample gas, the smaller will be the error.

Case 2. Diffusional Loss of Sample Gas Through the Capillary

Even when the rates of permeation of sample gas and reference gas are equal and no flow of gas occurs through the capillary tube, there is a transport of the sample gas from the Thermistor cavity by pure diffusion through the capillary tube. For diffusion through 100 cm of capillary tube, the time lag of diffusion may be calculated from the following equation[5,6]:

$$\theta = L^2/6D' = 10^4/6 \times 0.65 = 2560 \text{ sec} = 42.7 \text{ min}$$

and in about 2 hr (3θ) the diffusion equilibrium is established.

This situation may be examined by an example of CO_2 as the sample gas and H_2 as the reference gas, since permeability constants of several polymers are about the same for these two gases. The loss of CO_2 through a H_2-filled capillary can be estimated by the time lag of diffusion using the interdiffusion constant D' of CO_2 in H_2 at 1 atm pressure ($D' = 0.65 \text{ cm}^2/\text{sec}$).

The time lag of CO_2 in the Thermistor cavity can also be calculated as follows:

$$\theta = 1.5^2/6 \times 0.65 = 0.58 \text{ sec.}$$

Therefore, it seems justified to assume that the effective mixing of the sample gas with the reference gas takes place only in the Thermistor cavity.

For measurements which take longer than this time lag of the capillary, the effect of the diffusion may become important. The transport of the sample gas through the capillary by diffusion depends on the concentration of the sample gas in the Thermistor cavity, and its effect can be estimated. Since the concentration of the sample gas at the outside end of the capillary is always zero, the rate of sample gas loss (dQ_1'/dt) can be approximated by the integrated form of Fick's diffusion equation:

$$dQ_1'/dt = (D'A/L)c \tag{7}$$

where D' is the interdiffusion constant, A is the cross-sectional area, and L is the length of the capillary.

Then, the change of concentration in the Thermistor cavity can be given by

$$V \, dc/dt = R_1 - (D'A/VL)c. \tag{8}$$

With the boundary condition ($c = 0$) at $t = 0$, eq. (8) can be integrated to

$$c = \frac{R_1 L}{D'A} \left(1 - e^{\frac{-D'At}{VL}} \right). \tag{9}$$

As it can be seen in eq. (9), the concentration of the sample gas in the Thermistor cavity approaches the value $c_\infty = R_1 L/D'A$ asymptotically and

stays at this value. For fast membranes (R_1 large), c_∞ is far beyond the practical limit of measurement (which is approximately 1%); however, for very slow membranes (R_1 small), this asymptotic behavior may be noticeable at concentrations reached during measurement. In that case, a straight line for a steady-state permeation may not be obtained. Using a longer capillary tube, the value of c_∞ can be increased to prevent this situation from occurring.

For small $R_1 t$, eq. (9) can be approximated by

$$C = \frac{R_1 t}{V} - \frac{1}{2}\frac{D'A}{L}\frac{R_1 t^2}{V^2} \tag{10}$$

Therefore, the error due to the diffusional loss of the sample gas is $\frac{1}{2}$ $(D'A/VL)t$.

In the derivation of error due to the flow of the sample gas in case 1, the effect of diffusion of sample gas was ignored. This would be a reasonable assumption if the flow is much faster than the diffusion. In order to check the validity of this assumption, we can compare the errors obtained in eqs. (6) and (10).

The diffusional error is given as $D'A/2VL$, and it depends only on the interdiffusion constant D', which varies only by a magnitude of 10 at most for many combinations of permanent gases, e.g., 1.13 for He–H_2 to 0.165 for CO_2–N_2. On the other hand, the error due to the flow of sample gas depends on k and R_1. Since $(1 - k)R_1 = [(1/k) - 1]R_2$, we can estimate the magnitude of this factor by assuming that N_2 is the slowest reference gas and $[(1/k) - 1] = 30$ at most.

For the maximum, we may take the case of silicone rubber of 20-micron thickness; and for the minimum, we may take the case of poly(vinylidene chloride) of 250-micron thickness. Using the values of sample area = 5 cm², driving pressure = 76 cm Hg, $2V$ = 1.3 cm³, and L = 100 cm, we obtain

$$1.2 \times 10^{-1} > (1 - k)R_1/2V > 3.5 \times 10^{-8}$$

and

$$2.8 \times 10^{-6} > D'A/2VL > 3.9 \times 10^{-7}.$$

The maximum case we used for this calculation may not represent a normal range of error, since the permeability of silicone rubber is exceptionally high and the thickness used is very small for such material. If we take as an example low-density polyethylene of 10-micron thickness, the value 2.3×10^{-5} is given for $(1 - k)R_1/2V$.

In calculating the diffusional flux of sample gas through the capillary, we assumed a steady flow. However, the diffusional flux through the capillary occurs after quite a long time lag, and consequently, except for very slow permeation, the error considered here may not be significant.

Therefore, we may consider that the flow and diffusion of the sample gas through the capillary tube may influence the measurement to a comparable

extent for very slow permeation if a reference gas which permeates slower than the sample gas is used. Use of H_2 as the reference gas will eliminate this error as well as the error due to the flow of sample gas for most cases.

DESCRIPTION OF INSTRUMENT

The heart piece of the instrument is shown schematically in Figure 2. It consists of two cylindrical brass blocks (A and A'), identical except that they are mirror images of each other. The two pieces are mounted inside a copper tube (not shown on picture; length, 13 cm; inner diameter, 5 cm; outer surface polished and nickel-plated) and are firmly pressed against a third brass block (B) by springs. The latter block, which is secured at the
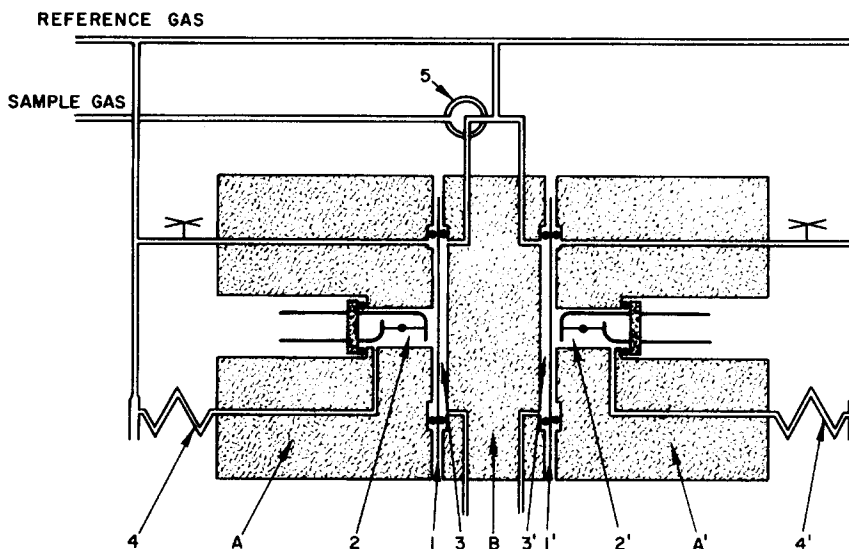

Fig. 2. Schematic representation of main part of instrument (shown through cutaway in Fig. 3): (A) sample thermistor; (A') reference thermistor blocks; (B) center block; (1) sample membrane; (1') reference membrane; (2) sample Thermistor cavity; (2') reference Thermistor cavity; (3) sample gas cavity; (3') dummy sample gas cavity for reference membrane; (4, 4') pressure-equalizing capillaries; (5) main valve to switch reference gas flow in sample gas cavity to sample (test) gas flow.

center of the copper tube, houses a shaft with *an oval disc*. When manually turned, the two outer blocks can be moved away from the center block a few millimeters.

Four O-rings are located in specially designed grooves in the contacting faces on the three blocks. Between the O-rings, the sample (1) and the reference (1') membranes are inserted. Bounded by the membranes and the O-rings, four cavities are defined, designated for further references 2, 2', 3, and 3'. All O-rings facing cavities 2 and 2' are made of Viton (du Pont trademark).

Cavity 2 is the actual receiving volume during measurements, with 2' as the identical twin for reference purposes. Both cavities consist of two parts, a shallow one next to the membrane and a narrow one surrounding the Thermistor. When these cavities are being swept, reference gas enters through an orifice and emerges into a deeper groove in the shallow part just inside the O-ring. The purpose of this arrangement is to facilitate an efficient sweeping of the whole membrane surface. The gas escapes through a hole in the narrow part behind the Thermistor (outlet not shown in figure). The inlet and outlet are regulated by different sections of on-off valves located in holes in the two brass blocks, respectively.

Cavities 2 and 2' are in contact with the surrounding atmosphere through capillary tubes 4 and 4', each 1 m long, with inner diameter of 0.2 mm (see above). To prevent diffusion of air through these capillaries, their outer ends are continuously purged with a small stream of reference gas.

For calibration purposes, each of the two outer brass blocks houses a turnable, small, closed cavity (not shown on figure). In one position it can be connected to cavities 2 and 2', respectively, the opening (of about 7 mm²) being in the shallow part close to the membrane. In the opposite position, the hole toward the membrane cavity is closed, and the turnable cavity can be purged by a gas mixture of known composition. The function of this valve is further described in the next section together with the calibration procedure.

The Thermistors (Victory Engineering Co.) are of a doubly glass-coated bead type of high stability which have been carefully matched. The operating temperature of the bead during measurements is some 50°C above that of the membrane. To prevent heat radiation from the bead to cause local warm spots on the membrane, light traps making very little obstacle to gas diffusion are inserted between Thermistors and membranes (not shown in figure).
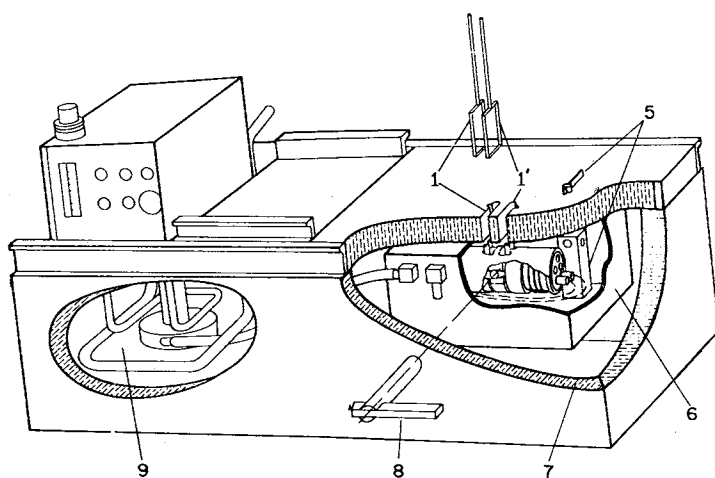

Fig. 3. Cutaway sketch of gas permeability measuring unit.

In order to maintain a constant temperature during measurements despite the heat evolved in the Thermistors, the two blocks A and A' are equipped with a number of fine channels for thermostated water circulation. Inlet and outlet plastic tubes are connected to the outer ends.

Cavities 3 and 3' are continuously being swept during measurement. The gas sweeping through cavity 3 can be either reference or sample gas, depending on the position of the main valve, 5. The volume of the cavity as well as the tube from the main valve is kept small to make it possible to complete the gas change in a few tenths of a second.

In order to facilitate the insertion of sample and reference membranes, these are mounted in a metal frame. This can be accommodated in slits made in the contacting surfaces of the three brass blocks. The three brass blocks in the copper tube are mounted on an aluminum plate together with the main valve, a needle valve to regulate reference glass flow, and equipment for internal gas connections. The mounting plate is secured to the bottom of a thick-walled, nickel-plated copper vessel (6, Fig. 3) having a heavy copper lid firmly held in place by two screws. Thus, all surfaces facing the copper tube with the cavities are at equal temperatures.

The copper vessel is partly immersed in a stainless-steel thermostat vessel containing about 20 liters of water. Foamed polystyrene, 7, forms the outer insulation as well as a lid covering the copper vessel. During measurements, the plastic handle of the frames can be unscrewed and the slits covered with a small insulating lid. A watertight connection reaching through the side of the thermostat into the copper vessel can accommodate a plastic handle, 8, for turning the oval disc during membrane insertion.

The thermostat is an on-off type having a mercury contact thermometer as temperature sensor. The power dissipated in the heating element can be regulated continuously. The outlet from pump 9 is divided into two streams: one is used to circulate the liquid in the thermostat vessel, the other is connected to the channels for thermostatted water in the blocks A and A'. During preliminary tests of the instrument, a Thermistor was inserted in the plastic tube connecting the pump with the blocks. The temperature variations during the on-off cycles of the instrument never exceeded $1/1000°C$.

MEASURING PROCEDURE

For measuring the permeability, test and reference specimens secured in sample holders are placed in the respective positions, and both sides of the specimens are swept by the reference gas until a steady bridge current is obtained (see position A in Fig. 4). The actual permeability measurement can be made by the following three methods.

Integral Measurement

Before the sample gas is sent into the sweeping gas cavity, both the test and the reference Thermistor cavities are completely closed off from the
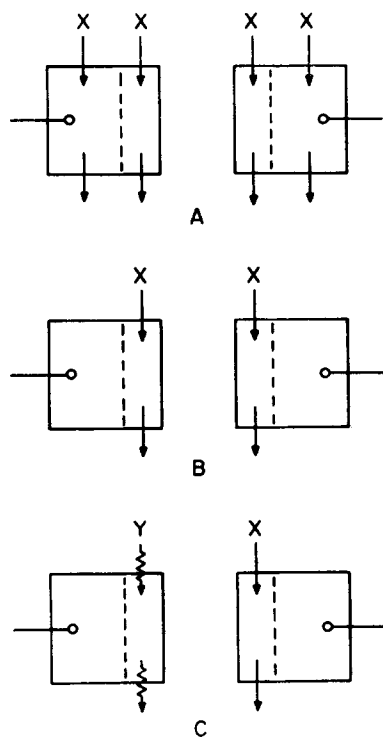
Fig. 4. Schematic representation of steps used in integral measurement. Left- and right-hand squares represent left and right portions shown in Figs. 1 and 2; (X) reference gas; (Y) sample gas; dotted lines represent membranes.
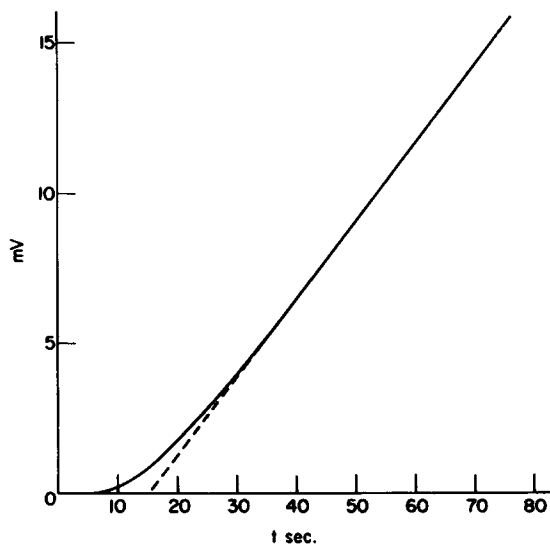

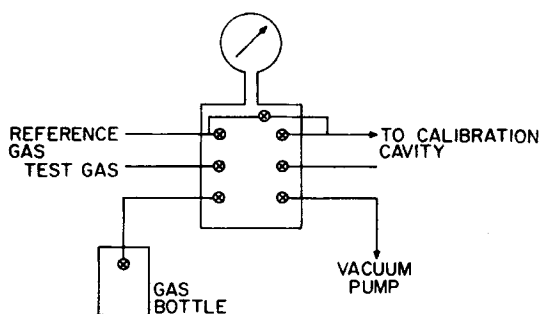Fig. 5. Typical curve obtained with integral measurement.

Fig. 6. Schematic representation of gas-mixing device used for calibration of instrument.

reference gas stream.   Thus, small known volumes of reference gas in which the Thermistors are contained are isolated (see position B in Fig. 4).   Then the sweeping gas on the test specimen is switched to a sample gas, while the sample gas cavity in the reference specimen is continued being swept by the reference gas (see position C in Fig. 4).

The increase in concentration of sample gas in the test Thermistor cavity is directly recorded as a function of time.   From the slope of the straight portion of the curve and the proportionality constant K, in terms of mV output per ml (STP) of gas in the cavity, the permeability constant is calculated.   A typical bridge output versus time is shown in Figure 5.

The time lag of the concentration buildup, in the integral measurement, can be used for calculating the diffusion constant by the equation derived by Daynes[5] and Barrer,[6] assuming that the reference gas does not affect the diffusion of sample gas in the polymer.   However, for permeations that yield a very short time lag, the delay in response of the detecting device should be considered.   The response time of the Thermistor bead is approximately 1 sec, irrespective of the surrounding gas.   However, the total delay in response of the instrument is longer than the response time of the Thermistor due to the transport of sample gas within the Thermistor cavity and is highly dependent on the reference gas.   When H_2, which has a very high interdiffusion coefficient with other gases, is used as the reference gas, this delay factor was estimated as 2.7 ± 0.2 sec irrespective of sample gas, as described in a later section.

If the time lag found on a recorder chart is orders of magnitude higher than the delay factor, it can be reasonably considered as the time lag due to the diffusion of sample gas in the membrane, and the diffusion constant may be calculated from the time lag without any further correction.

Since the measurement is carried out at constant volume with varying barometric pressure, the bridge current m should be proportional to p_i/B, i.e.,

$$m \text{ (in mV)} = \alpha p_i/B \tag{11}$$

where p_i is the partial pressure of the sample gas and B is the barometric pressure.   The proportionality constant α is a convenient way to express
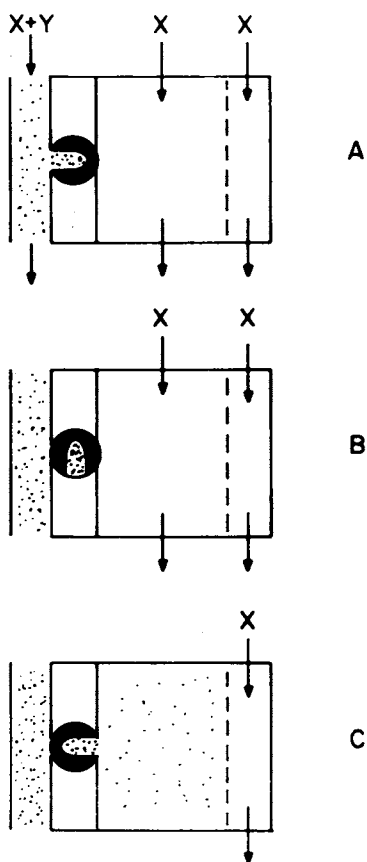
Fig. 7. Schematic representation of steps used in calibration of instrument. Sketches represent only the sample side (left) of instrument shown in Figs. 1 and 2. Calibration cavity (not shown in Figs. 1 and 2) is shown in three positions: (A) open to sample gas–reference gas stream; (B) closed to both sides; (C) open to Thermistor cavity; (X) Reference gas; (Y) sample gas.

the sensitivity of the instrument toward various sample gas–reference gas combinations. The value of α (in mV or V) indicates the potential across the bridge if the Thermistor cavity was completely filled with sample gas (providing that eq. (3) would be valid for X_2 in the whole range of 0 to 1). For calibration purposes, the instrument is equipped with a gas-mixing device and calibration cavities of known volume. The former consists of a gas bottle and a valve block with a precision pressure gauge connected with copper tubing, as shown schematically in Figure 6. The latter is placed in the main apparatus adjacent to the Thermistor cavities, as shown schematically in Figure 7.

First, the valve block and a gas bottle are evacuated by a vacuum pump. After a sufficient evacuation (which can be reduced by washing the system with test gas and reevacuating), a test gas is let into the system (valve block

and a gas bottle) until the manometer stays well above zero. The excess amount of the test gas collected in the system is allowed to escape through a bleeding outlet which is connected to a soap flow meter. When the movement of soap bubbles becomes slower, the outlet valve is closed and the system is left for about 5 min to let the gas equilibrate at room temperature. During this period, barometric pressure B_1 (in mm Hg) is read.

Then the outlet valve is opened again and left open until no outward movement of soap film is detected, and the system is closed. After closing the gas bottle, the valve block and copper tubing are evacuated again, and the reference gas is introduced into the valve block up to 9–10 kg/cm² maximum pressure (controlled by the regulator on the reference gas cylinder). The valve on the gas bottle is opened, and the reference gas is allowed to fill into the gas bottle until pressure on the manometer reads about 0.1–0.2 kg/cm² less than the maximum pressure, and then the valve on the gas bottle is closed.

The gas bottle, which now contains a mixture of reference gas and test gas, is shaken strongly enough to move around the rolls of stainless-steel net inside the bottle for mixing. After this, it is left for approximately 10 min to allow the gas mixture to reach room temperature (for highest precision and to avoid heating it by hand, handling of the gas bottle is done with asbestos gloves).

The inlet valve of the reference gas is closed, and the valve on the bottle is opened for a few seconds and the pressure on the manometer, p_0 kg/cm², is read accurately. The gas bottle is now shaken 40–50 times. The manometer and copper tubing are evacuated before the gas mixture is let into the valve block.

The fraction of the partial pressure of test gas in the final mixture is given by

$$\frac{B_1}{(p_0)(0.9678)(760) + B_1} .$$

After the gas mixture is collected in the valve block, the valve on the gas bottle is closed and the gas mixture is sent to the calibration cavity by opening the valve which connects the block to the calibration cavity. The calibration cavity is placed in position A in Figure 7, which represents a schematic arrangement of the calibration cavity in the test Thermistor cavity.

A needle valve which is placed on the line between the valve block and calibration cavity is adjusted so that the pressure drops at a rate of approximately 1 kg/cm² per 10–15 sec. After a total pressure drop of 3–5 kg/cm² on the manometer, the valve on the block is closed and the calibration cavity is turned to position B in Figure 5 within a few seconds.

Thus, a known amount (volume V_0 of the calibration cavity at barometric pressure B_0) of test gas mixture is trapped. By turning the calibration cavity (after closing Thermistor cavities) to position C in Figure 7, the test gas mixture is allowed to diffuse into the reference gas, which is retained in

Thermistor cavity of volume V at pressure B_0, and the bridge output signal is read.   After a short time, the bridge output reaches a constant and the shift from the baseline is read as m_0 (in mV).

From this measurement, factor α is calculated as follows:

volume of calibration cavity: V_0 cm^3

partial pressure of sample gas in calibration cavity: $\dfrac{B_1}{(p_0)(0.9678)(760) + B_1} \cdot B_0$

volume of thermistor cavity: V

total volume in position C (Fig. 7): $V + V_0$

partial pressure of sample gas in Thermistor cavity in position C:

$$p_i = \frac{V}{V + V_0} \cdot \frac{B_1 B_0}{(p)(0.9678) \cdot (760) + B_1}$$

From eq. (11), α is given by

$$\alpha = m_0 \frac{B_0}{p_i} = \frac{V + V_0}{V} \frac{(p)(0.9678) \cdot (760) + B_1}{B_1} m_0 \qquad (12)$$

In this calibration procedure, a metal foil or polymer film of very slow permeability can be used, since the mixing of gases is usually complete within 30 sec.

The permeability constant P is generally given by

$$P = (\text{rate of gas flux}) \cdot \frac{l}{A} \cdot \frac{1}{\text{driving pressure}}. \qquad (13)$$

With this instrument, measurement is done under barometric pressure B as the driving pressure:

$$P = (\text{rate of gas flux}) \frac{l}{A} \cdot \frac{1}{B} \qquad (14)$$

where l is the film thickness, A is the membrane area, and B is the barometric pressure when the measurement is carried out.   Rate of gas flux is customarily expressed by cc(STP) of gas, which is given by

$$\text{rate of gas flux} = \left(\frac{dp_i}{dt}\right)_{\text{steady state}} \cdot \frac{V}{760} \cdot \frac{273}{T_1} \qquad (15)$$

where $(dp_i/dt)_{\text{steady state}}$ is the steady-state rate of partial pressure increase and T_1 is the temperature of the measurement.   From eq. (11) we obtain

$$\frac{dp_i}{dt} = \frac{B}{\alpha} \frac{dm}{dt}. \qquad (16)$$

Therefore, P can be given by

$$P = \frac{1}{\alpha} \left(\frac{dm}{dt}\right)_{\text{steady state}} \frac{V}{760} \frac{273}{T_1} \frac{l}{A}. \qquad (17)$$

TABLE I
Sensitivity and Calibration Factors

	$\alpha \times 10^{-3}$, mV	$K \times 10^7$, cm^3 (STP)/ mV cm^2 cm Hg
H$_2$ as Reference Gas		
CO$_2$	6.10	2.57
N$_2$	5.04	3.11
O$_2$	4.76	3.29
He	0.947	16.5
He as Reference Gas		
CO$_2$	7.03	2.23
N$_2$	5.89	2.66
O$_2$	5.43	2.89

Since A is a constant with the instrument,

$$P = \left(\frac{dm}{dt}\right)_{\text{steady state}} K \cdot l \tag{18}$$

where

$$K = \frac{V\ 273}{\alpha\ 760\ T_1\ A}. \tag{19}$$

The values of α and K at 25°C are shown in Table I.

Dependence of α on Bridge Current and Temperature

At constant measurement temperature, the sensitivity of the instrument is dependent on the bridge current. As seen in Figure 1, the bridge is fed symmetrically; thus half of the bridge current goes through each Thermistor. The bridge current giving highest instrument sensitivity is experimentally found by measuring the steady-state flow rate of an arbitrarily chosen film. A low-density polyethylene film was used for this purpose. A steady-state flow of sample gas was established before the test, and $(dm/dt)_{\text{steady state}}$ was examined with various bridge currents. Results obtained with H$_2$ as reference gas are shown in Table II. For all test gases, the same behavior is found: the sensitivity increases rapidly when current is increased, whereafter a plateau is reached. Recent refined measurements indicate a minor drop in sensitivity at still higher current. Working at the current showing maximum sensitivity minimizes disturbances from variations in the current; hence, for measurement at 25°C, 8 mA was selected as the standard bridge current for H$_2$ and He as the reference gases. When gases of lower thermal conductivities are used as reference gas, a lower bridge current should be used, e.g., 3.5 mA for N$_2$ as the reference gas.

A number of experiments have been performed at higher instrument temperatures. By using He as the reference gas, the bridge current giving maximum sensitivity at 25°C, 40°C, 60°C, and 80°C was found to be 8, 11, 16, and 20 mA, respectively.

TABLE II
Effect of Bridge Current on Sensitivity α^{a}

Gas	Bridge current, mA	$\alpha \times 10^{-3}$ mV	Gas	Bridge current, mA	$\alpha \times 10^{-3}$, mV
CO$_2$	6.0	5.42	O$_2$	6.0	4.28
	6.5	5.64		6.5	4.45
	7.0	5.78		7.0	4.61
	7.5	6.01		7.5	4.70
	8.0	6.10		8.0	4.76
	8.5	6.10		8.5	4.85
	9.0	6.13		9.0	4.85
	9.5	6.14		9.5	4.85
N$_2$	6.0	4.51	He	6.0	0.829
	6.5	4.70		6.5	0.867
	7.0	4.87		7.0	0.906
	7.5	5.02		7.5	0.923
	8.0	5.04		8.0	0.947
	8.8	5.11		8.5	9.947
	9.0	5.16		9.0	0.958
	9.5	5.11		9.5	0.960

^{a} H$_2$ as reference gas.

When calibrations were made at different temperatures (using the bridge currents showing maximum sensitivity), a drop in sensitivity was found at higher temperatures. Taking the values at 25°C as 100%, the sensitivities for CO$_2$ and O$_2$ at 40°C were reduced to 74.2% and 74.2%; at 60°C, to 59.3% and 60.1%; and at 80°C, to 48.9% and 50.0%, respectively.

Differential Measurement

Instead of closing the Thermistor cavity, a known rate of reference gas flow can be maintained in the cavity. This flow method can be used for the differential measurement of the permeation flux by simply changing the sweeping gas to a sample gas, as shown schematically in Figure 8.

In this flow method, the partial pressure of sample gas, p_i, in the gas mixture stream is given by

$$p_i = B \left(\frac{R'}{R' + F} \right) \tag{20}$$

where R' is the rate of sample gas flux through the membrane, F is the flow rate of the reference gas, and B is the barometric pressure.

Since $R' \ll F$,

$$p_i \cong B \frac{R'}{F}. \tag{21}$$

From eqs. (11) and (21), the steady-state bridge output in the differential method, m', can be given as

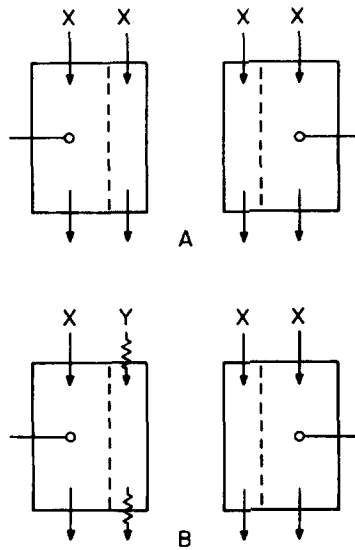$$m' \text{ (in mV)} = \alpha \frac{R'}{F}. \tag{22}$$

Fig. 8. Schematic representation of steps used in differential measurement (flow method). Symbols used are same as those in Fig. 4.

As R is expressed in cc(STP)/sec, rather than cc/sec at the temperature of measurement,

$$R \text{ (in cc(STP)/sec)} = R' \frac{273}{T_1} \frac{B}{760} = \frac{273}{T_1} \frac{B}{760} \frac{Fm'}{\alpha} \tag{23}$$

where F is flow rate of reference gas in cc/sec at the temperature of the measurement, T_1.

From eqs. (14) and (23) one obtains

$$P = \frac{273}{T_1} \frac{F}{760} \cdot \frac{l}{A} \cdot \frac{m'}{\alpha} \tag{24}$$

which can be simplified for an equipment as

$$P = K'Fm'l \tag{25}$$

where

$$K' = \frac{273}{\alpha \cdot 760 \cdot A \cdot T_1} . \tag{26}$$

Consequently,

$$P = \frac{K}{V} Fm'l \tag{27}$$

$$V \left(\frac{dm}{dt} \right)_{\text{steady state}} = Fm'_{\text{steady state}} \tag{28}$$

TABLE III
Effect of Flow Rate on the Differential Measurement

Gas	F, cm³/sec	m', mV	Fm'	$P_2 \times 10^{10}$, cm³ (STP) cm/cm² sec cm Hg
	Polydimethylsiloxane ($l = 1.53 \times 10^{-2}$ cm)			
N₂	0.2293	16.05	3.680	289
	0.2688	13.00	3.656	287
	0.3759	9.82	3.691	290
	0.4807	7.69	3.697	291
	0.5290	6.93	3.667	288
O₂	0.1594	44.6	7.109	591
	0.2024	35.0	7.084	589
	0.2873	25.0	7.183	597
	0.3773	19.0	7.169	596
	0.5291	13.6	7.196	599
He	0.1408	6.37	0.8968	375
	0.1984	4.65	0.9225	386
	0.2923	3.19	0.9324	390
	0.3745	2.50	0.9365	391
	0.5347	1.65	0.8822	369
	Poly(phenylene Oxide) ($l = 1.04 \times 10^{-2}$ cm)			
CO₂	0.2036	8.90	1.8120	80.0
	0.2824	6.32	1.7847	78.8
	0.3571	5.02	1.7926	79.2
	0.4854	3.72	1.8056	79.7
	PMP ($l = 1.076 \times 10^{-2}$ cm)			
O₂	0.1636	2.77	0.4539	2.650
	0.2272	2.02	0.4589	2.684
	0.2976	1.56	0.4642	2.715
CO₂	0.2132	9.00	1.9188	8.767
	0.2409	8.00	1.9272	8.805
	0.3105	6.23	1.9328	8.831
	0.3875	4.93	1.9103	8.728
He	0.1584	1.625	0.2574	7.567
	0.2164	1.225	0.2650	7.791
	0.3067	0.8625	0.2645	7.776
	0.3802	0.6875	0.2613	7.682
	PMP ($l = 7.84 \times 10^{-3}$ cm)			
N₂	0.1721	1.05	0.1807	7.280
	0.2232	0.86	0.1919	7.731
	0.3300	0.58	0.1914	7.711
	0.3921	0.475	0.1862	7.502
O₂	0.2197	3.20	0.7030	2.996
	0.3205	2.18	0.7010	2.988
	0.3731	1.88	0.6995	2.981
	0.4739	1.486	0.6930	2.953

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Examples of the constancy of Fm' and P_2 calculated from eq. (27) are presented in Table III. As seen, the relationship

$$Fm' = \text{constant}$$

held for all practical ranges of flow rates and for different sample gases; however, the values of Fm' were found not to be always the same as the value of $V \left(\dfrac{dm}{dt} \right)_{\text{steady state}}$.

There seem to be several possibilities which cause the discrepancy in eq. (28). They are (a) the sensitivities of Thermistors in a stagnant system and in flow might be different; (b) possible asymmetric flow rates may exist in Thermistor cavities; (c) the volume in which the mixing of gas takes place may not be identical with the static volume of the Thermistor cavity; (d) the flow rate measured may be less than the actual flow in the Thermistor cavity due to the additional flow resistance of the bubble.

However, the fact that Fm' always becomes a constant seems to preclude all these possibilities in a practical range of accuracy, and it is found that $(dm/dt)_{\text{steady state}}$ is not accurate for membranes that have very high permeability (for which the flow method can be used). This situation is explained in a later section.

In differential measurement, the electrical output is reduced by a factor proportional to the flow rate. For this reason, it is not suitable for estimating the permeability constant for slow membranes nor for the gas pair which does not give a large enough α. On the other hand, this method seems to be quite useful for determination of very high permeability constants due to high solubility, because the steady-state permeation of such a membrane often cannot be observed within the limit of time in which the concentration of the sample gas in the small receiving volume reaches the upper limit of the measurement.

In this method, as seen in eq. (28), the bridge output is proportional to the rate of permeation, whereas the integral method output is proportional to the total amount of the sample gas in the Thermistor cavity. Equation (23) is derived for a steady-state flux of sample gas through the membrane. However, as long as the flow rate of the reference gas is high enough in comparison to the sample gas flux through the membrane and practically instantaneous mixing can be assumed, the equation should hold for the transient state of permeation. Thus, the recorder output at a given time represents the differential of the concentration buildup curve which would be obtained by the integral measurement. An example of m' versus time is presented in Figure 9.

Since the output is the differential of the concentration buildup, this method has the special advantage of estimating the diffusion constant by applying the early-time method.[7,8,9]

The usefulness of the early-time method in the study of diffusion of gas through polymer membranes has been indicated by Barrer and Chio.[10]
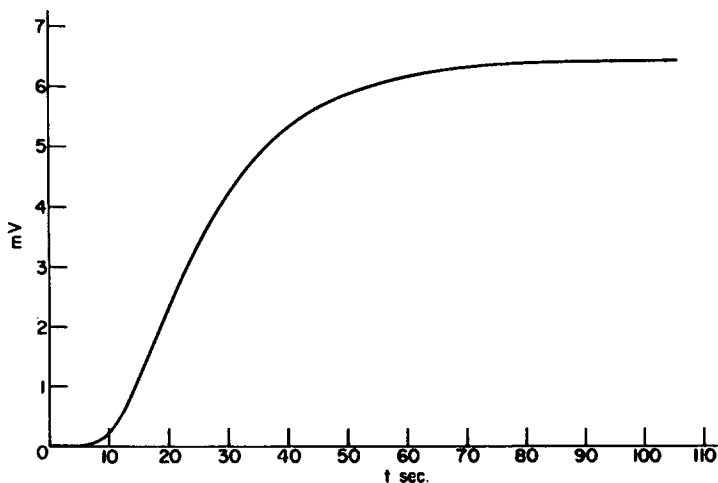
Fig. 9. Typical curve obtained with differential measurement.

In this early-time approach, the diffusion constant D_E, for the early stage of permeation, is given by the following expression:

$$\ln \left(t^{1/2} \frac{dp_2}{dt} \right) = \ln \left[\frac{2A}{V} \sigma p_1 \left(\frac{D_E}{\pi} \right)^{1/2} \right] - \frac{l^2}{4D_E t} \qquad (29)$$

where A is the membrane area, V is the volume in which the diffused gas is contained at pressure p_2, p_1 is the pressure of the high pressure side, and σ is the solubility constant of the gas in the polymer. Thus, a plot of $\ln \left[t^{1/2} \frac{dp_2}{dt} \right]$ versus $1/t$ is a straight line of slope $l^2/4D_E$.

By the differential measurement, the value proportional to dp_2/dt is directly given on the curve, and, therefore, the slope of eq. (29) can be obtained by plotting the logarithm of the product of the recorder displacement and the square root of time against $1/t$. Applicability of this analysis is discussed in a later section.

Decay Rate Measurement

The measurement of decay rate of the sample gas through a sample film can be used as the third method of permeability measurement by the instrument. In this method, the calibration cavity is utilized to introduce sample gas into the closed Thermistor cavity following the procedure described in the calibration of the instrument for the integral method. This situation is schematically represented in Figure 10. At position A in Figure 10, while both sides of the sample film are swept by the reference gas, the calibration cavity is filled by a sample gas–reference gas mixture. In order to trap the sample gas mixture at atmospheric pressure, the flow of sample gas mixture is stopped a fraction of a second before the calibration cavity is

turned to position B.   Then, the Thermistor cavity is closed to the reference gas stream (position C in Fig. 10), and the calibration cavity is turned to the Thermistor cavity to let the sample gas diffuse into the entire Thermistor cavity (position D in Fig. 10).   As the sample gas diffuses into the Thermistor cavity and the mixing is completed, the bridge signal will remain at a constant if no gas permeates through the sample film (as is the case during the calibration procedure).   When the sample gas permeates through a sample, the entire bridge signal will follow the curve shown in Figure 11.
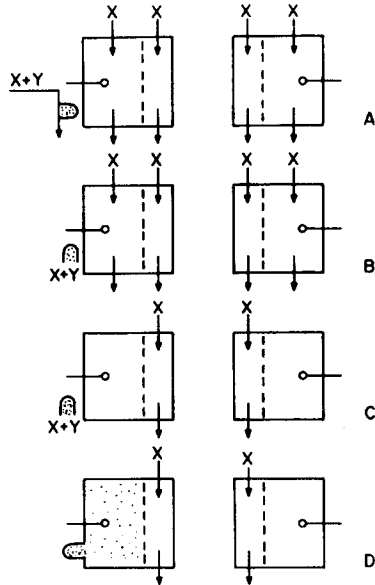

Fig. 10. Schematic representation of steps used in the decay-rate measurement.   Symbols used are same as those in Figs. 4 and 7.

The first part of the curve is exactly the same as the one used for calibration; however, the decay part of the curve generally follows the first-order decay, and the permeability of gas through the film can be calculated by the decay rate:

$$\frac{dp_i}{dt} = \frac{PA}{Vl}\,p_i \tag{30}$$

where P is the permeability constant and p_i is the partial pressure of the test gas.   (With very fast permeation, the constant value is never reached. Even in this case, the decay curve is quite normal except in the very early stage.)   Since the bridge output m (mV) is related to the partial pressure of of the test gas in the Thermistor cavity as follows:

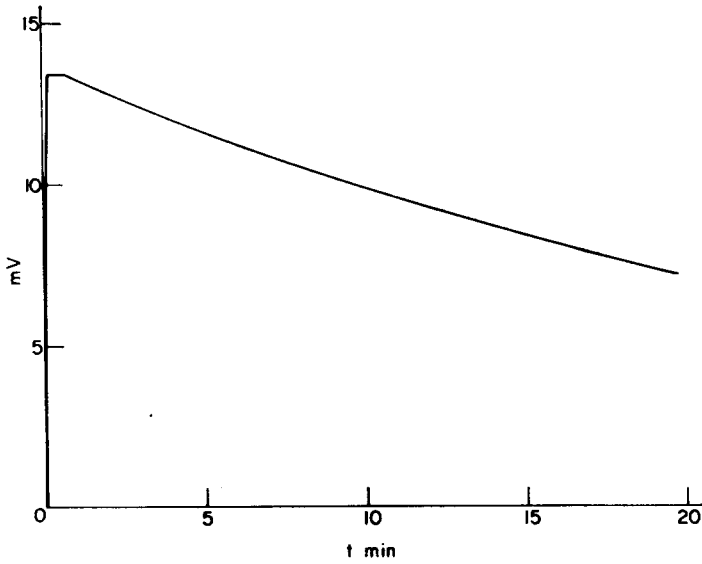$$p_i = \frac{B}{\alpha}\,m, \tag{11}$$

Fig. 11. Typical curve obtained by decay-rate measurement.

dp_i/dt is given by

$$\frac{dp_i}{dt} = \frac{B}{\alpha} \frac{dm}{dt}. \tag{16}$$

Hence,

$$\frac{dm}{dt} = \frac{PA}{Vl} m \tag{31}$$

$$\frac{d \ln m}{dt} = \frac{PA}{Vl}. \tag{32}$$

Using the conversion factor of the pressure unit, permeability, in units of $cm^3(STP)$ cm/cm^2 sec cm Hg, is obtained by

$$P = \frac{\dfrac{d \ln m}{dt} \cdot V \cdot l}{A \cdot 76} \tag{33}$$

For values of V, the volume of the Thermistor cavity plus the volume of the calibration cavity should be used for the procedure described here; $\dfrac{d \ln m}{dt}$ can be obtained from the semilog plot of m versus t.

Using the half-time of decay, P can also be calculated by

$$P = K'' \cdot \frac{l}{t_{1/2}} \tag{34}$$

where

$$K'' = \frac{2.3 \cdot \log 2 \cdot V}{A \cdot 76}. \tag{35}$$

This method is very useful when the permeability of polymer film is too high and the accurate measurement by the integral method becomes difficult.

The measurement by this method takes a much longer time than the two methods previously described, due to the much smaller driving forces involved; however, because of this fact, the method is very useful for extremely fast membranes for which the two other methods cannot be used. A unique advantage of this method is that the calculation does not depend on the calibration. Therefore, this method is useful for permeability measurement of condensible vapor which cannot be calibrated by the ordinary procedure, providing that permeation is fast enough to be detected.

This method can also be used without a calibration cavity. For this procedure, the ordinary integral measurement is performed until an appropriate output signal is obtained. Then the sample gas is switched back to the reference gas, keeping the Thermistor cavity closed.

RESULTS AND DISCUSSION

Gas permeabilities of various polymer films were examined using the instrument and compared with the values obtained by the conventional vacuum method. Permeabilities of gases through a sample of each polymer was first measured by the vacuum method; then the center part of the sample was cut out to be the sample for the thermal conductivity method. Results are summarized in Table IV, where P_v refers to the permeability values obtained by the vacuum method, P_1 by the integral method, P_2 by the flow method, and P_3 by the decay method.

The applicable ranges of each method are estimated as shown in Figure 12. Some of the values shown in Table IV are beyond the range suggested, and those are placed in parentheses. As seen in Figure 12, the applicable
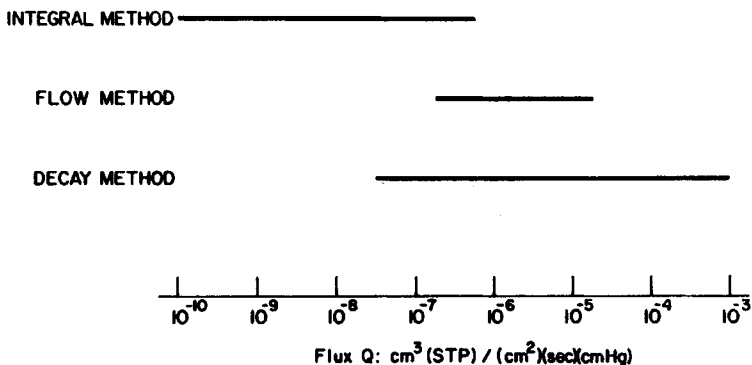

Fig. 12. Estimated ranges of permeation rate obtained by three different methods.

TABLE IV
Comparison of P Values Obtained by Various Methods[a]

Gas	P_v	P_1	P_2	P_3
	Poly(dimethylsiloxane) ($l = 1.53 \times 10^{-2}$ cm)			
N_2	281	220	288	233
O_2	605	(419)	595	429
CO_2	3240	(1690)	3210	2220
He	355	253	384	255
H_2	649	—	—	—
	Poly(phenylene Oxide) ($l = 1.04 \times 10^{-2}$ cm)			
N_2	3.81	3.16	—	—
O_2	15.8	15.3	—	17.8
CO_2	75.7	73.2	79.4	61.0
He	78.1	63.8	68.3	76.5
H_2	112.8	—	—	—
	Poly-4-methylpentene-1 ($l = 1.076 \times 10^{-2}$ cm)			
N_2	7.83	5.91	6.19	12.5
O_2	32.3	24.1	26.8	33.5
CO_2	92.6	78.7	87.8	87.5
He	101	72.0	77.0	103.
H_2	136	—	—	—
	Poly-4-methylpentene-1 ($l = 7.84 \times 10^{-3}$ cm)			
N_2	9.87	6.41	7.56	8.65
O_2	42.3	26.2	29.8	`28.9
CO_2	128	83.6	101	91.3
He	136	79.4	96.5	97.5
H_2	179	—	—	—
	Polyethylene (0.920), Low Density ($l = 4.0 \times 10^{-3}$ cm)			
N_2	0.973	0.932	—	—
O_2	3.15	2.88	—	—
CO_2	13.2	12.6	—	12.3
He	6.28	5.29	—	5.28
H_2	9.25	—	—	—
	Polyethylene (0.960), High Density ($l = 3.46 \times 10^{-3}$ cm)			
N_2	0.245	0.205	—	
O_2	0.829	0.705	—	
CO_2	3.39	2.85		
He	2.06	1.56	—	1.72
H_2	2.92	—	—	—
	Polystyrene (biaxially oriented) ($l = 3.0 \times 10^{-3}$ cm)			
N_2	0.788	0.389	—	0.621
O_2	2.63	1.94	—	2.38
CO_2	10.5	9.10	—	10.1
He	18.7	13.5	—	20.0
H_2	23.3	—	—	—
	Polypropylene (biaxially oriented) ($l = 2.1 \times 10^{-3}$ cm)			
N_2	0.219	0.185	—	—
O_2	0.872	0.879	—	—
CO_2	2.90	2.61	—	2.87
He	6.21	5.05	—	5.28
H_2	5.98	—	—	—
	Poly(vinyl Chloride) ($l = 1.21 \times 10^{-2}$ cm)			
CO_2	0.157	0.151	—	—

[a] P values $\times 10^{10}$, in units of $(cm^3\text{-STP})(cm)/(cm^2)(sec)(cmHg)$.

range of the three methods are overlapping and consequently compensating the disadvantage of having a very small receiving volume. Therefore, with proper choice of the testing methods, this instrument can be utilized for measurement of a wide range of permeation rates.

For the proper selection of the methods, the following basic factors involved in the measurement of gas permeability should be kept in mind.

Measurement of Permeability Constants

Upper Limit of Recorder Range

The linear increase of mV versus time as shown in Figure 5 cannot be expected if the mV range used exceeds a certain limit. This linear relationship is expected only when the partial pressure of test gas in the receiving volume is negligibly small compared to the driving partial pressure of the test gas, regardless of the method of detecting permeant gas in the receiving volume. Although the sensitivity α was found to be practically constant for a higher percentage of gas mixture than the concentration used for the calibration procedure (approximately 1%), the recorder output obtained by the calibration process may be considered as the maximum recorder output to be used, and measurement should not be extended beyond these values. The values of maximum recorder output for various gases (H_2 as the reference gas) are as follows: CO_2, 100 mV; N_2, 85 mV; O_2, 80 mV; He, 20 mV.

Integral Method

When a steady-state permeation rate is obtained for the ordinary integral (time-lag) measurement, a straight line should be obtained within the upper limit, and also the time span of the measurement should cover over three times the apparent time lag. This situation is explained in Figure 13, where integral measurement and differential measurement are superimposed in the same time scale for permeation of O_2 in a sample of poly(4-methylpentene-1). As is seen, it takes approximately 3τ to establish steady-state flow. Therefore, the straight line obtained from the line beyond 3τ represents the true steady-state rate of permeation, as is the case shown in Figure 13. However, when permeability of CO_2 through the same sample is measured, the Thermistor output reaches a maximum value before 3τ, as shown in Figure 14, due to higher solubility coefficient of CO_2 than that of O_2. Even in this case, an apparent straight line can be obtained, but the line does not represent the true steady-state permeation rate, as the curve obtained by the differential measurement clearly indicates. This situation can be detected either by checking if the data are taken beyond 3τ or by checking the time necessary to reach steady-state flow by differential measurement.

When the steady-state rate cannot be obtained by ordinary time-lag measurement, the steady-state permeation rate may be obtained by starting the flow method until a steady-state permeation is reached, then closing the Thermistor cavities to measure the steady-state rate. For these membranes

however, the steady-state rate observed by the integral method tends to give smaller values, owing to the following reasons.

The rate of partial pressure increase in the receiving volume is dependent upon not only the rate of permeation through the sample polymer film but
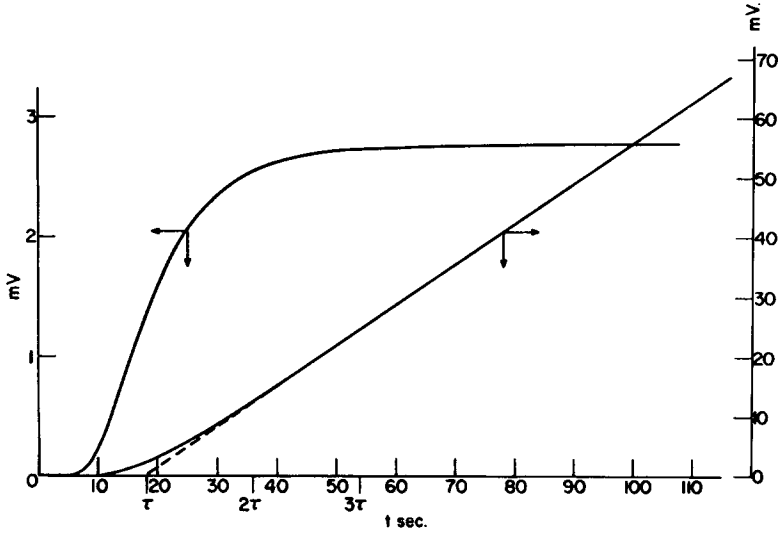

Fig. 13. Superimposed curves obtained by integral measurement (right ordinate) and differential measurement (left ordinate) for the ideal case. A steady-state rate measurement can be obtained by integral measurement.
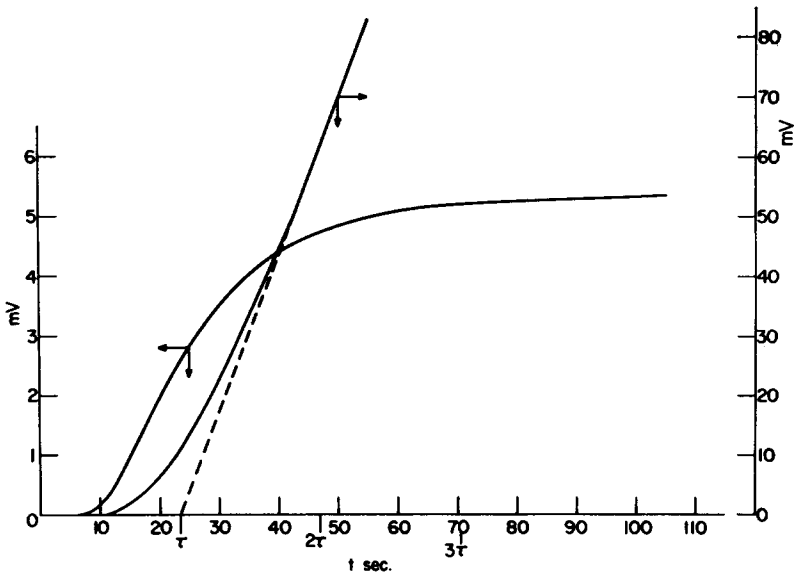

Fig. 14 Superimposed curve obtained by integral measurement (right ordinate) and differential measurement (left ordinate) for the case when steady-state rate of permeation cannot be obtained by integral measurement.
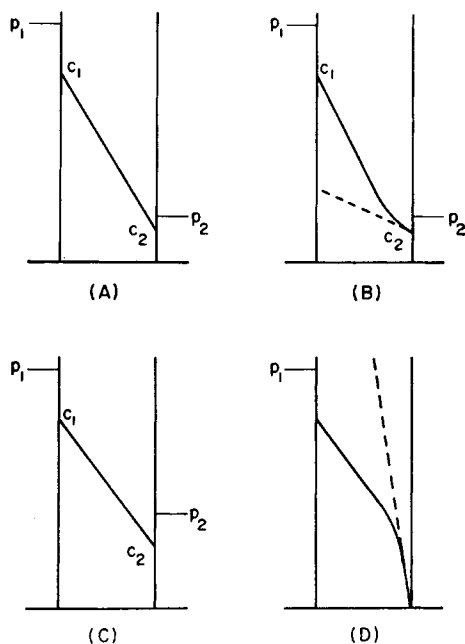
Fig. 15. Schematic representation of concentration profile of permeant (sample) gas within membranes.

also on the size of the receiving volume—to be exact, on the ratio of membrane area over volume of receiving volume. On the other hand, the permeation process of permeant gas is governed by the diffusion process which is the characteristic nature of a polymer. In the process of permeation, the time lag (which is a function of diffusion constant and thickness of the film) can be considered as a parameter analogous to the relaxation time of the process. If the time lag is large, any changes in the external concentration of the permeant will be reflected in the measurement only after the time-consuming step of establishing a new steady state is completed. Therefore, when the partial pressure of permeant in the receiving volume increases faster than the relaxation process characterized by the time lag, or partial pressure in the receiving volume is changed abruptly by sweeping the cavity by reference gas, the apparent permeation rate observed may not represent the steady-state permeation under the external condition, but it may merely represent a permeation rate controlled by the local concentration gradient in the vicinity of the downstream side of the membrane. These situations may be visualized by the schematic representation of the concentration profile of the permeant within a membrane shown in Figure 15.

Case A represents the situation when the upstream side of the membrane is exposed to a constant partial pressure p_1 and the measurement of partial pressure in the downstream side is carried out up to p_2 ($p_1 \gg p_2$) and the rate of p_2 increase is slow enough so that a linear concentration gradient in

the membrane phase is maintained (ideal case). In this case, the flux can be properly related to the driving pressure p_1 ($p_1 - p_2 \cong p_1$) to yield an accurate permeability constant.

If p_2 increases faster than the relaxation time of the permeation process due to very small receiving volume, however, a linear concentration gradient cannot be maintained, and distortion of the concentration profile results. In this case, the permeation is governed by the local concentration gradient near the downstream side of the membrane (dotted line) which is smaller than the ideal case, as seen in case B. Therefore, if the permeability is calculated by using p_1 as the driving pressure, smaller values than the true permeability are obtained. This seems to be the major reason why small values are obtained by the integral method for highly permeable membranes, even with steady-state rate measurement.

When the bridge output reaches the upper limit of measurement before a steady-state flux is obtained, the Thermistor cavity may be flushed with the reference gas and the steady-state rate may be measured by reclosing the cavity.

However, in this case, special precaution should be taken to obtain an accurate measurement of the steady-state flux. This situation is explained by the schematic representation in cases C and D. The polymer at the downstream surface is in equilibrium with the permeant concentration that was built up in the receiving volume during the measurement (close to the upper-limit concentration) as seen in case C (assuming the ideal case). If the permeant in the receiving volume is instantly flushed by reference gas, the partial pressure may drop down nearly instantaneously; however, it will take some time (characterized by the time lag) before the linear concentration profile is established. If the second measurement is started as soon as the bridge output drops to near zero, it may give a much higher permeation rate due to the higher local concentration gradient near the outgoing surface, as seen in case D. Therefore, the second measurement should be taken after a sufficient time to insure that a linear concentration profile is established in the membrane phase.

For these reasons, the measurements of high flux by differential measurement or by the decay rate measurement are more accurate, and the measurement of high permeation rates by the integral method is not recommended.

Differential Measurement (Flow Method)

As is clear from the previous discussion, the flow method has the advantage that the partial pressure of test gas in the receiving volume can be maintained low, and it overcomes the disadvantage of a very small receiving volume for the measurement of relatively fast permeation rates. This method, on the other hand, is limited to relatively fast permeation which gives enough signal at a reasonable flow rate such as 0.2–0.4 cm³/sec. This range seems to cover conveniently the range where the regular integral measurement becomes inapplicable. The bridge output is a function of flow

rate, and the measurement of flow rate should be carefully carried out for accurate measurement of permeability. A bubble flow meter was used for this purpose, and the meter is always connected to the outlet of test Thermistor cavity while this method is used. The flow rate is measured with the main valve in the test gas position.

Decay Rate Measurement

This method was found to be accurate and versatile for measurement of fast to very fast permeation rates. It also has the advantage that the measurement is independent of the type of gas (i.e., calibration is not necessary). This method had an applicable range wider than that of the differential method, though the time necessary for measurement is much longer for relatively slow membranes.

Permeability values obtained by the instrument represent true diffusional permeability regardless of the membrane structure. Therefore, appreciable differences were found between values obtained by the instrument and the pressure methods for porous membranes. This is believed to reflect a difference in transport mechanism; details will be presented elsewhere.

Measurement of Diffusion Constants

Delay Factor of the Instrument

As mentioned in the previous section, there is a certain delay time after a fraction of transmitted gas molecules leave from the outgoing surface of the membrane until they are registered on the recorder. This delay time does not affect the steady-state slope of the recorded result; however, it may become important for estimating the diffusion constant by the time-lag method.

In order to estimate the delay time, a thin brass plate was used instead of a sample membrane, and the following measurements and calculations were carried out. The brass plate had a number of very fine holes evenly distributed over the surface. At the beginning of the experiment, the Thermistor cavities are closed and the sample gas cavities are purged with the reference gas.

At time zero, the main valve is turned to the sample gas for a fraction of a second and then back to the reference gas. This will introduce a small amount of sample gas over the outer surface of the brass plate, and a part of this will immediately go into the cavity by interdiffusion. This will produce a movement of the recorder, which quickly increases to a maximum peak and then starts to reduce. This decay curve, caused by back diffusion of the sample gas through the brass plate, reaches a characteristic logarithmic decay in 8 to 9 sec. The logarithmic decay curve (after 8 to 9 sec) can be easily extrapolated back to time zero, resulting in a decay curve that we would have had if the sample had been evenly distributed inside the Thermistor cell at the beginning. (Athough this situation does not exist in actual measurement, it may be used for estimating the delay time as a first approximation.)

TABLE V
Estimation of the Delay Time of Instrument From Decay Curve Obtained with A Brass Plate With Small Holes[a]

Time interval, sec	5 mV			10 mV			50 mV		
	a	b	$\left(1 - \dfrac{b}{a}\right) \times 100$	a	b	$\left(1 - \dfrac{b}{a}\right) \times 100$	a	b	$\left(1 - \dfrac{b}{a}\right) \times 100$
8–			0			0			0
7–8	156.5	156	0.5	166	165.3	0.8	101.7	100.7	1.0
6–7	162.2	159.7	1.9	175.2	172	1.9	107.3	104.0	3.0
5–6	171.0	162.2	4.2	185.2	173.5	6.3	113.0	105.0	7.2
4–5	180.3	159.2	12.0	196	170.1	13.2	119.1	101.8	14.7
3–4	191.0	145.2	24.1	207.5	154	25.8	125.5	91.6	27.0
2–3	206.5	113	45.3	222	117	47.4	132.1	67.6	49.0
1–2	218	58	73.3	239	55.5	76.8	139	31.3	77.5
0–1	241	4.8[b]	98	261	4[b]	98.5	147	1.5[b]	99.0
Total			259			270			278

[a] a = Signal (in mm) if sample gas had been in cavity at $t = 0$; b = real signal (in mm). All values taken at center of time interval.
[b] Area under irregular curve averaged out.

Now we can compare the extrapolated curve with the real curve to calculate a correction for the delay. This is shown in Table V for three experiments for N_2/H_2. (The amount of sample gas entering the Thermistor cavity depends on the pressure of the sample gas in the main valve, and it can be controlled and adjusted.)

To use this correction, let us look at a typical curve obtained in an ordinary integral permeability measurement where the slope of the straight part of the curve is b mV/sec (see Fig. 16). The main valve is turned to a sample gas at time zero; at time t_1, the total recorder deflection is v_1. This deflection, however, is lower than it should be if there has been no delay in
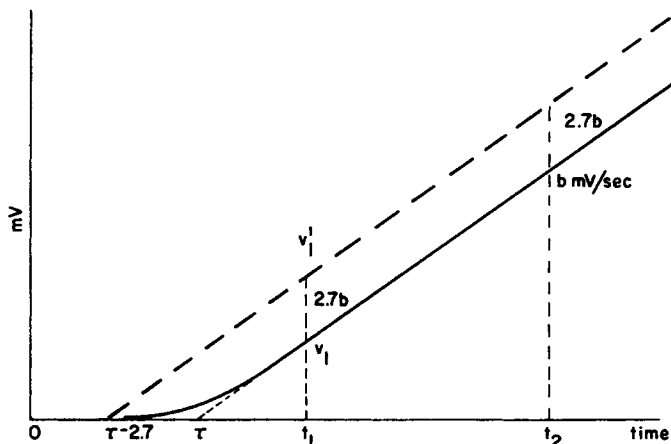

Fig. 16. Schematic representation of integral measurement curve to show effect of delay factor of instrument on the time lag obtained by the measurement.

the gas phase in the Thermistor cavity. From the experiment with the brass plate, we know that the sample gas which has arrived in the Thermistor cavity during the last 8 sec has not yet fully affected the recorder output. We can now make a correction for the gas arriving at each one of these eight 1-sec intervals.

The corrected deflection v_1' would be (figures are from the 10-mV experiment in Table V):

$$v_1' = v_1 + 0.08b + 0.019b + 0.063b + \dots$$

$$= v_1 + 2.70b$$

At time t_2, the vertical distance between the measured and the corrected value should be, of course, the same, $2.70b$; and the corrected straight part of the curve is thus parallel to the measured one. Since the slope of these two lines is b (in mV/sec) and their vertical distance is $2.70b$, the horizontal distance is 2.7 sec. Therefore, the true time lag to be used to determine the diffusion coefficient is thus $\theta - 2.7$ sec.

Similar experiments were done with four different sample gases, which gave the following values:

N_2	259, 270, 278
A	269
O_2	276
CO_2	269
mean	270

Thus, the delay time of the instrument is estimated as 2.70 sec.

Comparison of D Values Obtained by Thermal Conductivity and Vacuum Methods

Measurement of diffusion constants by time lag is not always possible regardless of the method used. The time lag is obtained from the plot of the partial pressure of permeant in the receiving volume or values proportional to it against time over an interval sufficiently long to identify the straight line and the intercept of the line on the time axis, τ. The diffusion constant D can be calculated by the relation

$$D = \frac{l^2}{6\tau} \tag{36}$$

when l is the thickness of the membrane.

The intercept of the straight line on the pressure axis p_c is related to the solubility constant S as follows:

$$S = \frac{6V}{Al} \cdot \frac{p_c}{p_1}. \tag{37}$$

Figure 17 illustrates t_c and p_c schematically for two imaginary cases where the time lag is identical (same diffusion constant), but the solubility constants are different. Since the instrument utilizes the barometric pressure of the permeant gas, p_1 is always a constant, and the upper limit of the measurement is also fixed. In both cases (with identical D but with different S), a steady-state flow will be established in approximately the same time characterized by 3τ. Therefore, the total amount of permeant gas accumulated in the receiving volume when a steady-state flow is established is proportional to S. Consequently, if the solubility is sufficiently high, the amount of transported permeant reaches the upper limit of the measurement before a steady-state flow will be established (as seen in Figs. 13 and 14, where time-lag measurement is possible for O_2 but not for CO_2). With fixed membrane area, volume, and driving pressure, the only experimental variable is the thickness of the membrane. Therefore, the possibility of obtaining D by time lag entirely depends on the combination of D, S, and l of the sample.

In Table VI, the diffusion constants obtained by the time-lag method (with correction of 2.7 sec) are compared with values obtain on the identical
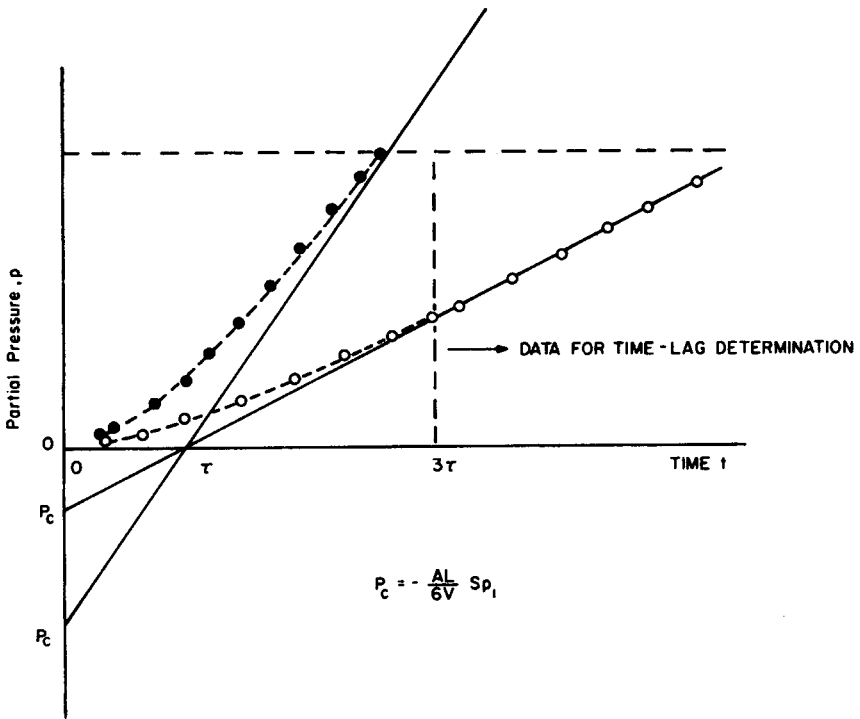
Fig. 17. Schematic representation of factors involved in obtaining accurate time-lag measurement by the integral method.
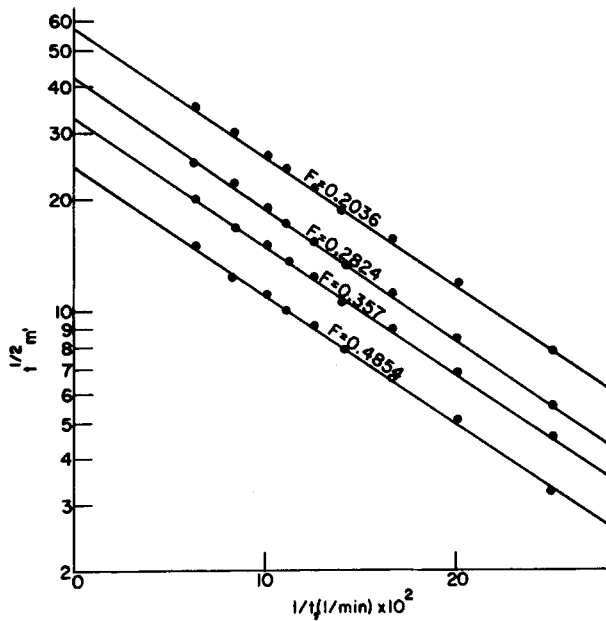

Fig. 18. Typical early-time plot. F represents flow rate of reference gas in ml/min.

samples by the vacuum method. Results indicate quite a good agreement between the two methods. If an apparent time lag is close to 2.7 sec, the error of estimating D from the time lag would be high, and the method is not recommended.

The Early-Time Analysis

The early-time analysis, previously shown eq. (29), can be used with this instrument in the following two ways: (a) differential measurement by flow method (for fast membranes) and (b) measurement of the differential rate

TABLE VI
Diffusion Constants Obtained by Time-Lag of Integral Method Compared With Those Obtained by Vacuum Method

Polymer	Film thickness, $cm^3 \times 10^3$	Gas	D, $cm^2/sec \times 10^7$ Integral method	Vacuum method
Polyethylene (0.960)	3.46	CO_2	1.37	1.49
Polyethylene (0.920)	4.00	CO_2	4.04	3.90
Poly-4-methylpentene-1	10.76	N_2	5.86	5.50
		O_2	12.2	10.1
Poly-4-methylpentene-1	7.84	N_2	8.20	8.12
		O_2	15.4	16.6

TABLE VII
Flow Rate Dependence of D_E

Gas	F, cm^3/sec	$D_E \times 10^7$, cm^2/sec	$D_T \times 10^7$, cm^2/sec^a
	PMP ($l = 7.84 \times 10^{-3}$ cm)		
N_2/H_2	0.172	5.11	8.12
	0.223	5.61	
	0.330	5.96	
	0.392	6.10	
	PMP ($l = 1.076 \times 10^{-2}$ cm)		
CO_2/H_2	0.213	5.58	6.84
	0.241	5.65	
	0.311	5.92	
	0.388	6.30	
	0.446	6.58	
	0.485	6.77	
	PPO ($l = 1.04 \times 10^{-2}$ cm)		
CO_2/H_2	0.204	0.570	0.601
	0.282	0.567	
	0.357	0.568	
	0.485	0.566	

[a] D_T measured by vacuum method.

of permeation by integral method intermittently applied during the transient state of permeation for very slow membranes.

An example of (a) is shown in Figure 18 as a plot of log $(m') \cdot t^{1/2}$ versus $1/t$ for carbon dioxide through a poly(phenylene oxide) film at 25°C. In this case, the logarithm plot is nearly independent of the flow rate; by early-time analysis it gave a diffusion constant D_E of 5.68×10^{-8}, compared to a D value obtained by time lag (vacuum method) of 6.01×10^{-8}.

For smaller diffusion constants, however, D_E was found to be dependent on the flow rate and smaller than D values obtained by time lag, as shown in Table VII. It may be generally used as a method for obtaining approximate values of diffusion constants; however, the absolute values should be carefully interpreted.

An example of (b) is seen with measurements of CO_2 permeation through poly(vinylchloride). In this case, the measurement was started as a flow method, and the integral measurement was taken at a certain interval for approximately 5 min. Since it took approximately 24 hr before a steady-state flow was obtained, the slope obtained in a 5-min time span can be considered as the differential rate of transient permeation. The early-time plot of the data gave a diffusion constant of 4.62×10^{-10}.

Estimate of Time Lag From Differential Measurement

The time to reach half of the steady-state flux, $t_{1/2}$ is related to the diffusion constant D by

$$D = \frac{l}{7.199 \cdot t'_{1/2}}. \tag{38}$$

Consequently, the time lag τ obtained by integral measurement is given by

$$\tau = 1.2 \cdot t'_{1/2}. \tag{39}$$

The value of $t'_{1/2}$ also slightly depends on the flow rate; however, the dependence reflected in the diffusion constant is less than half of the flow rate dependence of D_E. Consequently, this simple method offers a better estimate of D than the early-time analysis, and the values seem to be slightly smaller (average 16%) than D obtained by the time lag of the vacuum method. Comparison of D values obtained by this method with values obtained from time lag by integral measurement and by the vacuum method is presented in Table VIII.

Considering the simplicity of the calculation (compared with early-time analysis), this method adds a great practical value to the differential measurement.

In general, it might be considered that the instrument is capable of obtaining diffusion constant nearly as good as many other methods. Methods that have a variable receiving volume and are applicable to varying driving pressures may have a little more freedom for obtaining the diffusion constants. However, the accuracy of the value does not seem to be superior to the values obtained by this instrument.

TABLE VIII
Comparison of D Values Calculated From Time Lag Obtained by
Various Methods[a]

Gas	Flow method[b] D_F	D_F'	Integral method D_I	Vacuum method D_v	$\dfrac{D_F - D_v}{D_v} \times 100$	$\dfrac{D_F' - D_v}{D_v} \times 100$
	Poly-4-methylpentene-1 ($l = 7.84 \times 10^{-3}$ cm)					
N_2	7.26	6.05	8.20	8.12	−10.6	−25.5
O_2	13.0	10.8	15.4	16.6	−21.7	−34.9
CO_2	9.31	7.26	—	10.2	−8.8	−28.8
	Poly-4-methylpentene-1 ($l = 10.76 \times 10^{-3}$ cm)					
N_2	6.53	5.44	5.86	5.50	+18.7	−1.1
O_2	10.3	8.6	12.2	10.1	+1.9	−15.0
CO_2	8.12	6.77	—	6.84	+18.8	−1.0
	Poly(phenylene Oxide) ($l = 10.40 \times 10^{-3}$ cm)					
CO_2	0.693	—		0.601	+15.3	−3.83
		0.578				−15.87

[a] D in units of cm^2/sec, $\times 10^7$.

[b] $D_F = \dfrac{l^2}{6\,t'_{1/2}}$; $D_F' = \dfrac{l^2}{7.20\,t'_{1/2}}$.

CONCLUSIONS

The instrument described in this paper seems to be at least as accurate and useful as any other method and has several unique advantages over many conventional methods. These advantages are as follows:

Sample Size. The instrument needs a sample size of 3.6 centimeter square (actual membrane area to be measured is 5 cm^2), yet the overall sensitivity is at least as great as that of any other method which requires a considerably larger membrane area.

No Pressure Differential Across the Membrane. The samples are held between the O-rings, and no pressure difference exists across the membrane during the measurement. Therefore, the permeabilities obtained by this instrument represent true diffusive permeability.

This membrane holding also makes it possible to measure permeabilities of fragile or brittle membranes which cannot be clamped to give a pressure-tight seal.

Short Degassing Period Required and No Loss of Relatively Volatile Components. Since a reference membrane taken from an identical sample film is placed in the reference Thermistor, interference of gases and vapors sorbed in membranes is minimized; and, together with the easy sample-mounting procedure, the overall time necessary to obtain permeability constants is greatly reduced. Degassing can be achieved in a separate box in which the reference gas is constantly flowing without occupying the instrument. This feature becomes significantly important in

reducing the total time necessary for accurate measurement of very small permeabilities. For instance, the time lag of N_2 permeability through 0.01 cm poly(vinyl chloride) film is roughly 7–8 hr. If the permeability measurement is carried out up to 5τ, the measurement will take roughly 35–40 hr. This time is characteristics of the polymer, and measurement should take this long regardless of the method of measurement. However, the degassing process necessary before the measurement (including the degassing after a run) is generally estimated to be 6τ. Therefore, if membranes must be degassed in a test equipment, the sample should be degassed for 42–48 hr before the measurement can be started. Thus, with preconditioned samples, this long degassing process can virtually be eliminated so far as the occupancy of the instrument is concerned.

Degassing is achieved at barometric pressure, and consequently possible change of permeability due to loss of relatively valatile components such as plasticizer is minimized, and it is possible to measure the actual permeability of plasticized polymer films.

True Membrane Area. When the temperature dependence of permeability is measured in a conventional test cell in which a membrane is clamped at room temperature and subjected to various temperatures, the actual membrane area is not measured at each temperature. Most polymers have considerably higher thermal expansion rates than metals, and it is often observed that the size and shape of the membrane are considerably changed after they have gone through a series of measurements at various temperatures. In other words, the temperature dependence of permeability obtained by a fixed sample includes the temperature dependence of total membrane area and thickness, though not much attention has been given to this effect.

With this instrument, the polymer samples can be equilibrated at the temperature of the measurement before they are clamped for measurement. Therefore, it is possible to eliminate the thermal expansion effect from the temperature dependence of permeation, diffusion, and sorption processes.

Among these advantages, perhaps the most significant feature may be the fact that this instrument measures true diffusive permeability. Most methods that utilize pressure difference across the membrane may not represent diffusive permeability, depending on the structure of the membrane. The distinction of these two permeabilities is discussed in more detail by Yasuda and Lamaze.[11] This instrument, therefore, when used with conventional methods, can supply additional information which cannot be obtained by the ordinary techniques for the structure of membranes and mechanism of transport of gases.

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