

Measurement of Gas Permeability of Polymers.

II. Apparatus for Determination of Permeabilities of Mixed Gases and Vapors

D. G. PYE, H. H. HOEHN, and M. PANAR, *Central Research and Development Dept., E. I. duPont de Nemours & Co., Wilmington, Delaware, 19898*

Synopsis

A gas permeability apparatus has been constructed to facilitate the study of permeation of mixtures of gases and vapors. The apparatus utilizes the carrier gas method with gas-chromatographic analysis to determine individual permeation values and in-line thermal conductivity detectors to provide simultaneous overall diffusion and permeability data. The effects of film type, structure, and morphology on permeability may be studied from atmospheric to 100 psi feed pressure and from ambient to 300°C. Feed stocks may be custom mixed, and a vaporizing bath permits introduction of vapors either as contaminants or as primary permeants in an inert carrier. The experiments which illustrate the use of the equipment suggest that the noninteracting gases H₂ and CH₄ permeate a number of polymer films independently over a wide concentration range and that water vapor retards their permeation in polyimide films.

INTRODUCTION

The gas permeability equipment most generally employed in membrane research is usually based on either the volumetric or manometric methods, well known examples being the Linde¹ and Dow² cells. Modifications of these concepts have been devised³⁻⁸ as experimenters have sought to extend studies to more severe test conditions.

Although it is possible to study permeability of mixed gases and vapors in these types of apparatus,⁹⁻¹³ more convenient sampling and analytical procedures can be applied when the carrier gas/concentration analysis system is employed. In recent years, several forms have been developed and at least one has been offered commercially.¹⁴ They are based on the principle of flowing a permeant gas on one side of a film and allowing the permeate to be picked up by an inert carrier gas flowing past the other side of the film and transported to an analysis system. In one form,¹⁵⁻¹⁸ the carrier gas passes through a thermal conductivity detector, and the output is registered as an integral curve showing the dynamic approach of the permeation to steady-state conditions. The contributions of more than one permeate component are not easily separated unless their diffusion times are significantly different.

In a second form, the carrier gas may be sampled for gas-chromatographic analysis. In this method, the amount of each component in a permeate may

be readily determined as shown by Caskey¹⁹ and Kapanin et al.²⁰ The work described in this paper utilizes a similar approach with the aim of developing an instrument that will permit study of membrane behavior to permeation of mixed gases and vapors under a variety of test conditions. The equipment contains provisions for (1) operation from atmospheric to 100 psi feed pressure; (2) operation from ambient to about 300°C; (3) custom mixing of gas feeds; (4) introduction of vapors either as contaminants or permeants; (5) on-line monitoring of permeation activity and diffusivity determination; and (6) on-line analysis by gas chromatography or gas sampling for special off-line analysis.

DETAILS OF APPARATUS

Permeation Test System

A system that accomplishes the objectives set forth in the introduction is shown in schematic form in Figure 1. All parts including tubing are of 304 stainless steel. In the simplest form, a feed gas is passed through one side of a test cell containing a film specimen, and the reject stream, after passing through a variable back pressure regulator, is directed either to an analyzer or discarded. Simultaneously, an inert carrier gas stream is passed over the other side of the film, and the permeate diffusing into it is carried to a suitable analyzer. Although both a thermal conductivity detector and an on-stream gas-chromatographic (GC) analyzer are routinely employed, attachment of sampling devices to the exit lines permits off-line analysis by mass spectrometry or other means. The cell and all feed systems were designed to be operable from 0 to 100 psi, and suitable safety, relief, and check valves were installed. Higher equipment pressure ratings would permit extension of the pressure test range.

Permeation Cell

The permeation cell consists of two flanges between which the test specimen is clamped and sealed with O-rings. Above and below the film, the flanges are cut back to a depth of 10 mils to provide thin cavities. The feed gas sweeps across the bottom, and the carrier gas flows over the top of the film in the same direction. Small, raised dimples on the lower face prevent gas flow blockage by a sagging film. The top cavity contains a Regimesh-type NK screen, Pall-Trinity Corp., which consists of a porous (2-micron) mesh material laminated to a coarse screen to provide film support when feed pressure is applied. Although the screen can be removed if zero differential pressure is used, no apparent effect on carrier gas pickup of permeate has been noted, and we have tended to leave the screen in place for all tests.

Gas Flow Systems—General

Four gas flow systems were used. The first is the feed gas flowing past the film. The second is the carrier gas flowing past the downstream side of the film. The third is a flush gas which is the same as the carrier gas and is used on the feed side of the film to condition it before the start of an experiment.

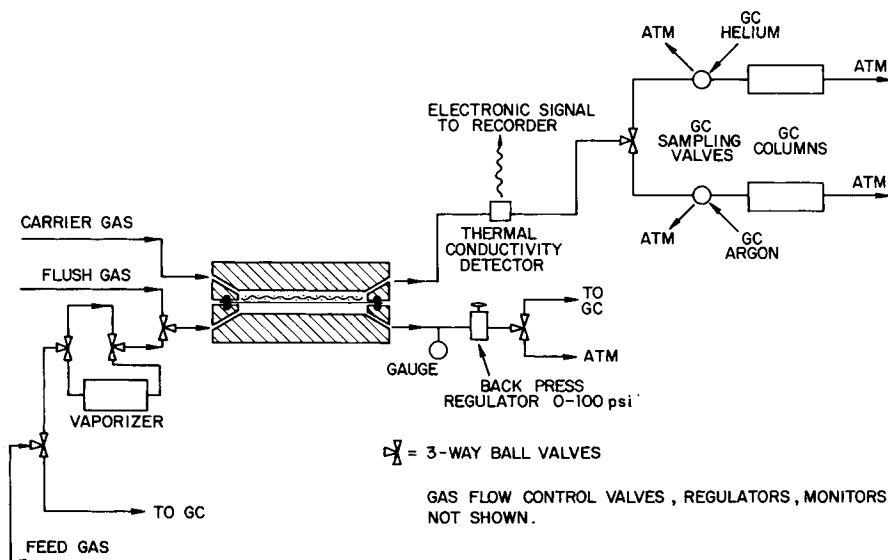


Fig. 1. Schematic diagram of carrier gas permeation apparatus.

The fourth is the gas supply for the GC.

Accurate flow control of the feed gas does not appear important as long as the flow is sufficiently high that permeation through the film does not deplete one or more components and change the composition. At high permeation rates, possible concentration polarization should not be overlooked. Flush gas flow rate is not important. However, constant carrier flow at a known rate is essential since the permeation constant is calculated from the permeate gas concentration in the carrier stream and the carrier gas flow rate. Similarly, the GC supply flow governs the peak height and position from which the permeate concentration is calculated. For these reasons, the carrier and GC streams are carefully controlled and independent of the flush stream.

Gas Feed System

A schematic diagram for a multigas feed system is shown in Figure 2. In the "custom mixing" section, any one or two gases may be selected and passed through individual rotometers to a gas mixing device and thence into the feed line leading to the cell. Flow control is obtained by pressure regulators and Brooks metering valves upstream from the mixer. A Brooks No. 8601 pressure regulator with range to 200 psi is preferred to standard regulators because of better flow control. Although flow can be monitored by rotometers, mixing to a desired concentration requires more accurate knowledge of flow in the 0-200 cc/min range; and, in practice, soap-bubble flow tubes have been useful. Unless feed gas pressures are identical, a custom-mixed feed established at atmospheric pressure will have a different composition at higher pressures. For pressure experiments, the desired mixture is conveniently prepared at the desired pressure and sent to GC analysis by passing it through an alternate back-pressure regulator set at the appropriate value in-

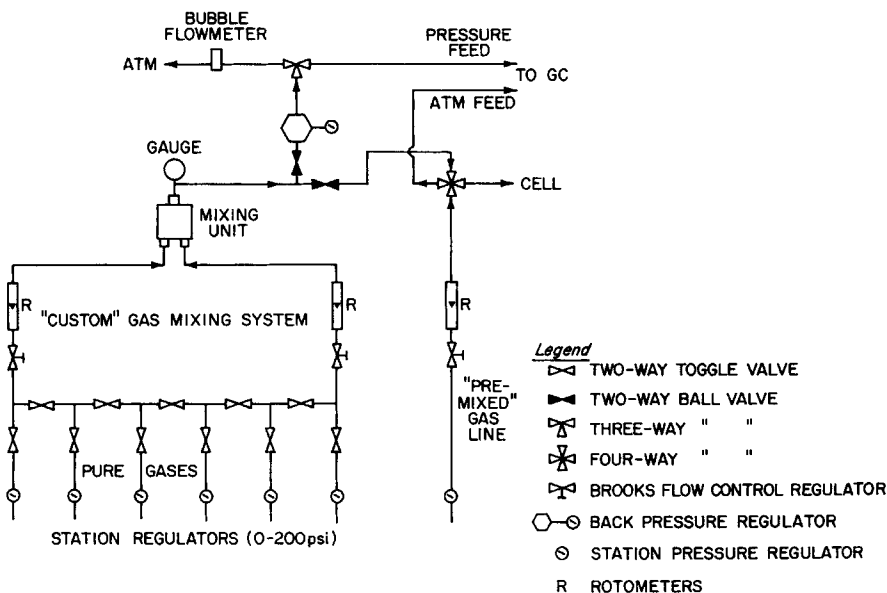


Fig. 2. Gas feed system.

stead of through the cell system. Necessary flow adjustments can then be made prior to initiating the experiment. These connections are shown in the upper part of Figure 2.

Because considerable work with mixed gases can be accomplished with a fixed composition which may be purchased premixed, an alternate line is used for this feed, and a four-way valve permits selection of sending either feed directly to the cell or to the GC units for analysis before use.

Carrier and Flush Gas Systems

The carrier and flush gas flows are controlled with Brooks metering valves and the carrier gas pressure is also maintained with a Brooks pressure regulator to give maximum flow uniformity. Rotometers indicate approximate flow rates, but the precise flow of the carrier is measured by a soap-bubble flowmeter.

The choice of carrier gas is dependent on the permeate to be analyzed. All gases and vapors but H_2 can be analyzed by GC in helium, and it was chosen as the primary carrier. Argon was selected as a second carrier for H_2 analysis. Appropriate switching was achieved with three-way valves.

Vaporizer

Introduction of vapor is useful both for studying permeabilities of vapors themselves either in an inert carrier or as part of a mixture and for studying the effect of a vapor on the permeability of a gas. As shown in Figure 1, two valves permit switching the feed gas through a vaporizing unit. The vaporizer can saturate gases at pressures up to 100 psi and temperatures from $-20^\circ C$ to $100^\circ C$. A combination circulating heating and refrigeration unit gives

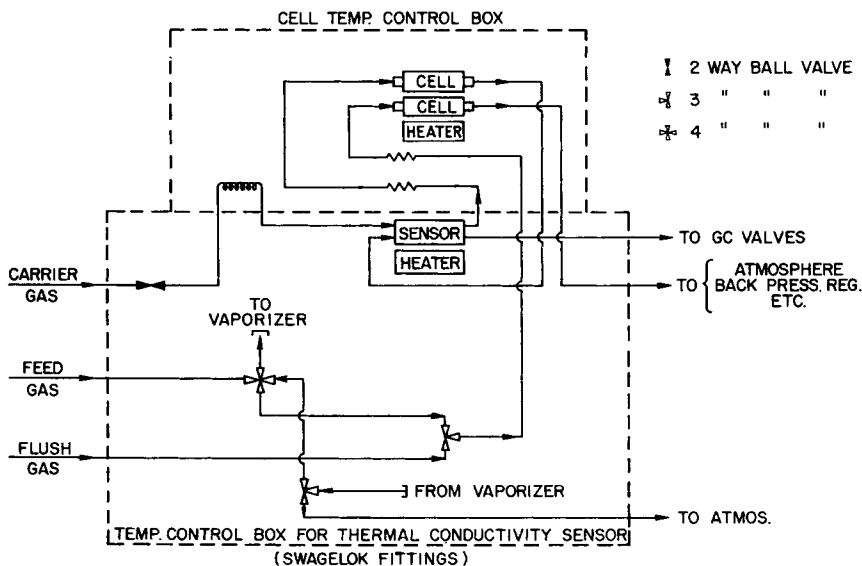


Fig. 3. Gas flow system in temperature control boxes.

wide temperature range. The vaporizer temperature should always be less than that of the detector and cell or vapor will condense in the feed stream. A differential of about 10°C is advisable. The vapor pressure at the cell can be calculated from the cell and vaporizer temperatures or determined by analysis.

Temperature Control

Since thermal uniformity is an essential requirement for operation of the thermal conductivity detectors, they and associated piping are arranged in an insulated control box which is held at a fixed temperature (normally 50°C , but at least 10° above the vaporizer temperature when it is in use). The temperature of the test cell itself in an adjacent, independently controlled box can be varied from ambient to 300°C . To maintain temperature uniformity in the thermal detectors, a coil of the incoming carrier gas line is placed in the cell box and brought back to the detector parallel to the carrier line bringing the sample from the cell. This arrangement maintains equal thermal history for the reference and test gases. Figure 3 is a schematic diagram that also shows the connection with the vaporizer unit.

ANALYSIS AND MATHEMATICAL TREATMENT

Two methods for analyzing the carrier stream are used. In a method similar to that of Ziegel et al.,¹⁵ a Gow-Mac thermal conductivity detector Model JDC-301 is located in the carrier line near the test cell so that the incoming carrier stream will pass through the reference side before going on to the cell to pick up permeate for return to the detector. Since the flow is continuous, the signal from the thermal conductivity cell beginning at zero permeation

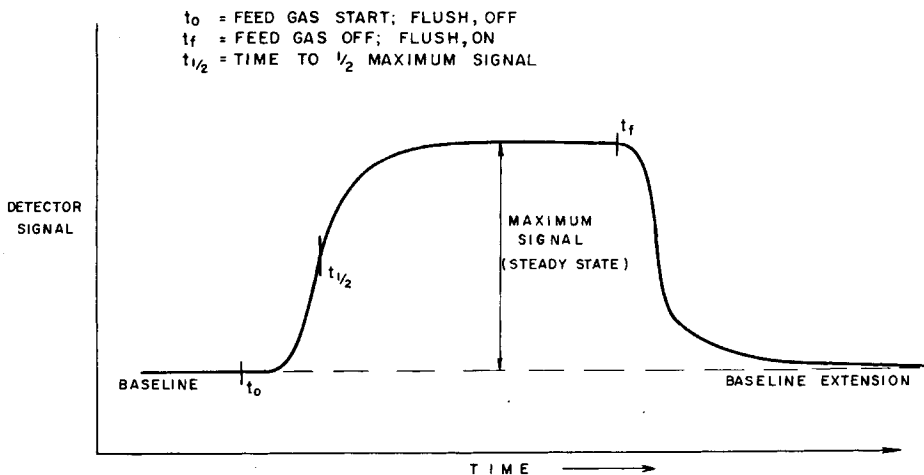


Fig. 4. Thermal conductivity detector output as function of time.

time is integral; and at steady state, no further rise in a concentration-versus-time recording occurs (Fig. 4). This form of recording the initial stages of permeation is more sensitive than the pressure method for determining variations that may be related to diffusion of gas through a film. When not used to study the time lag portion of the permeation curve, the thermal detectors are used as monitors to follow the overall course of the permeation.

As shown by Ziegel,¹⁵ the diffusion constant of a permeating gas may be determined from the curve by the equation

$$D = \frac{L^2}{7.2 \times t_{1/2}} \quad (1)$$

where $t_{1/2}$ is the time in seconds for the permeation to reach steady state and L is the film thickness in mils. Permeability constants are also determinable when pure gases are used by calibrating the detector signal.

Analysis of gas mixtures has been done by GC. All gases other than H_2 are analyzed in a He carrier system. When H_2 is the component to be analyzed, the carrier is switched to argon and a second GC is employed to avoid delays in column conditioning. Column conditions affording sharp peaks are used and in-line sampling loops of 0.25 and 5 cc permit analysis over a wide concentration range.

Calibration of the GC columns for the low concentrations (<1%) encountered in permeates was accomplished with a geometric dilution flask following the work of Lovelock²¹ and Green.²² The high concentration range of the feed gases was calibrated by direct injection of known gas concentrations.

Since theoretical and mathematical treatments of permeation may be found in many texts and articles,²³⁻²⁵ only relationships relating to carrier gas analysis as used herein will be described. In accordance with ASTM standards,²⁶ the following relationships for permeability in gas transmission rate (GTR) and centibarrer (cB) units exist:

$$P_{(GTR)} = \frac{\text{cc (S.T.P.)}}{24 \text{ hr} \cdot 100 \text{ in.}^2 \cdot \text{atm}} \quad (2)$$

and

$$P_{(cB)} = P_{(GTR)} \cdot (0.6) \text{ (thickness, mils)} \quad (3)$$

when

$$1 \text{ cB} = \frac{10^{-12} \text{ cc (S.T.P.)} \cdot \text{cm}}{\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}}$$

and

$$1 \text{ GTR} = \frac{1 \text{ cc (S.T.P.)}}{24 \text{ hr} \cdot 100 \text{ in.}^2 \cdot \text{atm}}$$

Equation (2) may be altered to accommodate the analytical data and flow and sensitivity parameters of the carrier gas permeation equipment by utilizing the gas laws and the following relationships. The permeate flow rate in cc (S.T.P.)/24 hr is

$$\frac{(D)(Attn)(K \cdot S_1)(Y)}{S_2} \cdot \frac{(273)(P)}{(T)(760)} \cdot \frac{(60 \times 24)}{1} \quad (4)$$

where D is the GC peak height, $Attn$ is the recorder attenuation, K is the GC calibration for the gas in cc gas/division for calibration sample volume S_1 , Y is the carrier flow rate in cc/min, and S_2 is the actual analytical sample size. If the same sample loop is used for calibration and test, S_1 and S_2 are the same, and accurate volume determination is unnecessary. The second term is the conversion from the GC measurement conditions, P and T , to S.T.P., and the last term is the conversion factor from min to 24 hr. The feed partial pressure in atmospheres is

$$\frac{(VF)(psia)}{14.7}$$

where VF is the feed volume fraction of the gas being tested and $psia$ is the absolute feed pressure assuming zero or negligible concentration on the carrier side of the membrane. With a film specimen of an effective area of 3.08 in.² (7.82 cm²), the area conversion factor is 3.08/100.

If the above values are substituted in eq. (2) and if, to simplify carrier flow measurement, $600/X$ is substituted for Y , where X is the time in seconds for a flow of 10 cc, a complete working equation is obtained, with constant factors separated on the right as C :

$$P_{GTR} = \frac{(D)(Attn)(K_{gas})}{(VF)(psia)(X_{sec})} \cdot (C). \quad (5)$$

When the sample sizes S are the same (5.0 cc) and average atmospheric conditions of $P = 755 \text{ mm}$ and $T = 298^\circ \text{K}$ are used,

$$C = 3.75 \times 10^6.$$

When the permeant is a pure gas, VF is 1.0.

OPERATIONAL PROCEDURES

Since there are a number of choices as to the type of permeation that may be made in the carrier gas apparatus, the method of carrying out the tests will

depend to some extent on the objective. After film installation and while temperature is equilibrating, both carrier gas and flush gas of the same type are passed through the cell (Fig. 1) to condition the film. Choice of argon in place of helium is dependent on whether H_2 is to be analyzed.

Feed Gas Adjustment

In preparation for a test, if a pure or premixed gas of known composition is to be used, analysis is not needed and the only adjustment necessary is to establish a tank feed pressure 10 to 20 psi above the desired operating pressure. When an experiment is begun by switching the flow from flush to feed gas and after the planned test pressure is attained, final flow adjustment can be made by monitoring the feed flow at the feed exit beyond the pressure let-down regulator. To avoid depletion of a rapidly permeating gas, e.g., H_2 or He, from a mixed gas when high permeation rates are expected, a flow rate of at least 20 atmospheric cc/min should be used, and rates as high as 40 to 80 cc/min may be needed occasionally. At atmospheric pressure, these flow rates are easily monitored with the rotometers but at higher pressures, bubble flow meters after the letdown valves must be used.

If a custom mix is to be tested, the desired composition is established before the experiment is begun. The simplest procedure is to adjust the individual gas flow rates at the desired pressure and pressure differential to give the approximate composition and to make final flow adjustments following GC analysis. In the middle range of compositions, few problems arise; but to obtain an accurate 99/1 composition which will remain constant at 100 psi operating pressure, the minor component probably must flow at not much more than 2 cc/min while the major component would then need to flow at 200 cc/min. Final measurement of the feed composition and adjustment, if needed, should be made after the permeation test has begun and before final permeation measurements are made.

Carrier Flow Rate

Since carrier gas flow rate is the key to permeation calculation, constant known flow rate is essential. For normal operation at 20 psi pressure, reliable control (within 1–2%) can be maintained at 20 cc/min. As long as the permeation of feed gas through the membrane is small compared with the carrier flow, no problem should occur; but higher carrier flows will be necessary with highly permeable membranes or the carrier will become significantly diluted with permeate and inaccurate results will be obtained unless appropriate changes are made in the calculations.

Gas Analyses

After a permeation test is begun, the carrier stream is monitored by either occasional GC analysis or by the thermal conductivity monitors, or both, until constant values are obtained. If mixtures including H_2 are being tested, the carrier gas is then switched to the second carrier, and the operating conditions for the monitor are adjusted to the appropriate values for the new car-

rier. When the first carrier has been swept out of the system, analysis for the second component is made. When other types of analysis are to be made, sampling loops are attached to the carrier exit line.

Vaporizer

If the vaporizer is to be used, the unit is two thirds filled with the appropriate liquid and the circulating bath is adjusted to the temperature that will give the desired vapor pressure. Normally, permeabilities are first measured under dry conditions. The feed gas is then switched through the vaporizer and measurements are continued until equilibrium is reestablished. Bypassing the vaporizer again will then permit a study of the permanent or transitory effects of the vapor.

Thermal Conductivity Monitors

The thermal conductivity monitors have their best use with pure gases on membranes of medium or higher permeability. With low permeability membranes (below 30 cB) the diffusion constant is usually small and approach to equilibrium becomes rather long. When the detectors are to be used, the same steps in preparing for tests as those described in previous sections are used. After a constant base line is achieved, a permeation test is begun and maintained till equilibrium is achieved. Switching the feed gas back to flush gas permits the permeation decay to be followed until the signal returns to the baseline.

EXPERIMENTAL EXAMPLES

Materials

With the exception of polyethylene, the film materials used in the permeation studies were soluble polyimides prepared by reaction of various diamines with 4,4'-hexafluoroisopropylidenediphthalic anhydride (6F) by conventional methods. To simplify the tables, the following designations have been employed for the diamines and attached to the 6F designation for the anhydride (films were usually cast from polymer solutions in dimethylacetamide): MPD = 1,3-diaminobenzene; PPD = 1,4-diaminobenzene; 3,5 DBA = 3,5-diaminobenzoic acid; 1,5 ND = 1,5-diaminonaphthalene; 3,5 DDMBA = 3,5-diaminodimethylbenzamide.

Gas Flow Parameters

Studies of permeations with mixed gases that involve high fluxes can be hampered by such phenomena as concentration polarization and depletion of one component. The potential for the occurrence of these effects has been minimized by the small feed gas and carrier gas cavities in the cell (about 0.5 cc each over a 10-mil depth) which result in relatively low residence times even at modest flow rates. Experiments with a 0.5 H₂/0.5 CH₄ molar feed mixture on a number of film samples having H₂ permeabilities up to 10,000

TABLE I
Comparison of Carrier Gas with Manometric Data

Material ^a	Permeability, cB ^b	
	Carrier gas	Manometric
	<i>Hydrogen</i>	
Polyethylene	915	975
3,5 DBA-6F	3440	3630
1,5 ND-6F	7810	9730
PPD-6F	4820	4410
3,5 DBA-6F	3270	2900
	<i>Methane</i>	
Polyethylene	280	305
3,5 DBA-6F	12.5	11
1,5 ND-6F	72.1	62.3
PPD-6F	31.6	30.5
3,5 DBA-6F	7.2	7.1

^a See text for polyimide description.

^b 115 psia, 30°C.

cB and CH₄ permeabilities up to 400 cB showed no influence of flow rates between 10 and 120 atmospheric cc/min at pressures up to 115 psia. Since these permeability ranges cover a high proportion of polymer films, feed gas flow does not appear to be a critical factor.

Permeabilities as a function of feed gas pressure up to 115 psia have followed essentially the same course as those reported previously⁸ in pressure cell studies. Films having little interaction with the permeant showed little permeability change at these low pressures.

Experiments on the effect of carrier gas flow have shown that rates should be adjusted to accommodate permeate fluxes. When the flux is low, rates as low as 5 cc/min improve sensitivity. However, when gas transmission rates (P_{GTR}) are 40,000, a feed pressure of 15 psia will produce a flux of 0.8 cc/min; and at 115 psia, the flow will be about 6 cc/min. These represent dilution factors of 5% and 30% at a normal carrier flow of 20 cc/min, and higher carrier flow rates must be used to avoid calculation errors and prevent overloading of the GC column.

Comparison of Carrier Gas Data with Manometric Data

The data in Table I provide a comparison of permeabilities obtained by the carrier gas procedure with those obtained by manometric methods previously described.⁸ The materials were a commercial polyethylene and several soluble polyimides. The same film specimen was used in both tests. Good agreement exists between the test results.

Effect of Feed Composition on Permeability

An important element in obtaining separation of one or more gases by selective permeability is the knowledge of how the permeabilities of the gases are affected by concentration. Such data are readily obtainable with the car-

TABLE II
Effect of Feed Composition on Permeability Constants

Feed comp., mole fraction		Pressure, psia	Permeability, cB ^a	
H ₂	CH ₄		H ₂	CH ₄
<i>PPD-6F^b</i>				
	Pure gas	14.7	5210	34.0
0.51	0.49	14.7	5060	30.9
0.51	0.49	114.7	4895	34.5
0.97	0.03	114.7	5360	25.9
0.99	0.01	114.7	—	33.9
<i>3,5 DBA-6F^b</i>				
	Pure gas	14.7	3270	7.2
0.51	0.49	14.7	3238	7.0
0.51	0.49	114.7	3168	7.5
0.94	0.06	114.7	3136	8.2
0.98	0.02	114.7	3364	8.8

^a At 30°C.

^b See text for polyimide description.

rier gas system. An illustrative set is shown in Table II for H₂/CH₄ mixtures permeating through two polyimide films. It will be evident that in this system, which involves *noninteractive* materials, the gases permeate independently even at very low partial pressures. The capability of making measurements at elevated pressures facilitates study of permeabilities of minor components. The partial pressure for a 1 mole-% component at atmospheric pressure is only 7.6 mm; whereas at 115 psia, it is about 60 mm. These results are in agreement with those of Meyer and co-workers¹² and the conclusions of Stern²⁵ and Rogers²⁷ in their discussions of mixed gas permeability.

Temperature Effects

The temperature control system in which the test cell compartment is isolated from the thermal conductivity monitors and the gas analysis system permits simple adjustment of permeation test temperature without upsetting the detector systems so that equilibrium conditions are quickly achieved. Thermal studies have been conducted up to 150°C. An example is shown in Table III using a H₂/CH₄ feed. The excellent stability of these films is shown by the return of permeability values to the original measurements at the conclusion of the experiment. Arrhenius plots of methane permeability of several polymer films in Figure 5 illustrate typical data fits. Hydrogen permeabilities gave similar results.

The drop in selectivity of H₂ over CH₄ of over 50% between 30° and 150°C is noteworthy. It corresponds to the difference in activation energies for the permeation process for H₂ and CH₄ as calculated from the Arrhenius plots. The data in Table IV for several films illustrate these differences and underscore the value of determining the temperature dependence of permeability of the various species in a mixed gas to permit optimization of permeation

TABLE III
Effect of Temperature on Permeability Constants and Selectivity^a

Temp, °C	Permeability, cB ^b		Selectivity, H ₂ /CH ₄
	H ₂	CH ₄	
30	7814	71.8	109
50	9602	103	93
76	11733	157	75
99	13853	228	61
149	17816	424	42
30	7637	70.5	108

^a 1,5 ND-6F. See text for polyimide description.

^b Feed gas: 0.5/0.5 mole fraction H₂/CH₄; feed pressure: 14.7 psia.

conditions for maximum gas separation. Similar conclusions have been noted elsewhere.¹³

Effects of Vapors on Permeabilities

The inclusion of a vaporizer in the gas feed system permits evaluation either of the permeability of a vapor transported to the cell by a carrier gas or

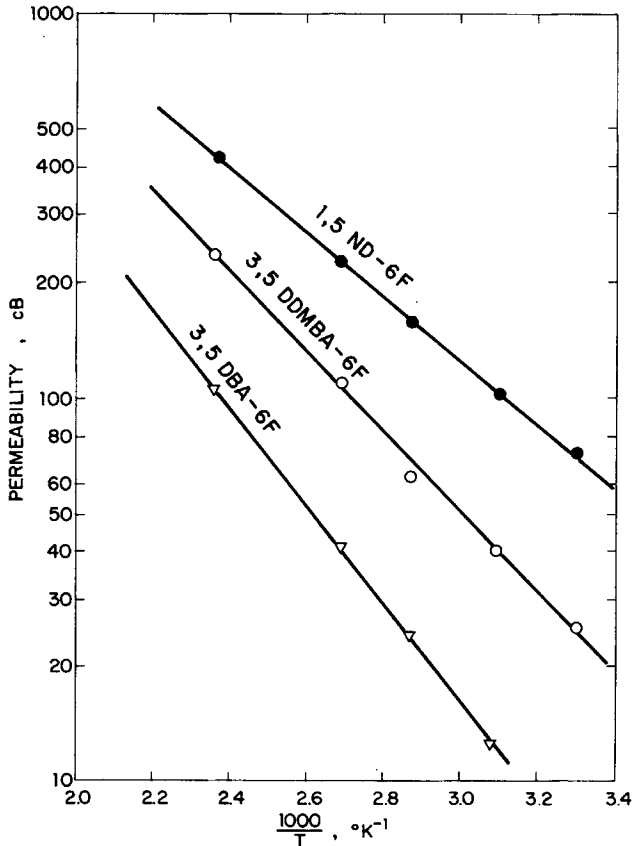


Fig. 5. Temperature dependence of permeability constant for methane through polyimides.

TABLE IV
Permeability Activation Energies for Several Polyimide Films^a

Polyimide ^b	Hydrogen		Methane	
	Perm, cB	E_p^c	Perm, cB	E_p^c
1,5 ND-6F	7814	1760	72	3820
3,5 DDMBA-6F	3400	2680	25	4740
3,5 DBA-6F	3444	2770	13	5490

^a From $P = P_0 e^{-E/RT}$, feed gas = 0.5/0.5 mole fraction H₂/CH₄, 14.7 psia.

^b See text for polyimide description.

^c Cal-deg⁻¹-mole⁻¹.

the effect of vapors on permeabilities of other gases. Water vapor, for example, may cause extensive changes and is frequently present in mixed gas streams. The data in Table V are some examples of water vapor effects on the permeability of a 0.5 H₂/0.5 CH₄ mole fraction mixture through polyimide films. The temperature of the vaporizer was adjusted to give 15 mm Hg partial pressure of H₂O in the feed (equivalent to 50% R.H. at the permeation temperature of 30°C). The data indicate that in all cases there was a significant reduction in the permeabilities of both H₂ and CH₄ relative to the initial dry film values. Return to initial permeabilities was slow, in some cases requiring one to two days after dry gas permeation was reintroduced.

The results differ from some data on other systems reported in the literature.^{12,25,27-30} Most of these systems concerned organic vapors, and those relating to inert gases usually involved hydrophilic polymers and did not include amorphous hydrophobic materials such as the aromatic polyimides which still retain a few carbonyls as hydrogen bonding sites. A possible explanation for the observed permeability reductions is that a small amount of water binds to these active groups, effectively reducing the microvoid content of the film and the available diffusion paths for the nonreactive gases. Several independent water absorption measurements on polyimides using a Cahn balance have indicated less than 5% water absorption at 15 mm Hg vapor

TABLE V
Effect of Water Vapor on Permeability Constants

Material ^a	Gas	Permeability, cB ^c		
		Dry	Wet ^b	Re-dry
MPD-6F	H ₂	3557	2817	2858
3,5 DBA-6F	H ₂	3168	1273	3010
1,5 ND-6F	H ₂	7637	6160	7759
MPD-6F	CH ₄	13.2	11.1	12.1
3,5 DBA-6F	CH ₄	7.5	3.3	7.3
1,5 ND-6F	CH ₄	68.2	57.0	69.2
1,5 ND-6F ^d	H ₂	13,900	13,900	—
1,5 ND-6F ^d	CH ₄	228	205	—

^a See text for polyimide description.

^b 15 mm H₂O vapor pressure/20°C.

^c Feed gas: 0.5/0.5 mole fraction H₂/CH₄; pressure = 14.7 psia; temp. = 30°C.

^d Temp. = 100°C.

pressure and 24°C. The amount was equivalent to about 1 molecule per 4 carbonyl groups.

The data in the last line of Table V indicate that when the permeation temperature was raised to 100°C in a wet system, there was no reduction in H₂ permeability and only a small reduction in CH₄ permeability, suggesting that at this temperature the binding energy for water may be negligible and that it thus may not be retained to impede the flow of other gases.

Other vapors can be incorporated in the feed stream. By vaporizing pentane at 2°C, 200 mm Hg pentane partial pressure was introduced to the H₂/CH₄ feed stream. Permeability reductions roughly equivalent to those obtained with water vapor were obtained. They were fully reversible indicating again that no significant interaction with the polyimide was occurring.

CONCLUSIONS

The carrier gas permeability apparatus that has been assembled offers wide latitude in the types of measurements that can be made and complements the constant volume/variable pressure system described previously.⁸ The carrier system is especially valuable for the study of permeabilities of mixed gases, for defining the effects of additives such as vapors, for the study of vapor permeabilities themselves, and for evaluation of temperature effects over a wide range. The pressure capability significantly improves sensitivity for study of minor components. Data have been shown to be comparable to those obtained by manometric methods.

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