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Flow of Air, Nitrogen, and Hydrogen through Porous Glass Tubes

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Abstract

A simple apparatus for obtaining diffusion data for porous tubes is described. It was used for determining the permeation rates of air, nitrogen, and hydrogen through porous 96% SiO_2 glass tubes. To increase flow, these tubes were subjected to multiple etch/wash treatments using aqueous NH_4F solutions at room temperature followed by successive hot washes in dilute mineral acid and distilled water. Further increases in permeation rates were achieved by subjecting the base glass used in the preparation of the porous glass to long heat treatments at its phase-separation liquidus prior to leaching and etching. Diffusion data show that the permeability of porous glass is not degraded on heating at temperatures up to 800°C, and that the separation ratios of the experimental glasses are in good agreement with values expected from Graham's law of diffusion. The role of heat treatment of the base glass, etch/wash treatments of the porous glass, and moisture in the gas stream are discussed.

INTRODUCTION

The ability of organic and inorganic membranes to separate permanent gases has been known for a long time, but it is only in recent times that industry has begun to use such materials for separating some important industrial gas mixtures. Although palladium and fused silica glass have received considerable attention because both of these materials are highly selective to hydrogen permeation, they have not found application in gas separation on a commercial scale.

Henis and Tripodi (*1*) in recent years introduced the prism membrane consisting of a silicone-coated hollow fiber made from a polysulfone that is useful in separating hydrogen from process streams. There is considerable activity in studying the flow through various organic polymers such as

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polysulfones, polycarbonates, polyphenylenes, and various copolymers in hopes that the separation properties can be engineered by coating them with special polymers.

Although membranes prepared from organic polymers are very rugged, they are not useful at temperatures above 100°C. Hwang (*2*) increased the temperature capability of membranes by filling the pores of porous inorganic supports with an appropriate silicone monomer and polymerizing it *in situ* to produce a composite membrane. Permeation tests with hydrogen, helium, and other gases showed that the polymerization of polydimethylsiloxane in a porous glass provided a viable separation medium up to 200°C.

Gavalas and Megiris (*3*) made hydrogen permselective membranes by depositing dense amorphous oxide layers within the pores of microporous ceramic support tubes, using chemical vapor deposition techniques. The stability of such inorganic composite membranes at elevated temperatures has been dealt with by Nam and Gavalas (*4*). Their studies indicate that the incorporation of a thin SiO_2 layer within a porous glass tube results in membranes with extremely high hydrogen selectivity that can operate at 500°C or higher.

In the preparation of composite membranes, the permeation of the gases through them depends not only on the intrinsic resistance of the coating or the embedded layer but also on the resistance of the substrate itself. The latter is generally selected from materials that do not seriously impede flow.

The purpose of this paper is to describe a simple diffusion apparatus for measuring gas flow through porous tubing, and to show how the permeability of porous 96% SiO_2 glass can be tailored by chemical etching treatments. Porous glass was chosen for this study because it is a unique microporous material that retains its porosity even when heated to high temperatures and, consequently, is well suited for incorporating thin films or layers in its pore structure over a wide range of temperatures.

EXPERIMENTAL SECTION

Porous Glass

Porous glass is an intermediate glass obtained by heat-treating and leaching a special soft alkali-borosilicate glass (*5*). It was used in this study in the form of tubing. The specimens were 5.8 cm long by 1.2 cm in diameter with a 1.1-mm wall thickness.

The composition of the porous glass tubing, on the basis of ignited weight, was 96% SiO_2, 3% B_2O_3, 0.4% R_2O_3 + RO_2 (chiefly Al_2O_3 and ZrO_2), and traces of Na_2O. It has a pore size of 5 nm and a surface area of 200 m^2/g as determined by the BET method (*6*) using nitrogen as the adsorbate, and an internal pore volume of 28%.

Diffusion Apparatus

The apparatus consists of a mercury manometer, Pyrex brand tubing, stopcocks, and ground joints as shown diagrammatically in Fig. 1. The porous glass tube whose permeation rate was to be measured was mounted between two flanges by means of Neoprene rubber gaskets tightened by means of an Allen head bolt provided with an air passage as shown in Fig. 2. This assembly was connected to the diffusion apparatus through ground joints.

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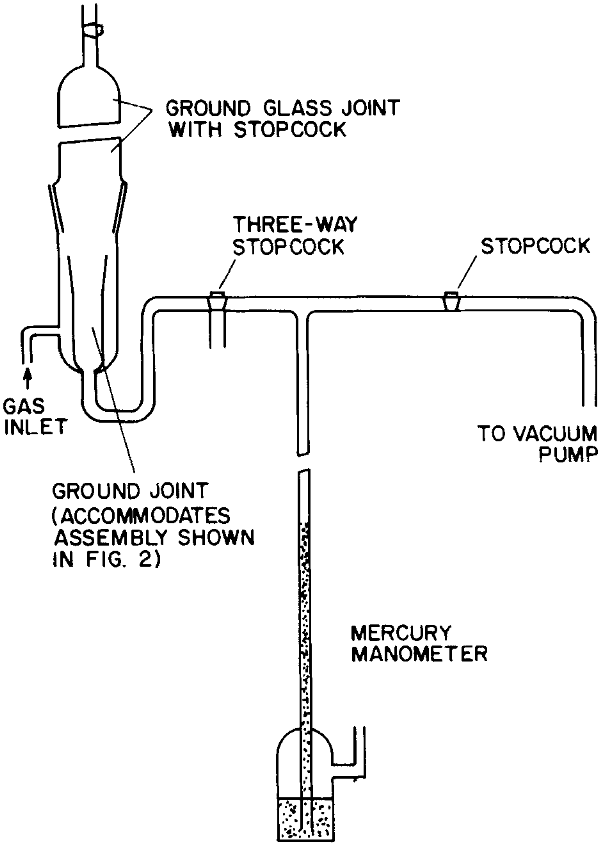

FIG. 1. Schematic drawing of diffusion apparatus.

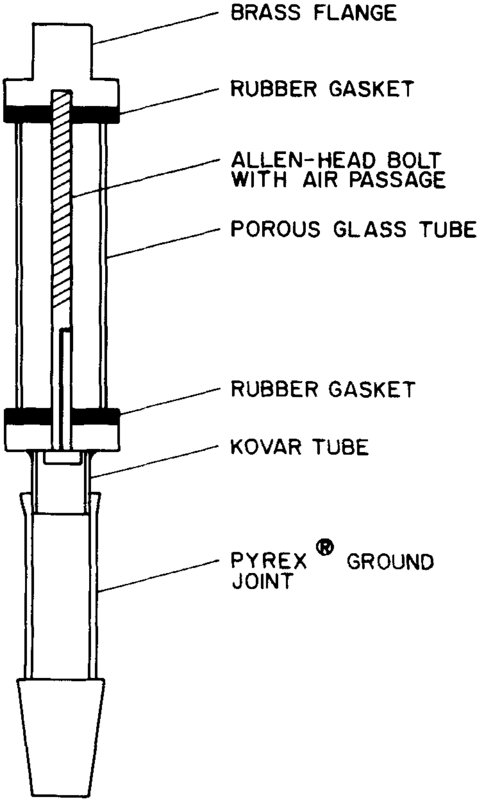

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FIG. 2. Cross-sectional view of device for attaching tubular sample for flow measurements.

Measuring Procedure

After attaching the porous glass tube to the sample support apparatus, the air was pumped away from the inside of the sample and the rest of the system by means of a Welch Duo-Seal vacuum pump. The desired gas was then introduced in the chamber containing the sample and pumped through the porous glass. Pumping was continued for about 15 min to assure thorough flushing of the porous glass with the gas. After reading the equilibrium position of the manometer, the stopcock connecting the pump was closed. The rate at which the gas passing through the porous glass filled the evacuated space was then determined by the rate of fall of the mercury manometer. All permeation measurements were made at room temperature with the gas on the outside of the porous tubes being at atmospheric pressure.

It should be pointed out that the apparatus used in this study is partly based on the experimental setup used by Schwertz (*7*). In the course of developing equations for calculating parameters such as specific surface area, pore diameter, and pore-population density for porous glass, Schwertz found that plotting $\ln (P_b - P)$ against the elapsed diffusion time gives a straight line, where P_b = pressure outside membrane (generally atmospheric pressure) and P = pressure inside membrane. Although there is little merit in using Schwertz's approach for calculating physical parameters of microporous materials, plots of diffusion data on semilog paper using his $\ln (P_b - P) \propto t$ equation are useful for making a visual comparison of permeabilities.

Pore Enlargement Treatments

The pore enlargement treatments involve impregnating the porous glass body with a weakly reactive fluoride-containing compound, reacting the compound *in situ* with a dilute mineral acid to release hydrofluoric acid at a temperature sufficient to dissolve a portion of the glass body, and washing the body to remove the soluble constituents (*8*).

In this study the porous glass tubes were heated overnight to 85°C to remove most of the physically adsorbed water from the pores and then were immediately immersed in aqueous etch solutions containing 10% $NH_4F \cdot HF$, or 10, 20, and 30% NH_4F. After 5 min immersion at room temperature, the impregnated tubes were transferred into 0.25 *N* HNO_3 at 95°C. After 4–5 h in the hot dilute acid solution, the tubes were washed for 1 h in hot distilled water, and after cooling in water were set to dry in room air.

The permeability of the porous glass tubes was measured after each of the above etch/wash treatments using Drierite-dried air at 22°C. The weight loss resulting from the etching treatments of the porous glass tubes and changes in their wall thickness were also determined. The percentage weight loss in the tables is based on the weight of untreated porous glass that had been baked at 85°C, the same temperature as that used prior to weighting the treated glass.

RESULTS AND DISCUSSION

Role of Moisture

Preliminary studies showed that water in the porous glass and in the air stream affect the rate of gas flow, making it necessary to dry both the glass and air to assure consistent results. This was not surprising since porous glass is an excellent moisture getter (*9*).

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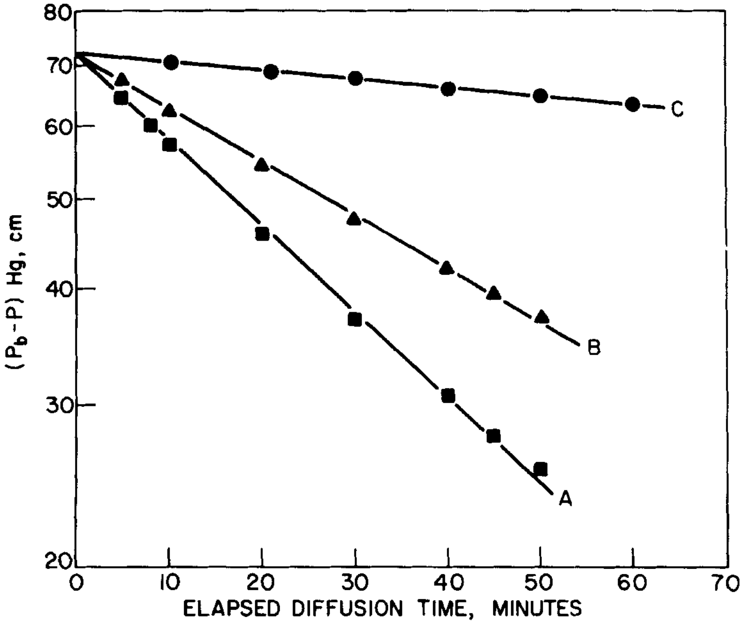

FIG. 3. Diffusion data for a porous 96% SiO_2 glass tube exposed to (A) dry air, (B) air with 44% relative humidity, and (C) air saturated with moisture.

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Figure 3 shows plots of experimental data for porous glass that had been exposed to a stream of air that had been bubbled through water at 22.5°C, a stream of air having a relative humidity of 44%, and a stream of air that had been dried with Drierite to a dew point of −79°C. The figure shows that plotting log $(P_b - P)$ versus time produces a straight line. The slopes of the lines are an indirect measure of the rate of gas flow. The steepest slope, and hence the highest flow rate, was obtained with dry air. Exposure to 44% r.h. air markedly reduced the flow due to adsorption of moisture on the pore walls of the glass. The slope was reduced still further with air that had been essentially saturated with water at room temperature.

Thermal Stability

The linear shrinkage and permeability of a porous glass tube were determined after successive heating for 1 h at temperatures of 100, 200, 400, 600, 900, 1000, 1050, and 1100°C. The results are summarized in Table 1. For the sake of brevity, only the slopes of the straight lines obtained from the plots of ln $(P_b - P)$ versus elapsed time are given in the table.

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TABLE 1
Shrinkage and Diffusion Data for Porous Glass Obtained after Successive Heating at Temperatures Ranging from 100 to 1100°C

Heat treatment (°C)	Linear shrinkage (%)	$\frac{\Delta \ln (P_b - P)}{\Delta t} \times 10^{-2}$
22	NM[a]	−5.90
100	NM	−5.90
200	NM	−5.90
400	0.84	−5.90
600	1.67	−6.08
800	2.51	−6.08
900	3.01	−5.91
950	4.01	−5.56
1000	5.33	−4.21
1050	9.38	−0.30
1100	13.90	0

[a] Not measured.

Both the slopes and shrinkage data in Table 1 are shown graphically in Fig. 4. Curve A shows that the slope, which is a measure of permeability, remains constant on successive heating at temperatures ranging from room temperature to 400°C. The slope goes through a maximum in the temperature range from about 500 to 800°C, and then decreases rapidly above 900°C. The slight increase in permeability in the 500–800° range is due to removal of space-filling hydroxyl groups and consolidation of colloidal deposits in the pore structure (*10*).

Curve B in Fig. 4 shows that the porous glass undergoes a steady contraction on heating from room temperature to 900°C. Above 900°C the shrinkage is greatly accelerated and stops after reaching 1100°C, a temperature above which all the pores are completely consolidated and the tube is no longer permeable to air as shown by Curve A.

Role of Etching

Table 2 summarizes diffusion times for dry air through a porous glass tube that had been subjected to multiple etching and washing treatments. The table also includes the weight loss and decrease in wall thickness of the tube that resulted from the treatments.

The diffusion times given in Table 2 represent the times required for dry air flowing through the porous glass tube to increase the pressure inside the tube from 0 to 37 cmHg, the 37 figure having been chosen arbitrarily. It should be noted that the multiple treatments reduced the diffusion time

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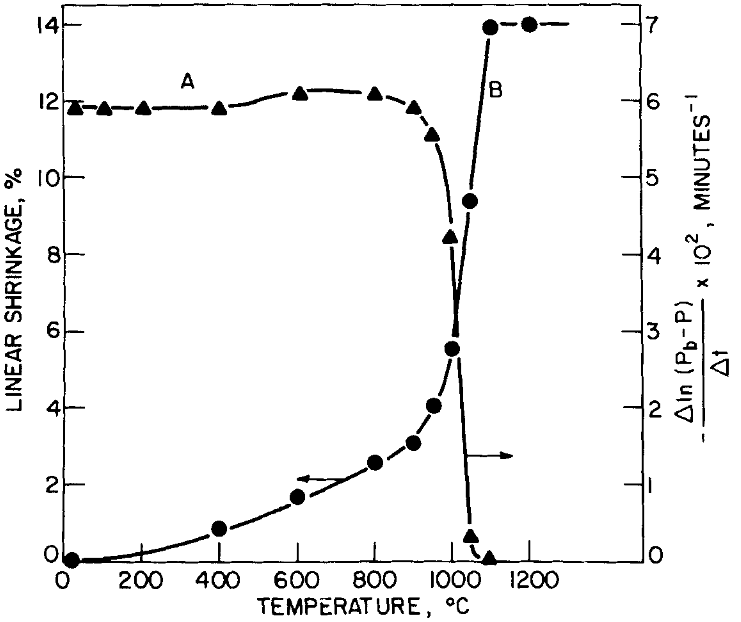

FIG. 4. Shrinkage of porous glass on heating and accompanying changes in diffusion of dry air through such glass in terms of $\Delta \ln (P_b - P)/\Delta t$.

from 13.65 to 2.98 min. This indicates that multiple etching and washing treatments greatly increase the permeability of porous glass. A plot of the diffusion time versus the number of treatments is shown in Fig. 5. It shows that the first treatment resulted in the greatest decrease in diffusion time. Since the data in Table 2 show that this decrease is accompanied by a

TABLE 2

The Effect of Multiple Etch/Wash Treatments[a] of a Porous Glass Tube on Weight Loss, Wall Thickness, and Diffusion Time in Dry Air

Number of treatments	Weight loss (%)	Wall thickness (mm)	Thickness loss (%)	Diffusion time (min)
1	6.45	1.08	0.92	5.52
2	12.78	NM		4.40
3	18.84	0.94	13.76	3.72
4	24.86	0.89	18.35	3.37
5	30.95	0.84	22.94	2.98
Before treatment		1.09		13.65

[a] 30% NH_4F/0.25 *N* HNO_3, 4 h; H_2O, 1 h.

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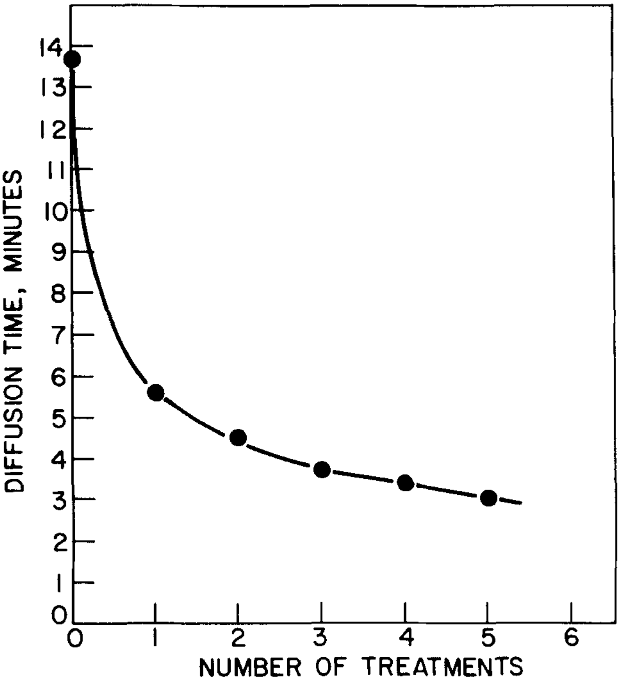

FIG. 5. Diffusion time for porous glass versus number of treatments in etch/wash solutions.

substantial weight loss (6.45%) without causing a corresponding loss in wall thickness of the porous glass, it can be concluded that this decrease in diffusion time is due to removal of colloidal siliceous deposits in the pores of the porous glass. Such deposits are known to result from acid leaching of the base glass used for making porous glass, their presence having been demonstrated by several investigators (*11–13*). Their removal

TABLE 3
Diffusion Time in Minutes of Etch/Wash-Treated Porous Glass Tubes after Baking at 80, 500, and 800°C

Sample	Etchant	80°C	500°C	800°C	Permeation[a]
1	10% $NH_4 \cdot HF_2$	4.32	4.22	4.17	35.0
2	20% NH_4F	3.88	3.87	3.85	39.5
3	30% NH_4F	3.30	3.27	3.25	45.6
4	Untreated	13.14	ND[b]	ND	10.9

[a] Permeation rate of air at 22°C in $cm^3/cm^2 \cdot atm \cdot h$.
[b] Not determined.

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TABLE 4
Nitrogen and Hydrogen Diffusion Data for Untreated and Treated Porous Glass Tubes

Nitrogen		Hydrogen		
Time (min)	$P_b - P$ (cmHg)	Time (min)	$P_b - P$ (cmHg)	Porous glass
0	74.2	0	74.2	Untreated
1.46	67.3	1.22	57.3	
4.12	58.7	2.27	46.3	
7.72	48.3	3.60	37.2	
9.97	43.0			
12.82	37.2			
0	74.4	0	74.3	Treated 5 times in 30% NH_4F
1.06	57.2	0.26	57.2	
1.97	47.2	0.52	47.2	
2.53	42.2	0.87	37.0	
3.20	37.4			

accounts for the fact that the weight loss after multiple etch/wash treatments greatly exceeds the loss in wall thickness, e.g., 30.95 versus 22.94% in Table 2.

Role of Temperature

Table 3 gives information regarding the thermal stability of porous glass tubes prepared by multiple etching and washing treatments. The pore enlargement treatment for these tubes was carried out in aqueous solutions

TABLE 5
Diffusion Times for Nitrogen and Hydrogen and Separation Ratios for Treated Porous Glass Tubes

	Diffusion time (min)			
Sample	N_2	H_2	K_{H_2}/K_{N_2}	Number of treatments
5	2.84	0.76_6	3.71	5[a]
6	3.22	0.87_5	3.68	5
7	3.20	0.86_6	3.70	5

[a] This sample was treated for 5 min in 0.5 *N* NaOH at 19°C and sequentially washed in H_2O at 95°C for 2, 1, and 1 h prior to subjecting it to 5 etch/wash treatments using 30% NH_4F, 0.25 *N* HNO_3, and H_2O as described in the Experimental Section.

TABLE 6
Permeation Data and Separation Ratios for Specially Prepared Porous Glass Tubes[a]

Sample	Diffusion time (min)		K_{H_2}/K_{N_2}	Gas flux[b] ($cm^3/cm^2 \cdot atm \cdot h$)	
	N_2	H_2		N_2	H_2
8	2.05	0.55	3.73	67.0	248
9	1.47	0.40	3.68	89.2	327

[a] The base glass tubes used in preparing Samples 8 and 9 were both subjected to a prolonged heat treatment at 575°C (25 h) with Sample 9 being cooled more slowly from the hold temperature. After leaching, both samples were subjected to five 30% NH_4F/wash treatments prior to gas flow measurements.

[b] At 20°C through 1 mm thickness.

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containing 10% $NH_4F \cdot HF$, 20% NH_4F, or 30% NH_4F followed by washes in dilute nitric acid and distilled water as described earlier. The treated porous glass tubes were heated for 1 h at 80, 500, and 800°C to determine the effect of temperature on permeability. The heating rate of the air-dried tubes to the hold temperatures was 160°C/h, starting at room temperature.

The data in Table 3 show that the diffusion time decreases slightly on heat treating at 500 and 800°C, indicating that the permeability of such inorganic membranes is not impaired by temperatures up to 800°C. The permeation rates for dry air at 22°C for these tubes are shown in the last column of the table.

Table 4 shows diffusion data for nitrogen and hydrogen for an untreated and treated porous glass tube. By dividing the diffusion time for nitrogen by that for hydrogen [both at the same ($P_b - P$) values], one obtains K_{H_2}/K_{N_2} separation ratios of 3.56 and 3.64 for the untreated and treated tubes, respectively. Additional separation ratios are given in Table 5. The values are in good agreement with the 3.73 value expected from Graham's law of diffusion for these gases.

Table 6 gives permeation data for two experimental porous glasses prepared from tubing that had been subjected to long heat treatments at its separation liquidus to coarsen the microstructure of the base glass prior to leaching. The resulting porous tubes were subjected to similar etching and washing treatments as the regular porous glass tubes described above.. The table shows that these experimental porous glasses are considerably more permeable than the regular porous glass* after similar etch/wash treatments. Furthermore, the data show that gas permeation rates for hydrogen of >300 $cm^3/cm^2 \cdot atm \cdot h$ are attainable with porous glass tubing of 1 mm

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*See Sample 3 in Table 3.

thickness. By reducing the thickness to 0.25 mm, it is possible to increase the rates to well above 1000 $cm^3/cm^2 \cdot atm \cdot h$. This makes such inorganic membranes attractive for recovery of hydrogen from industrial waste gases.

An electron micrograph of a replica of a fractured surface prepared from pore enlarged Sample 8 of Table 6 is shown in Fig. 6. The silica-rich phase is randomly interconnected in three dimensions. The vermicular structure that resulted from the growth by coalescence of the silica-rich phase on heat treatment of the base glass is evident in the micrograph. A typical pore size distribution curve of pore-enlarged porous glass is shown in Fig. 7.

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FIG. 6. Electron micrograph of fractured surface of pore-enlarged porous glass. White marks indicate 1 μm.

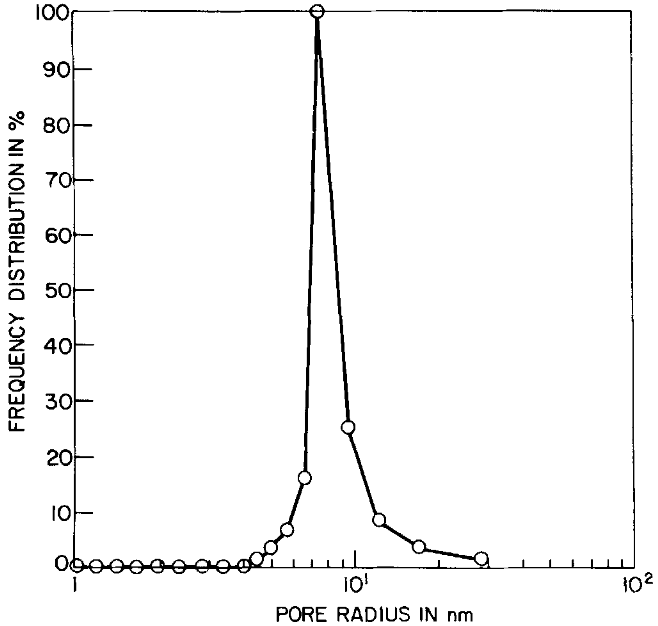

FIG. 7. Pore size distribution of pore-enlarged porous glass.

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In recent years considerable effort has been directed to the development of composite membrane gas separation systems that can operate successfully at elevated temperatures. For industrial applications there is a need for inorganic microporous membranes with minimum resistance to flow, chemical inertness, and high temperture capabilities. This study shows that porous glass meets these requirements and should prove useful as a substrate material in the development of composite membranes for gas separation.

CONCLUSIONS

The rate of flow of permanent gases such as nitrogen, hydrogen, and dry air through porous 96% SiO_2 glass is markedly increased by subjecting porous glass to a pore-enlargement treatment involving multiple etch/wash treatments, each consisting of a brief immersion in an ammonium fluoride solution at room temperature followed by washes in hot dilute mineral acid and hot distilled water.

The increase in the permeability of gases that results from such etch/wash treatments is due to removal of colloidal deposits in the pores and dissolution of some of the structural silica that comprises the porous glass body.

The rate of diffusion through the porous glass is not degraded on heating to temperatures up to 800°C, indicating that porous 96% SiO_2 glass, unlike organic membranes, possesses high temperature capabilities.

A further increase in gas permeation is achieved by subjecting the base glass used in the preparation of the porous glass to long heat treatments prior to leaching. However, to obtain high flows, the porous glass must be subjected to etch/wash treatments since the colloidal deposits in the pores of the leached glass resulting from acid leaching of the heat-treated base glass impede the flow of gases. The gas permeation rates for hydrogen through such treated porous glass tubes are well above 300 and 1000 $cm^3/cm^2 \cdot atm \cdot h$ for tubes having wall thicknesses of 1 and 0.25 mm, respectively. Their K_{H_2}/K_{N_2} separation ratio is in good agreement with that expected from Graham's law of diffusion.

The high permeation rates of the gases combined with high thermal resistance, chemical inertness, and mechanical rigidity make porous glass a suitable substrate for preparing permselective composite membranes for gas separation.

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