

Permeability of Silicone Polymers to Ammonia and Hydrogen Sulfide

S. A. STERN* and B. D. BHIDE, *Department of Chemical Engineering and Materials Science, Syracuse University, Syracuse, New York 13244*

Synopsis

Permeability coefficients, \bar{P} , for NH_3 and H_2S in 11 different types of silicone membranes were measured in the temperature range from 10.0 to 55.0°C and at pressures up to 115 psig (~ 7.8 atm). The values of \bar{P} for NH_3 and H_2S in different silicone polymers decrease considerably as the bulkiness of the functional groups in the side and backbone chains of these polymers increases. The substitution of Si—O bonds with stiffer Si—C bonds in the backbone chains also results in a considerable decrease in gas permeability. The values of \bar{P} for NH_3 and H_2S increase exponentially with increasing Δp , the pressure difference across the membranes. The temperature dependence of NH_3 and H_2S varies greatly: \bar{P} can increase, decrease, or pass through a minimum with increasing temperature, depending on the nature of the silicone polymer. The temperature dependence of \bar{P} is also affected in some cases by Δp . The permeability behavior of silicone polymers to NH_3 and H_2S is compared with that to other penetrant gases, and the factors which might affect this behavior are discussed.

INTRODUCTION

Considerable work is in progress in a number of academic and industrial laboratories with the objective of elucidating the relationships between the chemical structure of polymers and their gas permeability. A better understanding of these relationships will greatly facilitate the development of polymer membranes with "tailored" gas selectivities and permeabilities. Such membranes are necessary to increase the efficiency and range of applications of membrane processes for the separation of gas mixtures.

During the past few years, an extensive study on the structure/permeability relationships of silicone polymers, polyorganosiloxanes, was made in this laboratory.¹ The permeability of 11 different types of silicone polymers to He, N_2 , O_2 , CO_2 , CH_4 , C_2H_4 , C_2H_6 , and C_3H_8 was measured at temperatures between 10.0 and 55.0°C (mostly at 35.0°C) and at pressures up to 115 psig (~ 7.8 atm). These penetrant gases are characterized by relatively low solubilities in silicone polymers.²

The present study is an extension of the above work to two penetrant gases that exhibit much higher solubilities in polymers, namely, NH_3 and H_2S . These gases are also components of some important gas mixtures of industrial interest and their separation is often desirable. The permeability measurements were made at temperatures from 10.0 to 55.0°C and at pressures up to 115 psig (~ 7.8 atm). Silicone polymers were selected for this study because of

*To whom correspondence should be addressed.

the versatility of silicone chemistry, which allows the substitution of many different functional groups in the side and backbone chains of these polymers. Additionally, silicone polymers have a relatively high *intrinsic* gas permeability as compared to that of other types of polymers. The polymers were employed in the form of thin, planar (sheet) membranes.

EXPERIMENTAL

Apparatus and Procedure

Mean permeability coefficients, \bar{P} , for NH_3 and H_2S were determined from the steady-state rates of permeation of these gases through the silicone membranes studied. Values of \bar{P} were calculated from the isothermal relation^{3,4}

$$P = G_s \cdot \delta / A(p_h - p_l) \quad (1)$$

where G_s is the steady-state permeation rate (flow rate) through a membrane of area A and thickness δ , when the pressures p_h and p_l ($< p_h$) are maintained constant at opposite membrane interfaces. In the most general case \bar{P} depends on the nature of the gas and of the polymer, the temperature, and both p_h and p_l . \bar{P} is reported here in units of $\text{cm}^3(\text{STP}) \text{ cm}/(\text{s} \cdot \text{cm}^2 \cdot \text{cm Hg})$.

The apparatus and procedure used to measure G_s have been described previously.¹ However, due to the high rates of permeation of NH_3 and H_2S , the measurements were made by means of an electronic mass flow meter, rather than by monitoring the displacement of a mercury slug in a precision-bore capillary. The flow meter (Type 249B, range 0–100 $\text{cm}^3(\text{STP})/\text{min}$) and its readout (Type 246) were obtained from MKS Instruments Co. of Burlington, MA. The flow meter was calibrated by the manufacturer for N_2 . In order to determine the actual flow rate of NH_3 or H_2S , a factor dial on the readout was set at the correction factor for the gas of interest. Correction factors for NH_3 and H_2S , relative to N_2 , were provided by the manufacturer. These correction factors were also verified experimentally in the range of 0–10 $\text{cm}^3(\text{STP})/\text{min}$. and the agreement between the two was found to be within $\pm 1.5\%$. It should be noted that in this study p_h was varied while p_l was always close to atmospheric pressure.

Polymer Membranes

Eleven different silicone polymers, which are listed below, were used in the present study in the form of 8–12 mil (203–305 μm)-thick membranes. These polymers were synthesized by the Silicone Research Dept. of Dow Corning Corp., Midland, MI. The polymers will be hereafter referred to as polymers A–L; the designation is the same as that used in a previous study.¹

(A) Poly(dimethyl siloxane), $[(\text{CH}_3)_2\text{SiO}]_x$ or $(\text{Me}_2\text{SiO})_x$

Side-chain modifications

(B) Poly(ethyl methyl siloxane), $(\text{C}_2\text{H}_5\text{CH}_2\text{SiO})_x$ or $(\text{EtMeSiO})_x$

(C) Poly(methyl propyl siloxane), $(\text{CH}_3\text{C}_3\text{H}_7\text{SiO})_x$ or $(\text{MePrSiO})_x$

(D) Poly(methyl octyl siloxane), $(\text{CH}_3\text{C}_8\text{H}_{17}\text{SiO})_x$ or $(\text{MeOcSiO})_x$

(E) Poly(trifluoropropyl methyl siloxane), $[(\text{CF}_3\text{CH}_2\text{CH}_2)\text{CH}_3\text{SiO}]_x$ or $(\text{F}_3\text{PrMeSiO})_x$

- (F) Poly(methyl phenyl siloxane), (CH₃C₆H₅SiO)_x or (MePhSiO)_x
Backbone modifications
- (G) Poly(dimethyl silmethylene), [(CH₃)₂SiCH₂]_x or (Me₂SiCH₂)_x
- (H) Poly(silethylene siloxane), [(CH₃)₂Si(CH₂)₂Si(CH₃)₂O]_x or [Me₂Si(CH₂)₂SiMe₂O]_x
- (I) Poly(silhexylene siloxane), [(CH₃)₂Si(CH₂)₆Si(CH₃)₂O]_x or [Me₂Si(CH₂)₆SiMe₂O]_x
- (K) Poly(*meta*-silphenylene siloxane), [(CH₃)₂Si *m*-C₆H₄Si(CH₃)₂O]_x or [Me₂Si *m*-C₆H₄SiMe₂O]_x
- (L) Poly (*para*-silphenylene siloxane), [(CH₃)₂Si *p*-C₆H₄Si(CH₃)₂O]_x or [Me₂Si *p*-C₆H₄SiMe₂O]_x

In polymers B–F one of the methyl groups in the side chains of polymer A is replaced by different alkyl groups, while in polymers H–K alternate oxygen atoms in the backbone chain of polymer A are replaced by different alkylene groups. In polymer G all the oxygen atoms in the backbone chain of polymer A are replaced by methylene groups.

Polymers B, C, E, and G–L were filler-free, whereas polymers A, D, and F contained 4.9, 2.0, and 2.9 vol % of a silica filler, respectively. The glass transition temperatures and densities of the above polymers were determined by the Silicone Research Dept. of Dow Corning Corp. Midland, MI, and are listed in Table I.

Gases

Pure ammonia (NH₃) and hydrogen sulfide (H₂S) were obtained from the Linde Division of Union Carbide Corp. The purity of the gases was reported

TABLE I
 Polymer Characterization^a

Polymer	Density at 25.0°C, ρ (g/cm ³)	Glass transition temperature ^b , T _g (°C)	Cohesive energy density, δ ² (cal/cm ³)
A. (Me ₂ SiO) _x	0.971	–123	53.24
<i>Side-chain Modifications</i>			
B. (MeEtSiO) _x	0.978	–135	60.15
C. (MePrSiO) _x	0.916	–120	60.15
D. (MeOcSiO) _x	0.906	–92	63.62
E. (F ₃ PrMeSiO) _x	1.292	–70	76.36
F. (MePhSiO) _x	1.138	–28	92.88
<i>Backbone Modifications</i>			
G. (Me ₂ SiCH ₂) _x	0.917	–92	64.24
H. [Me ₂ Si(CH ₂) ₂ SiMe ₂ O] _x	0.890	–88	64.24
I. [Me ₂ Si(CH ₂) ₆ SiMe ₂ O] _x	—	–90	62.68
J. [Me ₂ Si(CH ₂) ₆ SiMe ₂ O] _x	0.889	–88	65.26
K. [Me ₂ Si <i>m</i> -C ₆ H ₄ SiMe ₂ O] _x	1.025	–48	75.50
L. [Me ₂ Si <i>p</i> -C ₆ H ₄ SiMe ₂ O] _x	1.058	–18	—

^aSource: Data from Silicone Research Department, Dow Corning Corporation, Midland, MI.

^bMeasured by differential scanning calorimetry.

by the supplier to be 99.5 vol % or higher. The gases were used without further purification.

RESULTS

Permeability coefficients, \bar{P} , for NH_3 and H_2S in 11 different types of silicone membranes were measured in the temperature range from 10.0 to 55.0°C and at pressures up to 115 psig (~ 7.8 atm). The values of \bar{P} for NH_3 and H_2S in polymers A, D, and F, which contained 4.9, 2.0, and 2.9 vol % of silica filler, respectively, were divided by the amorphous volume fraction of the polymer to obtain approximate values of \bar{P} for filler-free membranes. The values of \bar{P} in this study varied from a maximum of 151.4×10^{-8} for NH_3 in polymer A at 10.0°C and $\Delta p = 60$ psig to a minimum of 1.38×10^{-8} for H_2S in polymer L at 10.0°C and $\Delta p = 20$ psig [\bar{P} is in the units of $\text{cm}^3(\text{STP}) \text{ cm}/(\text{s} \cdot \text{cm}^2 \cdot \text{cm Hg})$]. The experimental error in \bar{P} was estimated to be within $\pm 10\%$, except for polymers F and L for which the error was within $\pm 13\%$ because of their low permeability. All the silicone polymers were found to be chemically and thermally stable to NH_3 and H_2S in the temperature range investigated over a period of several days.

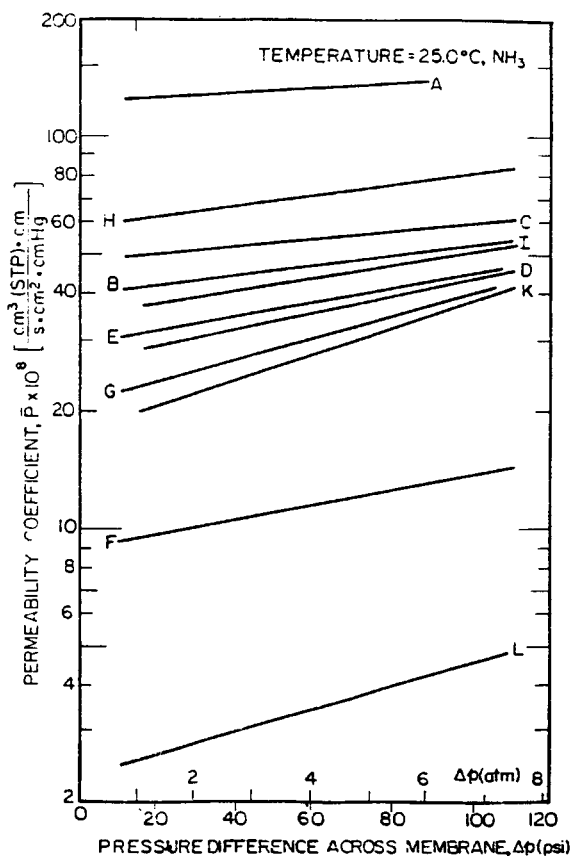


Fig. 1. Mean permeability coefficients as a function of pressure difference across membrane for NH_3 in several silicone polymers at 25.0°C.

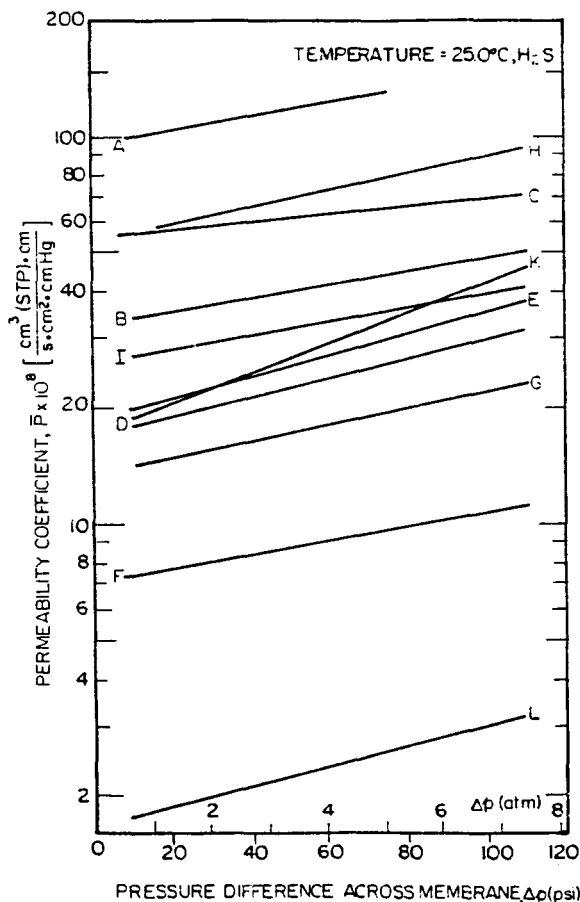


Fig. 2. Mean permeability coefficients as a function of pressure difference across membrane for H₂S in several silicone polymers at 25.0°C.

The permeabilities of *different silicone polymers* to NH₃ and H₂S at 25.0°C are compared in Figures 1 and 2, respectively. These figures show semi-logarithmic plots of \bar{P} as a function of the pressure difference across the membrane $\Delta p (= p_h - p_l)$. The permeabilities of membranes prepared from polymers A, D, and L to *different gases*, including NH₃ and H₂S, at 35.0°C are shown in Figures 3-5.¹ The values of \bar{P} for NH₃ and H₂S at this temperature were obtained by interpolation from Arrhenius plots in the temperature range from 10.0 to 40.0°C.

Typical results of gas permeability measurements are presented in Figures 6-8 in the form of semi-logarithmic plots of \bar{P} vs. Δp at different temperatures for H₂S in polymers C and E, and for NH₃ in polymer K. Similar plots were obtained for NH₃ and H₂S in the other polymers studied. The plots in Figures 6-8 are linear, and thus can be represented by relations of the form:

$$\log \bar{P} = \log \bar{P}(\Delta p = 0) + m \cdot \Delta p \quad (2)$$

where $\bar{P}(\Delta p = 0)$ and m are constants at a given temperature, and $\Delta p =$

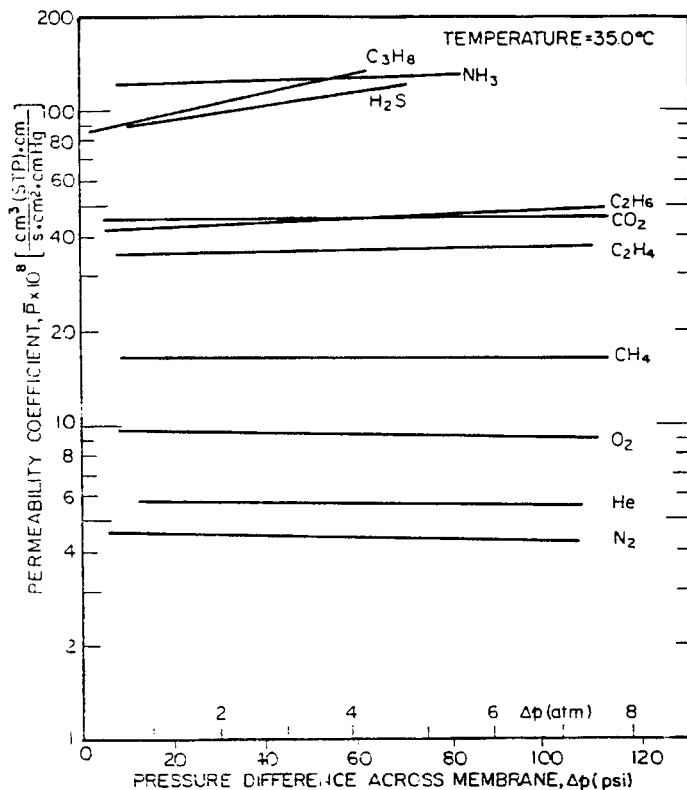


Fig. 3. Mean permeability coefficients as a function of pressure difference across membrane for different gases in poly(dimethyl siloxane) [(Me₂SiO)_x] at 35.0°C. The polymer contained 4.9 vol % silica filler.

$p_h - p_l$. The values of $\bar{P}(\Delta p = 0)$ and m for NH₃ and H₂S in silicone polymers are listed in Table II. These values were obtained from least-squares fits of eq. (2) to the experimental data.

The permeability coefficients for NH₃ and H₂S in polymer A [poly(dimethyl siloxane)] at 25.0°C have been determined previously by Robb.⁵ The values of \bar{P} for NH₃ and H₂S, as reported by Robb, are 88.0×10^{-8} and 149.2×10^{-8} cm³(STP) · cm/(s · cm² · cmHg), respectively, after correcting for the filler content of the polymer. By comparison, the values of $\bar{P}(\Delta p = 0)$ determined in this study are 124.2×10^{-8} and 96.5×10^{-8} in the same units, respectively. These two sets of data differ considerably. Thus, Robb reports that $\bar{P}(\text{H}_2\text{S}) > \bar{P}(\text{NH}_3)$ whereas the opposite was observed in the present study. The reasons for this discrepancy are not known.

The temperature dependence of \bar{P} for NH₃ and H₂S in different silicone polymers can vary greatly, as is exemplified by Figures 9–11. These figures show semilogarithmic plots of \bar{P} vs. the reciprocal absolute temperature, $1/T$, for H₂S in polymers C and E (Figs. 9 and 10, respectively) and for NH₃ in polymer K (Fig. 11). The plots were made at constant values of Δp . It is seen that all plots in Figures 9 and 10 are linear and can be represented by

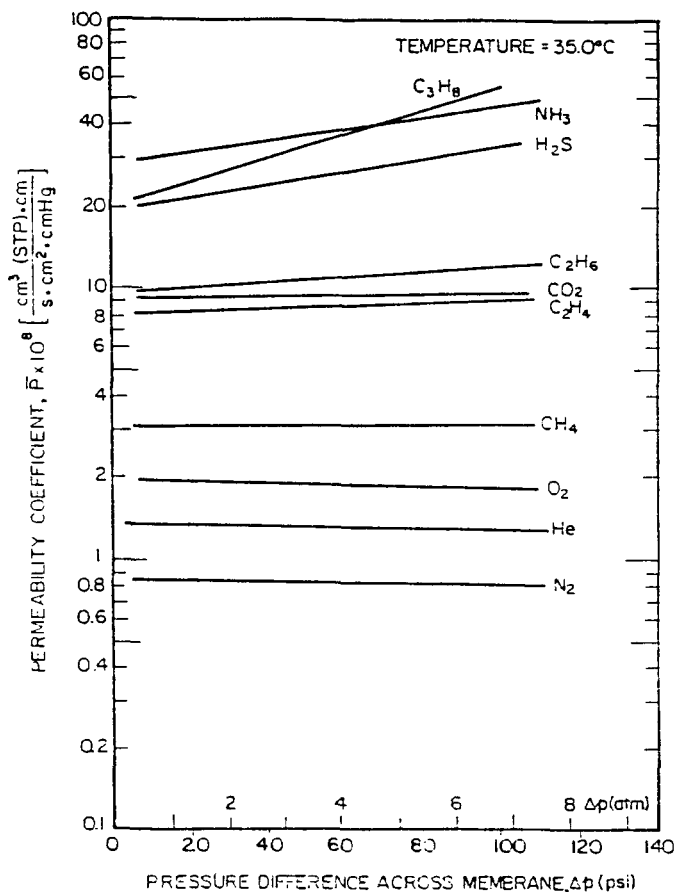


Fig. 4. Mean permeability coefficients as a function of pressure difference across membrane for different gases in poly(methyl octyl siloxane) [(MeOcSiO)_x] at 35.0°C. The polymer contained 2.0 vol % silica filler.

Arrhenius-type relations of the form:

$$\bar{P} = P_0 \exp(-E_p/RT), \quad \Delta p = \text{const} \quad (3)$$

where P_0 is a constant, E_p is the energy of activation for the permeation process, R is the universal gas constant, and T is the absolute temperature. The value of E_p for H₂S in polymer C is negative (Fig. 9), i.e., \bar{P} decreases with increasing temperature, whereas E_p for H₂S in polymer E is positive (Fig. 10) and indicates that \bar{P} increases with increasing temperature. The temperature dependence of \bar{P} for NH₃ in polymer K is more complex: \bar{P} increases with increasing temperature at low Δp 's, but passes through a minimum as Δp is raised (cf. Fig. 11). Possible causes for this behavior are suggested in the following section.

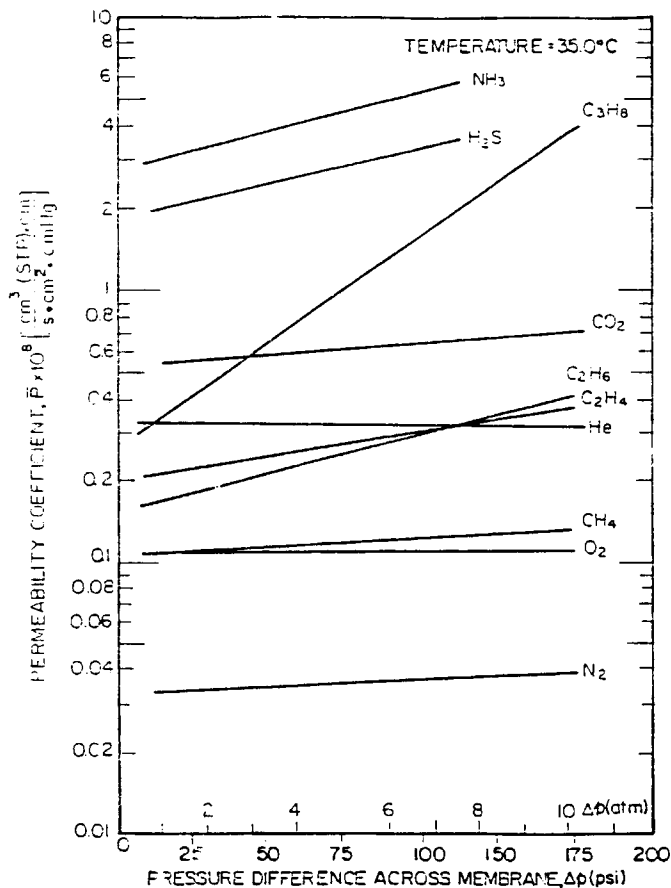


Fig. 5. Mean permeability coefficients as a function of pressure difference across membrane for different gases in poly(*para*-silphenylene siloxane) $\{[\text{Me}_2\text{Si}p\text{-C}_6\text{H}_4\text{SiMe}_2\text{O}]_x\}$ at 35.0°C. The polymer was filler-free.

DISCUSSION

Effect of Polymer Structure

The substitution of different functional groups in the side and backbone chains of silicone polymers was found to have the same effect on the values of \bar{P} for NH₃ and H₂S as was observed with many other gases.¹ Thus, the values of \bar{P} for NH₃ and H₂S decreased markedly as the bulkiness of the substituted functional groups was increased. This effect was more pronounced with the side-chain substitutions. The replacement of the flexible Si—O bonds with stiffer Si—C bonds in the backbone chains, as in polymer G, was also found to result in a considerable decrease in \bar{P} .

An interpretation of the above permeability behavior requires a knowledge of the solubility and diffusivity of NH₃ and H₂S in silicone polymers, since \bar{P} is a product of a mean diffusion coefficient, \bar{D} , and of a solubility coefficient,

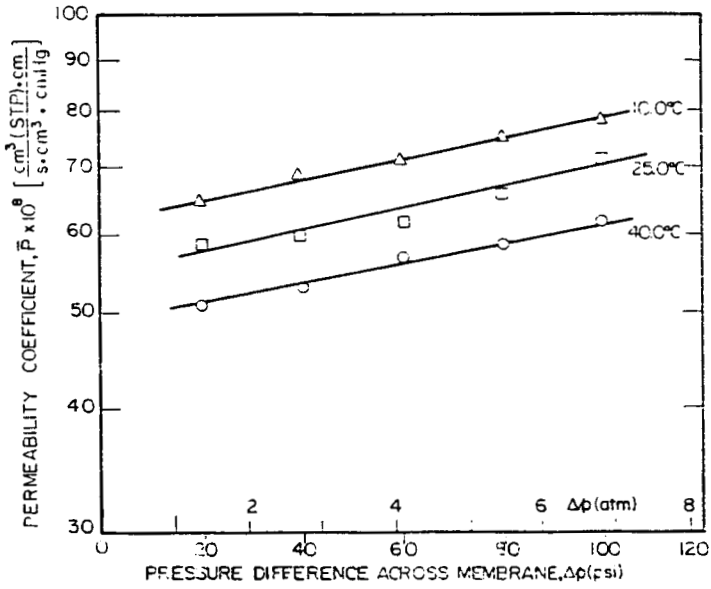


Fig. 6. Mean permeability coefficients as a function of pressure difference across membrane for H₂S in poly(methyl propyl siloxane) [(MePrSiO)_x].

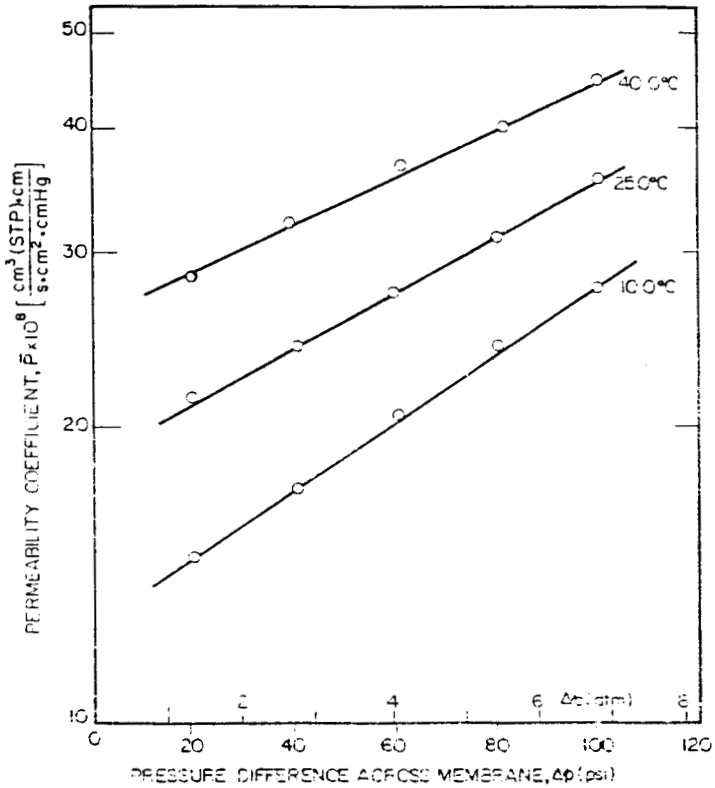


Fig. 7. Mean permeability coefficients as a function of pressure difference across membrane for H₂S in poly(trifluoropropyl methyl siloxane) [(F₃PrMeSiO)_x].

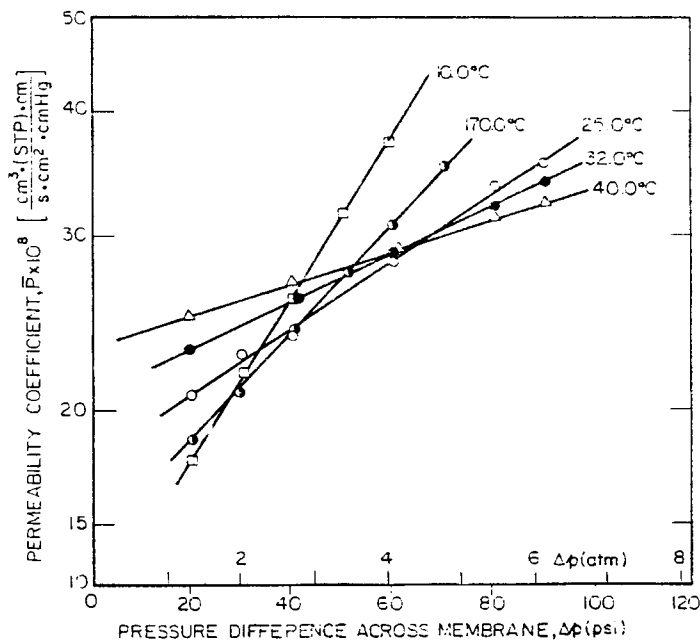


Fig. 8. Mean permeability coefficients as a function of pressure difference across membrane for NH_3 in poly(*meta*-silphenylene siloxane) $\{[\text{Me}_2\text{Si}m\text{-C}_6\text{H}_4\text{SiMe}_2\text{O}]_x\}$.

S:^{1,3,4}

$$\bar{P} = \bar{D} \cdot S, \quad (p_h \gg p_l) \quad (4)$$

\bar{D} and S have been defined elsewhere. No measurements of \bar{D} and S appear to have been reported in the open literature for NH_3 and H_2S in silicone polymers. However, it was observed in a study on the transport of other gases in the same polymers as used here that the decrease in \bar{P} discussed above was mainly due to a decrease in \bar{D} .¹ By comparison, S decreased to a much lesser extent.^{1,2}

The decrease in \bar{D} resulting from the substitution of bulkier functional groups in the silicone polymers is caused by an increasing loss in the segmental mobility, i.e., an increasing stiffness, of the polymer chains. This was evidenced by a corresponding increase in the glass transition temperature, T_g , of the polymers (cf. Table I). The increase in chain stiffness probably is accompanied by a decrease in the free volume of the polymers.

The decrease in the \bar{P} values of NH_3 and H_2S in silicone polymers with increasingly bulkier functional groups is probably also due to the decrease in \bar{D} .

Effect of Penetrant Gas

The above discussion was concerned with the permeability of different silicone polymers to *specific penetrant gases*. The permeabilities of *specific silicone polymers* to different penetrant gases are illustrated in Figures 3–5. These figures show semilogarithmic plots of \bar{P} vs. Δp for NH_3 , H_2S , and eight other gases in polymers A, D, and L at 35.0°C. Additionally, values of

TABLE II
Parameters in Eq. (2)^a

Gas	Temperature, <i>t</i> (°C)	$\log[\bar{P}(\Delta p = 0) \times 10^8]$	$m \times 10^2$ (atm ⁻¹)
<u>Polymer A: (Me₂SiO)_x</u>			
NH ₃	10.0	2.1416	0.9914
	25.0	2.1002	0.7730
	40.0	2.0782	0.5163
H ₂ S	10.0	2.0581	2.0889
	35.0	1.9271	(3.1734)
	55.0	1.8939	0.8255
<u>Polymer B: (MeEtSiO)_x</u>			
NH ₃	10.0	1.6443	2.9233
	25.0	1.6030	1.9101
	40.0	1.5653	1.2285
H ₂ S	10.0	1.5603	3.0382
	25.0	1.5115	2.5150
	40.0	1.4713	1.8914
<u>Polymer C: (MePrSiO)_x</u>			
NH ₃	10.0	1.7133	2.2742
	25.0	1.6931	1.3351
	40.0	1.6765	0.9253
H ₂ S	10.0	1.7831	1.5774
	25.0	1.7332	1.5012
	40.0	1.6745	(1.5811)
<u>Polymer D: (MeOcSiO)_x</u>			
NH ₃	10.0	1.3052	4.3576
	25.0	1.4236	3.2790
	40.0	1.5118	2.8752
H ₂ S	10.0	0.9942	6.7574
	25.0	1.2273	3.7024
	40.0	1.3284	2.9742
<u>Polymer E: (F₃PrMeSiO)_x</u>			
NH ₃	10.0	1.3631	3.7162
	25.0	1.4722	2.7680
	40.0	1.5758	1.8915
H ₂ S	10.0	1.1007	4.9837
	25.0	1.2673	4.0720
	40.0	1.4133	3.3902
<u>Polymer F: (MePhSiO)_x</u>			
NH ₃	10.0	0.7178	4.3175
	25.0	0.9568	2.8433
	40.0	1.0737	(3.8949)
H ₂ S	10.0	0.7610	1.8354
	25.0	0.8450	2.6683
	40.0	0.9629	3.0021

TABLE II
(Continued from the previous page.)

Gas	Temperature, <i>t</i> (°C)	$\log[\bar{P}(\Delta p = 0) \times 10^8]$	$m \times 10^2$ (atm ⁻¹)
<u>Polymer G: (Me₂SiCH₂)_x</u>			
NH ₃	10.0	1.2008	5.5321
	25.0	1.3263	4.1703
	40.0	1.4609	2.8738
H ₂ S	10.0	0.9759	6.9099
	18.0	1.0420	5.3615
	25.0	1.1222	3.0728
	40.0	1.1547	2.9161
<u>Polymer H: [Me₂Si(CH₂)₂SiMe₂O]_x</u>			
NH ₃	10.0	1.8358	2.4842
	25.0	1.7763	2.0269
	40.0	1.6969	2.0949
H ₂ S	10.0	1.7185	5.0193
	25.0	1.7258	3.3732
	40.0	1.7199	2.3167
<u>Polymer I: [Me₂Si(CH₂)₆SiMe₂O]_x</u>			
NH ₃	10.0	1.4682	3.0577
	25.0	1.5489	2.4892
	40.0	1.6000	2.6926
H ₂ S	10.0	1.3376	2.4497
	25.0	1.4176	2.6447
	40.0	1.4867	2.5826
<u>Polymer K: [Me₂Si <i>m</i>-C₆H₄SiMe₂O]_x</u>			
NH ₃	10.0	1.1033	11.6609
	17.0	1.1650	8.0700
	25.0	1.2594	4.9138
	32.0	1.3275	3.3402
	40.0	1.3766	2.1426
H ₂ S	10.0	1.0747	10.8600
	17.0	1.1650	8.0810
	25.0	1.2329	5.8368
	32.0	1.3089	4.4970
	40.0	1.3606	3.5072
<u>Polymer L: [Me₂Si <i>p</i>-C₆H₄SiMe₂O]_x</u>			
NH ₃	10.0	0.2054	5.2453
	25.0	0.3740	4.3143
	40.0	0.5232	3.8138
H ₂ S	10.0	0.0714	4.4318
	25.0	0.2180	3.7423
	40.0	0.2934	(4.2625)

* $\log_{10}(\bar{P} \times 10^8) = \log_{10}[\bar{P}(\Delta p = 0) \times 10^8] + m \cdot \Delta p$. Units: \bar{P} is in cm³(STP) · cm/(s · cm² · cmHg); Δp is in atm.

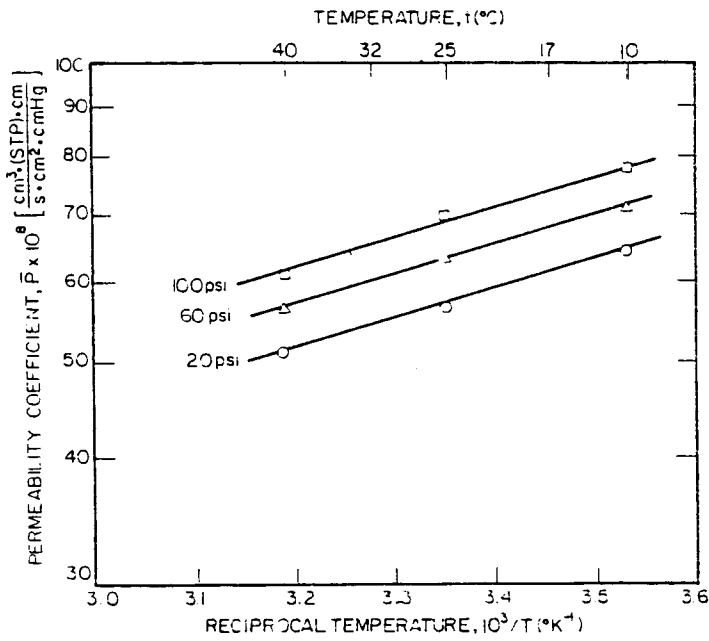


Fig. 9. Arrhenius plots of mean permeability coefficients for H₂S in poly(methyl propyl siloxane) [(MePrSiO)_x].

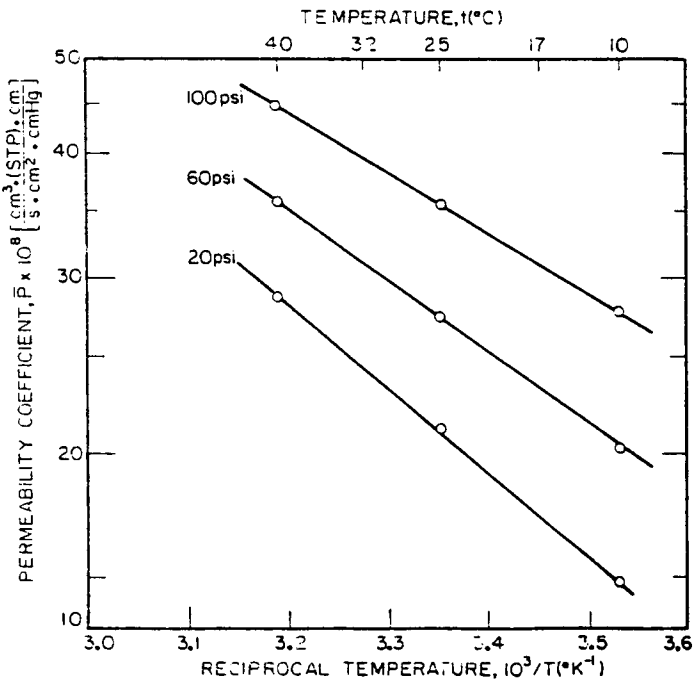


Fig. 10. Arrhenius plots of mean permeability coefficients for H₂S in poly(trifluoropropyl methyl siloxane) [(F₃PrMeSiO)_x].

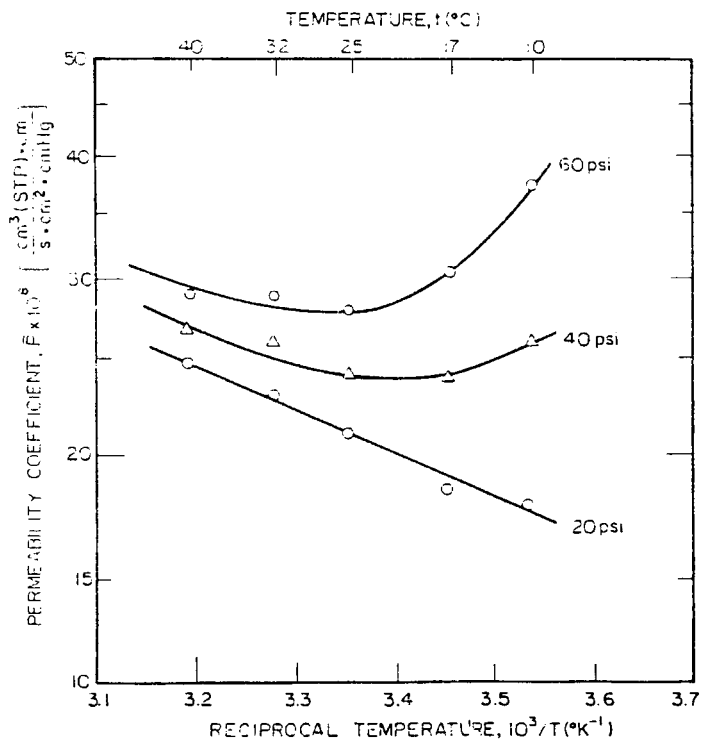


Fig. 11. Arrhenius plots of mean permeability coefficients for NH_3 in poly(*meta*-silphenylene siloxane) $\{[\text{Me}_2\text{Si } m\text{-C}_6\text{H}_4\text{SiMe}_2\text{O}]_x\}$.

$\bar{P}(\Delta p = 0)$ for the above gases in these three polymers are listed in Table III, together with the values of the critical temperature, T_c , and the Lennard-Jones diameter, σ , of the penetrants. The values of $\bar{P}(\Delta p = 0)$, rather than \bar{P} , were selected for comparing the polymer permeabilities to different gases because the plasticizing effects of the penetrants on the polymers are minimized in the limit of $\Delta p = 0$ ($p_h = p_l = 1$ atm). It should be noted that the data for NH_3 and H_2S at 35.0°C were obtained by extrapolation from other temperatures, and therefore could be less accurate than indicated in the previous section.

It can be seen from Figure 3 and Table III that the values of $\bar{P}(\Delta p = 0)$ for different gases in polymer A (polydimethylsiloxane), which is the most highly permeable silicone polymer, generally increase with increasing T_c of the penetrant gas. It has been shown previously that T_c is a "scaling" factor for the solubility of different gases in rubbery polymers.^{2-4,6} This indicates that the *relative* permeability of polymer A and of other highly permeable polymers to different penetrant gases is controlled by the solubility of these gases in the polymers. NH_3 and H_2S have the highest T_c 's of all the gases investigated, and therefore should also exhibit the highest solubility in polymers. This could account for the fact that the highest values of $\bar{P}(\Delta p = 0)$ obtained with the gas/silicone systems studied are those for NH_3 and H_2S . The value of $\bar{P}(\Delta p = 0)$ for NH_3 is higher than that for H_2S not only because $T_c(\text{NH}_3) > T_c(\text{H}_2\text{S})$, and hence the solubility of NH_3 in the silicone polymers

TABLE III
Permeability Coefficients of Penetrant Gases in Three Different Silicone Polymers
at 35.0°C

Penetrant gas	Critical temperature, T_c (K)	Lennard-Jones diameter, σ (Å)	Permeability coefficient, $\bar{P}(\Delta p = 0) \times 10^{10}$ ^a , polymer		
			A	D	L
NH ₃	405.6	2.900	120.2	29.5	2.97
H ₂ S	373.2	3.623	85.5	19.6	1.88
C ₃ H ₈	369.8	5.118	84.5	19.9	0.26
C ₂ H ₆	305.6	4.443	42.0	9.6	0.15
CO ₂	304.2	3.941	47.5	9.2	0.51
C ₂ H ₄	282.4	4.163	36.5	8.1	0.20
CH ₄	190.6	3.758	13.2	3.14	0.102
O ₂	154.6	3.467	9.6	1.92	0.109
N ₂	126.2	3.798	4.7	0.87	0.032
H ₂ ^b	33.2	2.827	9.4	3.11	—
He	5.2	2.551	5.6	1.33	0.324

^aUnits of $\bar{P}(\Delta p = 0) \times 10^{10}$: cm³(STP) cm/(s · cm² · cm Hg).

^bTo be reported elsewhere.

should be higher than that of H₂S, but also because $\sigma(\text{NH}_3) < \sigma(\text{H}_2\text{S})$, and consequently the diffusivity of NH₃ in the polymers should be higher than that of H₂S (cf. Table III).

The permeability of polymer A and of other silicone polymers to He is higher than that expected from the very low critical temperature of this gas ($T_c = 5.2$ K) because of its small molecular diameter ($\sigma = 2.55$ Å), which suggests that the diffusivity of He in the polymers is substantially higher than that of most other gases investigated (except perhaps of H₂ and NH₃). Similarly, the value of $\bar{P}(\Delta p = 0)$ for CO₂ in some silicone polymers is higher than that for C₂H₆, because CO₂ and C₂H₆ probably have similar solubilities in polymers [$T_c(\text{C}_2\text{H}_6) = 305.6$ K and $T_c(\text{CO}_2) = 304.2$ K], but the diffusivity of CO₂ may be higher than that of C₂H₆ [$\sigma(\text{C}_2\text{H}_6) = 4.44$ Å and $\sigma(\text{CO}_2) = 3.94$ Å].

Polymers which are much stiffer than polymer A can better discriminate between penetrant molecules of different sizes and shapes, and thus behave more like "molecular sieves." In such cases, the *relative* permeability of silicone polymers to different gases, i.e., their gas selectivity, is affected by differences in the penetrant diffusivity as well as in the solubility. This behavior is illustrated by the relative values of $\bar{P}(\Delta p = 0)$ for NH₃, H₂S, and other gases in polymer A ($T_g = -123^\circ\text{C}$), polymer D ($T_g = -92^\circ\text{C}$), and polymer L ($T_g = -18^\circ\text{C}$) listed in Table III. As the stiffness of the polymers is increased (T_g increases), the permeability of the polymers to all penetrant gases is decreased. Moreover, the permeability to larger penetrant molecules is decreased to a greater extent than to smaller ones.

Effect of Pressure

Figures 6 to 8 and Table II show that the values of \bar{P} for NH_3 and H_2S increase exponentially with increasing Δp (or p_h) at the temperatures of the present study. This indicates that either \bar{D} or S , or both these coefficients, are exponential functions of Δp (or p_h). Such a behavior is usually observed with penetrant gases which exhibit a high solubility in polymers, and therefore tend to plasticize the polymers. Moreover, the pressure dependence of \bar{P} for NH_3 and H_2S is markedly weaker than that for C_3H_8 , particularly in the case of the less permeable polymers, even though the values of \bar{P} for the three penetrants are of the same order of magnitude. Diffusivity and solubility measurements with the various penetrant/silicone systems are necessary to determine the causes of the above effects.

Effect of Temperature

The temperature dependence of \bar{P} for NH_3 and H_2S in silicone polymers is complex because it depends to different extents on that of \bar{D} and S . \bar{D} always increases with increasing temperature, i.e., the energy of activation for diffusion is positive ($E_d > 0$). The solubility coefficient, S , on the other hand, increases with a decrease in the temperature, i.e., the heat of solution is negative ($\Delta H_s < 0$) (except for very light gases such as He and H_2). The degree of plasticization of the polymer also increases with increasing solubility of the penetrant in the polymer. The energy of activation for permeation E_p , which is the sum of E_d and ΔH_s , can then be either positive or negative depending on the relative values of E_d and ΔH_s . Accordingly, three types of behavior have been observed:

(1) The values of \bar{P} for NH_3 and H_2S in polymers D, E, F, I, and L, and for NH_3 in polymer G, increase exponentially with increasing temperature. This indicates that the temperature dependence of \bar{P} for NH_3 and H_2S in these polymers is dominated by that of \bar{D} , i.e., $E_d > |\Delta H_s|$.

(2) The values of \bar{P} for NH_3 and H_2S in polymers A, B, C, and H decrease with increasing temperature. This indicates that the temperature dependence of \bar{P} is controlled in these cases by that of S , i.e., $|\Delta H_s| > E_d$.

(3) The values of \bar{P} for H_2S in polymer G, and for both NH_3 and H_2S in polymer K, pass through a minimum at high Δp 's as the temperature is raised. A similar behavior has also been observed previously by Stannett and co-workers⁷ for the permeation of organic vapors, such as methyl bromide and isobutene, through polyethylene. These authors have shown that such a behavior is due to the fact that the temperature dependence of \bar{P} is controlled at high temperatures by that of \bar{D} and at low temperatures by that of S [cf. eq. (4)]. Since \bar{D} always increases with increasing temperature whereas S decreases, \bar{P} passes through a minimum over a sufficiently wide temperature range.

CONCLUSIONS

The permeation behavior of NH_3 and H_2S in different types of silicone polymers is consistent with that of other penetrant gases studied earlier,¹ taking into account the critical temperature and the molecular size of these gases.

Direct measurements of \bar{D} and/or S for NH₃ and H₂S in different silicone polymers are necessary to quantify the relative contributions of these coefficients to the observed dependence of \bar{P} on polymer structure, nature of penetrant gas, pressure, and temperature.

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