Gas Permeation Through Lexan Polycarbonate Resin

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Introduction and Procedure

Lexan is a thermoplastic polymer, a polycarbonate [poly(dimethyl-methylene diphenylene carbonate)], made by General Electric Company. It has high impact strength and good optical, electrical, and heat-resisting properties. This study is the measurement of permeation rate, diffusion constants, and solubility of various gases in commercial-grade cast film, 0.005 in. thick.

The permeation cell, of stainless steel, clamped the film so it could be degassed with vacuum on each side. For the measurements, the low-pressure side led directly to a mass spectrometer. Gas was applied to the high-pressure side, and observation made of the mass peak for that particular gas. This came up to a steady-state flow and the peak height represented the permeation rate directly. It was calibrated by a subsidiary leak system[1] in cubic centimeters per second.

The time required to come to steady state yields the diffusion constant. Daynes[2] showed that for film thickness d in centimeters and time lag L in seconds, the diffusion constant $D = d^2/6L$. The units here used are: (1) permeation rate P in cubic centimeters of gas (STP) per second per square centimeter area per millimeter thickness for 1 cm. Hg gas pressure difference; (2) D is diffusion constant in square centimeters per second; (3) S is solubility in cubic centimeters gas (STP) per cubic centimeter polymer for 1 atm. (76 cm.) applied. For the preceding units, there is the relationship $7.6\,P = DS$.

Crank[3] has shown that, by using the proper boundary conditions, the solution of Fick's differential diffusion equations will yield the simple relationship above, if (1) the diffusion constant D is independent of solute concentration, and (2) the solubility of the gas, S, obeys Henry's Law. These conditions are, in general, fulfilled for the gases here studied. Some deviations might be expected for the highly soluble CO_2 and H_2O.

Results

The permeation rates measured at various temperatures were plotted as $\log_{10}P$ vs. $1000/T$, yielding straight lines with an inflexion (for Ar, O_2, and N_2) at about 130°C. This is just below the glass transition T_g of

TABLE I

Permeation Rate P of Oxygen and Nitrogen through Lexan

(Units: cm.³ gas (STP) per sec. per cm.² area per mm. thick per cm.
Hg gas pressure difference)

Temp., °C.	Nitrogen		Oxygen	
	P	$\log P$	P	$\log P$
0	1.1×10^{-10}	$\overline{10}.05$	6.7×10^{-10}	$\overline{10}.82$
25	3.0×10^{-10}	$\overline{10}.48$	1.4×10^{-9}	$\overline{9}.15$
50	6.7×10^{-10}	$\overline{10}.82$	2.6×10^{-9}	$\overline{9}.42$
75	1.3×10^{-9}	$\overline{9}.12$	4.5×10^{-9}	$\overline{9}.65$
100	2.2×10^{-9}	$\overline{9}.34$	6.8×10^{-9}	$\overline{9}.83$
125	3.7×10^{-9}	$\overline{9}.57$	1.0×10^{-8}	$\overline{8}.00$
150	9.0×10^{-9}	$\overline{9}.95$	1.8×10^{-8}	$\overline{8}.25$
175	1.9×10^{-8}	$\overline{8}.28$	3.0×10^{-8}	$\overline{8}.47$

TABLE II

Permeation Rate P of Hydrogen, CO_2, and SF_6 through Lexan

(Units: cm.³ gas (STP) per sec. per cm.² area per mm. thick per cm.
Hg gas pressure difference)

Temp., °C.	Hydrogen		CO_2		SF_6	
	P	$\log P$	P	$\log P$	P	$\log P$
25	1.2×10^{-8}	$\overline{8}.07$	8.0×10^{-9}	$\overline{9}.90$	6.5×10^{-15}	$\overline{15}.8$
50	2.5×10^{-8}	$\overline{8}.40$	1.3×10^{-8}	$\overline{8}.13$	3.3×10^{-14}	$\overline{14}.52$
75	4.5×10^{-8}	$\overline{8}.65$	2.2×10^{-8}	$\overline{8}.33$	1.2×10^{-13}	$\overline{13}.10$
100	7.1×10^{-8}	$\overline{8}.85$	2.7×10^{-8}	$\overline{8}.43$	5.0×10^{-13}	$\overline{13}.7$
125	1.1×10^{-7}	$\overline{7}.05$	—	—	1.3×10^{-12}	$\overline{12}.10$
150	1.7×10^{-7}	$\overline{7}.23$	—	—	1.1×10^{-11}	$\overline{11}.05$
175	2.4×10^{-7}	$\overline{7}.38$	—	—	1.0×10^{-10}	$\overline{10}.00$

TABLE III

Permeation Rate P of the Rare Gases through Lexan

(Units: cm.³ gas (STP) per sec. per cm.² area per mm. thick per cm.
Hg gas pressure difference)

Temp., °C.	Argon		Neon		Helium	
	P	$\log P$	P	$\log P$	P	$\log P$
0	4.3×10^{-10}	$\overline{10}.63$				
25	8.0×10^{-10}	$\overline{10}.90$			1.0×10^{-8}	$\overline{8}.00$
50	1.65×10^{-9}	9.22			1.9×10^{-8}	$\overline{8}.27$
75	3.2×10^{-9}	$\overline{9}.50$			3.3×10^{-8}	$\overline{8}.52$
100	5.0×10^{-9}	$\overline{9}.70$	1.45×10^{-8}	$\overline{8}.16$	4.8×10^{-8}	$\overline{8}.68$
125	8.0×10^{-9}	$\overline{9}.90$			7.1×10^{-8}	$\overline{8}.85$
150	1.8×10^{-8}	$\overline{8}.25$				
175	4.3×10^{-8}	$\overline{8}.63$				

TABLE IV
Activation Energies for the Permeation Process through Lexan

Gas	Below 125°C.	Above 125°C.
CO_2	3800	—
O_2	4600	7400
He	4800	—
Ar	5400	13000
H_2	5400	5400
N_2	6000	10000
SF_6	—	30000

TABLE V
Diffusion Constant D of Gases through Lexan
(Units: cm.²/sec.)

Temp., °C.	Ar	H_2	O_2	N_2	CO_2	SF_6
0	5.3×10^{-9}	3.0×10^{-7}	6.7×10^{-9}		1.2×10^{-9}	
25	1.5×10^{-8}	6.4×10^{-7}	2.1×10^{-8}		4.8×10^{-9}	(1.0×10^{-13})
50	3.3×10^{-8}	1.1×10^{-6}	5.4×10^{-8}		1.5×10^{-8}	
75	6.4×10^{-8}		1.3×10^{-7}		4.7×10^{-8}	
100	1.2×10^{-7}		2.4×10^{-7}		1.0×10^{-7}	
125	2.1×10^{-7}			2.0×10^{-7}		
150	3.3×10^{-7}					
175	5.3×10^{-7}					2.5×10^{-8}

TABLE VI
Activation Energies (cal./mole) for Diffusion of Gases through Lexan

H	5000
Ar	6000
H_2O	6200
O	7700
CO_2	9000
SF_6	20000 (approx.)

TABLE VII
Equilibrium Solubility in Lexan at 25°C.

Solute gas	Solubility S, cc. gas (STP)/cc. polymer (76 cm. applied)
H_2O	169.0
CO_2	12.6
O_2	0.51
SF_6	0.50
Ar	0.42
H_2	0.14

TABLE VIII

Lexan: Summary of Data at 25°C.

Gas	Diff. const. D	Permeation rate P	Solubility S
H_2	640×10^{-9}	120×10^{-10}	0.14
H_2O	68×10^{-9}	14000×10^{-10}	169.0
O_2	21×10^{-9}	14×10^{-10}	0.51
Ar	15×10^{-9}	8×10^{-10}	0.42
CO_2	4.8×10^{-9}	80×10^{-10}	12.6
SF_6	1.0×10^{-13}	6.5×10^{-15}	0.50

Lexan, at about 140°C. Above this the polymer is rubbery, below it is tough and glassy in nature.

From these plots, tables of permeation rates were constructed, and from the slopes of the graphs the activation energies for permeation were derived,
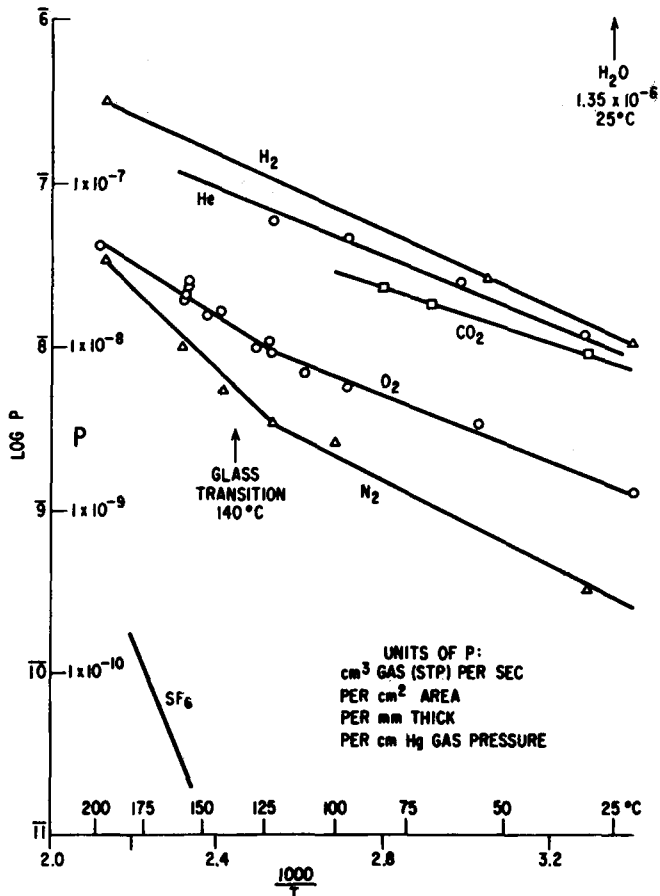
Fig. 1. Gas permeation rate P through Lexan.

as given in Table IV.   The time lag technique led to the graphs of diffusion constants (Table VI, the activation energy for diffusion).

The graph of $\log_{10}D$ vs. $1000/T$ does not show an inflexion.   This means that if the relationship 7.6 $P = DS$ holds, the solubility of the gas in the solid must go through a minimum with change of sign of the heat of solution as the temperature is raised.   This is shown in Figure 8 for O_2 and argon.
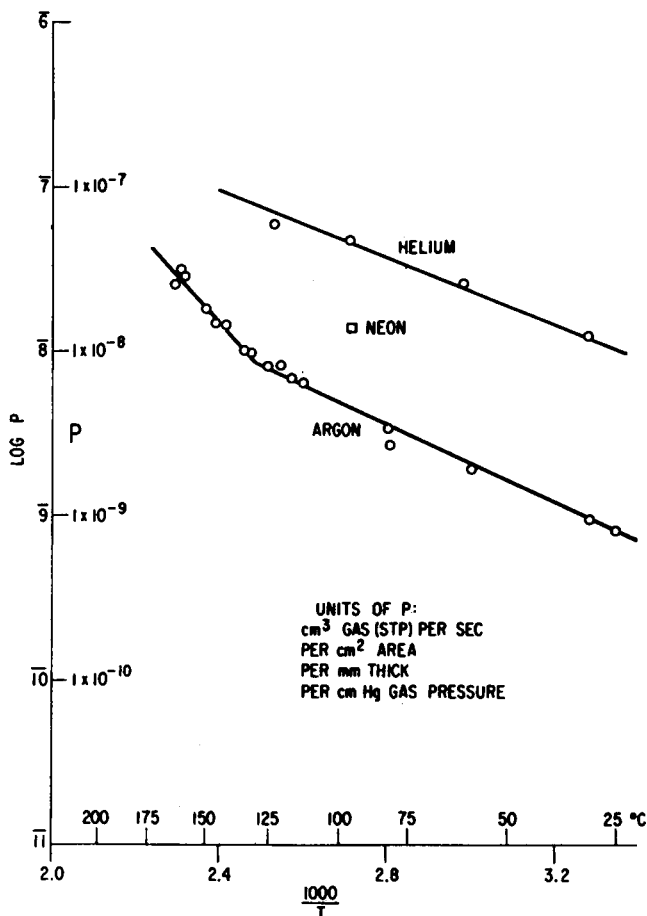
Fig. 2. Gas permeation rate P: rare gases through Lexan.

Such a minimum has also been observed by Meares[4] for various gases in polyvinyl acetate.

It was also found that a plot of $\log_{10}D$ vs. molecular weight gave a fairly linear relationship for the gases measured, with H_2O and argon somewhat off the curve.   A plot of activation energy for diffusion against molecular weight is also linear, with argon not on the line.   The big molecule SF_6 is on the line, and this has very large activation energies: 30,000 cal. for
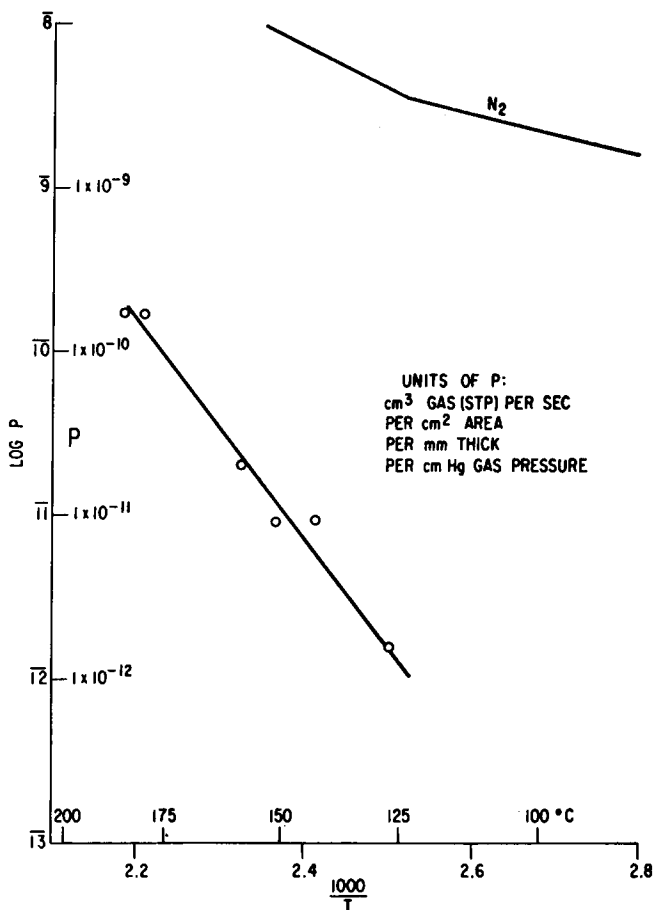
Fig. 3. Permeation rate P of SF_6 through Lexan.

permeation and about 20,000 cal. for diffusion of the SF_6 in Lexan. There are no such regularities relating permeation rates and gas molecular weight.

Discussion

The case of SF_6 permeating through Lexan is interesting because its rate, even at 175°C., is 150 times lower than any of the other gases measured, and it has a very steep decrease with diminishing temperature. This is measured by the activation energy which, for SF_6 above the T_g, is 30,000 cal. Other gases (except H_2) have about half as much activation energy for permeation below T_g as they have above. Applying this to SF_6–Lexan, we may extrapolate a permeation rate at 25°C. of 6.5×10^{-15}. This is very low for a gas–polymer system. A hollow cube, 1 cm. on a side with 5-mil walls of Lexan and filled with an atmosphere of SF_6, would lose only
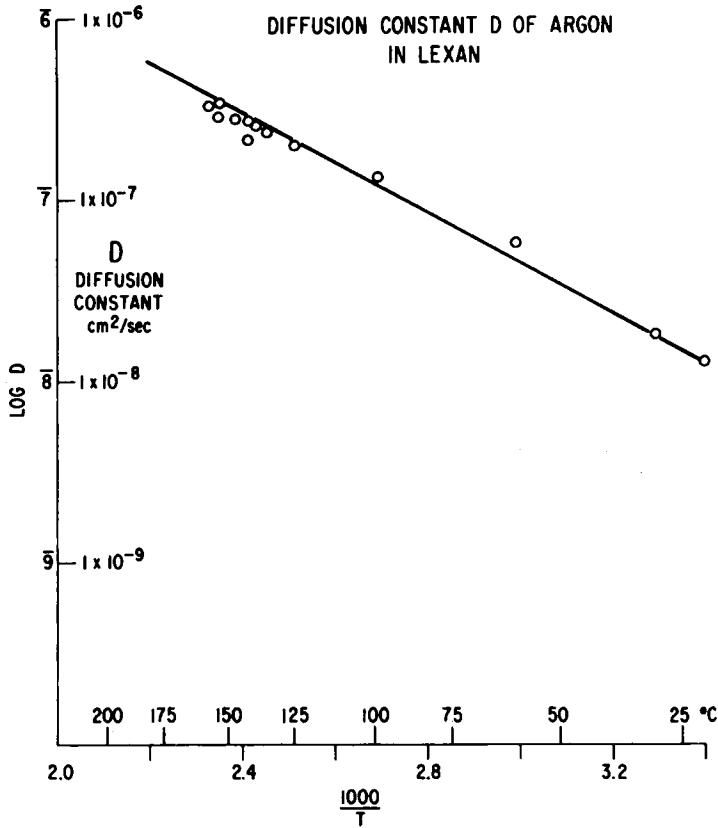
Fig. 4. Diffusion constant D of argon in Lexan.

1% of its charge in 13 years. If it were filled with argon this 1% would be lost in a little over 1 hr.

The permeation rates cover a great range, at 25°C., depending on the nature of the gas permeating the solid. For water,[6,7] $P = 1.4 \times 10^{-6}$, and for SF_6 (a good dielectric gas) $P = 6.5 \times 10^{-15}$ (extrapolated)—a range of nearly 10^9.

Another noteworthy fact is that CO_2 permeates nearly as fast as the small molecules H_2 and He. This undoubtedly related to the presence of CO_2-like units in the structure and the diffusing CO_2 interacting with the polar polycarbonate polymer. Water, being highly polar, has the highest permeation rate of all the gases at 25°C.

Related to these factors is the fact that at 25°C. the solubility of H_2O and CO_2 in Lexan is very high compared with that of other gases. So, even though their diffusion constants are not exceptionally large, the permeation rates for H_2O and CO_2 are high, because their solubilities are high, and this operates through the relationship 7.6 $P = DS$. From this relationship for CO_2, there was found the high solubility of 12.6 cc. of gas (STP) per cubic

centimeter of polymer, 76 cm. CO_2 gas pressure applied.   To check this by an independent method, 32 g. of 5-mil Lexan (this is 26.8 cc. of the polymer, density 1.2) were rolled and packed into a free volume of 61 cc., a vacuum manometer attached.   This system was evacuated at 27°C. overnight.   Then an atmosphere, 76 cm. of CO_2, was admitted and the system sealed.   The CO_2 pressure started to drop at once as the gas dissolved rapidly in the polymer.   After sealing, the CO_2 pressure was 520 mm. 6
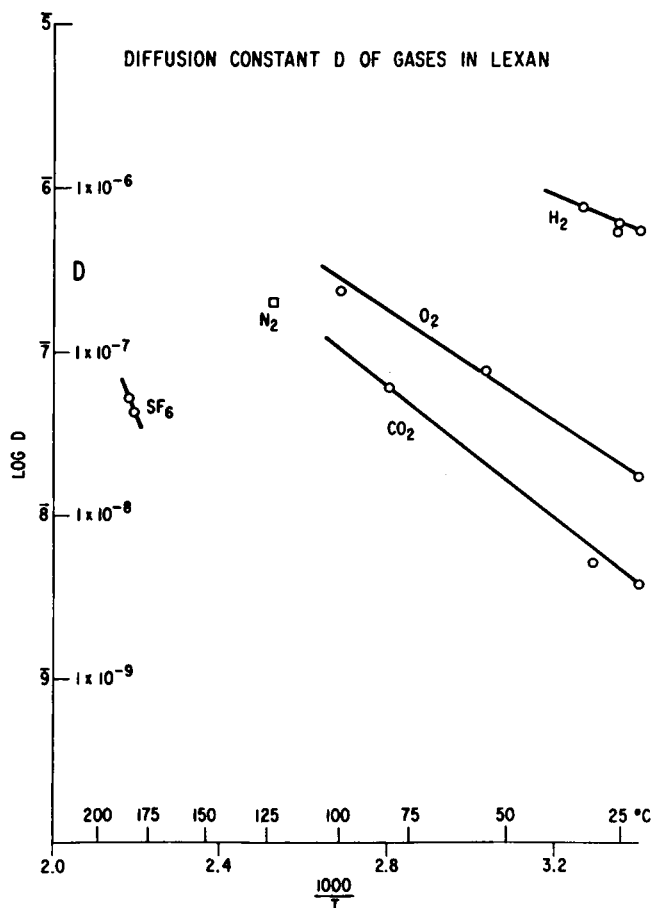
Fig. 5. Diffusion constant D of gases in Lexan.

min. later 370 mm., and after 30 min. (1800 sec.) it was 140 mm.   The final equilibrium pressure of CO_2 at 27°C. was 100 mm.   The volumes involved being known, the CO_2 absorbed was found to be 46.8 cc. STP; this is with 100 mm. equilibrium CO_2 pressure on the polymer.   If Henry's law holds, putting 760 mm. on would give (760 × 46.8 cc. gas)/(100 × 26.8 cc. polymer) = 13.3 as S, the solubility.   The other method gave 12.6 The solubility data by the two methods are given in Figure 9.
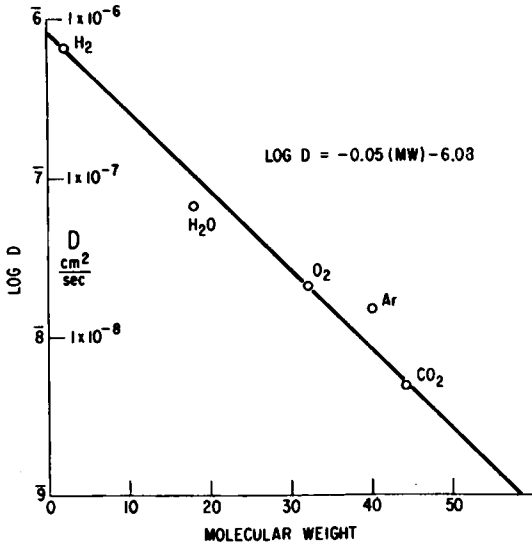
Fig. 6. Relationship between log of diffusion constant D and molecular weight for gases in Lexan 25°C.
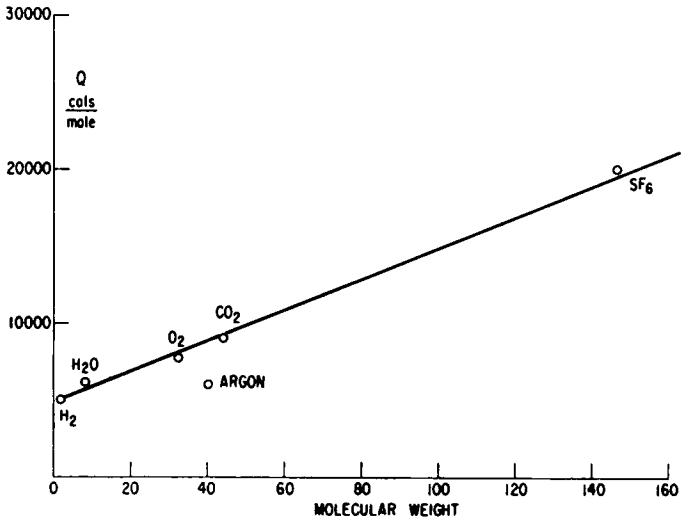

Fig. 7. Activation energy Q for gas diffusion in Lexan and gas molecular weight.

The diffusion constant for CO_2 in Lexan found by the mass spectrometer–time lag methods can also be checked from the rate of CO_2 uptake by the polymer. Several excellent papers and charts by Newman[5] describe the use of the very useful dimensionless Fourier number, F, in diffusion calculations. It is applied here for CO_2 pickup in a 5-mil Lexan sheet, $a = \frac{1}{2}$ thickness $= 2.5$ mil. For the diffusion process in an infinite slab, $Dt/a^2 = F$, where t is time in seconds and $a^2 = 4 \times 10^{-5}$ cm². At 360 sec. the
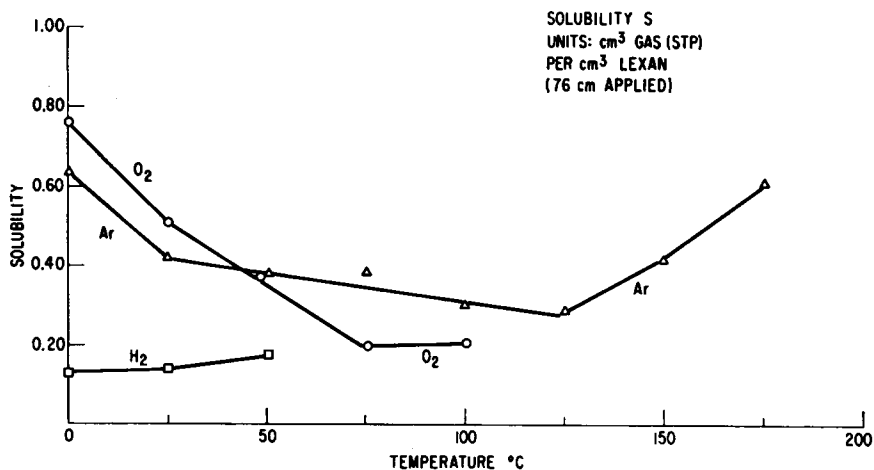
Fig. 8. Solubility S of gases in Lexan.
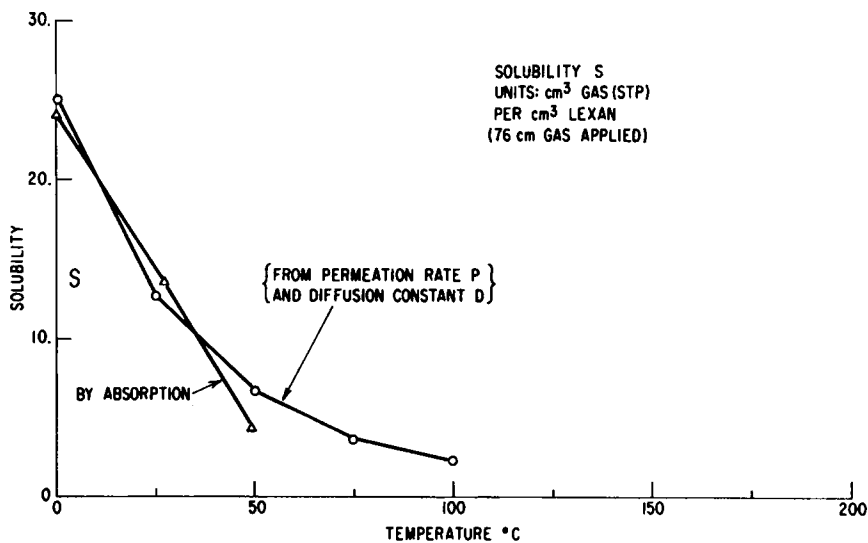
Fig. 9. Solubility S of CO_2 in Lexan.

pressure of 370 mm. is 0.71 of the initial CO_2 pressure of 520 mm. in the absorption apparatus. For the fraction 0.71 left, $F = 0.066$, $D = a^2F/t = (4 \times 10^{-5} \times 6.6 \times 10^{-2})/(3.6 \times 10^2) = 7.3 \times 10^{-9}$ by the absorption method. By the mass spectrometric–time lag technique $D = 5.4 \times 10^{-6}$.

Water and Lexan

The permeation rate, diffusion constant, and solubility of water in Lexan can be calculated from the data of General Electric Company[6] and Christopher and Fox.[7]

The equilibrium water absorption at 25°C. is 0.35 wt.-%. This is calculated to these units of S as follows: 18 g. H_2O = 22400 cc. gas STP,

or $18/2.24 \times 10^4 = 8 \times 10^{-4}$ g. H_2O/cc. gas, and 1.25×10^3 cc. gas (STP)/g. H_2O.

Hence, $0.35 \times 1.25 \times 10^3 = 438$ cc. gas/100 g. polymer or 4.38 cc./g. At density 1.2, this is 4.38 cc. gas/0.83 cc. polymer, yielding 5.28 cc. gas (STP)/cc. polymer. This is at 25°C. where the vapor pressure of water is 2.38 cm.

On calculating this to the theoretical condition of 76 cm. of gas pressure applied, S comes out $(76/2.38) \times 5.28 = 169.0$. This is about 13 times the CO_2 solubility. The diffusion constants of water in Lexan may be roughly estimated, together with the permeation rates as:

Temp.	P	D
25°C.	1.4×10^{-6}	6.8×10^{-7}
100°C.	—	6.0×10^{-8}

Tables I–VIII and Figures 1–9 present all of the measurements for the various gases.

Thanks are due T. R. Calkins for his experimental data on Lexan–water.

References

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7. Christopher, W. F., and D. W. Fox, *Polycarbonates*, Reinhold, New York, 1962, p. 48.

Synopsis

Values have been determined over a considerable temperature range for the permeation rate, diffusion constant, and solubility of the following gases in Lexan: H_2, H_2O, He, Ne, O_2, argon, CO_2, and SF_6. There is some discussion of the interrelationships and the variation of activation energies with molecular weight.

Résumé

Des valeurs de vitesse de perméation, de constante de diffusion et de solubilité ont été déterminées dans un domaine considérable de température pour les gaz suivants dans le Lexan: H_2, H_2O, He, Ne, O_2, argon, CO_2 et SF_6. On discute des relations entre ces valeurs, et de la variation des énergies d'activation avec le poids moléculaire.

Zusammenfassung

In einem grösseren Temperaturbereich wurden Werte der Permeations-geschwindigkeit, Diffusionskonstanten und Löslichkeit folgender Gase in Lexan bestimmt: H_2, H_2O, He, Ne, O_2, Argon, CO_2 und SF_6. Die gegenseitigen Beziehungen und die Abhängigkeit der Aktivierungsenergien vom Molekulargewicht werden diskutiert.