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Permeation of Sulfur Dioxide Through Polymers

R. M. Felder,[1] R. D. Spence, and J. K. Ferrell
Department of Chemical Engineering, North Carolina State University, Raleigh, N.C. 27607

Permeabilities, diffusivities, solubilities, and activation energies for permeation and diffusion are reported for the permeation of SO_2 through various polymers. Effects of gas pressure and humidity and membrane plasticization on SO_2 permeabilities are summarized.

The permeability of a polymer to a gas or vapor is the ratio $J/(\Delta p/h)$, where J is the flux of the gas through a flat membrane of thickness h, and Δp is the partial pressure difference across the membrane. If the equilibrium sorption of the gas in the polymer varies linearly with the partial pressure in the gas phase and diffusion of the gas through the polymer is Fickian with a constant diffusivity, then

$$P = DS \qquad (1)$$

where P is permeability, $cm^3(STP)/sec{\cdot}cm{\cdot}cm\ Hg$; D is diffusivity, cm^2/sec; and S is solubility, $cm^3(STP)/cm^3{\cdot}cm\ Hg$.

The temperature dependence of gas permeabilities frequently follows an Arrhenius relationship

$$P = P_0 \exp\left(-E_p/RT\right) \qquad (2)$$

where E_p is the activation energy for permeation. Techniques for the measurement of P, D, and S are reviewed by Crank and Park (*6*), and factors which affect the values of these parameters are discussed by Stannett (*34*).

SO_2 permeabilities of a number of materials have been measured at temperatures from 25° to 232°C, and activation energies for permeation have been calculated. This paper reports the results of these experiments. In the course of this study, a literature search on the permeation of SO_2 through polymers was carried out, covering references through April 1974. Relatively few reported permeabilities were found, but a number of papers presented permeation rate data from which permeabilities could be calculated. These calculations have been performed, and the results are also reported in this paper.

Experimental

Span gas mixtures of SO_2 in air with SO_2 concentrations in the range 1,000–10,000 ppm were passed on one side of a flat polymer membrane or on the outside of a hollow tube in a thermostatically controlled oven. SO_2 permeated through the polymer into a carrier gas stream of pure air, which passed to an SO_2 analyzer. The SO_2 permeation rate was calculated as the product of the carrier gas flow rate and the SO_2 concentration in this gas at steady state; the permeability of the polymer to SO_2 was then calculated from the permeation rate, the SO_2 partial pressures in the span gas and the carrier gas, and the dimensions of the membrane or tube.

The experimental and calculational procedures for determining permeabilities and the permeation chamber used for hollow tubes are described in detail by Rodes et al. (*23*). A two-piece hollow stainless-steel cylinder with o.d. = 7.62 cm, i.d. = 5.08 cm, and outside height = 7.0 cm was used as a permeation chamber for flat membranes. The membranes were clamped between the two halves of the chamber, and the span gas and carrier gas were fed into the chamber on opposite sides of the membrane. The entrance and exit ports were situated so that the gases entered tangentially and swept across the entire membrane surface before exiting.

Span gas SO_2 concentrations were determined by passing a measured volume of the gas through a 3% H_2O_2 solution to absorb the SO_2, and then titrating with a 0.01*N* barium perchlorate solution in the presence of Thorin indicator (*9*). Carrier gas SO_2 concentrations were measured with a Meloy Laboratories Model SA-160 total sulfur analyzer or an Envirometrics Model NS-300M SO_2 analyzer.

Permeabilities, Diffusivities, and Solubilities

Materials for which SO_2 permeabilities, diffusivities, and/or solubilities have been found include TFE Teflon, FEP Teflon, several silicone and fluorosilicone rubbers, polyvinyl fluoride (Tedlar), polyvinylidene fluoride (Kynar), polycarbonate (Lexan), polyethylene, polypropylene, polyvinyl chloride, copolymers of polyvinyl chloride and polyvinylidene chloride, several natural rubbers, polyisobutene, polymethyl methacrylate, polyethylterephthalate (Mylar), several cellulosic films, a

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[1] To whom correspondence should be addressed.

chlorinated polyether (Penton), and a polyethylene glycol liquid membrane. Although most of the data are for temperatures in the range 15–30°C, permeabilities have been measured over temperature ranges broad enough to permit the determination of activation energies for TFE and FEP Teflon, a fluorosilicone and a silicone rubber, polyethylene, polyvinyl fluoride, and polyvinylidene fluoride. Measured and estimated permeabilities, diffusivities, and solubilities are summarized in Table I, and Arrhenius law parameters are listed in Table II.

The permeabilities of TFE and FEP Teflon are similar, despite the probable differences in the degree of crystallinity of these two substances. This result supports a claim by Stern et al. (*35*) that the two substances have similar permeabilities but conflicts with assertions by Saltzman et al. (*24, 25*) that TFE may be as much as 10 times more permeable than FEP at the same temperature.

Extended use at temperatures close to 200°C did not affect either TFE or FEP, either in physical appearance or in permeability to SO_2. The fluorosilicone rubber (Dow-Corning: SILASTIC LS-63U®) maintained a constant permeability with extended usage, although it underwent a discoloration and deteriorated when subjected to an acid mist environment. The silicone rubber (Dow-Corning: SILASTIC 437®) became brittle at high temperatures (*23*), probably owing to attack by SO_2 (*16*).

Permeabilities of SO_2 in TFE Teflon are summarized on an Arrhenius plot in Figure 1. The high-temperature permeabilities determined in the present study and by Rodes et al. (*23*) are consistent with the permeability reported by Jordan (*15*) at a temperature presumably in the range 20–30°C. Values estimated from SO_2 permeation tube emission rate data (*17*) are substantially out of line with the other permeabilities, but the degree of uncertainty in the tube dimensions used to obtain these values is sufficient to account for the discrepancy.

An Arrhenius plot of SO_2 permeabilities in FEP Teflon is shown in Figure 2. A single line correlates the measured and estimated permeabilities reasonably well, except for values reported by Benarie and Bui-the-Chuong (*1*) and estimated from permeation tube emission rates reported by Stevens et al. (*36*) and Metronics, Inc. (*17*). Permeabilities obtained for flat membranes 0.02–0.1 mm thick were consistently 5–20% higher than values obtained for cylindrical tubes with wall thicknesses in the range 0.3–0.7 mm.

Stern et al. (*35*) indicate that a phase change occurs in FEP Teflon at 60°C which might affect its permeability. Figure 2 suggests that this effect is minimal, if it exists at all.

SO_2 permeabilities in silicone and fluorosilicone rubbers are shown in Figure 3. The permeability of SO_2 in these materials is between one and two orders of magnitude higher than that in Teflon, and the activation energy for permeation of the silicones is much lower than that of Teflon. High SO_2 permeabilities are also found for dimethyl silicone rubbers, which are discussed by Robb (*22*), Hodgson (*13*), and an undated General Electric brochure (*11*). Permeabilities calculated at high temperatures for a fluorosilicone rubber in the present study and by Rodes et al. (*23*) do not agree particularly well; however, the material in question was not available commercially when the latter measurements were made, and the differences in the permeabilities of different tubes might reflect a difference in fabrication methods from one batch to another.

SO_2 permeabilities in polyethylene are given by several authors (*1, 3, 7, 12, 15*). The permeability reported by Jordan

Table I. SO_2 Permeabilities, Diffusivities, and Solubilities

Material	Temp, °C	$P \times 10^{10a}$	$D \times 10^{10b}$	S^c	Source
TFE Teflon tube	99	64.7	...	...	Present study
o.d. = 0.959 cm	128	107.	...	...	
i.d. = 0.806 cm	131	105	...	...	
	154	157.^{d}	...	...	Felder et al. (*10*)
	154	147.^{d} (21.1% H_2O)	...	...	
	173	212.	...	...	Present study
	175	242.	...	...	
	175	249.	...	...	
	179	221.^{d}	...	...	Felder et al. (*10*)
	179	231.^{d} (21.1% H_2O)	...	...	
	202	407.^{d}	...	...	
	230	473.	...	...	Present study
	241	557.	...	...	
TFE Teflon tube	52	14.9	...	...	
o.d. = 0.604 cm	68	17.7	...	...	
i.d. = 0.544 cm	87	34.9	...	...	
	127	55.2	...	...	
TFE Teflon tube heat-shrunk on	152	145.	...	...	
a porous sintered stainless-	175	197.	...	...	
steel tube	201	285.	...	...	
TFE Teflon	20	11.4^{j,k}	...	...	Metronics (*17*)
	25^l	5.1	1300.	0.04	Jordan (*15*)
	30	17.8^{j,k}	...	...	Metronics (*17*)
	40	26.5^{j,k}	...	...	
	93.3	29.9	...	...	Rodes et al. (*23*)
	121	53.9	...	...	
	121	57.6	...	...	
	149	92.3	...	...	
	177	181.	...	...	
	177	154.	...	...	
	204	234.	...	...	
	232	448.	...	...	
	232	427.	...	...	

Table I. Continued

Material	Temp, °C	$P \times 10^{10}$[a]	$D \times 10^{10}$[b]	S[c]	Source
FEP Teflon tubes	127	60.	...	...	Present study
	158	124.	...	...	
	175	256.[d]	...	...	Felder et al. (*10*)
	175	262.	...	...	Present study
	180	203.[d]	...	...	Felder et al. (*10*)
	201	384.[d]	...	...	
FEP Teflon heat-shrunk on a porous sintered stainless-steel tube	126	68.4	...	...	Present study
	127	73.9	...	...	
	152	128.	...	...	
	181	242.	...	...	
	196	316.	...	...	
FEP Teflon tube heat-shrunk on a stainless-steel coil	211.5	457.	...	...	
FEP Teflon tube heat-shrunk with no support	124	62.4	...	...	
	125	65.5	...	...	
	150	120.	...	...	
	179	219.	...	...	
	194	285.	...	...	
FEP Teflon membrane 0.00263 cm thick	24	5.84	...	...	
	47	11.9[j]	...	...	
	48	13.6	...	...	
	73	26.5[j]	...	...	
	85	37.4 (32.5% H_2O)	...	...	
	94	50.9	...	...	
	97	44.7 (32.5% H_2O)	...	...	
	115	91.7	...	...	
	122	85.0	...	...	
FEP Teflon membrane 0.0144 cm thick	74	22.3	...	...	
	122	96.8	...	...	
	147	103.	...	...	
	149.5	179.	...	...	
FEP Teflon	13.8	1.6[k]	...	...	O'Keefe and Ortman (*19*)
	20	2.6[k]	...	...	Scaringelli et al. (*31*)
	20	3.2[k]	...	...	
	20	2.3[j,k]	...	...	Metronics (*17*)
	20.1	2.4[k]	...	...	O'Keeffe and Ortman (*19*)
	20.3	46.8[k]	...	...	Stevens et al. (*36*)
	22	65.8	70	0.922	Benarie and Bui-the-Chuong (*1*)
	25	3.3[j,k]	...	...	Saltzman et al. (*26*)
	25	3.4[j,k]	...	...	
	25	4.0[j,k]	...	...	
	25	4.2	...	...	
	25	4.0[j,k]	...	...	
	25	4.0[j,k]	...	...	
	25	3.3[j,k]	...	...	
	25	3.5[j,k]	...	...	
	29.1	3.6[k]	...	...	O'Keeffe and Ortman (*19*)
	30	7.1[j,k]	...	...	Dietz et al. (*8*)
	30	3.8[j,k]	...	...	Metronics (*17*)
	30	4.5	...	...	
	40	5.8[j,k]	...	...	
	40	7.4[j,k]	...	...	
	50.5	17.4[j,k]	...	...	Dietz et al. (*8*)
	60	24.6[j,k]	...	...	
Tecsil (silicone rubber)	22	11,800	...	...	Benarie and Bui-the-Chuong (*1*)
Silastic LS-63® (silicone rubber)	121	2,620	...	...	Rodes et al. (*23*)
	177	2,810	...	...	
	204	3,130	...	...	
	232	3,480	...	...	
Dimethyl silicone (25%)	25	11,450	...	...	General Electric (*11*)
	25	13,730	...	...	Robb (*22*)
Dimethyl silicone peroxide cured, silica filler	25[l]	43,630[j]	...	...	Hodgson (*13*)
Silastic LS-63U® (fluorosilicone rubber) tube o.d. = 0.929 cm i.d. = 0.521 cm	129	3,180	...	...	Present study
	160	3,330	...	...	
	175	3,130[d]	...	...	Felder et al. (*10*)
	177	3,240[d] (21.1% H_2O)	...	...	
	183	3,350	...	...	Present study

(Continued on page 238)

Table I. Continued

Material	Temp, °C	$P \times 10^{10}$[a]	$D \times 10^{10}$[b]	S[c]	Source
	195	3,290[d]	...	...	Felder et al. (*10*)
	195	3,350[d] (21.1% H_2O)	...	...	
	225	3,340[d]	...	...	
	225	3,430[d] (21.1% H_2O)	...	...	
Silastic LS-63U® tube	27	2,720	...	...	Present study
o.d. = 0.848 cm	44	2,950	...	...	
i.d. = 0.744 cm	68	3,290	...	...	
	100	3,350	...	...	
	129	3,650	...	...	
Silastic LS-63U tubes	121	2,360	...	...	Rodes et al. (*23*)
	149	2,580	...	...	
	177	2,880	...	...	
	204	3,160	...	...	
Polyvinyl fluoride (Tedlar)	70	15.5	...	...	Present study
membrane	80	23.7	...	...	
0.006196 cm thick	88	31.4	...	...	
	100.5	61.5	...	...	
	104	54.1	...	...	
Polyvinylidene fluoride (Kynar)	39	3.20	...	...	
membrane	45	4.62	...	...	
0.00417 cm thick	55	7.56	...	...	
	65	12.2	...	...	
(Kynar)	23	2.51 (100 psig)[j]	...	...	Seibel & McCandless (*32*)
		2.68 (200 psig)[j]	...	...	
		2.28 (300 psig)[j]	...	...	
		3.47 (400 psig)[j]	...	...	
		9.49 (500 psig)[j]	...	...	
(Kynar + 8.2% sulfolane)	13	7.29 (300 psig)[j]	...	...	
		15.9 (400 psig)[j]	...	...	
	23	3.79 (100 psig)[j]	...	...	
		5.36 (200 psig)[j]	...	...	
		13.7 (300 psig)[j]	...	...	
		19.4 (400 psig)[j]	...	...	
		36.1 (500 psig)[j]	...	...	
	32	16.4 (300 psig)[j]	...	...	
		26.4 (400 psig)[j]	...	...	
		42.3 (500 psig)[j]	...	...	
	42	18.2 (300 psig)[j]	...	...	
		24.2 (400 psig)[j]	...	...	
		38.1 (500 psig)[j]	...	...	
	47	16.4 (300 psig)[j]	...	...	
		27.8 (400 psig)[j]	...	...	
		38.8 (500 psig)[j]	...	...	
	64	29.3 (300 psig)[j]	...	...	
		32.6 (400 psig)[j]	...	...	
		47.2 (500 psig)[j]	...	...	
	73	31.9 (300 psig)[j]	...	...	
		38.8 (400 psig)[j]	...	...	
		47.9 (500 psig)[j]	...	...	
Polycarbonate (Lexan)	25	22.4	...	Eq. 5 in text	Davis and Rooney (7)
Polyethylene (Visqueen)	6.5	9.0	...	...	Brubaker and Kammermeyer (*3*)
	11.5	13.0	...	...	
	13	13.0	...	...	
	15	17.0	...	...	
	20.5	24.0	...	...	
(Polyane)	22	43.4	30.	1.45	Benarie and Bui-the-Chuong (*1*)
(Visqueen)	23	28.0	...	...	Brubaker and Kammermeyer (*3*)
	25	20.9[e]	1120	0.0191	Davis and Rooney (7)
	25	16.2[f]	854[g]	...	
	25[l]	840.0	1800	0.47	Jordan (*15*)
(NSR)	25	24.5 (0% RH)[m]	...	...	Hanousek and Herynk (*12*)
	25	21.8 (84% RH)[m]	...	...	
(CSSR)	25	31.6 (0% RH)[m]	...	...	
	25	21.3 (84% RH)[m]	...	...	
(Visqueen)	30	42.0	...	...	Brubaker and Kammermeyer (*3*)
	41.5	70.0	...	...	
	42	70.0	...	...	

Table I. Continued

Material	Temp, °C	$P \times 10^{10}$[a]	$D \times 10^{10}$[b]	S[c]	Source
Polypropylene (Maurylene)	22	6.18	3.5	1.71	Benarie and Bui-the-Chuong (*1*)
Polyvinyl chloride	0	...	...	Eq. 6 in text	Perret et al. (*20*)
	20	...	...	Eq. 7 in text	
	22	132.	400.	0.329	Benarie and Bui-the-Chuong (*1*)
	25[l]	0.042	1.4	0.03	Jordan (*15*)
	25	412 (0% RH)[m]	...	...	Hanousek and Herynk (*12*)
	25	45 (84% RH)[m]	...	...	
Copolymer of vinylidene chloride and vinyl chloride	25	0.201	...	...	Davis and Rooney (7)
Polyamide (Rilsan)	22	21.1	10.	1.84	Benarie and Bui-the-Chuong (*1*)
(Nylon 11)	25	6.58	...	Eqs. 3, 4 in text	Davis and Rooney (7)
(CSSR)	25	8.54 (0% RH)[m]	...	...	Hanousek and Herynk (*12*)
	25	11.4 (84% RH)[m]	...	...	
Vinyril 11 Rilsan and Saran (copolymer of vinyl and vinylidene chloride)	22	1.18	0.6	1.97	Benarie and Bui-the-Chuong (*1*)
Vulcanized natural rubber	0	...	...	0.528	Chappuis (*4*)
	18.5	...	...	0.322	Reychler (*21*)
	20–22	...	...	0.256	Venable and Fuwa (*42*)
	22	1,450	10,000	0.158	Benarie and Bui-the-Chuong (*1*)
	25	...	...	0.311	Van Amerongen (*41*)
	43	...	...	0.153	
Buna S	25	...	...	0.227	
	43	...	...	0.129	
Perbunan	25	...	...	0.632	
	43	...	...	0.310	
Neoprene G	25	...	...	0.239	
	43	...	...	0.138	
Polyisobutene (Oppanol B 200)	25	...	...	0.047	
	43	...	...	0.032	
Polymethyl methacrylate (Plexiglas)	22	0.132	...	...	Benarie and Bui-the-Chuong (*1*)
	25[l]	2.6	6.2	0.42	Jordan (*15*)
Polyethylterephthalate (Mylar)	22	5.27	1.6	3.29	Benarie and Bui-the-Chuong (*1*)
Cellulose films	22	52.7	27.0	1.98	
(Cellafan, CSSR)	25	0.256 (0% RH)[m]	...	...	Hanousek and Herynk (*12*)
	25	7.14 (84% RH)[m]	...	...	
(Cellofen, English)	25	2.43 (0% RH)[m]	...	...	
	25	20.4 (84% RH)[m]	...	...	
(Ethylcellulose)	25	264	530[h]	0.498[h]	Hsieh (*14*)
			734[i]	0.360[i]	
(Nitrocellulose)	25	176	7.9[h]	0.222[h]	
			18.0[i]	0.0977[i]	
(Nomex)	22	0.132	...	...	Benarie and Bui-the-Chuong (*1*)
Regenerated cellulose film	28.1	0.77×10^{-7}	...	...	Simril and Hershberger (*33*)
	24.5	0.77×10^{-7}	...	...	
	24.5	0.00169 (100% RH)	...	...	
(22% glycerol plasticizer)	24–25	33.6×10^{-7}	...	...	
Paper Imp II	25.	3.09 (0% RH)[m]	...	...	Hanousek and Herynk (*12*)
	25.	3.03 (84% RH)[m]	...	...	
Paper PLP II	25.	6.74 (0% RH)[m]	...	...	
Paper PLP I	25.	1.31 (84% RH)[m]	...	...	
Chlorinated polyether (Penton)	25.[l]	$<10^{-15}$	...	0.01	Jordan (*15*)
Polyethylene glycol liquid membrane: porous polymer backing of Solvinert® coated with TFE dispersion	100.	81,300.	...	...	Ward (*43*)

[a] Permeability, $cm^3(STP)/sec \cdot cm \cdot cm$ Hg. [b] Diffusivity, cm^2/sec. [c] Solubility, $cm^3(STP)/cm^3 \cdot cm$ Hg. [d] Values published by Felder et al. (*10*) were based on a nominal cylinder span gas concentration reported by the supplier. A more accurate concentration has since been obtained, and the given value reflects the correction. [e] SO_2 partial pressure >25 cm Hg. [f] Calculated as $(DS)_{p_{SO_2}} \rightarrow 0$. [g] SO_2 partial pressure → 0. [h] Author measures S by a volumetric method and calculates $D = P/S$. [i] Author measures S by a gravimetric method and calculates $D = P/S$. [j] Rough estimate. [k] Deduced from permeation tube emission rate. [l] Speculation—author did not report a temperature. [m] Speculation—author did not report time units.

(*15*) appears far too high, assuming that it was obtained in the temperature range 20–30°C; the other values are shown on an Arrhenius plot in Figure 4.

Studies of SO_2 transport in polymers which are not referenced in Table I have been carried out by Sano and coworkers (*27–30*), Stoeckli (*37*), and Svoboda and coworkers (*38–40*). References *27–30* deal with the permeation of SO_2 through polyethylene and plasticized polyvinyl chloride membranes, ref. *37* with sorption of SO_2 on polyvinylidene chloride, and refs. *38–40* with penetration of SO_2 into alkyd resins.

Effect of Temperature on Permeability

The Arrhenius plots of Figures 1, 2, and 4 for TFE Teflon, FEP Teflon, and polyethylene have been fit by linear regression to obtain the preexponential factors and activation energies listed in Table II. The following data points were excluded from the regressions: Figure 1, Metronics; Figure 2, Stevens

Table II. Arrhenius Parameters for SO_2 Permeability

Material	ln P_0	SD[a]	$P_0 \times 10^{5}$[b]	E_p[c]	SD	Source
TFE Teflon	−10.39	0.27	3.07	6.54	0.23	Regression on Figure 1
	...	...	...	6.99	0.83	Rodes et al. (*23*)
FEP Teflon	−9.54	0.20	7.23	7.18	0.14	Regression on Figure 2
	...	...	...	7.14[e]	...	Dietz et al. (*8*)
	...	...	...	9.08[e]	...	Saltzman et al. (*26*)
	...	...	...	9.08[e]	...	Brocco and Possanzini (*2*)
	...	...	...	8.45[d]	0.86[d]	
Silastic LS-63U® (fluorosilicone rubber)	−14.65	0.13	0.0435	0.253	0.118	Present study
	−14.01	0.13	0.0826	0.651	0.088	
	...	...	...	1.33	0.38	Rodes et al. (*23*)
Silastic LS-63® (silicone rubber)	...	...	...	0.94	0.87	
PVF (Tedlar) membrane	−6.49	0.28	152.	9.39	0.20	Present study
Polyvinylidene fluoride (Kynar) + 8.2% sulfolane						
(300 psig)	−13.24[d]	0.97[d]	0.178[d]	4.32[d]	0.60[d]	Seibel and McCandless (*32*)
(400 psig)	−15.51[d]	0.51[d]	0.0183[d]	2.67[d]	0.32[d]	
(500 psig)	−17.62[d]	0.55[d]	0.00223[d]	1.07[d]	0.35[d]	
Polyethylene	−2.44[d]	0.56[d]	8700.[d]	10.2[d]	0.33[d]	Regression on Figure 4

[a] Standard deviation. [b] cm³(STP)/sec·cm·cm Hg. [c] kcal/g-mol. [d] Calculated from data reported by author. [e] Calculated by subtracting a heat of evaporation $\Delta H_{\text{evap}} = 5.46$ kcal/g-mol (*5*) from the published activation energy, which was for the combined processes of evaporation and permeation.

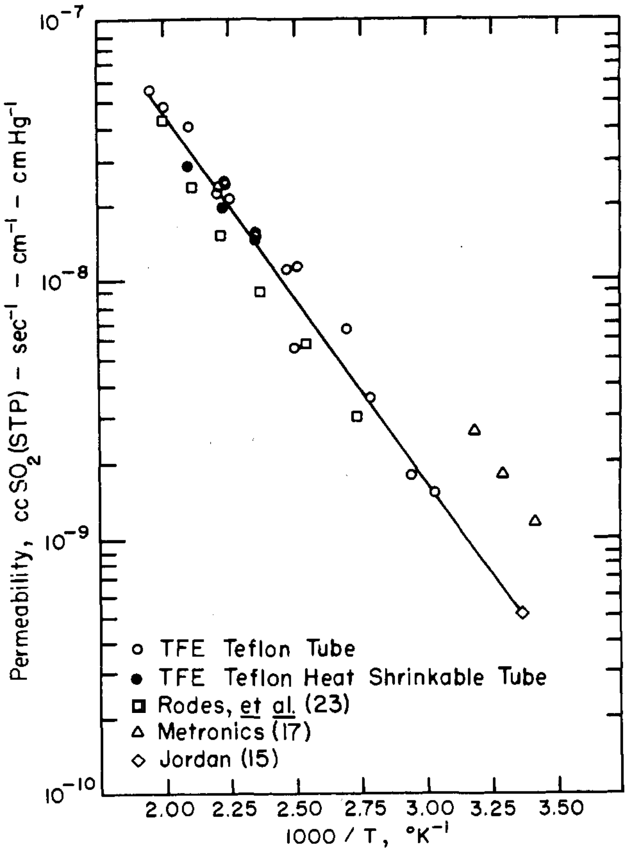

Figure 1. SO_2 permeabilities of TFE Teflon

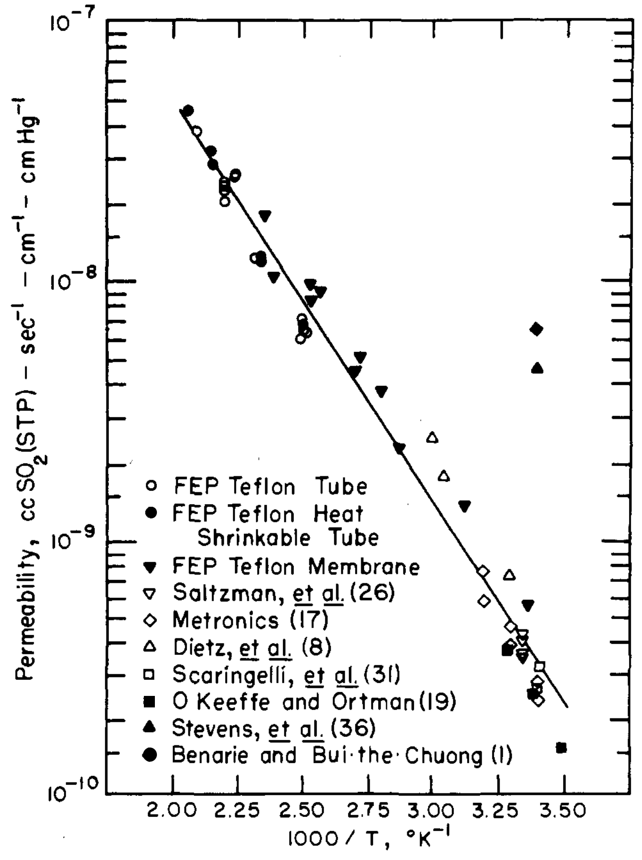

Figure 2. SO_2 permeabilities of FEP Teflon

et al. and Benarie and Bui-the-Chuong; Figure 4, all but Brubaker and Kammermeyer. Also listed in Table II are published activation energies for permeation of SO_2 through polyvinyl fluoride, polyvinylidene fluoride, and polyethylene.

The permeabilities of silicone and fluorosilicone rubbers shown in Figure 3 are too scattered to permit meaningful regressions; however, the following ranges for P and E_p may be deduced from the data:

$$\left.\begin{array}{l}\text{SILASTIC 437®}\\ \quad\text{silicone rubber}\\ \text{SILASTIC LS-63U®}\\ \quad\text{fluorosilicone}\\ \quad\text{rubber}\\ 50°\text{C} \le T \le 232°\text{C}\end{array}\right\} \begin{array}{l} 10^{-7} \le P \le 5 \times 10^{-7}\ \dfrac{\text{cm}^3\text{(STP)}}{\text{sec·cm·cm Hg}} \\[2ex] 0.1 \le E_p \le 2\ \text{kcal/g-mol}\end{array}$$

Effect of Pressure on Permeability

At low pressures, gas permeabilities, diffusivities, and solubilities are characteristically independent of pressure (*34*). The high-temperature permeation measurements reported in Table I—for which the total pressures were close to atmospheric and partial pressures of SO_2 were in the range 0.08–1.3 cm Hg—show this behavior: plots of permeation rate vs. SO_2 partial pressure obtained by Rodes et al. (*23*) and in the present study were linear, with correlation coefficients usually in excess of 0.99.

Under some circumstances, however, the effective permeability of a substance depends on the partial pressure of the permeating species and/or the total pressure on the high concentration side of the interface. The cause may be the departure of the solubility of the material from Henry's law behavior, a concentration-dependent diffusivity, or the occurrence of permeation by a mechanism other than solution followed by activated diffusion.

Pressure-dependent SO_2 permeabilities have been observed by Davis and Rooney (*7*) for polyethylene, polycarbonate, and polyamide membranes and by Seibel and McCandless (*32*) for polyvinylidene fluoride (Kynar). Seibel and McCandless worked at total pressures of 100–500 psig—pressures at which any or all of the factors indicated could cause the observed pressure dependence of the effective permeability.

Solubilities of SO_2 in polyethylene and polymethyl methacrylate reported by Jordan (*15*) show a considerable departure from Henry's law. Davis and Rooney (*7*) report a Henry's law dependence for SO_2 in polyethylene, deviations from this behavior in polycarbonate and polyamide, and concentration-dependent diffusivities for all three materials.

Davis and Rooney (*7*) and Perret et al. (*20*) present diffusivity and solubility correlations for SO_2 in the range 0–25°C. In the equations that follow, p_{SO_2} is the SO_2 partial pressure in cm Hg, C_{SO_2} the absorbed SO_2 concentration in cm^3 SO_2(STP)/cm^3 polymer, and D the SO_2 diffusivity in cm^2/sec. Polyamide at 25°C (*7*):

$$C = \frac{0.98\, p_{SO_2}}{1.0 + 0.169\, p_{SO_2}} + 0.298\, p_{SO_2} \tag{3}$$

$$D \times 10^{10} \left\{\begin{array}{l} = 3.63 \times (10)^{0.05C} \quad (4a) \\ = 2.63 \times (10)^{0.06C} \quad (4b) \end{array}\right\} \begin{array}{c}\text{(Determinations by}\\ \text{two different}\\ \text{methods)}\end{array}$$

Polycarbonate at 25°C (*7*):

$$C = \frac{2.44\, p_{SO_2}}{1.0 + 0.241\, p_{SO_2}} + 0.522\, p_{SO_2} \tag{5}$$

Polyvinyl chloride (*20*):

$$0°\text{C:}\quad C = 0.719\, p_{SO_2} + 2.155 \qquad P_{SO_2} > 3\ \text{cm Hg} \tag{6}$$

$$20°\text{C:}\quad C = 0.393\, p_{SO_2} + 1.472 \qquad P_{SO_2} > 54\ \text{cm Hg} \tag{7}$$

The sorption isotherms given by Equations 3, 5, 6, and 7 are consistent with the dual-mode mechanism proposed by Michaels et. al. (*18*) for sorption in glassy polymers. According to this mechanism, sorption is a combination of ordinary

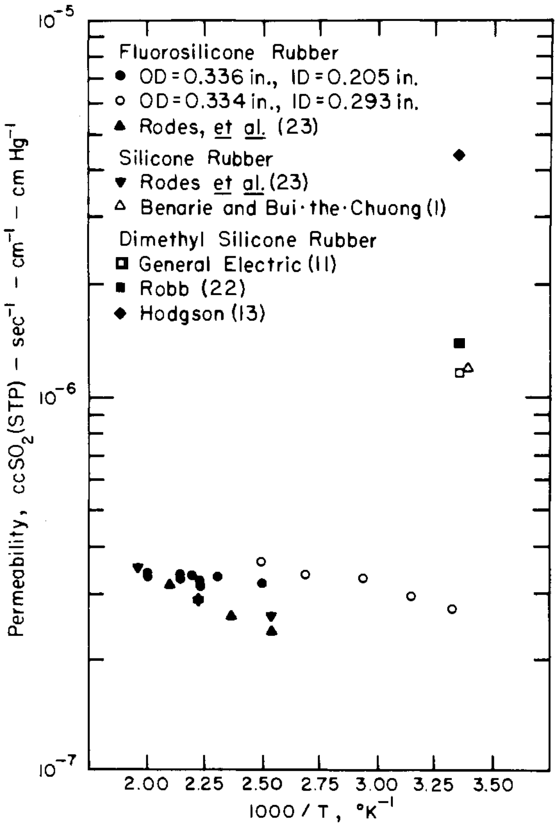

Figure 3. SO_2 permeabilities of silicone rubbers

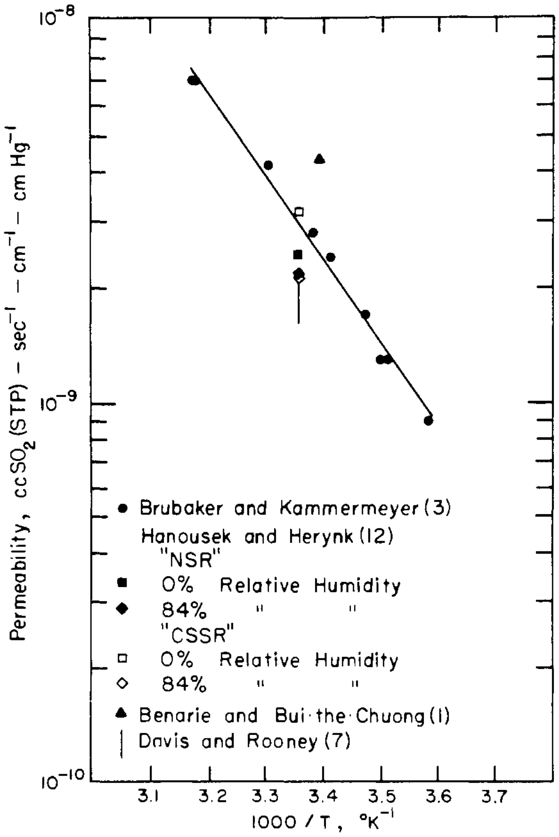

Figure 4. SO_2 permeabilities of polyethylene

Henry's law solution—which leads to a linear component of the isotherm—and microvoid or hole filling, which gives rise to a Langmuir expression. Both components of the isotherm appear explicitly in Equations 3 and 5. At sufficiently high pressures the isotherm becomes linear, with a slope equal to the Henry's law constant and a positive intercept, cf., Equations 6 and 7.

Effect of Humidity on Permeability

Stannett (*34*) observes that humidity has little effect on the permeability of gases through polymers in which water is only slightly soluble; but when water is highly sorbed, the gas permeation rate may be significantly increased by an increase in humidity.

The few reported studies of the effects of humidity on SO_2 permeation confirm this observation. Felder et al. (*10*) report that the SO_2 permeabilities of TFE Teflon, FEP Teflon, and SILASTIC LS-63U® fluorosilicone rubber tubes measured for dry gases and gases containing up to 21% water by volume are statistically indistinguishable at temperatures up to 200°C. Hanousek and Herynk (*12*) found that the permeability of polyethylene at 25°C decreased by 10–30%, and the permeabilities of several types of paper decreased or remained unchanged when the relative humidity was raised from 0 to 84%, whereas the permeability of a polyamide increased by 33% and that of polyvinyl chloride increased by 10% for the same change in humidity. On the other hand, both Hanousek and Herynk (*12*) and Simril and Hershberger (*33*) report increases of an order of magnitude or more in the permeability of cellulosic films when the humidity was raised from 0 to 84–100%.

Effect of Plasticizers on Permeability

The presence of a plasticizer in polymeric materials may increase the solubility and hence the permeability of these materials to gases (*34*). Seibel and McCandless (*32*) utilized this principle to fabricate SO_2-permeable membranes by adding sulfolane (an SO_2 solvent) as a plasticizer to polyvinylidene fluoride films. The addition of the sulfolane increased the permeability of SO_2 relative to that of N_2, with the separation factor increasing with decreasing temperature.

Sano has been the author or coauthor of several patents and papers on the separation or removal of SO_2 by polyvinyl chloride membranes plasticized with dioctyl phthalate and tricresyl phosphate (*27–30*).

Summary

Permeabilities of SO_2 in various polymers have been measured or calculated from published permeation rate data. Activation energies for permeation have been determined by fitting Arrhenius functions to permeability data for TFE Teflon, FEP Teflon, silicone and fluorosilicone rubbers, polyvinyl fluoride (Tedlar), polyvinylidene fluoride (Kynar), and polyethylene.

The permeabilities of TFE and FEP have been found to be similar, contradicting published assertions that TFE is considerably more permeable than FEP. Silicone and fluorosilicone rubbers are 10–100 times more permeable than Teflon, but they are also subject to embrittlement and attack by acid mist.

A transport model based on Henry's law for solution and Fick's law for diffusion correlates permeation data well for many materials at pressures of 1 atm or less. At higher pressures, deviations from these laws have been reported for polyethylene, polycarbonates, and polyamides, polyvinyl chloride, polyvinylidene fluoride, and polymethyl methacrylate.

The observation of Stannett (*34*) that relative humidity affects the permeability of a gas through a polymer to the extent that the polymer absorbs water is borne out by the results of several experiments. As the humidity increases, the permeabilities of TFE Teflon, FEP Teflon, and fluorosilicone rubber tubes were unchanged, that of polyethylene decreased slightly, and those of a polyamide and of polyvinyl chloride increased slightly, whereas the permeabilities of cellulosic films increased substantially.

The addition of certain plasticizers to a polymer film may increase the permeability of the film to SO_2. This effect has been observed in sulfolane-plasticized polyvinylidene fluoride and dioctyl phthalate and tricresyl phosphate-plasticized polyvinyl chloride films.

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