Table IV. Parameters of Various Equations for Excess Gibbs Free Energy

System	Temp, °C	Redlich-Kister, 3-parameter[a] B	C	D	σ^d	Wilson, 2-parameter[b] A_{12}	A_{21}	σ^d	NRTL, 3-parameter[c] τ_{12}	τ_{21}	α	σ^d
DMSO(1)–acetone(2)	25	0.6910	−0.0651	0.0233	0.37	0.5498	0.8271	0.37	0.3153	0.5585	0.9068	0.36
	35 (Run 1)	0.6553	−0.0455	0.0125	0.24	0.5948	0.8078	0.24	0.2689	0.4916	0.6763	0.26
	(Run 2)	0.6524	−0.0333	0.0303	0.27	0.6321	0.7684	0.45	0.3556	0.4702	1.0147	0.29
	45	0.6247	−0.0345	0.0095	0.33	0.6273	0.7987	0.33	0.2641	0.4470	0.6456	0.33
DMSO(1)–tetrahydrofuran(2)	25	1.2506	−0.1919	0.1228	0.56	0.2941	0.6543	0.61	0.6240	1.2174	0.6627	0.35
	35	1.2188	−0.1934	0.1198	0.58	0.2981	0.6756	0.63	0.5991	1.1984	0.6772	0.38
	45	1.1779	−0.1836	0.1077	0.51	0.3128	0.6906	0.53	0.5656	1.1405	0.6825	0.28
DMSO(1)–ethyl acetate(2)	25	1.2212	−0.0831	0.1031	0.27	0.4008	0.5499	0.62	0.7352	0.9875	0.6836	0.27
	35	1.1813	−0.0763	0.0917	0.40	0.4177	0.5642	0.62	0.7029	0.9381	0.6894	0.36
	45	1.1514	−0.0741	0.0944	0.32	0.4300	0.5725	0.64	0.6932	0.9188	0.7174	0.29

[a] Redlich-Kister equation (*13*): $\frac{G^E}{RT} = x_1x_2[B + C(x_1 - x_2) + D(x_1 - x_2)^2]$

[b] Wilson equation (*18*): $-\frac{G^E}{RT} = x_1 \ln (x_1 + A_{12}x_2) + x_2 \ln (x_2 + A_{21}x_1)$

[c] NRTL equation (*14*): $\frac{G^E}{RT} = x_1x_2\left[\frac{\tau_{21} \exp (-\alpha\tau_{21})}{x_1 + x_2 \exp (-\alpha\tau_{21})} + \frac{\tau_{12} \exp (-\alpha\tau_{12})}{x_2 + x_1 \exp (-\alpha\tau_{12})}\right]$

[d] Standard deviation in relative pressure, %; N, number of experimental points: $100 \times \sqrt{\Sigma \left(\frac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}}\right)^2 / N}$

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Permeability of Teflon Polytetrafluoroethylene Resin and Buna-*N* Butadiene-Nitrile Rubber to Deuterium[1]

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The permeability, ϕ, of Teflon and buna-*N* to deuterium at 0.16–5 atm between 196 and 441K is given by: $\phi_{\text{Teflon}} = 2.8 \times 10^{-4} \exp (-4950/RT)$ and $\phi_{\text{Buna-}N} = 1.02 \times 10^{-2} \exp (-6700/RT)$ cm^3 (NTP gas) cm^{-1} atm^{-1} sec^{-1}. Temperature dependence of deuterium diffusivity, *D*, in these materials was calculated from measurements of the rate of rise to, and decline from, steady-state permeation. Deuterium solubilities, *S*, were also calculated.

Teflon polytetrafluoroethylene resin and buna-*N*, a nitrile rubber, are often used as gasket materials to seal valves, transducers, and/or secondary containers in hydrogen handling systems (*1, 3, 5*). Systems handling deuterium, an hydrogen isotope, are similarly constructed. Permeation data for Teflon and buna-*N* are necessary to predict system responses to various deuterium exposures where low-level permeation through the gaskets must be controlled. The permeability and the diffusivity of deuterium in these gasket materials were measured over a range of temperatures.

Experimental

The permeability was calculated from measurements of the steady-state deuterium flux through membranes exposed to 0.16–5 atm deuterium gas in the test apparatus sketched in Figure 1. Test specimens were ~0.050 cm thick by about 4.83 cm in diameter. High-purity

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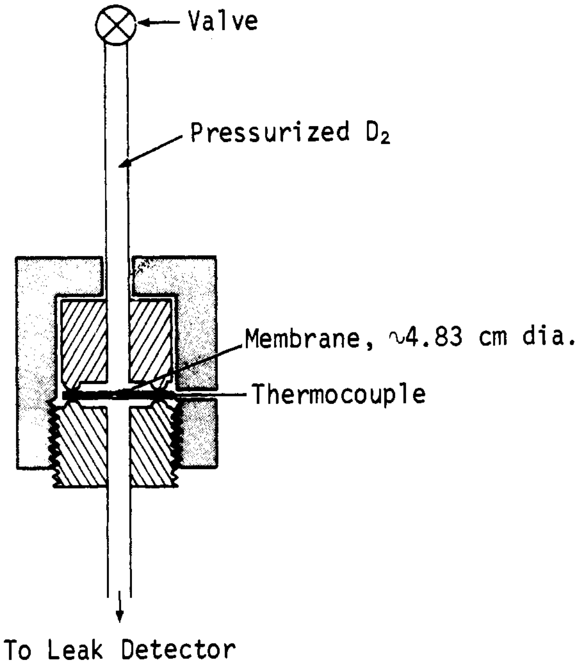

Figure 1. Cell for measuring permeation of deuterium through membranes

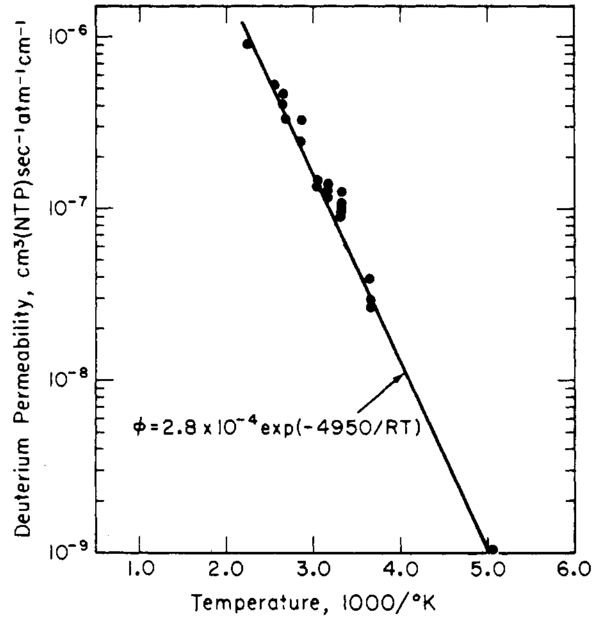

Figure 2. Permeability of Teflon to deuterium

Table I. Deuterium Permeability and Diffusivity in Teflon

Temp, K	Press, atm	Permeability, cm³ (NTP) sec⁻¹ atm⁻¹ cm⁻¹	Diffusivity, cm² sec⁻¹	
			Rise	Decline
196	0.16	1.07×10^{-9}	6.98×10^{-8}	...
273	0.16	3.91×10^{-8}	6.79×10^{-7}	5.31×10^{-7}
273	1.0	2.70×10^{-8}	7.48×10^{-7}	5.76×10^{-7}
273	5.0	2.90×10^{-8}	7.91×10^{-7}	4.96×10^{-7}
300	0.16	1.00×10^{-7}	1.80×10^{-6}	1.53×10^{-6}
300	0.50	1.06×10^{-7}	1.28×10^{-6}	1.38×10^{-6}
300	1.0	1.25×10^{-7}	1.46×10^{-6}	1.52×10^{-6}
300	3.0	0.97×10^{-7}	...	...
300	5.0	0.90×10^{-7}	...	1.61×10^{-6}
313	3.0	1.20×10^{-7}	2.39×10^{-6}	2.00×10^{-6}
313	5.0	1.40×10^{-7}	...	2.20×10^{-6}
315	0.16	1.25×10^{-7}	2.13×10^{-6}	...
315	0.50	1.20×10^{-7}	...	2.20×10^{-6}
328	0.16	1.39×10^{-7}	3.10×10^{-6}	3.07×10^{-6}
328	0.50	1.41×10^{-7}	3.40×10^{-6}	2.60×10^{-6}
328	3.0	1.43×10^{-7}	3.81×10^{-6}	3.00×10^{-6}
328	5.0	1.42×10^{-7}	4.19×10^{-6}	2.88×10^{-6}
348	0.16	3.34×10^{-7}	5.13×10^{-6}	4.88×10^{-6}
348	1.0	2.51×10^{-7}	4.19×10^{-6}	4.17×10^{-6}
348	3.0	2.50×10^{-7}	5.24×10^{-6}	4.42×10^{-6}
378	0.16	4.75×10^{-7}	5.99×10^{-6}	6.80×10^{-6}
378	0.5	4.10×10^{-7}	7.31×10^{-6}	6.88×10^{-6}
378	1.0	3.30×10^{-7}	7.62×10^{-6}	6.58×10^{-6}
396	1.0	5.15×10^{-7}	1.02×10^{-5}	1.02×10^{-5}
441	1.0	9.25×10^{-7}	1.94×10^{-5}	1.95×10^{-5}

Table II. Deuterium Permeability and Diffusivity in Buna-*N*

Temp, K	Press, atm	Permeability, cm³ (NTP) sec⁻¹ atm⁻¹ cm⁻¹	Diffusivity, cm² sec⁻¹	
			Rise	Decline
296	1.0	9.77×10^{-8}	1.56×10^{-6}	1.12×10^{-6}
312	1.0	1.85×10^{-7}	2.63×10^{-6}	1.93×10^{-6}
325	1.0	3.02×10^{-7}	2.96×10^{-6}	4.10×10^{-6}
353	1.0	7.33×10^{-7}	7.70×10^{-6}	7.13×10^{-6}
362	1.0	8.51×10^{-7}	1.38×10^{-5}	1.05×10^{-5}
389	1.0	1.33×10^{-6}	1.53×10^{-5}	1.97×10^{-5}
401	0.16	2.40×10^{-6}	1.98×10^{-5}	1.94×10^{-5}

(99.9%) deuterium gas was introduced to one side of the membrane, and the quantity passing through the membrane (flux) was monitored with a Consolidated Electrodynamics Corp. Type 24-120B leak detector. The system was evacuated to 10^{-5} torr before deuterium was introduced. Specimen temperature during the test was controlled to ±1K. Measurements of flux at steady state, J_∞, were converted to permeability, ϕ, by

$$\phi = \frac{J_\infty l}{A(p_1 - p_2)} \text{ cm}^3 \text{ (NTP } D_2\text{) cm}^{-1} \text{ atm}^{-1} \text{ sec}^{-1} \quad (1)$$

where l was the membrane thickness and A, the area exposed to hydrogen at pressure p_1 on the entrance side and p_2 on the exit side. Under the experimental conditions, p_2 was neglected because p_1 was much greater than p_2.

Deuterium diffusivities, D, were calculated from measurements of the rate of rise to, or decline from, steady-state permeation. During rise to steady state, the ratio of flux at any time (J_t) to the steady-state flux (J_∞) is given by

$$\frac{J_t}{J_\infty} = 1 + 2\sum_{n=1}^{\infty}(-1)^n[\exp(-Dn^2\pi t/l^2] \quad (2)$$

Solution of this equation for a flux ratio of 0.90 gives

$$\frac{Dt_{0.9}}{l^2} = 0.312 \quad (3)$$

Equation 3 was used to calculate diffusivities from rise to steady-state measurements. A similar equation, valid at a flux ratio of 0.45, is

$$\frac{Dt_{0.45}}{l^2} = 0.150 \quad (4)$$

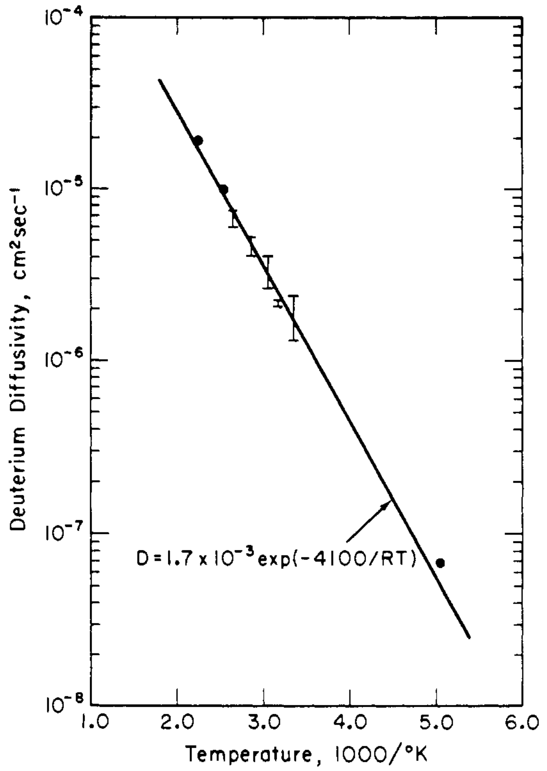

Figure 3. Diffusivity of deuterium in Teflon

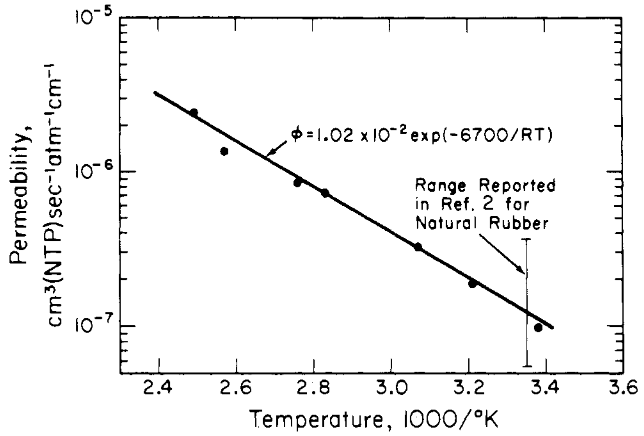

Figure 4. Permeability of buna-*N* to deuterium

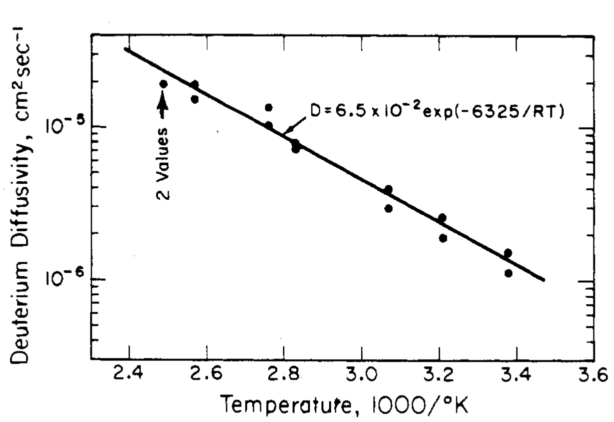

Figure 5. Deuterium diffusivity in buna-*N*

Diffusivities from measurements of decline from steady-state permeation were calculated from Equation 4.

Deuterium solubilities, *C*, were calculated from the relationship:

$$C = \frac{\phi p}{D_A}\ ,\ \mathrm{cm^3\ (NTP\ } D_2)\cdot\mathrm{cm^{-3}\ (sample)} \qquad (5)$$

Results and Discussion

Teflon. The permeability of Teflon to deuterium at 0.16–5 atm between 196 and 441K can be expressed by the equation:

$$\phi = 2.8 \times 10^{-4} \exp(-4950/RT)\ \mathrm{cm^3\ (NTP\ } D_2)\ \mathrm{sec^{-1}\,atm^{-1}\,cm^{-1}} \qquad (6)$$

Data used to develop this equation are given in Table I and Figure 2. The lack of significant scatter in Figure 2 indicates that the assumption is valid that the permeation rate of deuterium through Teflon depends directly on pressure. This result indicates that the permeation process involves solution and diffusion of molecular deuterium.

The permeability of Teflon to deuterium and the activation energy for permeation are lower than for hydrogen (*6*). Similar isotopic effects have been observed in other elastomeric membranes and have been attributed to differences in zero-point energies (*4*). However, detailed comparison of permeabilities to the three hydrogen isotopes was not attempted in this study because the experimental apparatus was only sensitive to deuterium.

Deuterium diffusivities are summarized in Table I and Figure 3. For the range studied, the diffusivity does not depend upon pressure (concentration), and *D* can be represented by

$$D = 1.7 \times 10^{-3} \exp(-4100/RT)\ \mathrm{cm^2\,sec^{-1}} \qquad (7)$$

The solubility of deuterium, therefore, is proportional to the pressure and can be represented by

$$C = 0.16\, p \exp(-850/RT)\ \mathrm{cm^3\ (NTP\ } D_2)\cdot\mathrm{cm^{-3}\ (sample)} \qquad (8)$$

The solubility range investigated in these studies is from approximately 0.003 to 0.060 cc $(D_2)/\mathrm{cm^3}$ (sample).

Buna-N. The permeability of buna-*N* to deuterium between 296 and 401K at 1-atm pressure, calculated from the data in Table II, is given by:

$$\phi = 1.02 \times 10^{-2} \exp(-6700/RT)\ \mathrm{cm^3\ (NTP\ } D_2)\ \mathrm{sec^{-1}\,atm^{-1}\,cm^{-1}} \qquad (9)$$

As shown in Table II and Figure 4, the observed permeability is in reasonable agreement with published data for hydrogen in natural rubber (*2*). The one measurement at 0.16 atm indicates that deuterium transport through buna-*N* is also by molecular diffusion. The calculated temperature dependence of deuterium diffusivity in buna-*N* (Figure 5) is given by

$$D = 6.5 \times 10^{-2} \exp(-6325/RT)\ \mathrm{cm^2\,sec^{-1}} \qquad (10)$$

and the solubility (assuming no dissociation on solution) is

$$C = 1.57 \times 10^{-1}\, p \exp(-375/RT)\ \mathrm{cm^3\ (NTP\ } D_2)\ \mathrm{cm^3\ (sample)} \qquad (11)$$

The low values for the calculated heats of solution, 850 cal for Teflon and 350 cal for buna-*N*, indicate that the solubility of deuterium in both materials is not very dependent on temperature.

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Carbon Dioxide Solubility in Aqueous Carbopol Solutions at 24°, 30°, and 35°C

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Solubilities for carbon dioxide in 0.25, 0.75, and 1.00 wt % aqueous Carbopol (carboxy polymethylene) solutions are determined at 24°, 30°, and 35°C. The rheological behavior of these solutions can be described by the Ostwald-de Waele power-law model with the flow behavior index varying between 0.916 and 0.594. The solubilities are expressed in terms of Henry's Law and decrease with increasing Carbopol concentration and temperature.

Aqueous Carbopol-934 (carboxy polymethylene) solutions are often used as model nonNewtonian fluids since their rheological behavior is well characterized by the power-law relationship. For interphase gas-liquid mass-transfer studies, with nonNewtonian fluids, carbon dioxide is a convenient choice as the solute to be transferred since large mass-transfer rates can be achieved owing to its relatively high solubility in aqueous solutions.

Another advantage with the use of carbon dioxide in aqueous solutions is that concentrations may be measured in a straightforward manner by wet chemistry techniques. To experimentally determine interphase mass-transfer coefficients it is necessary to know equilibrium solubilities for the binary gas-liquid system. In the work described here, solubilities for carbon dioxide in 0.25, 0.75, and 1.00 wt % aqueous Carbopol solutions were determined for partial pressures near atmospheric and for temperatures of 24°, 30°, and 35°C. The Carbopol solutions were pseudoplastic with the flow behavior index varying from 0.916 to 0.594.

Experimental

A schematic drawing of the experimental apparatus is shown in Figure 1. The solutions were saturated by bubbling "bone-dry" grade carbon dioxide through a fritted-glass disc in a gas-washing bottle for approximately 1 hr. Initially, several runs were made lasting 2 hr, and these showed no differences with runs lasting 1 hr. Thus, the majority of the runs were made with a 1-hr bubbling period. A liquid seal was provided for the saturation vessel by placing a 500-ml Erlenmeyer flask in series with the saturation vessel as shown in Figure 1.

After turning the gas to the bubbler off, a sufficient period of time, usually about ½ hr, was allowed to elapse to ensure that the pressure which initially was slightly in excess of atmospheric was reduced to atmospheric. The saturation vessel was shaken manually at 5-min intervals during this period. The initial excess pressure was approximately 1 in. of water. The temperature was controlled to within ±0.1°C by placing the saturation vessel in a constant-temperature water bath. The use of low gas flow rates minimized evaporation losses of water which would have altered the solution compositions.

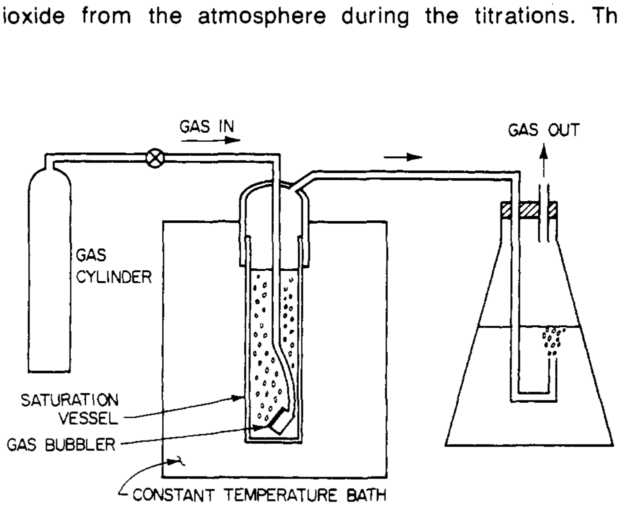

Figure 1. Solubility apparatus

A 50-ml pipet was used to transfer samples out of the saturation vessel for concentration measurements. Carbon dioxide concentrations were determined by precipitation as barium carbonate from standard barium hydroxide solutions with the excess hydroxide determined by titration with hydrochloric acid to a phenolthalein end point. Since Carbopol solutions are acidic, it was necessary to perform blank titrations on carbon dioxide-free solutions. Care was taken to avoid the loss of carbon dioxide to the atmosphere during the transfer of samples from the saturation vessel and to prevent the introduction of carbon dioxide from the atmosphere during the titrations. The

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