

Permeation of Several Gases through Elastomers, with Emphasis on the Deuterium/Hydrogen Pair

M. W. FITCH,¹ W. J. KOROS,^{1,*} R. L. NOLEN,² and J. R. CARNES²

¹Department of Chemical Engineering, University of Texas at Austin, Austin, Texas 78712, and ²Group WX-5, Los Alamos National Laboratories, Los Alamos, New Mexico 87545

SYNOPSIS

The diffusion and permeation coefficients for He, H₂, D₂, O₂, and N₂ in a variety of elastomers were measured by simple manometric methods. The elastomers studied were butyl rubber; Hypalon® 40 and 45; Viton® E60 and GF; Hydrin® 100 and filled Hydrin® 100; Kraton® G, FG, and KG VTEOS; EPDM; epoxidized natural rubber; and neoprene. Consistent with earlier studies, elastomers with higher glass transition temperatures exhibited lower diffusion coefficients. The ratio of diffusion coefficients of the hydrogen isotope pair differed from the purely molecular-weight-based prediction. Deuterium's slightly smaller size relative to hydrogen is consistent with observed deviations from the molecular-weight-based diffusion coefficient ratio. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Inhibition of polymer segmental motions tends to reduce gas permeation and elasticity of rubbery polymers. This suggests a need to suitably balance these properties for barrier elastomers used in many gasket and seal applications. Earlier studies¹ have reported elastomeric properties, as well as permeation data, for a variety of gases in numerous polymers. Relatively few studies²⁻⁶ have treated the permeation properties of the deuterium isotope and its relationship to hydrogen permeation in polymers. The present study considers this isotope pair, as well as three other important gases—He, O₂, and N₂—in various elastomers that have either not been studied to date or have been only partially characterized for these gases. In addition to the practical utility of such work, by considering the structure-permeability relationships that emerge, improved insight into the mechanisms of diffusion and sorption responsible for permeation of gases through elastomers is possible.

BACKGROUND

For a flat membrane with one-dimensional diffusion, Fick's first law is simply

$$N = -D\partial C/\partial x \quad (1)$$

In 1866, Graham⁷ postulated that the process of permeation involved a solution-diffusion mechanism by which the diffusing molecule first is dissolved in the membrane and then transported through it by diffusion. von Wroblewski⁸ defined a coefficient, the permeability, P , equal to the flux at steady state divided by the driving pressure, Δp , across the membrane, normalized by the thickness of the membrane, l , giving rise to

$$P \equiv N/(\Delta p/l) \quad (2)$$

If dissolved penetrant within the membrane obeys Henry's law, a constant solubility coefficient, S , relates the concentration, C , to the external pressure, p , at equilibrium:

$$C = Sp \quad (3)$$

* To whom correspondence should be addressed.

Further, if Fick's law with a constant diffusion coefficient applies, von Wroblewski showed that the permeability is equal to the product of solubility and diffusivity coefficients:

$$P = DS \quad (4)$$

The time lag method of Daynes⁹ and Barrer¹⁰ yields two observable parameters, the time lag (Θ) and the permeability. For systems obeying both Henry's and Fick's laws, the time lag is related to the diffusion coefficient by

$$(\Theta) = l^2/(6D) \quad (5)$$

When a constant gas pressure is applied to one side of an initially degassed membrane, a period of transient transport occurs. At a time greater than three times the time lag, a steady-state rate of permeation is established and the slope of the recorded pressure can be related to the flux, while an extrapolation of this steady-state line back to the time axis yields the time lag. Experience has shown that for permanent gases the diffusion coefficient is generally independent of concentration in rubbery polymers so that both the permeability and the time lag for this case are independent of the pressure applied to the membrane.

The time lag technique allows direct evaluation of the diffusion and permeation coefficients; therefore, the Henry's law solubility coefficient can be calculated from eq. (5) for these elastomers.

The diffusivities of different gases in a single polymer are related to the molecular size of the various gases, typically ranked by critical volume, zeolite sieving diameter, or the Lennard-Jones collision diameter. The diffusion coefficient for a given gas in a variety of polymers decreases as the segmental packing efficiency of the polymers increases. An increased segmental packing efficiency tends to decrease the segmental motions that allow penetrants to move within the polymer, further reducing the diffusion rate of the penetrant. Similarly, polar groups increase intersegmental attractions and also tend to reduce the diffusion coefficient of penetrants. The lowest diffusivities in elastomers are found in highly polar, bulky rubbers with minimal double bonds, such as butyl rubbers.

Henry's law solubility coefficients in a polymer correlate strongly to the respective gas condensibilities as measured by their boiling or critical temperature. Accommodation of a sorbed penetrant in a matrix includes an endothermic contribution in-

volving the formation of the sorbed cage needed to accommodate the penetrant. This contribution tends to be largest, and hence least favorable to sorption, for polar polymers with high cohesive energy densities. For a given gas, therefore, polar media typically have a lower solubility coefficient than in a corresponding nonpolar medium. In the case of polar or polarizable penetrants such as H₂O or CO₂, favorable exothermic polymer-penetrant interactions can overcome the endothermic sorbed cage energy contribution, but this is not the case for He, H₂, O₂, N₂, etc.

The implication of these statements is that a lower permeability, and hence better barrier materials for most standard gases, may be realized by increasing the segmental packing efficiency of a polymer and increasing polymer polarity. These general expectations are considered in the context of a range of polymers, with special emphasis on the He/D₂ pair as a means of probing details of the diffusional process in elastomers.

EXPERIMENTAL

Equipment

In this study, permeability and diffusivity were measured for a number of elastomers to helium, hydrogen, deuterium, oxygen, and nitrogen. Permeabilities and time lags were measured in a simple manometric device, and diffusion and solubility coefficients were calculated from these data via eqs. (3) and (5). All measurements were made at 35°C ($\pm 1^\circ\text{C}$).

Membranes of 7.99 cm² area, typically 0.025-in thick, were mounted in the permeation cell on filter paper on top of a porous metal support. The cell was sealed with a Viton® O-ring. The entire system, upstream and down, was then evacuated for 24 h, after which gas was introduced to the upstream side. Upstream pressures varied from 30–270 psia, and results were generally independent of upstream pressure, indicating the applicability of Henry's law and Fick's law with a constant diffusion coefficient in these elastomers. On the permeant side, the changing pressure was measured with a Baratron pressure transducer (0–10 torr) and plotted against time on a stripchart recorder. Stripchart data in the region of steady state (at least three time lags beyond the initial gas introduction) were fit by least squares as a linear function of time to give values for the rate of pressure increase with time and the time lag. At the end of an experiment, the membrane was ex-

posed to vacuum (~ 0.03 torr) for at least 10 times the measured time lag to degas the membrane.

Each polymer-gas pair, except for the filled epichlorohydrin sample, was measured at least twice to ensure reproducible results with less than 5% deviation. The filled epichlorohydrin sample data were not reproduced due to time constraints on the equipment.

Materials

The polymers examined were butyl rubber; Hypalon[®] 40 and 45; Viton[®] E60 and GF; Hydrin[®] 100 and filled Hydrin[®] 100; Kraton[®] G, FG, and KG VTEOS; EPDM; epoxidized natural rubber; and neoprene. The structures and glass transition temperatures of these polymers are shown in Table I.

Enjoy butyl rubber types 065, 165, 268, and 365 were provided in a noncrosslinked form by Exxon. The four samples varied in molecular weight as sent but after crosslinking were expected to have only minor differences in membrane properties. These were studied to see what effect, if any, would appear from polymer sample to polymer sample. The samples contained no filler, and were crosslinked by sulfur with zinc oxide and tetramethylthiuramdisulfide (TMTD) as an accelerator. All but two measurements showed less than a 20% variation between these membranes. Therefore, the results of the type 165 sample are used for butyl rubber data throughout the remainder of this article.

Hypalon[®] 40 and 45 were provided by Dr. Wolfgang Honsberg of E. I. Du Pont de Nemours. The polymer was crosslinked by sulfur with zinc oxide and TMTD. The 40 sample contained 35% chlorine and the 45 sample contained 24% chlorine. They were unfilled.

Viton[®] E60 and GF were provided by Dr. Walter Schmiegel of E. I. Du Pont de Nemours. The E60 sample contained 65% fluorine and was sent cured (bisphenol cure) and unfilled. The GF sample contained 70% fluorine and was sent cured (peroxide cure) and unfilled.

Hydrin[®] 100 and filled Hydrin[®] 100 were provided by Dr. Don Mittendorf of B. F. Goodrich. The unfilled sample was sent cured by a diamine agent. The filled sample was similarly cured with a hydrous magnesium silicate filler (70 parts per hundred), as well as antioxidants and reinforcing fillers.

Kraton[®] G, FG, and KG VTEOS were provided by Dr. Len Gerlowski of Shell. Kraton[®] is an SBS thermoplastic elastomer. The G sample was control Kraton[®] polymer. The FG sample was maleic an-

hydride modified. The KG sample was vinyl triethoxysilane modified.

The EPDM sample was provided by Los Alamos National Laboratories and was filled and cured. The filler was carbon black and antioxidants. The base polymer was Nordel 1470 from Sargent.

The ENR 25 sample was provided by Dr. Ian Gelling of the Tun Abdul Razak Laboratory. The sample was sent crosslinked and carbon black filled and is a 25 mol % epoxidized natural rubber.

The neoprene sample was provided by Dr. T. Takeshita of E. I. Du Pont de Nemours. It was crosslinked by sulfur with TMTD as an accelerator and was unfilled.

The O₂, N₂, He, and H₂ gases were obtained from Wilson Oxygen & Supply and deuterium was provided by Los Alamos National Laboratories. The minimum gas purities were: helium 99.995%; hydrogen 99.999%; deuterium 99.5%; oxygen 99.99%; and nitrogen 99.998%.

RESULTS AND DISCUSSION

The results of the investigation are reported in Table II. The error was calculated from standard deviation between repetitive trials.

Van Amerongen¹ noted that the diffusion coefficient of one gas in many different elastomers appears to correspond well to a measure of the mobility of the polymer, as measured by the difference in the temperature of measurement and a given polymer's glass transition temperature. Such results are illustrated for N₂ in Figure 1, which shows values from this study as well as Van Amerongen's data. Clearly, there is a trend toward linearity of the results for the temperature range of $T - T_g$ over 40–140°C corresponding to experimental temperatures of 20–70°C regardless of the material. Similar results were seen for all the gases examined. This linear trend is violated by only three substances: butyl rubber, filled Hydrin[®], and EPDM.

In the case of butyl rubber, Van Amerongen argued that this elastomer's unique deviation arises from the combination of the bulky side methyl groups with the absence of double bonds in the butyl group. It is of interest to note, however, that Viton[®], a fluorinated elastomer, seemingly shares the lack of double bonds and has bulky fluorine side groups but lies on the common line. It does, however, have a diffusion coefficient of similar magnitude to butyl rubber.

The filled Hydrin[®] deviates from the general line as well. In this case, the use of a control, unfilled

Table I

Elastomer		T_g (°C)
Butyl rubber	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{C} \\ \\ \left[\begin{array}{c} \text{H} \\ \\ \text{C} - \text{C} \\ \quad \\ \text{H} \end{array} \right]_{0.98} - \left[\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{C} - \text{C} = \text{C} - \text{C} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{array} \right]_{0.02} \\ \\ \text{C} \\ \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	-70
Hydrin®	$\begin{array}{c} \left[\begin{array}{c} \text{H} \\ \\ \text{C} - \text{C} - \text{O} \\ \quad \\ \text{H} \end{array} \right] \\ \\ \text{C} \\ \\ \text{H} \quad \text{Cl} \quad \text{H} \end{array}$	-17
EPDM ($Z \sim 0.02$)	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{C} \\ \\ \left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} - \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_x - \left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} - \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_y - \left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{C} - \text{C} \\ \quad \\ \text{H} \quad \text{C} = \text{C} - \text{H} \\ \quad \\ \text{C} - \text{H} \\ \\ \text{C} \\ \\ \text{H} \quad \text{H} \quad \text{H} \end{array} \right]_z \end{array}$	-60 to -92 ^a
Neoprene	$\left[\begin{array}{c} \text{H} \quad \text{Cl} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{C} - \text{C} = \text{C} - \text{C} \\ \quad \\ \text{H} \quad \quad \text{H} \end{array} \right]$	-45
Hypalon®	$\begin{array}{c} \left[\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\ \quad \quad \quad \\ \text{Cl} \quad \text{H} \quad \text{H} \quad \text{H} \end{array} \right] \\ \\ \text{O} = \text{S} = \text{O} \\ \\ \text{Cl} \end{array}$	40: -22 45: -26
Kraton G® (A1 + A2 ~ 0.25 , B ~ 0.75)	$\begin{array}{c} \left[\begin{array}{c} \text{H} \quad \text{C}_6\text{H}_5 \\ \quad \\ \text{C} - \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_{A1} - \left[\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{C} - \text{C} = \text{C} - \text{C} \\ \quad \quad \\ \text{H} \quad \quad \text{H} \end{array} \right]_B - \left[\begin{array}{c} \text{H} \quad \text{C}_6\text{H}_5 \\ \quad \\ \text{C} - \text{C} \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_{A2} \end{array}$	-50

sample shows that the effect arises from the filler, a plate-like substance that greatly reduced the observed diffusion coefficient, presumably by making the diffusional path longer and more tortuous by

presenting an impermeable obstacle to diffusion, as argued by Van Amerongen.

EPDM also deviates somewhat significantly from the common linear relationship, but in this case the

Table I. Continued

Elastomer	T_g (°C)
	-48
	E60: -23 GF: -8

^aThis value varies widely based upon technique.

true value of the glass transition temperature of the sample is of some doubt.

Diffusion coefficients in polymers have also been linked to the diameter of the gas molecules as measured, e.g., by zeolite sieving diameters or Lennard-

Jones collision diameters.¹¹ A plot for several of the polymers examined in this work, shown in Figure 2, reflects this size-dependent trend well.

As noted earlier, solution coefficients of different gases in a given polymer are related to the conden-

Table II

Elastomer	He			H ₂			D ₂			O ₂			N ₂		
	P^a	D^b	S^c	P^a	D^b	S^c	P^a	D^b	S^c	P^a	D^b	S^c	P^a	D^b	S^c
Butyl 165	16.4	1020	0.0122	13.8	331	0.0316	11.3	216	0.0398	2.80	18.3	0.1164	0.76	8.9	0.0643
Butyl 268	16.4	946	0.0132	13.7	248	0.0420	11.7	248	0.0360	2.92	17.0	0.1304	0.76	8.5	0.0676
Butyl 365	16.3	1020	0.0122	14.0	303	0.0352	13.7	336	0.0311	3.35	21.8	0.1167	0.86	11.6	0.0561
Butyl 065	14.1	418	0.0256	11.7	257	0.0346	11.0	227	0.0368	2.50	14.7	0.1290	0.69	9.2	0.0569
Butyl average	15.8	851	0.0158	13.3	285	0.0359	11.9	257	0.0359	2.89	18.0	0.1231	0.76	9.5	0.0612
Hypalon® 40	8.8	631	0.0106	11.0	265	0.0314	10.2	232	0.0334	2.37	20.4	0.0881	0.63	9.8	0.0487
Hypalon® 45	11.5	1030	0.0085	15.6	484	0.0245	14.9	535	0.0211	4.20	48.6	0.0657	1.28	34.4	0.0283
Viton® E60	30.5	810	0.0286	10.6	187	0.0429	10.0	179	0.0426	2.28	13.9	0.1244	0.85	6.4	0.1007
Viton® GF	43.9	1830	0.0182	21.8	345	0.048	20.9	278	0.0571	4.20	38.6	0.0827	2.13	12.9	0.1255
Hydrin® 100 w/filler	1.5	73	0.0154	1.4	23	0.0474	1.6	18	0.0675	0.31	3.1	0.0743	0.15	0.8	0.1450
Hydrin® 100	5.5	526	0.0079	8.9	292	0.0233	8.8	293	0.0229	1.05	16.6	0.0481	0.44	9.2	0.0362
Kraton® G1652	45.3	1990	0.0173	68.6	1225	0.0426	64.3	1010	0.0484	26.60	192.0	0.1053	9.80	118.0	0.0631
Kraton® FG	46.2	2240	0.0157	66.9	1156	0.0439	59.8	968	0.0470	24.53	143.0	0.1304	8.63	98.1	0.0668
Kraton® KG VTEOS	45.1	2050	0.0167	69.7	1334	0.0397	63.6	993	0.0487	25.48	181.0	0.1070	9.91	114.0	0.0661
EPDM	33.6	1090	0.0234	49.4	502	0.0748	45.8	471	0.0738	21.14	147.0	0.1093	8.33	90.6	0.0699
ENR 76	23.6	647	0.0277	33.9	268	0.0962	31.7	247	0.0976	10.90	87.2	0.0950	4.90	67.4	0.0552
Neoprene	20.0	6040	0.0025	27.6	933	0.0224	26.7	1070	0.0190	8.83	101.0	0.0664	2.97	53.3	0.0424

^a In barrer. 1 barrer = 10^{-10} [cc(STP)cm]/(cm² cm Hg). Error: $\pm 10\%$.

^b Diffusion coefficients in units of cm²/s $\cdot 10^8$. Error: $\pm 10\%$.

^c Solubility coefficients reported in cc (STP)/cc atm. Error: $\pm 15\%$.

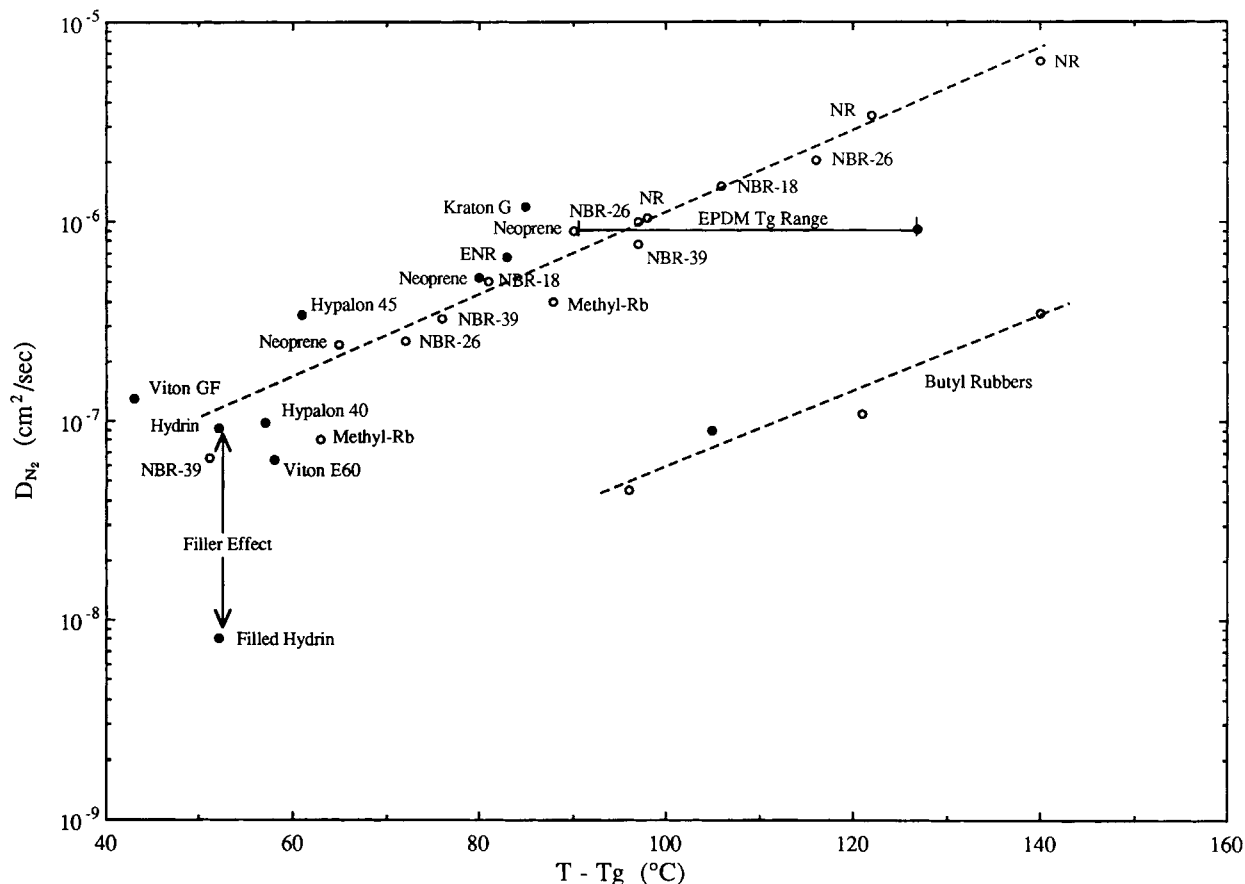


Figure 1 D_{N_2} dependence on mobility. Open circles are van Amerongen's data, closed are this study's.

sibility of each gas, as measured by boiling or critical point, which are in turn complex functions of the mass and polarity of the gas molecule.¹ Such a relation is shown in Figure 3, where the solubility coefficients of He, H₂, D₂, O₂, and N₂ are given as a function of the boiling point of these gases in different polymers. Note that the solubility coefficient of the gases is higher in the filled Hydrin® than in the nonfilled sample. This suggests that the filler may be acting as an absorption site within the polymer.

As a barrier, the filled Hydrin® sample had the lowest permeability of the samples for any gas measured. This is attributable in part to the filler in the material, magnesium silicate, which decreased diffusivity coefficients by approximately an order of magnitude. However, this filler also almost doubled the solubility coefficient of most gases so that the overall permeability measured was generally one fifth that of the control Hydrin® elastomer. If the enhanced solubility effect associated with the filler

could be eliminated, the filled Hydrin® would be even more attractive. Presumably, a similar filler could be used to great benefit for the other elastomers with an intrinsic low permeability such as butyl rubbers and Hypalon®.

The unfilled Hydrin®, Hypalon® 40, butyl rubber, and Viton® samples all had similarly low diffusion coefficients, and the unfilled Hydrin®, Hypalon 45®, and neoprene samples had the lowest solubility coefficients. The combined low solubility and diffusivity of gases in Hydrin® gave it the lowest permeability value aside from the filled sample.

The Hypalon® samples showed the effect of polar groups on solubility and diffusivity in these elastomers. The 35% chlorine (Hypalon 40®) version had significantly lower diffusion and solubility coefficients than the 24% (Hypalon 45®) version. The increasing chlorine content apparently increased the interchain attractions in the polymer, giving the material good barrier characteristics. This is an interesting case in that decreasing the chlorine content

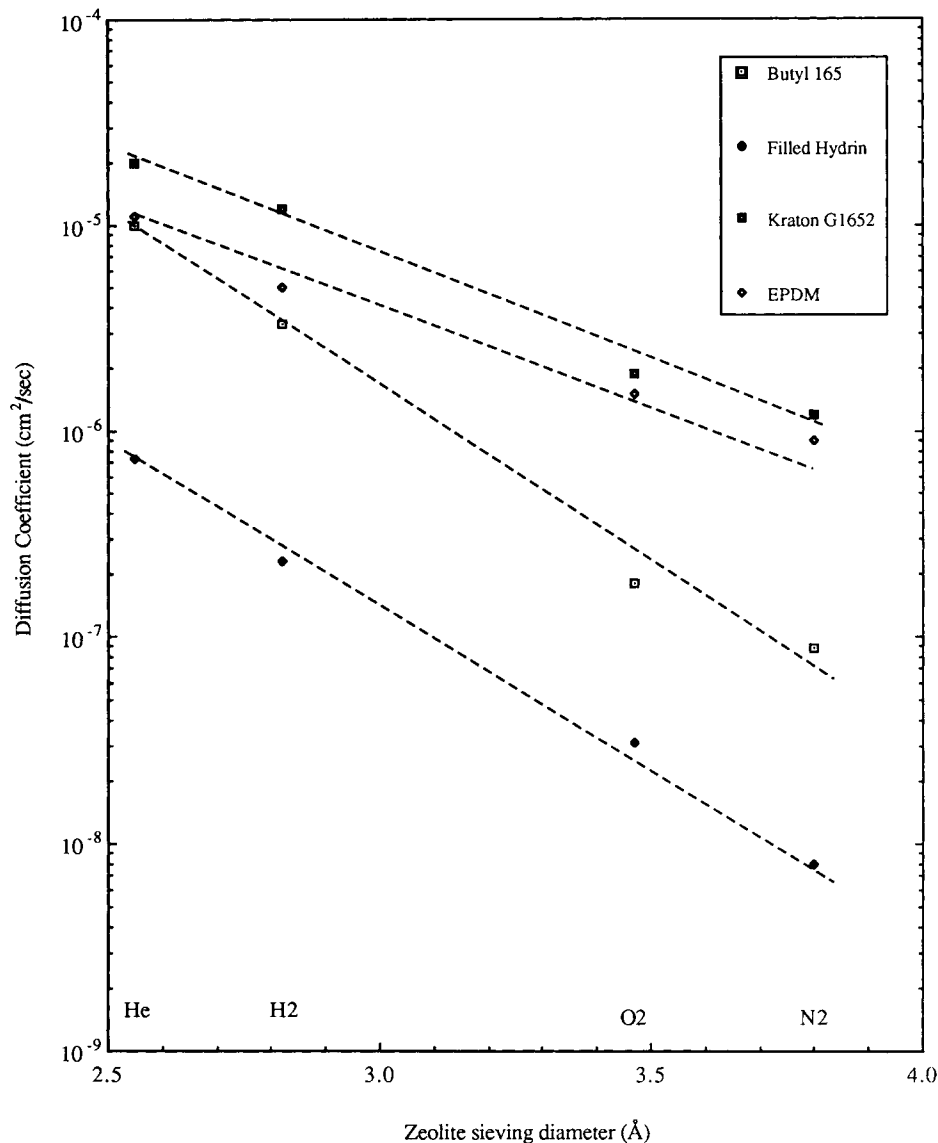


Figure 2 Diffusion coefficient against effective zeolite sieving diameter.

below that of the Hypalon 45[®] sample will begin to give polyethylene crystal regions, significantly changing all properties of the polymer.

In general, the more polar polymers had lower solubility coefficients, although the Viton[®] samples had relatively high solubility coefficients. This might be explainable by the high degree of fluorination, which tends to decrease the polarity or polarizability of the medium because of the scarcity of hydrogen in the polymer, much as polytetrafluoroethylene has a very low polarizability. Similarly, in the EPDM sample, with a completely hydrocarbon backbone, high solubility coefficients were measured, relative to the rest of the samples.

But, butyl rubber breaks this trend; it is com-

pletely hydrocarbon in content and was measured to have a low solubility parameter, but displayed fairly low solubility coefficients for all gases but oxygen. It seems the reason for this is that the packing of the chains is still tight enough to provide little free volume to promote gas dissolution. This effect can be rationalized by consideration of space-filling models of the polyisobutylene chain, which is extremely compact and prone to efficient packing while also being inhibited in its rotational freedom.

Isotopic Results

The permeability, diffusivity, and solubility selectivities of several polymers are given in Table III

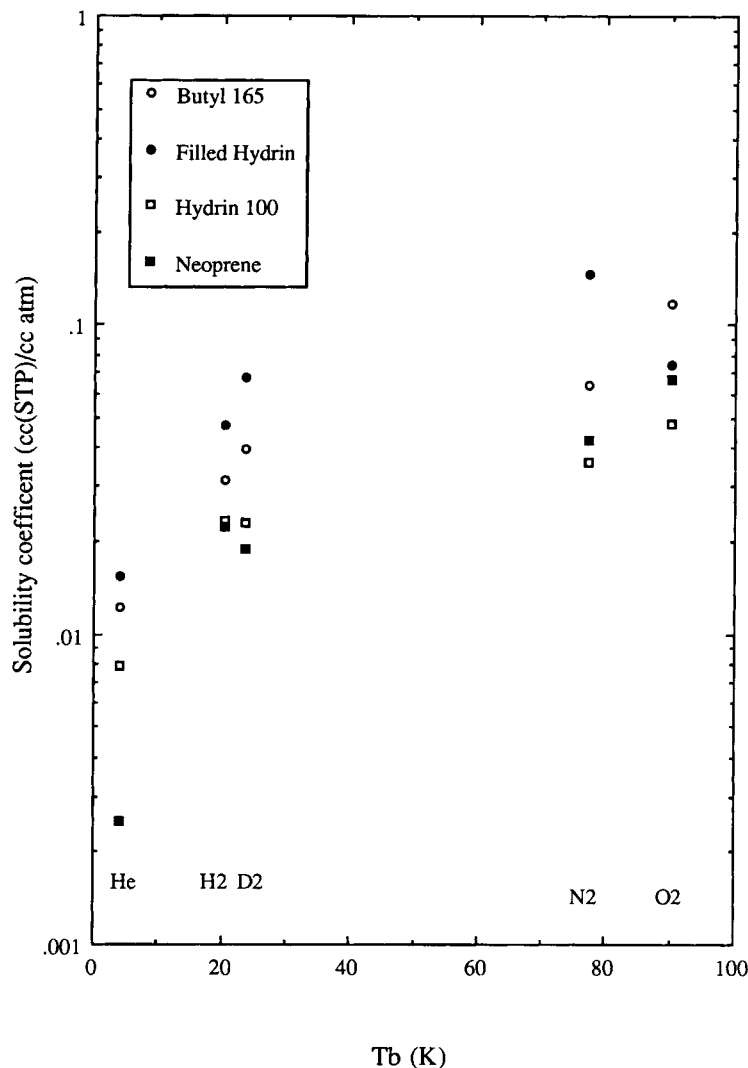


Figure 3 Solubility coefficient relation to gas condensability.

for hydrogen and deuterium. The diffusive selectivity for H₂/D₂ is generally in the range of 1.0–1.3 and the solubility selectivity is from 0.8–1.1.

The variation in solubility selectivity may reflect the calculated nature of the coefficients which were determined from the ratio of steady state permeation and diffusion coefficients measured by time lag. Small uncertainties in both P and D are accumulated in the calculated solubility coefficient based on these two parameters. Static H₂/D₂ sorption measurements have not been done in these polymers to our knowledge; however, precise measurements in organic liquids¹² revealed a solubility ratio of 0.95–0.98 in the range of –25 to 35°C. This solubility ratio was observed to be independent of the liquid but slightly dependent upon temperature. Such a solubility ratio of H₂ to D₂ is readily explained by

the difference in condensibilities of the two gases, as reflected by their critical and normal boiling temperature differences, $T_c = 33.24$ K and $T_b = 20.4$ K for H₂ and $T_c = 38.35$ K and $T_b = 23.7$ K for D₂.

The difference in diffusion coefficients between the isotopes is more difficult to explain fully. Previous publications have used a square-well potential model to rationalize the isotope effect in diffusion. Ziegel and Eirich⁵ used Eyring's fundamental equation

$$D = \lambda^2 \chi \quad (6)$$

and evaluated the rate constant χ in terms of a partition function and an activation energy for the diffusant, where the partition function was modeled as a gas molecule in a matrix cage. They arrived at

Table III Ratios of P , D , and S for Isotopic Pair

Elastomer	$P_{\text{H}_2}/P_{\text{D}_2}$	$D_{\text{H}_2}/D_{\text{D}_2}$	$S_{\text{H}_2}/S_{\text{D}_2}$
Butyl 165	1.22	1.53	0.79
Butyl 268	1.17	1.00	1.17
Butyl 365	1.02	0.90	1.13
Butyl 065	1.07	1.13	0.94
Hypalon® 40	1.08	1.14	0.94
Hypalon® 45	1.05	0.90	1.16
Viton® E60	1.05	1.04	1.01
Viton® GF	1.04	1.24	0.84
Hydrin® 100 w/filler	0.91	1.29	0.70
Hydrin® 100	1.01	1.00	1.02
Kraton® G1652	1.07	1.21	0.88
Kraton® FG	1.12	1.19	0.94
Kraton® KG VTEOS	1.10	1.34	0.82
EPDM	1.08	1.07	1.01
ENR 76	1.07	1.08	0.99
Neoprene	1.03	0.87	1.18

$$D = [(\lambda^2/v_f^{1/3})(kT/2\pi m)^{1/2}]e^{-E_D/RT} \quad (7)$$

where λ is the average diffusive jump length, E_D is the activation energy for diffusion, and v_f is the average cavity volume. Using this model to predict the diffusive selectivity between isotopes, the following was derived:

$$D_{\text{H}_2}/D_{\text{D}_2} = [\lambda(\text{H}_2)/\lambda(\text{D}_2)]^2 [v_f(\text{D}_2)/v_f(\text{H}_2)]^{1/3} \\ \times [m(\text{D}_2)/m(\text{H}_2)]^{1/2} e^{\delta E_D/RT} \quad (8)$$

where δE_D is $E_D(\text{D}_2) - E_D(\text{H}_2)$. If the assumption is made that hydrogen and deuterium are the same size and will have the same jump distance and cavity size, eq. (8) is unsatisfactory to describe their observations. The preexponential term is reduced to the square root of the mass ratio, and the exponential term, for which δE_D has been generally found to be a small positive value, becomes larger than one such that the predicted diffusion ratio is much larger than the measured value. Further, extension of the data to find cavity sizes and jump lengths leads to numbers that seem unusually large. This suggests that the partition function derived from the gas molecule in a square well may be too simplified for diffusion in such polymers.

Clearly, for most penetrants the mass effect de-

rived from the modeling the penetrant as a particle in a three-dimensional box plays a small role in determining the relative diffusivity of two penetrants. For example, in the CO_2/CH_4 gas pair penetrant size, not mass, is the determining factor in diffusion selectivity. We feel that consideration of subtle factors involving *both* size- and mass-related differences in velocities may be needed to arrive at a consistent physical picture of both the relative diffusivities of the H_2/D_2 gas pair, as well as the CO_2/CH_4 gas pair.

The articles on isotope diffusion to date have assumed H_2 and D_2 to be the same size. However, there is evidence to indicate that this is not strictly true. As a liquid at 20 K, the molar volume of H_2 is 28.3 ml, and of D_2 23.5 ml.¹² Fink and Ketkar¹⁴ measured the anharmonic bond length (the length of the bond for a molecule undergoing harmonic and anharmonic vibration) as 0.763 ± 0.002 and 0.749 ± 0.001 Å for gaseous H_2 and D_2 , respectively. In deuterated organic liquids and polymers, the volume of the deuterated unit has been found to be smaller than the protonated repeat unit by 0.2–0.4%.^{15,16} Therefore, it would seem quite reasonable to suppose that deuterium is smaller than hydrogen by some small but “measurable” amount. This difference in size would arise directly from the mass-induced quantum differences in the vibrational bond length of the gases. Because of the very small size of these molecules, the effect of the size difference may be insignificant to the diffusive process, but we feel this matter should be examined in more detail before one can assume that it plays no part in diffusive selectivity.

Bates¹⁶ has shown that the C—D bond is slightly less polarizable than the C—H bond. This amounts to only a 1–2% difference, and a similar difference may be expected in the molecular D_2 and H_2 bonds. This might produce a slight effect on the solution and diffusion of the two molecules in addition to direct volume and mass effects. One would expect the less polarizable molecule, deuterium, to interact less with the polymer and to be slightly less soluble than hydrogen. The very small difference in polarizability may play no measurable effect in these processes, but this is another physical effect to be considered in a precise treatment of this process.

With size and polarizability considered, the notion that D_2 is slightly smaller and slightly less polarizable than H_2 , when applied with the conventional understanding of gas-polymer activated diffusion, would lead to the conclusion that deuterium actually has a higher diffusion coefficient in a given polymer than does hydrogen. However, in every reported case hydrogen has a higher diffusion coeffi-

cient and, in most cases, a lower apparent activation energy of diffusion (E_d) and preexponential (D_0) value. How, then, can we develop a physical model to explain this?

The lower energy of diffusion and preexponential value for hydrogen are interrelated. Work by Barrer¹⁷ showed a dependence of D_0 upon E_d/T . This relationship is seen to apply to the reported deuterium values^{3,5,6} in Figure 4. Thus, we may consider only E_d when explaining the difference in diffusion coefficients for the two gases. Table IV sum-

marizes reported values of E_d for D_2 and H_2 in a variety of polymers, as well as the difference in the energies, ΔE_d . The reported values generally show a lower value of E_d for H_2 than for D_2 (ΔE_d positive), contrary to the previously presented ideas about size and polarizability for penetrants trapped in a polymeric cage.

If volume and polarizability favor deuterium to diffuse at a higher rate than hydrogen, then the mass difference is the most reasonable explanation of hydrogen's lower energy of diffusion. The model of

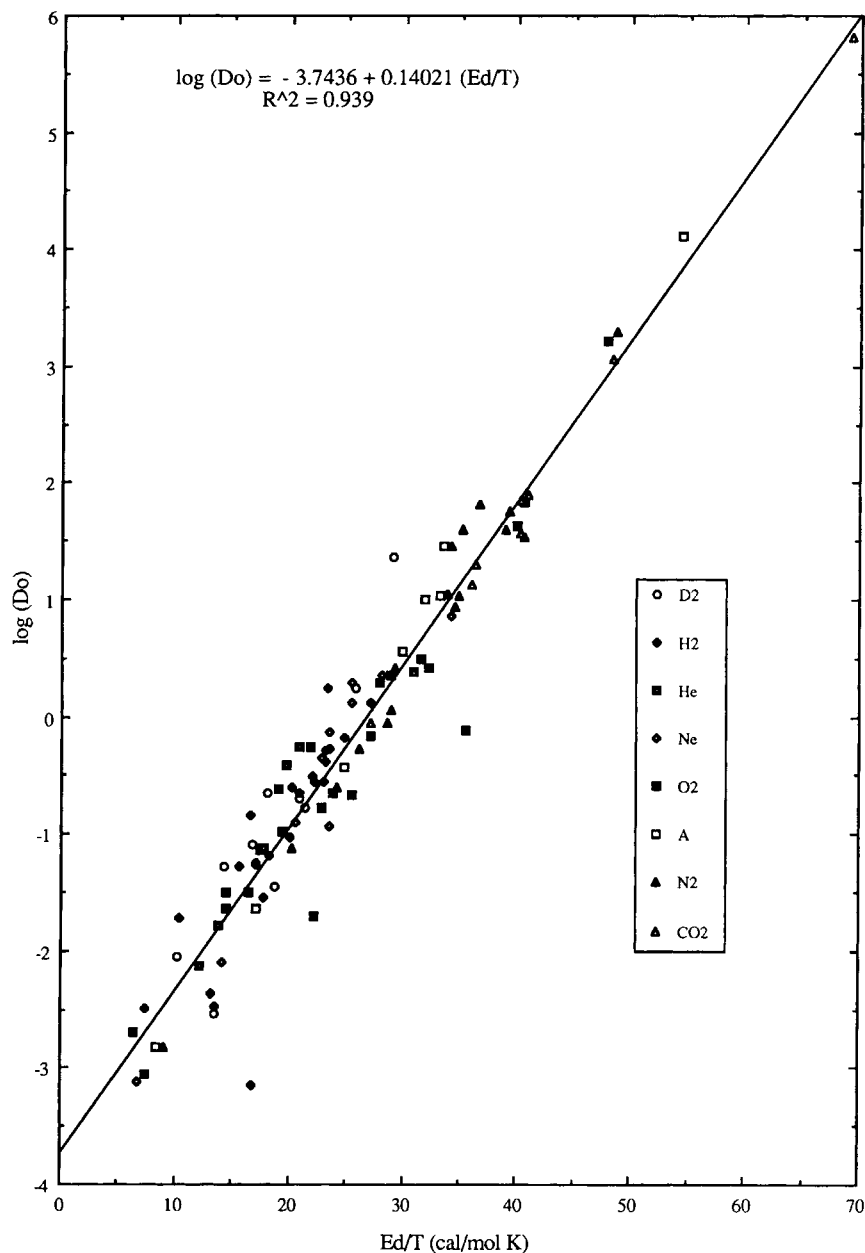


Figure 4 Correlation of D_0 to energy of diffusion. Data from references 1, 3, 5 and 6.

Table IV Isotope Activation Energies for Diffusion

Polymer	Temperature (°C)	E_d (H ₂) (cal/mol)	E_d (D ₂) (cal/mol)	ΔE_d (cal/mol)
Poly(dimethyl siloxane) ^a	44	3460	3390	-70
Polyurethane ^a	64	7780	9660	1880
Poly-cis-isoprene ^a	36	5530	6040	510
Poly(ethyl methacrylate) ^a	> 65	6060	6930	870
Poly(ethyl methacrylate) ^a	< 60	4250	4640	390
Poly(vinyl fluoride) ^a	> 46	4520	5280	760
Poly(vinyl fluoride) ^a	< 46	7800	7870	70
Polyethylene ^b	25-30	5314	5597	184
Poly(vinyl acetate) ^b	27-40	6749	7875	1126
Poly(vinyl acetate) ^b	15-19	4837	4842	5
Polystyrene ^b	25-40	4112	4120	8
Poly(vinyl chloride) ^b	25-40	5637	5876	239
Poly(ethylene terephthalate) ^b	25-40	6839	6671	-168
Synthetic Natural Rubber ^c	30-60	4969	5308	339
Polyethylene ^c	30-60	6369	6809	440

^a Ref. 5.^b Ref. 3.^c Ref. 6.

Ziegel and Eirich [eq. (8)] predicts gaseous hydrogen to diffuse at a higher rate than gaseous deuterium by the square root of mass, but we also question such purely gaseous models for activated diffusion. We are led instead to describe diffusion for these very small molecules as a process seemingly possessing aspects of both activated diffusion and a mass-based, Knudsen-like diffusion.

Knudsen diffusion offers a good model of a "penetrant" diffusing purely by mass effects. One can estimate the "apparent" ΔE_d of Knudsen diffusion for H₂ and D₂ if such diffusion were erroneously modeled as activated diffusion:

$$D = 9.7 \times 10^{-5} r_p [T/MW]^{1/2} \\ = D_0 \exp(-E_d/RT) \quad (9)$$

where D is in cm²/s, r_p is the pore radius in cm, T is in Kelvin, and MW is in g/mol of gas.¹⁸ That is, one could fit experimental data from Knudsen diffusion to an activated diffusion model over a small range of temperatures and produce some erroneous activation energy for diffusion. Using the above equality and substituting the linear relation described in Figure 4 for D_0 , we may express $\Delta E_d = E_d(D_2) - E_d(H_2)$ as

$$\Delta E_d = -0.3466T(0.323 - 1/R)^{-1} \quad (10)$$

where T is in Kelvin, ΔE_d is in cal, and R is 1.987 cal/mol K. Therefore, for Knudsen diffusion described arbitrarily as activated diffusion ΔE_d at 25°C is 571 cal/mol, at 35°C is 592 cal/mol, and at 60°C is 639 cal/mol. These energy differences are well within the range of energies reported in Table IV. This illustrates that mass-based diffusion, such as Knudsen diffusion, could provide an acceptable model for the difference in diffusion of the H₂ and D₂. A cage-based model would predict negative values for ΔE_d . We are not proposing that Knudsen diffusion occurs in these membranes, but showing that for these small penetrants mass plays a significant role in the energy of diffusive separation.

A possible physical model consistent with most of these observations considers the H₂ or D₂ as existing in an essentially static matrix over time scales of importance to a diffusive jump. The free volume of a polymer is clearly not well represented as a static pore network over time scales of more than micro- or even nanoseconds. However, over an arbitrarily short time scale the rapidly moving sorbed penetrants may interact with the chains comprising the matrix as if they are effectively immobile, with intersegmental spacings that are, in general, too small to allow free movement of typical penetrants. In this case, the sorbed penetrant behaves essentially as a three-dimensional oscillator, exploring the "walls" of its cage to find an opening of sufficient size to permit its escape. In the absence of such an opening,

the penetrant continues to explore its cage until a thermally generated rearrangement of the matrix (over a nano- or microsecond scale) produces an opening of sufficient size to allow the penetrant to escape, thereby performing a diffusive jump. Note that such a model becomes very dependent upon subtle properties of the macromolecular matrix.

For a "large" penetrant such as CO₂ or CH₄, the likelihood of finding an opening into a new cage before local rearrangement of the polymer matrix creates such an opening at the sorbed penetrant's site is very small because of the large dimension of the penetrant compared to the range of possible opening sizes in the matrix. Because the likelihood of openings at a given point of the matrix are thought to be inversely and exponentially dependent upon the size of the opening, increasingly larger penetrants must wait increasingly longer for local rearrangements to produce a sufficiently large opening. Thus, large penetrants can take fewer jumps per second than can smaller penetrants and have proportionally smaller diffusion coefficients. This is consistent with conventional visualizations that suggest that the major determinant of the ability to jump is rearrangement of the matrix, not differences in exploration rates of the sorbed cage.

However, if a penetrant were sufficiently small every opening in the polymer network would be large enough to allow a diffusive jump and the rate of diffusion would become a phenomenon controlled purely by the random movements of the penetrant itself. That is, for infinitely small isotopes the diffusive selectivity in any polymer network would be the same as if the isotopes were in a gas phase, which is the inverse square root of the mass ratio. For slightly larger penetrants, many openings would be sufficiently large for a diffusive jump without local rearrangement of the polymer matrix, and both size and mass become important in the diffusive process. Because of their very small size, penetrants such as He, H₂, and D₂ may have the ability to find multiple openings in the locally confining cage within which they oscillate. The mass ratio between H₂ and D₂ would suggest a roughly $(2/4)^{1/2} = 1.414$ times higher exploration rate for H₂ in its sorbed cage than for D₂. If the two molecules were the same size, H₂ should find an escape opening 1.414 times faster than D₂ and enter the next confined domain, where it begins to explore for another opening to continue its random walk. If the isotopes differ in size and D₂ is slightly smaller, the rate at which D₂ finds an opening of suitable size is greater than that of H₂, which would influence the diffusive selectivity to-

ward D₂. Therefore, the diffusive selectivity in a given polymer membrane becomes an interplay between the exploration rate and subtle size differences between the two penetrants.

For larger caged penetrants, the exploration rate diminishes in importance as the probability of finding a suitable opening decreases. Thus, for very large molecules mass differences become insignificant. For molecules such as CO₂ and CH₄, the mass ratio would suggest a roughly $(44/16)^{1/2} = 1.65$ times higher rate of exploration of the sorbed cage for CH₄ than for CO₂. Nevertheless, the ratio of diffusion coefficients in polymers typically favors CO₂ by a factor ranging from 1.2 to as much as 16, depending upon the rigidity and segmental packing of the matrix. The large sorbed penetrant is very unlikely to find an opening in the matrix once in a new cage until local rearrangement opens a sufficiently large hole for a jump. In this scenario, the penetrant must wait for polymer rearrangement to diffuse. This is markedly different from the case presumed to apply for small penetrants discussed above, in which every time a penetrant comes into a new cage there is a fair probability of a sufficiently large opening for diffusion to already exist in the cage. In this case, the small penetrant need merely find the opening to diffuse, not wait on local rearrangement to present such an opening.

Should the above be an accurate physical model of diffusion, it becomes clear that differences in diffusive selectivity between H₂ and D₂ arise from differences in opening size distributions in polymers. The more tightly packed a polymer is, the greater the effect of the isotope size difference, and therefore the lower the diffusive selectivity for H₂/D₂. Theoretically, selectivities of less than one might be measured in closely packed polymers.

Clearly, this physical model shows agreement with the model of Ziegel and Eirich if one leaves in the λ and v_f terms in eq. (9), i.e., if one does not assume H₂ and D₂ to be the same size.

Returning to Table III, it is apparent that the H₂/D₂ diffusive selectivity is somewhat dependent upon the packing of the polymer. Although all rubbers we studied are expected to be closely packed, butyl rubbers, Hypalon,[®] and Hydrin[®] may be considered the most tightly packed. For these rubbers, low selectivities are generally observed, contrasted to the relatively high selectivities found in polyethylene and styrene butadiene rubber (Kraton[®]), which may be considered open polymers. However, the high reproducibility of differing diffusive selectivities in four butyl rubber samples seems to show

that the local polymer arrangement in individual samples of one polymer may vary greatly enough to obscure the effect of the overall polymer properties.

Figure 5 shows the diffusion coefficient at 25°C of several progressively larger gases in three of the elastomers in this study. It is clear from this figure that the difference in the diffusion coefficient of a gas between the polymers increases in magnitude as the size of the penetrant increases. For example, the ratio of the diffusion coefficient for hydrogen in Hypalon® 45 to that of butyl rubber 165 is smaller than that of nitrogen. This trend suggests that the polymer-related effect on diffusion arises from size considerations and that differences in packing have substantially larger effects on diffusion coefficients as penetrant size increases. Importantly, the effect

of this packing is apparently negligible for hydrogen and helium for these polymer comparisons. This does not mean that the diffusion coefficient of hydrogen or helium is *independent* of the polymer matrix, but rather that *differences* in the matrix at larger levels, important to the diffusion of larger penetrants, are of lesser importance in the diffusion of small penetrants.

In summary, the above issues suggest that mass differences should play a minor role in the normally activated process and are dominant in the case of the H_2/D_2 pair. In comparing the diffusive selectivity for a small molecule (H_2 , D_2 , or He) with that of larger molecules, the above discussion also has important implications. It would seem that the optimum medium for such separations would be the

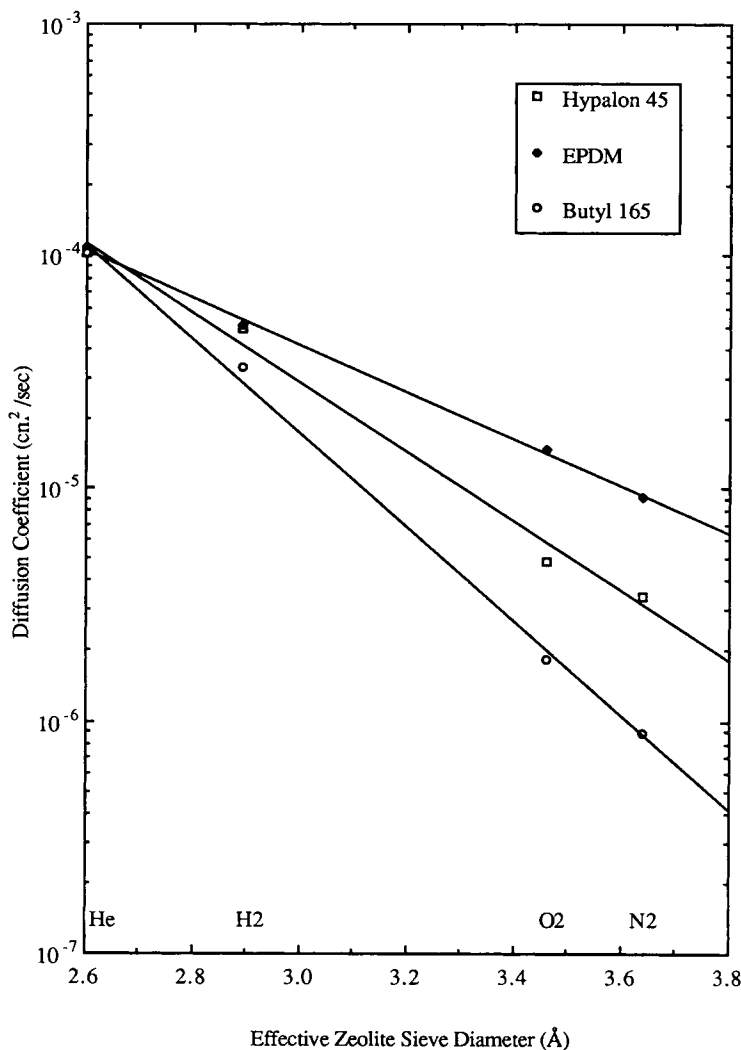


Figure 5 Relation between diffusion coefficient and penetrant size.

one with sufficient free volume between segments to allow the small molecule to make multiple high-frequency jumps in the time between the micro- or nanosecond periods when the matrix undergoes sufficient local rearrangements to permit a single diffusion jump by the large molecule. A good example of such materials are the glassy, packing-inhibited polyimides typically used for gas separation.

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Received December 1, 1991

Accepted April 28, 1992