Diffusion of Gases in Fluorocarbon Polymers

W. W. BRANDT, and G. A. ANYSAS, *Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois*

INTRODUCTION

Diffusion processes in high polymers have been studied by many workers,[1-12] because, aside from the technical interest of the resulting data, there exist certain correlations among diffusion parameters and to the known molecular structure parameters. As an example, it was observed long ago that the activation energy E_D appearing in the Arrhenius-type expression for the diffusion coefficient D

$$D = D_0 e^{-E_D/RT} \tag{1}$$

is linearly related to the logarithm of the frequency factor D_0 of the same equation. The symbols e, R, and T have their usual meaning. To explain this, Barrer[3] postulated that a diffusion "jump" requires an activated region, or "zone," comprising the neighborhood of the diffusing molecule. The size of the zone determines both E_D and the activation entropy $\Delta S^{\ddagger}$ or log D_0 of eq. (1). Lawson[13] similarly showed that several relatively simple models of the diffusion process lead to a linear relation between the energy and entropy of activation:

$$\Delta S^{\ddagger} = 4\alpha H_D \simeq 4\alpha E_D \tag{2}$$

Here α is the thermal expansion coefficient at constant pressure, and H_D is the heat of activation.

In addition to the above model approaches, several attempts have been made to correlate the diffusion parameters E_D and D_0 (or $\Delta S^{\ddagger}$) to certain definite molecular structure variables. van Amerongen[2] found a correlation between the E_D values obtained on various rubbers and the cohesive energy density per unit length of the backbone chain. Meares[6] extended this approach by calculating activation energies as the energies required to produce a void of cylindrical shape in the high polymer matrix against the action of the cohesive energy density. The "jump" distances calculated by this treatment are manifold the solute molecular diameter.

One of us[14] suggested a different model for the diffusion process. The activation energy is thought to be required in part to "bend" the chain molecules, and in part to overcome the attractive forces between them. Segment lengths can be calculated on this model which compare well with those obtained by other methods.[15,16] Also, Michaels and Parker[17] have

shown that their extensive diffusion data on polyethylene support the model's feature which claims that any free or unoccupied volume found between the molecular chains serves to reduce the required activation energy for the diffusion jump, in that less work needs to be done to clear a path for the diffusing molecule.

Kumins and Roteman[18] recently fitted their diffusion data on a vinyl copolymer by adopting an expression for the jump frequency derived earlier by Bueche.[19]   Their data can equally well be represented by the expressions resulting from the aforementioned model calculation.[14]   In any case, an interpretation on the basis of Bueche's theory implies that the solute diffusion jumps always require the cooperation of the neighboring polymer segments, while the model proposed by Brandt[14] requires such cooperation only for solute molecules which are too large to pass through the existing free spaces.   It is very likely that a full description of the diffusion process will ultimately require a synthesis of these two approaches.

The present research was undertaken to further elucidate the merits of the different semitheoretical treatments.

Fluorocarbon polymers were chosen in this work because they have some unusual molecular properties, such as a high chain stiffness, and weak intermolecular forces.   Also, there seem to be no diffusion data on these materials available in the literature.

EXPERIMENTAL

The perfluorocarbon polymers used in this study were experimental compositions supplied by the Polychemicals Department of the Du Pont

TABLE I
Sample Characteristics[a]

Polymer	Crystallinity, %	Void content, %	Density, g./ml.	Abbreviation
Polytetrafluoroethylene	52	0.1	2.144	PTFE-52
Polytetrafluoroethylene	89	1.2	2.236	PTFE-89
Tetrafluoroethylene–hexafluoropropylene copolymer (86/14)	~33	—	~2.15	Copolymer
Polychlorotrifluoroethylene (Kel-F, Type 1270-25-10 Lot 902P)[b]	~55	—	~2.1	PCTFE

[a] All information from the suppliers.
[b] PCTFE contains about 25% of a low molecular weight fraction; the molecular weight distribution is therefore anomalous.

Company.   The polychlorotrifluoroethylene used was a commercial sample, from the M. W. Kellogg Co.   Sample descriptions and suitable abbreviated designations are listed in Table I.

Film samples were prepared from the original pieces of polytetrafluoro-ethylene, PTFE-52 and PTFE-89, and from a compression-molded sheet of the polychlorotrifluoroethylene, PCTFE, using a Spencer model 820 precision microtome. The copolymer was compression molded into films of suitable size. The average film thickness of 10–35 mils was determined, using a dial gauge, with a standard deviation close to 0.3%.

Most of the diffusion and solubility coefficients were determined by the conventional spring balance method using a helical nichrome spring with a sensitivity of approximately 1 mg./mm. extension and load capacity of about 300 mg. The reported data are usually averages of two or more runs.
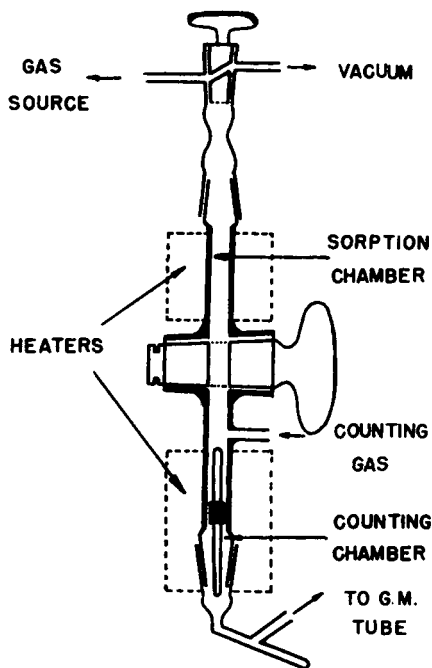

Fig. 1. Schematic drawing of the tracer diffusion apparatus.

A second method used consists of measuring the rate of desorption of tagged carbon dioxide from the polymer sample. The experimental arrangement is shown in Figure 1. The carbon dioxide containing the carbon-14 is prepared from barium carbonate with a specific activity of approximately 1 mc./mmole by the addition of concentrated sulfuric acid and is then stored. The polymer sample is placed in the sorption chamber and degassed. Next, the tracer gas is admitted to this chamber and the pressure adjusted to a level which is suitable for the rate measurement proper, as described below. Enough time is allowed for sorption equilibrium to be attained. A thin layer of mercury lying on top of the

large stopcock prevents or reduces contamination of the lubricant by the active gas. While the sorption is in progress, counting gas is flowing through the empty counting chamber and the background count is obtained using a windowless detector (Wood Laboratories, Chicago) and a Nuclear Chicago Model 182 scaler unit.

To start the desorption the gas pressure in the sorption chamber is reduced quickly to a few millimeters of mercury, and the large stopcock is opened so that the sample falls into the desorption chamber. Since it is attached to a small glass rod, it ends up somewhere near the center of this chamber. The mercury also falls down and flows to the end of the long and narrow tubing. According to blank experiments the additional count due to the mercury is negligible. While the sample falls into place, a stream of counting gas rushes upward and effectively rinses the sample of the tracer gas. The large stopcock is closed immediately after the sample has passed through and the total count is obtained as a function of time. The zero time of the experiment is taken to be the moment when the first active gas reaches the Geiger tube. The precision of the data and the agreement of experimental and theoretical desorption curves depend markedly on the accurate determination of the background. The carbon dioxide pressures used in the sorption steps of these experiments were less than 75 mm. Hg; the limited pressure range and the present level of precision mean that the concentration dependence of the diffusion coefficients is not discernible. This effect is expected to be quite small in the gas–polymer systems used here. In many experiments the active carbon dioxide was diluted with air. This also appeared to have no effect on the resulting diffusion coefficients. The probable errors in the diffusion coefficients are estimated to lie below 5%, provided there is good temperature control.

The tracer method described here was used to measure the diffusion coefficients of CO_2 in PTFE-52, in the copolymer, and in the PCTFE. The gravimetric method was found to be useless for the latter polymer because some of the low molecular weight component present is desorbed under the experimental conditions leading to nonsignificant weight readings and to a bad distortion of the sample films. The agreement of the results obtained from the tracer method and from the spring balance is quite satisfactory, as can be seen from Figure 2.

Solubility coefficients are not available from the tracer method in its present form.

RESULTS

Figures 2 and 3 show the logarithms of the diffusion coefficients (in cm.^{2}/sec.) plotted against the inverse of the absolute temperatures. The effects of the solute molecular size and the polymer crystallinity are easily discerned and will be discussed in the next section. Table II sum-

marizes the frequency factors D_0, the activation energies E_D, the heats of solution ΔH, and constants s_0 of the solubility-temperature relation

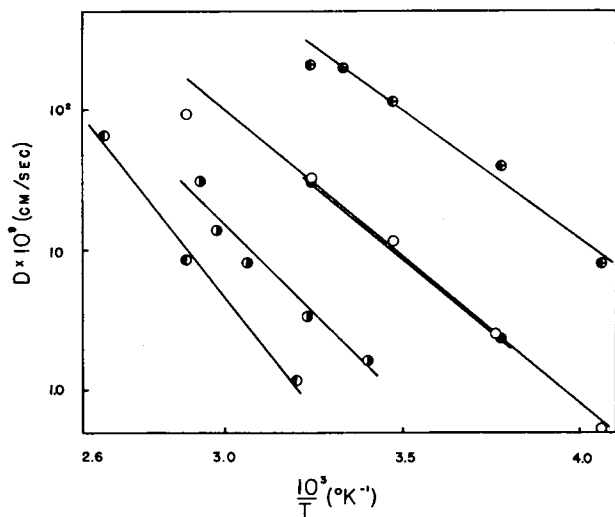$$s = s_0 e^{-\Delta H/RT} \tag{2}$$

Fig. 2. Logarithms of the diffusion coefficient D, against $1/T$: carbon dioxide (●) by spring balance, (◐) by tracer method; (○) methyl chloride; (●) fluoroform; (◐) sulfur hexafluoride, all in PTFE-52; (◑) methyl chloride in PTFE-89.
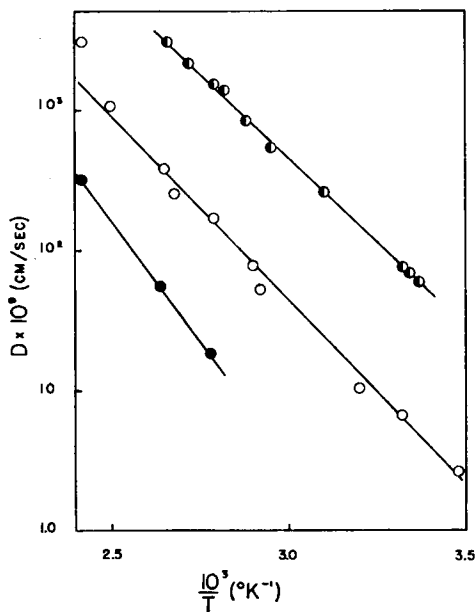

Fig. 3. Logarithms of the diffusion coefficient D, against $1/T$ for the copolymer: (◐) carbon dioxide, tracer method; (○) methyl chloride; (●) sulfur hexafluoride.

The data obtained on the polychlorotrifluoroethylene are presented in tabular form only.

TABLE II

Frequency Factors D_0, Activation Energies E_D, of the Arrhenius Equation, Eq. (1); Solubility Constant s_0, and Heats of Solution ΔH of Eq. (2)

	D_0, cm.^{2}/sec.	E_D, kcal./mole	s_0, cc. (STP)/ cc. $\times$ atm.	ΔH, kcal./mole
PTFE-52				
Carbon dioxide	0.25	8.4	1.7×10^{-3}	-3.7
Methyl chloride	0.21	9.6	1.1×10^{-3}	-4.6
Fluoroform	0.16	9.5	4.1×10^{-4}	-5.6
Sulfur hexafluoride	17.2	14.6	4.9×10^{-4}	-5.2
PTFE-89				
Methyl chloride	0.46	11.4	1.4×10^{-3}	-3.7
Copolymer				
Carbon dioxide	7.65	11.0	—	—
Methyl chloride	3.5	12.0	1.2×10^{-2}	-2.9
Sulfur hexafluoride	68.3	15.8	9.9×10^{-3}	-2.6
PCTFE				
Carbon dioxide	0.35	9.8	—	—

DISCUSSION

Solute Molecular Diameter

As expected,[6, 14] the measured diffusion coefficients decrease and the activation energies increase with increasing solute molecular size (Fig. 4). Data from this research and from other sources show similar trends; in particular, the curve for polyvinyl acetate may be considered typical for many polymers. The data for fused silica[3] are included to show that the resistance offered to diffusion by the amorphous or liquidlike regions of the high polymer is considerably lower than that offered by typical ionic solids.

The curves in Figure 4 do not converge to the origin, and there is no single set of molecular diameters which would remedy the situation. The present plot used the values derived from gas viscosities by Hirschfelder and co-workers,[20] because these seem to be the most complete.[21] If one extrapolates the curves shown in this Figure to the abscissa, one finds that the activation energy vanishes for hypothetical molecules of $\sigma^2 = 5-8$ A^2. The model for the diffusion process described earlier[14] relates this intercept at the abscissa to the average free distance between the chain molecular surfaces, or the "free cross section" corresponding to the chain molecular cross section. An approximate calculation of this free cross section from the difference of the specific volumes of the amorphous polymers and the van der Waals volume yields values for the limiting σ^2 which overlap the above values. This tends to support the new model in contrast to Meares' proposal which cannot account for the intercept.

The rather precise data of Meares[6,7] and Ryskin[8,9] on polyvinyl acetate, and of van Amerongen[1,2] on polybutadiene, as well as other data of the latter author which are not reproduced here, show a distinct curvature in
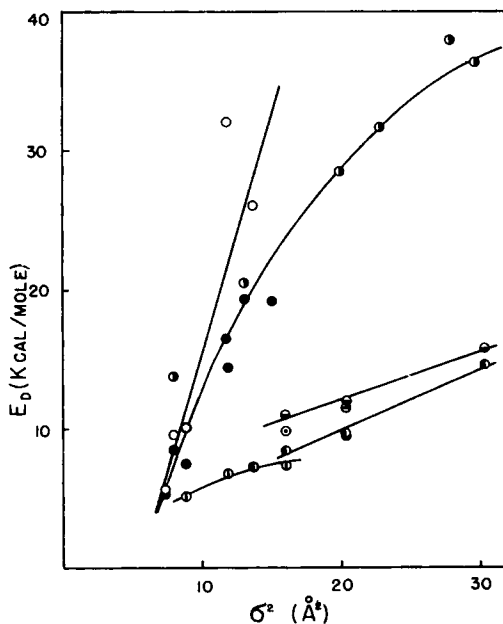

Fig. 4. Correlation of the activation energy of diffusion E_D, and the square of the solute molecules diameter σ^2: (●) polyvinyl acetate (data of van Amerongen[2]); (◑) polyvinyl acetate (data of Ryskin[9]); (◐) polybutadiene (data of van Amerongen[1]); (◒) PTFE-52 (this work); (⊖) PTFE-83 (this work); (◓) copolymer (this work); (○) PCTFE (this work); (○) fused silica (data of Barrer[3]). The σ^2 values are derived from gas viscosities.[6]

the plot of activation energies vs. the solute molecular diameter squared. This feature remains unexplained; it is not consistent with any one of the simple models proposed to date.

The Intermolecular Forces

Meares' model of channel formation discussed above implies that the activation energy for the diffusion of a given solute molecule in different polymers increase with the strength of the intermolecular forces present in these polymers, assuming similar jump lengths. The data of Figure 4 do not support this suggestion; the cohesive energy densities of polyvinyl acetate, ethyl cellulose, PTFE-52, and polybutadiene have been estimated to be 88, 120, 39, and 71 cal./ml., respectively.[22] This implies that the variations of the intermolecular forces do not, without further assumptions, permit one to describe the diffusion process.

The Polymer Chain Stiffness

Krigbaum's work on the polymer solution properties[23] shows that ethyl cellulose has very inflexible molecules. Also polytetrafluoroethylene can be assumed to have stiff and twisted backbone chains, and it is clear from Figure 4 that both polymers offer relatively small energy barriers to diffusion. In terms of the zone theory of diffusion,[3] one can say that relatively few degrees of freedom are involved in the diffusion process. A possible explanation of these findings lies in a comparison of the experimental heats of solution with the values calculated from the solubility parameters, following Barrer's suggestion.[5] For polyvinyl acetate, ethyl cellulose, PTFE-52, and polybutadiene the differences between observed and calculated heats of sorption are -1.4, -6.0, -4.8, and 0.2 kcal./mole, respectively. That is to say, the sorption process in ethyl cellulose and PTFE-52 is much more exothermic than one would expect from the solubility data obtained on low molecular weight compounds. Barrer suggested this to be an indication of the existence of numerous preformed cavities of molecular dimensions which can serve as sorption sites and make the expenditure of energy for hole formation unnecessary. If we assume these preformed interspaces to consist partly of holes and partly of irregular channels, then the low activation energies of diffusion in ethyl cellulose and PTFE-52 are reasonable. The hypothesis advanced here does not explain the very low activation energies needed for the diffusion of gases in polybutadiene. The data obtained by van Amerongen[1,2] on other types of rubber are not shown in Figure 4, but they would lie between the curves for the polybutadiene and the polyvinyl acetate.

The rubbery materials in question can be expected to have exceedingly flexible chains judging from Krigbaum's data,[23] and this may be the reason for the relatively low activation energies.

The Activation Entropy

The very good correlation of the logarithms of the frequency factors and the activation energies shown in Figure 5 is well known. Again, the center line refers to the precise data of Meares,[6,7] which may be considered typical of many organic high polymers. The data for the PTFE-52, PTFE-89, and PCTFE lie distinctly below this reference line. The correlation shown here is consistent with Barrer's zone theory[3] and several continuum models of diffusion, as pointed out by Lawson.[18]

Figure 5 shows that the self-diffusion data obtained by various authors on low molecular weight liquids probably follow a steeper correlation line. The self-diffusion data of McCall and Anderson[24] on the homologous methylsiloxanes of low molecular weight demonstrate that for a given value of the activation entropy chain molecules will need a larger activation energy to diffuse than their low molecular weight counterparts. Liquid sulfur, having long chains, leads to a very high activation energy of self-diffusion.[25] Data on homologous hydrocarbons found in the literature[26]

show similar trends. According to the transition state theory,[27] and the zone theory, the pre-exponential factor D_0 of the Arrhenius eq. (1) contains $\lambda^2\nu$, where λ is the "jump distance" of the diffusing molecule and γ is its thermal vibration frequency (actually, $\nu = ekT/h$, where e, k, T, and h have their usual meanings).

Extrapolating the polymer correlation line to the ordinate, one can obtain an estimate of the quantity $\lambda^2\nu$, which is in good agreement with the
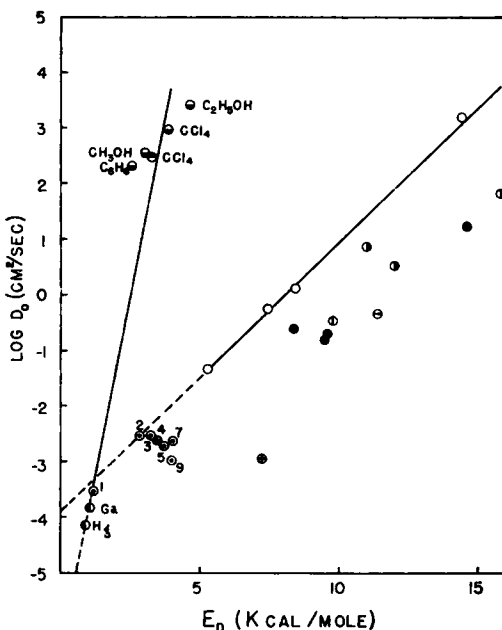

Fig. 5. Correlation of the logarithms of the frequency factors D_0, and activation energies E_D: (O) gases and vapors in polyvinyl acetate (data of van Amerongen[2] and Barrer[4]); (◐) self-diffusion in low molecular weight liquids (data of Rathbun and Babb[30]); (◓) data of Watts, Adler, and Hildebrand;[31] (◉) in liquid metals (data of Nachtrieb and Petit[32]); (⊙) in $(CH_3)_3Si—[O—Si(CH_3)_2]_{N-2}—OSi(CH_3)_3$ where N is given in the figure (data of McCall and Anderson[24]); (⊕) in liquid sulfur (data of Saxton and Drickamer[25]); (●) gases in PTFE-52 (this work); (◒) gases, in the copolymer (this work); (⊖) gases in PTFE-89 (this work); (⊕) gases in PCTFE (this work).

values typically assumed.[3,6] The extrapolated values of $\lambda^2\nu$, lead to ratios of $\Delta S^{\ddagger}/E_D$ which are constant within the experimental error for various solutes diffusing in a given high polymer as seen on Table III. The frequency ν is probably a very weak function of the solute molecule's size and mass and hence on the present logarithmic scale appears to be constant, within the experimental uncertainties, for a given high polymer.

Interestingly, the very approximate $\lambda^2\nu$, values one obtains by this method for low molecular liquids are very small, suggesting that in this case the diffusion proceeds by small steps, while in high polymers solute molecules seem to jump by distances of the order of molecular diameters.

As an example, for $\nu = 10^{12}$ sec.$^{-1}$, and $\lambda^2\nu = 10^{-4}$ cm.^{2}/sec., one gets $\lambda = 1$ A.

The values of $\Delta S^{\ddagger}/E_D$ as derived by the above procedure are listed in Table III. Obviously they are fairly close to four times the thermal expansion coefficient, in those cases where experimental values of this quantity are available. In addition the $\Delta S^{\ddagger}/E_D$ ratios are remarkably constant, and consequently there are no clear-cut correlations between this quantity and the cohesive energy densities, the measures of the chain stiffness summarized by Krigbaum,[23] or the glass transition temperatures. In short,

TABLE III

Extrapolated Frequency Factors ($\lambda^2\nu$), Slopes of the Correlation Line ($\Delta S^{\ddagger}/E_D$) of log D_0 and E_D, Thermal Expansion Coefficients (α), and Square Roots of Cohesive Energy Densities, (C.E.D.)$^{1/2}$

Polymer	No. of data used for correlation	Log $(\lambda^2\nu)$, cm.^{2}/sec.	$(\Delta S^{\ddagger}/E_D)$ $\times 10^3$	$\alpha \times 10^4$, deg.$^{-1}$	(C.E.D.)$^{1/2}$ cal.$^{1/2}$/ ml.^{2}	Reference
Polyvinyl acetate	17	−4.4	2.26			Ryskin[8,9]
''	7	−3.7	2.17	—	8.91	Meares[6,7]
''	4	(−7)	2.72			Wilkens
Polyvinyl alcohol	2	−2.2	0.84	—	8.68	Ryskin[8,9]
Polystyrene	4	−3.2	1.73	—	8.84	''
Polymethyl acrylate	4	−4.0	2.18	—	9.04	''
Polymethyl methacrylate						
$T > T_g$	3	−3.0	1.66	4.60	8.55	''
$T < T_g$	3	−3.5	1.19	2.15		
Polyethyl methacrylate	5	−3.9	1.79	5.40	8.32	''
Polybutyl methacrylate	2	(−3)	(1.65)	6.10	8.45	''
Rubber A						
$T = 30°C.$	4	−5.0	2.7	—	7.36	Barrer[3]
$T = 50°C.$	5	(4.3)	(2.4)			

we find the behavior of many different polymers well represented by the zone theory,[3] or by one of several continuum theories.[18]

As discussed previously, the diffusion in fluorocarbon resins involves anomalously low activation energies. Yet their points in the present Figure 5 lie below the correlation line. This can be assumed to be a consequence of the pre-existing holes and channels discussed above—a situation of this type will make for a tortuous diffusion path, much longer than the actual geometrical dimensions of the sample would indicate. This in turn leads to a low apparent frequency factor or activation entropy.

The Polymer Crystallinity

The changes are similar in magnitude to what was found by Jeschke and Stuart[12] on polypropylene and polyethylene terephthalate. In general, the effects are not large compared to the experimental errors and they go in various directions. Hence it is premature to seek a detailed interpretation in terms of the state of order of the noncrystalline portions of the polymer.

The Polymer Transitions

The room temperature transition of polytetrafluoroethylene is a crystalline transition.[28] Most or all of the diffusion, however, occurs in the amorphous regions of the polymer. The activation energies of diffusion are therefore the same, above and below the transition (Fig. 2).

An amorphous transition occurs in the copolymer at about 78°C., according to McCrum.[29] This transition also does not clearly affect the copolymer diffusion data, probably because many different molecular mechanisms can contribute to this overall diffusion process and the freezing or thawing out of one particular motion leads to only very minor changes in the overall process. This is in accord with the new model proposed previously.[14]

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Synopsis

The diffusion and solubility coefficients and their temperature coefficients of several gases in fluorocarbon polymers were measured by a spring balance and radiotracer method. The activation energies of small molecule diffusion in polytetrafluoroethylene increase with the diffusate molecular diameter squared. The increase is less than that found in many other typical polymers and this is probably due to pre-existing holes or channels. The latter are most likely to occur in polymers consisting of stiff chain molecules which have a low packing efficiency. Furthermore, the activation energies are not simply proportional to the cohesive energy density. These findings and the general relation between activation energy and solute molecular size can be explained in terms of the model proposed earlier. The apparent frequency factors in the Arrhenius expression for the diffusion coefficients also are low in comparison to other typical polymers presumably because the diffusate molecules are forced to follow a tortuous path through the polymer. The effect of polymer crystallinity and transitions are discussed briefly. Many molecular motions apparently lead to successful diffusion events, again in agreement with the model mentioned above. A simple and rather unambiguous method to derive activation entropies is reported and the diffusion processes in low and high molecular weight materials have been compared.

Résumé

On a mesuré les coefficients de diffusion et de solubilité et les coefficients de température correspondants de différents gaz dans de polymères fluorocarbonés au moyen d'une balance à ressort et d'une méthode à radiotraceur. Les énergies d'activation de diffusion des petites molécules dans le polytétrafluoroéthylène augmentant avec le carré de diamètre moléculaire. Cette croissance est inférieure à celle trouvée dans beaucoup d'autres polymères typiques et ceci est probablement dû aux trous et aux canaux préoxidants. Ces derniers se présentent le plus vraisemblablement dans des polymères constitués de molécules en chaînes rigides ayant une faible densité de tassement moléculaire. De plus les énergies d'activation ne sont pas simplement proportionnelles à la densité d'énergie de cohésion. Ces résultats et la relation générale entre l'énergie d'activation et le volume moléculaire du soluté peuvent être expliqué en termes du modèle proposé précédemment. Le facteur de fréquence apparent dans l'expression d'Arrhénius pour les coefficients de diffusion sont également bas comparés aux autres polymères typiques vraisemblablement parce que les molécules diffusées sont formées de suivre un chemin tortueux à travers le polymère. On discute brievement l'effet de critallinité du polymère et des transitions. Beaucoup de mouvements moléculaires conduisent apparemment à des phénomènes de diffusion, en accord avec le modèle mentionné ci-dessus. On signale une méthode simple et nonambigue pour déterminer les entropies d'activation et on compare les processus de diffusion dans du matériel de bas et de haut poids moléculaire.

Zusammenfassung

Die Diffusions- und Löslichkeitskoeffizienten mehrerer Gase in Fluorkohlenstoffpolymeren sowie ihre Temperaturabhängigkeit wurden unter Benützung einer Feder-

waage und nach einer Methode mit radioaktiver Markierung gemessen. Die Aktivierungsenergie für die Diffusion kleiner Moleküle in Polytetrafluoräthylen nimmt mit dem Quadrat des Moleküldurchmessers des diffundierenden Moleküls zu. Die Zunahme ist geringer als sie bei vielen anderen Polymertypen gefunden wird, was wahrscheinlich durch vorgebildete Löcher oder Kanäle bedingt ist. Letztere treten mit grösser Wahrscheinlichkeit in Polymeren auf, die aus steifen Kettenmolekülen mit niedriger Packungsdichte bestehen. Die Aktivierungsenergien zeigen ausserdem keine einfache Proportionalität zur Kohäsionsenergiedichte. Diese Befunde sowie die allgemeine Beziehung zwischen Aktivierungsenergie und Molekulgrösse des Gelösten kann auf Grund eines früher vorgeschlagenen Modells erklärt werden. Die scheinbaren Frequenzfaktoren in der Arrheniusbeziehung für die verschiedenen Diffusionskoeffizienten sind ebenfalls niedrig im Vergleich zu anderen Polymertypen, wahrscheinlich weil die diffundierenden Moleküle gezwungen werden, einen verschlungenen Weg durch das Polymere zu verfolgen. Der Einfluss der Kristallinität des Polymeren und von Umwandlungserscheinung wird kurz diskutiert. Es führen offenbar viele Molekülbewegungen zu erfolgreichen Diffusionsschritten, was wieder mit dem oben erwähnten Modell in Einklang steht. Eine einfache und recht eindeutige Methode zur Ableitung von Aktivierungsentropien wird mitgeteilt und der Diffusionsvorgang in nieder- und hochmolekularen Stoffen verglichen.