

A Free-Volume Interpretation of the Influence of the Glass Transition on Diffusion in Amorphous Polymers

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Synopsis

A new version of the free-volume theory of diffusion is used to describe polymer-solvent diffusion both above and below the glass transition temperature. Expressions are derived for the temperature dependence of the mutual diffusion coefficient and for the effective activation energy in the limit of zero penetrant concentration. The theory also describes the effect of the glass transition on the diffusion process. Predictions of the theory are compared with available diffusivity data for amorphous polymer-solvent systems.

INTRODUCTION

Numerous studies have been concerned with the temperature dependence of the mutual diffusion coefficient for amorphous polymer-penetrant systems in the vicinity of the glass transition temperature. Of particular interest is the effect of the glass transition on the mutual diffusion coefficient in the limit of zero penetrant concentration. An effective activation energy for diffusion, E_D , can be derived from the mutual diffusion coefficient, D , using the expression

$$E_D = RT^2 \left(\frac{\partial \ln D}{\partial T} \right)_p \quad (1)$$

and the variation of E_D with temperature can be determined in the temperature range where the classical theory of diffusion is valid. A variety of behavior has been observed in the experiments which have been reported in the literature, and results from a few of these investigations are cited here as examples.

Meares^{1,2} measured the diffusion coefficients of six gases in poly(vinyl acetate) in temperature intervals approximately 20°C on either side of the glass transition temperature. He observed three linear regions on a logarithm of D -versus- $1/T$ plot, separated by step changes in E_D , near the glass temperature and at about 10°C below the glass temperature. Kishimoto et al.³ examined the diffusion of water in poly(vinyl acetate) in the temperature interval of 5°–60°C. The plot of the logarithm of D versus $1/T$ was curved, and E_D reached a maximum value in the vicinity of the glass transition temperature. Zhurkov and Ryskin⁴ and Ryskin⁵ obtained diffusion coefficients for a number of polymer-solvent systems, and in all cases considered a step change in E_D was observed near the glass temperature. Stannett and Williams⁶ obtained diffusivity data for eight gases in poly(ethyl methacrylate) and observed constant activation energy and no discernible effect of the glass transition on the diffusion process. They observed a step change in E_D with water as a penetrant, but attributed this to be the

plasticizing effect of the water molecule above the glass temperature. Ziegel and Eirich⁷ used the same polymer as Stannett and Williams, but they observed that the glass transition caused a step change in E_D when hydrogen and deuterium were used as penetrants. Burgess et al.⁸ measured diffusion coefficients for four gases in poly(methyl acrylate) and observed a step change in E_D near the glass temperature for each of the gases. Kumins and Roteman,⁹ Tikhomirov et al.,¹⁰ and Michaels et al.¹¹ also conducted comprehensive investigations of the effect of the glass transition on the diffusion process, but these studies are not considered here because of the possible complicating effects of the crystalline regions in the polymers which were utilized.

It would prove valuable if this diverse behavior could be explained theoretically. Hopfenberg and Stannett¹² have discussed mechanisms for diffusion in glassy polymers and for the effect of the glass transition on the diffusion process. The purpose of this paper is to provide an alternative description of the diffusion process near the glass transition by using a new version of the free volume theory of diffusion.¹³⁻¹⁶ Expressions are derived for the temperature dependencies of D and E_D , and the predictions of the theory are then compared with available diffusivity data for amorphous polymer-solvent systems.

Unfortunately, comparison of experimental results with any theory must be viewed with caution because there exist several sources of uncertainty in the reported diffusivity data. In the first place, very accurate diffusion data are needed to determine the temperature dependence of E_D using eq. (1). At the present, it appears that an insufficient amount of such data is available for adequate testing of any proposed theory. Furthermore, in some experimental investigations, additional uncertainty is introduced by the need to extrapolate diffusivity data near the glass transition temperature to zero penetrant concentration. Finally, some reported diffusion coefficients may be in doubt because of possible anomalous diffusion effects near the glass temperature.

Conditions under which anomalous diffusion effects can be expected for amorphous polymer-solvent systems can be anticipated by using the concept of a diffusion Deborah number¹⁷ and by constructing Deborah number diagrams.¹⁸ For small Deborah numbers, the molecular relaxation process is fast compared to the diffusive transport, and the diffusion process can hence be described by the classical theory of diffusion. Since this transport involves a purely viscous binary mixture, it can be called viscous diffusion. For large Deborah numbers, there is effectively no time variation of the polymer structure during the diffusion process. A diffusing solvent molecule undergoes movement in a material which appears to have the properties of an elastic solid, and this type of diffusional transport can be called elastic diffusion. Meares,^{1,2} Kishimoto et al.,³ and Zhurkov and Ryskin⁴ collected diffusion data using small amounts of penetrants below the glass temperature, and they concluded that the diffusional transport could be described by the equations of the classical theory with a concentration independent D . Since the Deborah numbers for these experiments were presumably large, it is reasonable to conclude tentatively that diffusional transport for large Deborah numbers can be satisfactorily described by the classical theory even though the system is obviously not a purely viscous fluid mixture. Finally, for Deborah numbers of the order of 1, the molecular relaxation and diffusive transport processes occur in comparable time scales. The relative movement of polymer and solvent can thus be affected by the rearrangement

of polymer chains, and the diffusional transport can be denoted as viscoelastic diffusion. There is no experimental or theoretical justification for using the classical theory to describe this diffusion process. Clearly, meaningful diffusion coefficients can generally be obtained only if experiments are conducted so that viscoelastic diffusion is avoided.

The existence of viscoelastic effects in unsteady sorption or permeation experiments at temperatures near the glass transition can also be determined by conducting appropriate auxiliary experiments. For example, diffusion coefficients determined from sorption experiments can be compared with those obtained using steady-state permeation experiments.³ Alternatively, viscoelastic effects in sorption experiments can be detected by carrying out a sequence of such experiments using different sample thicknesses.⁴ Unfortunately, very few investigators have adequately scrutinized unsteady sorption or permeation data for the possibility of viscoelastic effects. Since diffusivities near the transition temperature which are measured using unsteady experiments must be viewed with caution, so must the comparisons of data and theory which are presented below. However, these comparisons are useful since they at least show that the predictions of the proposed theory are plausible.

THEORY

Local density fluctuations occur both above and below the glass transition temperature, and it is reasonable to expect that free volume theory should provide an adequate description of transport in glassy materials. For example, Plazek and Magill¹⁹ and Rusch²⁰ applied free volume analyses with some success in describing creep and stress relaxation experiments performed on glassy polymers. There will, of course, be several important differences between transport processes above and below T_{g2} , the conventional glass transition temperature of the pure polymer. In the first place, polymers above T_{g2} possess an equilibrium liquid structure before a mass transfer or mechanical experiment is initiated, whereas materials below T_{g2} generally have a nonequilibrium liquid configuration. Furthermore, the thermal expansion coefficient changes rapidly near T_{g2} (usually approximated by a step function), reflecting the increasing difficulty for volume contraction with decreasing temperature.

In addition, the hole free volume, the portion of the unoccupied volume in the polymer which can be redistributed with no energy change, becomes very small below T_{g2} . Hence, the probability that a local fluctuation in density will produce a hole of sufficient size so that a polymeric jumping unit or a solvent molecule will move decreases rapidly near T_{g2} . Motion below T_{g2} becomes so hindered owing to the lack of hole free volume that significant movement of segments of polymer molecules does not occur in the time scales of rheological or diffusion experiments. It is thus reasonable to expect that the average hole free volume of the system does not change during the course of such experiments. The proposed model of the free-volume behavior of the system is depicted in Figure 1. The specific occupied volume of a material is defined to be the specific volume of the equilibrium liquid at 0°K, and the interstitial free volume is the part of the free volume which is distributed uniformly among the jumping units of a given species because the energy for redistribution is large. From this figure it is evident that transport below T_{g2} can be significantly enhanced by the extra

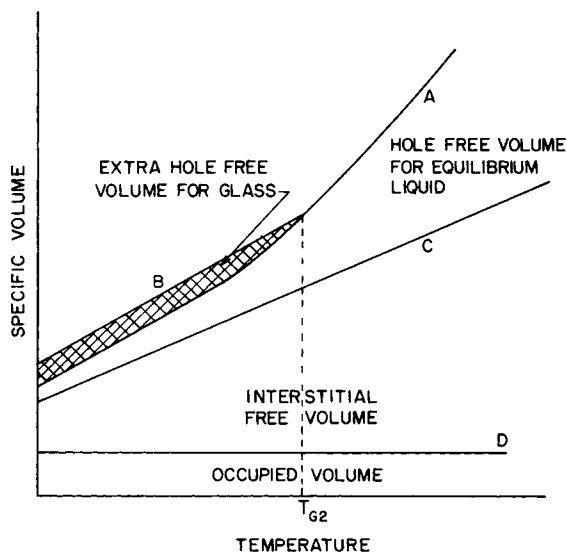


Fig. 1. Volume-temperature behavior of an amorphous polymer: (a) volume of equilibrium liquid; (b) volume of nonequilibrium liquid or glass; (c) sum of occupied volume and interstitial free volume; (d) occupied volume.

hole free volume which is effectively frozen into the polymer in the nonequilibrium liquid or glassy state.

We consider the temperature dependence of D for a system consisting of a trace of solvent and an amorphous polymer. The proposed theory is valid for systems that initially have an equilibrium liquid structure above the glass temperature and a nonequilibrium liquid structure, which remains invariant during the diffusion process, below the glass temperature. Thus, the theory describes the temperature dependence of D for elastic or viscous diffusion above T_{g2} and for elastic diffusion below T_{g2} . The volumetric behavior of the equilibrium liquid above T_{g2} is described by a thermal expansion coefficient α_2 , and the temperature dependence of the volume of the nonequilibrium liquid below T_{g2} is given by a pseudoexpansion coefficient for the glassy state, α_{2g} . The rapid change in the expansion coefficient in the vicinity of T_{g2} is idealized²¹ as a step change from α_{2g} to α_2 at T_{g2} . The expansion coefficient α_{2g} must be defined as the temperature derivative of volume with both pressure and some measure of the internal order of the nonequilibrium liquid being held constant.²¹ Over the moderate temperature ranges usually considered in diffusion studies, it is reasonable to assume that these expansion coefficients can be adequately approximated by suitable average values.

From a new version of the free-volume theory for self-diffusion coefficients,¹³ it can be shown that in the limit of zero penetrant concentration, both D and D_1 , the self-diffusion coefficient of the solvent, are given by the following expression for a classical diffusion process:

$$D = D_1 = D_{01} \exp\left(-\frac{\gamma \xi \hat{V}_2^*}{\hat{V}_{FH2}}\right) \quad (2)$$

where γ is an overlap factor (which should be between $1/2$ and 1) which is introduced because the same free volume is available to more than one molecule; \hat{V}_2^*

is the minimum or critical local hole free volume per gram of polymer required for displacement of a polymeric jumping unit; ξ is the ratio of the critical molar volume of the solvent to the critical molar volume of the polymeric jumping unit; and \hat{V}_{FH2} is the average hole free volume per gram of polymer which characterizes an equilibrium liquid structure. The preexponential factor D_{01} is considered to be a much weaker function of temperature than the exponential term and, hence, is treated as a constant.

From eq. (2) and from free-volume considerations discussed elsewhere,¹⁵ it can easily be shown¹⁶ that the mutual diffusion coefficients at T and T_{g2} are related by the following expression valid for $T > T_{g2}$:

$$\ln \left(\frac{D(T)}{D(T_{g2})} \right) = \frac{\gamma \hat{V}_{2\xi}^*}{K_{12} K_{22}} \frac{T - T_{g2}}{K_{22} + T - T_{g2}} \quad (3)$$

where

$$K_{12} = \hat{V}_2^0(T_{g2}) [\alpha_2 - (1 - f_{H2}^G) \alpha_{c2}] \quad (4)$$

$$K_{22} = \frac{f_{H2}^G}{\alpha_2 - (1 - f_{H2}^G) \alpha_{c2}} \quad (5)$$

$$f_{H2}^G = \frac{\hat{V}_{FH2}(T_{g2})}{\hat{V}_2^0(T_{g2})} \quad (6)$$

where \hat{V}_2^0 is the specific volume of the polymer and α_{c2} is the thermal expansion coefficient of pure polymer for the sum of the specific occupied volume and the specific interstitial free volume. It is assumed that α_{c2} is constant and is not affected by the glass transition. The parameter K_{22} depends on the properties of the polymer only, whereas the group $\gamma \hat{V}_{2\xi}^*/K_{12}$ is a function of both polymer and solvent properties.

The nonequilibrium liquid structure is considered invariant below T_{g2} during the course of a diffusion process. Since the average hole free volume is fixed, it is reasonable to assume that the self-diffusion coefficient below T_{g2} (and hence also D) can be determined using eq. (2), where \hat{V}_{FH2} now refers to the specific average hole free volume for the glassy polymer. By considerations completely analogous to those described above, it can be shown that the temperature dependence of D below T_{g2} is given by the expression

$$\ln \left(\frac{D(T)}{D(T_{g2})} \right) = \frac{\gamma \hat{V}_{2\xi}^*}{K_{12} K_{22}} \frac{T - T_{g2}}{K_{22}(\lambda) + T - T_{g2}} \quad (7)$$

with

$$\lambda = \frac{\alpha_{2g} - (1 - f_{H2}^G) \alpha_{c2}}{\alpha_2 - (1 - f_{H2}^G) \alpha_{c2}} \quad (8)$$

The parameter λ describes the character of the change of the volume contraction which can be attributed to the glass transition. Clearly, an infinite number of nonequilibrium liquid structures can be realized below T_{g2} depending on the mechanical and thermal history of the material. If $\lambda = 1$, the equilibrium liquid structure is realized at all temperatures; whereas, if $\lambda = 0$, the specific hole free volume equals $\hat{V}_{FH2}(T_{g2})$ everywhere below T_{g2} . It is evident from eqs. (3) and (7) that plots of the logarithm of D versus $1/T$ will not be linear, either above or below T_{g2} , if $\lambda > 0$.

The temperature dependence of E_D can be derived from eqs. (1) and (2). Above T_{g2} , the free volume result for E_D is simply

$$E_D = \frac{RT^2 \frac{\gamma \hat{V}_{2\xi}^*}{K_{12}}}{(K_{22} + T - T_{g2})^2} \quad (9)$$

and the temperature variation of E_D below T_{g2} is given by the following expression:

$$E_D = \frac{RT^2 \frac{\gamma \hat{V}_{2\xi}^*}{\lambda K_{12}}}{[(K_{22}/\lambda) + T - T_{g2}]^2} \quad (10)$$

Consequently, the step change for E_D at T_{g2} is given by the result

$$E_D(T_{g2}^+) - E_D(T_{g2}^-) = \frac{\gamma \hat{V}_{2\xi}^* (1 - \lambda) RT_{g2}^2}{K_{12} K_{22}^2} \quad (11)$$

Furthermore, it is evident that

$$\frac{E_D(T_{g2}^-)}{E_D(T_{g2}^+)} = \lambda \quad (12)$$

A more useful form of eq. (11) is the expression

$$E_D(T_{g2}^+) - E_D(T_{g2}^-) = \left(\frac{2.303(C_f^2)(1 - \lambda)RT_{g2}^2}{(C_g^2)\hat{V}_2^0(0)M_j} \right) \hat{V}_1^0(0) \quad (13)$$

where it has been assumed that the specific critical volume is equal to the specific occupied volume both for the solvent and for the polymeric jumping unit. In eq. (13), $\hat{V}_1^0(0)$ is the molar volume of the liquid solvent at 0°K, $\hat{V}_2^0(0)$ is the specific volume of the liquid polymer at 0°K, M_j is the molecular weight of a jumping unit of the polymer chain, and (C_f^2) and (C_g^2) are the WLF constants for the polymer.²² For a given polymer, the magnitude of the step change in E_D depends on the solvent size, the glass temperature and free volume characteristics of the polymer, and the change in the expansion coefficient at the transition temperature. Stannett and Williams⁶ have previously noted that penetrant size and the relative change in the expansion coefficient at T_{g2} should be of importance in determining the effect of the glass transition on the diffusion process.

The parameters T_{g2} , (C_f^2) , (C_g^2) , α_2 , and α_{2g} have been tabulated for a number of amorphous polymers,^{22,23} and $\hat{V}_1^0(0)$ and $\hat{V}_2^0(0)$ can be estimated using methods discussed by Haward.²⁴ Furthermore, ξ and hence M_j can be calculated by using viscosity data for the polymer and mutual diffusion data for a system consisting of a trace of solvent in the polymer.¹⁴ However, α_{c2} and f_{H2}^g cannot in general be extracted from polymer viscosity data above T_{g2} , and eqs. (12) and (13) cannot be utilized in a strictly predictive sense. However, it is evident that

$$0 \leq \lambda \leq \frac{\alpha_{2g}}{\alpha_2} \quad (14)$$

and this result can be used in eqs. (12) and (13) to provide bounds for $E_D(T_{g2}^-)/E_D(T_{g2}^+)$ and $E_D(T_{g2}^+) - E_D(T_{g2}^-)$ for fixed α_{2g} and α_2 . Furthermore, the bracketed quantity in eq. (13) depends only on properties of the polymer,

and thus the step change in E_D should be a linear function of the solvent size, as estimated using the solvent molar volume at 0°K. This prediction of the theory is tested below using diffusivity data collected for several solvents on the same polymer. Finally, from eq. (12), it is evident that the theory predicts that the ratio of activation energies at T_{g2} should be independent of the solvent for a given polymer. Comparison of this prediction with experiment is also considered below.

The above development immediately suggests a method for separating the free-volume parameters of a polymer, α_{c2} , f_{H2}^G , and γ . It can easily be shown that

$$\frac{\gamma \hat{V}_2^0(0)}{\hat{V}_2^0(T_{g2})[\alpha_2 - (1 - f_{H2}^G)\alpha_{c2}]} = 2.303(C_1^g)_2(C_2^g)_2 \quad (15)$$

$$\frac{f_{H2}^G}{\alpha_2 - (1 - f_{H2}^G)\alpha_{c2}} = (C_2^g)_2 \quad (16)$$

$$\frac{\alpha_{2g} - (1 - f_{H2}^G)\alpha_{c2}}{\alpha_2 - (1 - f_{H2}^G)\alpha_{c2}} = \frac{E_D(T_{g2}^-)}{E_D(T_{g2}^+)} \quad (17)$$

and the above three free-volume parameters can be determined from these equations using viscosity data above T_{g2} in conjunction with mutual diffusion coefficient data measured above and below T_{g2} in the limit of zero penetrant concentration. Berry and Fox²³ have proposed a method for separating the free-volume parameters using rheological data.

RESULTS AND DISCUSSION

The predictions of the free-volume theory can be tested using data for amorphous polymer-solvent systems taken from the investigations briefly described above.³⁻⁸ The data of Meares^{1,2} are not included in any comparisons; it is not clear how these results should be interpreted since the two linear regions below the glass temperature may possibly be evidence of anomalous diffusion behavior or of a changing activation energy for diffusion. Furthermore, the behavior reported by Meares has apparently not been observed by other investigators, and it seems reasonable to exclude these data from present consideration.

With the exception of the data presented by Kishimoto et al.³ and a few results of Ryskin,⁵ constant activation energies have been observed⁴⁻⁸ both above and below T_{g2} . However, as noted above, eqs. (3) and (7) indicate that plots of the logarithm of D versus $1/T$ will not be linear either above or below the glass transition temperature. It is easy to show that the data and theory are not necessarily in disagreement by examining curves depicting the temperature dependence of D near T_{g2} . A plot of this type is presented in Figure 2 for penetrants diffusing in polystyrene with $T_{g2} = 373^\circ\text{K}$ and $K_{22} = 45.3^\circ\text{K}$.^{15,16} A value of 200°K for $\gamma \hat{V}_2^0 \xi / K_{12}$ is typical of a small penetrant like nitrogen, whereas $\gamma \hat{V}_2^0 \xi / K_{12} = 1000^\circ\text{K}$ represents an organic solvent such as ethylbenzene.

It is evident from Figure 2 that the variation of D below T_{g2} is strongly dependent on λ . Furthermore, it is clear that a straight line representation for the logarithm of D versus $1/T$ is satisfactory for sufficiently small temperature intervals and for small solvents. Indeed, from Figure 2 it would appear that very accurate data are needed if the temperature dependence of E_D is to be deter-

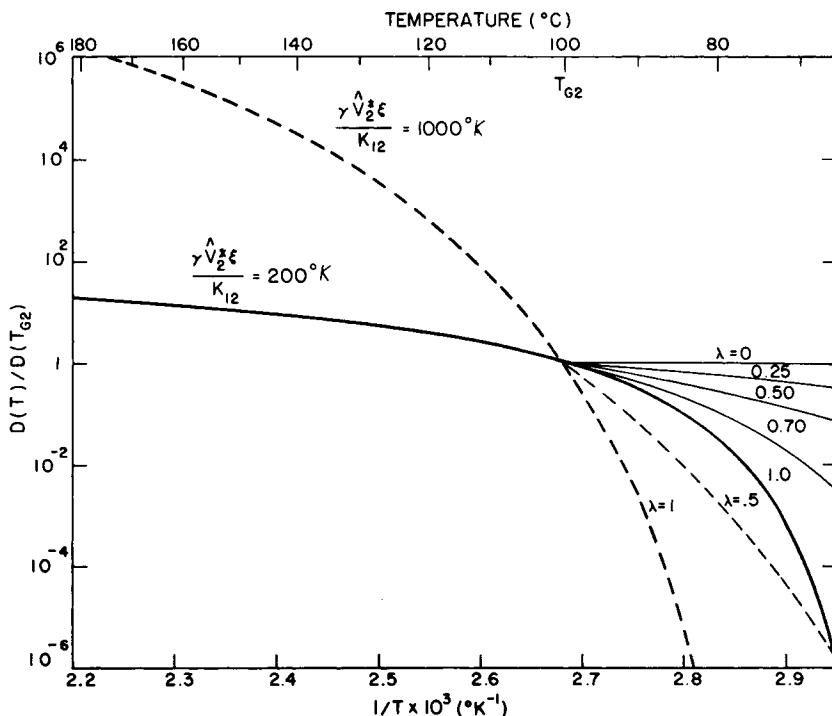


Fig. 2. Temperature dependence of D for polystyrene-penetrant systems with $K_{22} = 45.3^\circ\text{K}$.

mined for solvents with $\gamma \hat{V}_2^* \xi / K_{12} = 200^\circ\text{K}$ for temperature intervals as high as 80°C above T_{g2} . Furthermore, it can be seen from this figure that nonlinearities in the logarithm of D -versus- $1/T$ plots become easier to detect as the size of the solvent increases. These points are considered in greater detail elsewhere.¹⁶ The variation of E_D with temperature is similarly difficult to determine below T_{g2} for small solvents and small temperature intervals, especially if λ is less than about 0.6.

Since nonlinear behavior is difficult to detect for the diffusion of small solvents over relatively narrow temperature intervals, it is not surprising that constant activation energies have been reported for the majority of the studies listed above. The experiments of Stannett and Williams,⁶ Ziegel and Eirich,⁷ and Burgess et al.⁸ were conducted using small penetrants and temperature intervals above or below T_{g2} which were generally about 30°C , with a maximum interval of approximately 55°C . Zhurkov and Ryskin⁴ and Ryskin⁵ used bigger penetrants with temperature intervals which were generally 50 – 60°C with a maximum interval of approximately 110°C . For this large interval, a significant variation of E_D with temperature was reported. Kishimoto et al.³ also observed a significant temperature dependence of E_D using temperature intervals of about 25°C below T_{g2} and 30°C above the transition temperature. The determination of the temperature variation of E_D was accomplished by collecting data at smaller temperature increments than were generally used in the above investigations. It thus seems fair to conclude that the available data for the temperature dependence of D are not inconsistent with the predictions of the free volume theory. It is reasonable, therefore, to interpret a reported constant activation energy for a given temperature interval as a good estimate of E_D for the average temperature of that interval.

Kishimoto et al.³ reported a maximum in E_D in the vicinity of the glass transition temperature. If $\lambda < 1$, it follows that comparable behavior is predicted by the free-volume theory, as is evident from Figure 3. This figure describes the variation of E_D with temperature for polystyrene and a small penetrant ($\gamma \hat{V}_2^* \xi / K_{12} = 200^\circ\text{K}$) for five values of λ . The theory predicts that a local maximum value of E_D is achieved at T_{g2} if $\lambda < 1$, followed by a step decrease in E_D and a subsequent increase if $\lambda > 0$. These free-volume predictions differ qualitatively in two aspects from the results observed by Kishimoto et al.³ First, the E_D data of these investigators show a smooth curve for E_D and a gradual decrease of E_D below T_{g2} , as contrasted with the step discontinuity depicted in Figure

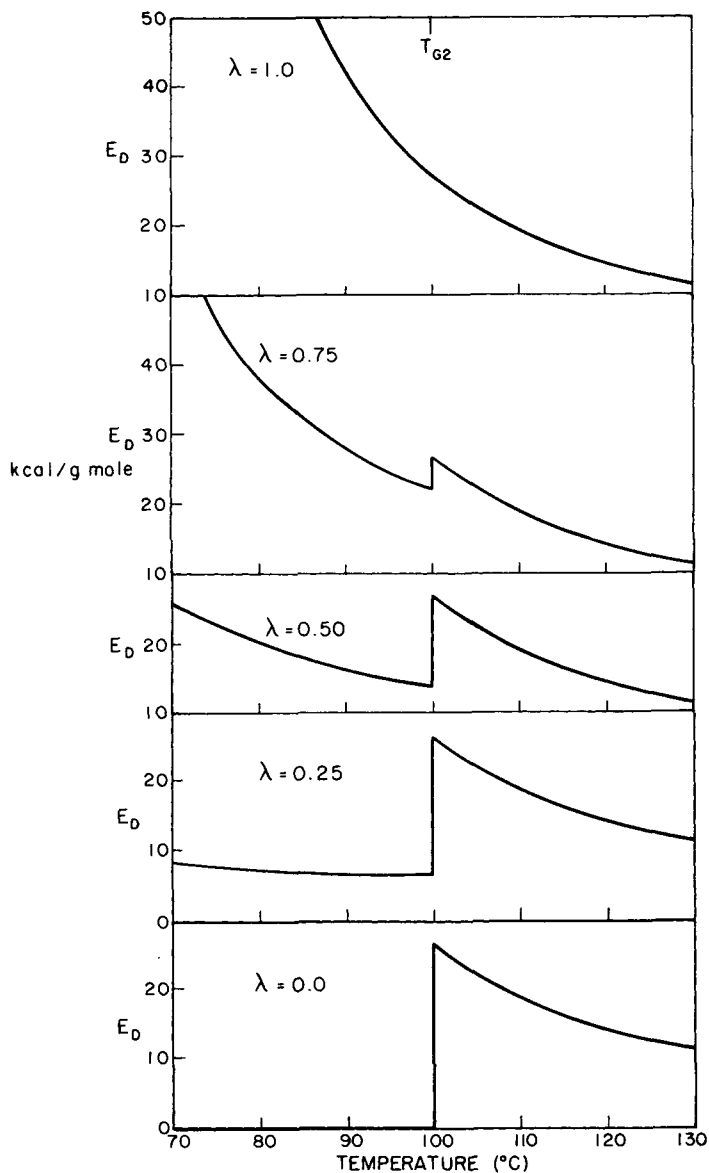


Fig. 3. Temperature dependence for polystyrene-penetrant system with $\gamma \hat{V}_2^* \xi / K_{12} = 200^\circ\text{K}$ and $K_{22} = 45.3^\circ\text{K}$.

3. This difference is presumably a consequence of the utilization of a step function as an idealization of the change in the thermal expansion coefficient near T_{g2} . A second difference is that Kishimoto et al.³ observed no increase in E_D below T_{g2} . There appears to be no explanation for this apparent discrepancy at this time.

Zhurkov and Ryskin⁴ and Ryskin⁵ collected data using six polymers and a variety of solvents, and it is of interest to use this data set to check the predictions of eqs. (12) and (13). The activation energies reported by these investigators are taken to be representative of the activation energies at the average temperatures T_1 and T_2 , above and below the glass temperature, respectively. Since some of the reported glass transition temperatures differ significantly from the usual values, the properties of the polymers which are utilized are somewhat uncertain. Furthermore, the temperature intervals studied are not particularly wide, and polymer properties are not derived directly from the diffusion data.¹⁵ Consequently, eqs. (12) and (13) are not utilized directly, and, with the exception of one calculation described below, the polymer properties are not utilized here in the comparison of data and theory.

An equation similar in form to eq. (13) can be derived for $E_D(T_1) - E_D(T_2)$. For diffusivity data obtained for a series of solvents and a single polymer, it follows from this result that $E_D(T_1) - E_D(T_2)$ is a linear function of the molar volume of the solvent at 0°K if T_1 and T_2 are the same for all solvents. This is approximately true for the polystyrene data reported by Zhurkov and Ryskin⁴ for four solvents and for the poly(vinyl acetate) data for two solvents. Values of $E_D(T_1) - E_D(T_2)$ are plotted versus molar volume of the solvent at 0°K in Figure 4. The values of $\bar{V}_1^0(0)$ were estimated using the methods of Sugden²⁵ and Biltz²⁶ as summarized by Haward.²⁴ The theoretical prediction is a straight

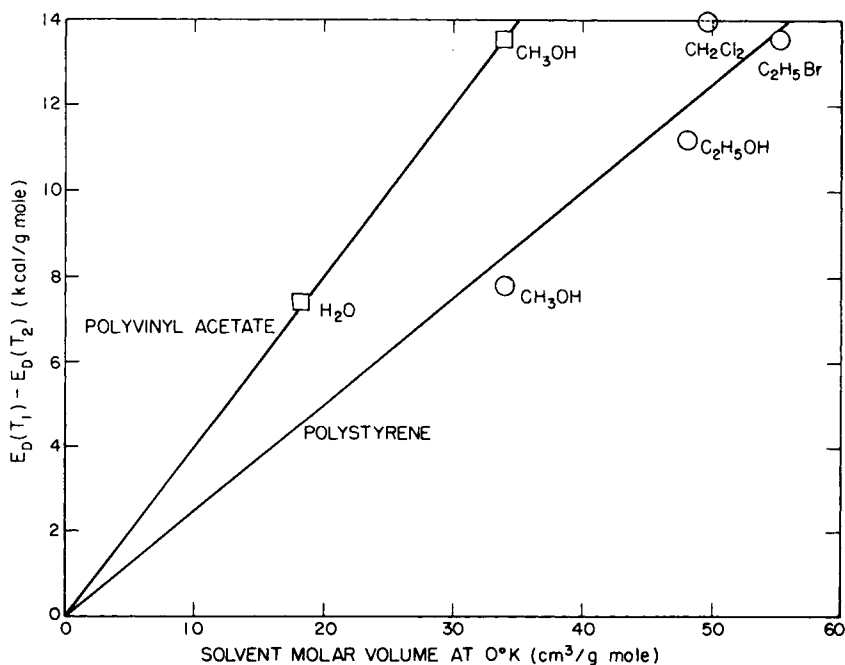


Fig. 4. Dependence of activation energy difference on solvent size.

TABLE I
Dependence of $E_D(T_2)/E_D(T_1)$ on Solvent

Polymer	Number of solvents	Average value of $E_D(T_2)/E_D(T_1)$	Maximum difference from average, %
Polystyrene	4	0.48	15
Poly(vinyl acetate)	2	0.42	11

line through the origin, and the data are in reasonable agreement with this result.

Since eq. (12) cannot be checked directly using the data of Zhurkov and Ryskin⁴ and Ryskin,⁵ we consider the following ratio of activation energies:

$$\frac{E_D(T_2)}{E_D(T_1)} = \frac{\lambda T_2^2(K_{22} + T_1 - T_{g2})^2}{T_1^2[K_{22} + \lambda(T_2 - T_{g2})]^2} \quad (18)$$

Again, if diffusivity data are measured for a single polymer and a series of solvents, then the above ratio of activation energies is independent of the solvent if T_1 and T_2 are the same for all solvents. This prediction is checked using the polystyrene and poly(vinyl acetate) data, and it is evident from Table I that reasonable agreement of the data with the theoretical prediction is obtained. Furthermore, it can easily be shown that

$$\frac{E_D(T_2)}{E_D(T_1)} > \lambda = \frac{E_D(T_{g2}^-)}{E_D(T_{g2}^+)} \quad (19)$$

Comparison of the ratios of activation energies listed in Table I with the maximum values of λ computed from eq. (14) and listed in Table II shows that the inequality of eq. (19) is satisfied.

TABLE II
Calculated Values of λ for Amorphous Polymer-Solvent Systems

Polymer	Calculated λ	Upper bound for λ	Reference
Polystyrene			
methanol	0.24	0.30	4
ethanol	0.22	0.30	
methylene chloride	0.20	0.30	
ethyl bromide	0.22	0.30	
Poly(vinyl acetate)			
water	0.20	0.37	4
methanol	0.16	0.37	
Poly(methyl methacrylate)			
methanol	0.33	0.41	4
ethanol	0.38	0.41	
Poly(ethyl methacrylate)			
water	0.44	0.50	5
methanol	0.34	0.50	
hydrogen	0.44	0.61	7
Poly(butyl methacrylate)			
methanol	0.47	0.62	5
Poly(methyl acrylate)			
water	0.24	0.39	5
neon	0.39	0.39	8
argon	0.35	0.39	
krypton	0.35	0.39	

The theory predicts that activation energies above and below the glass transition temperature are related by eq. (18). Since $E_D(T_2)/E_D(T_1)$, T_1 , T_2 , and T_{g2} are reported in some of the above diffusion studies and since K_{22} can be estimated using data summarized by Ferry,²² eq. (18) provides a convenient means of determining λ . The calculated value of λ must obviously be independent of the solvent utilized for a particular polymer, and, furthermore, λ must lie within the bounds given by eq. (14) if the theory is to have a valid basis. Calculated values of λ based on the data of Zhurkov and Ryskin,⁴ Ryskin,⁵ Ziegel and Eirich,⁷ and Burgess et al.⁸ are summarized in Table II. An estimate of the upper bound on λ was determined using data for α_2 and α_{2g} tabulated by Ferry²² and by Berry and Fox.²³ The expansion coefficients reported by Burgess et al.⁸ were not used because they do not appear to be consistent with the volume-temperature curve presented in their paper. Also, the helium data of these investigators are not included because of the large scatter in the reported diffusion coefficients. Finally, the tabulated activation energies for the poly(methyl methacrylate)-water data of Zhurkov and Ryskin⁴ are not consistent with the reported plot, and this system is not included in Table II.

It is evident from Table II that all of the calculated values of λ fall within the bounds given by eq. (14). Furthermore, with the exception of the poly(methyl acrylate) data, the variation of λ with solvent for a given polymer is relatively small, the maximum difference from the average being typically approximately 10%. The maximum deviation from the average is nearly 30% for the poly(methyl acrylate) data. This is not surprising since the above calculation is based on the assumption that the polymer samples utilized in the two investigations have identical properties. It is quite possible that this is not the case, and some variation in the calculated values of λ is not unexpected. Indeed, there is very good agreement among the values of λ calculated for three solvents using only the data of Burgess et al.⁸

Finally, we consider the poly(ethyl methacrylate) data presented by Stannett and Williams⁶ and by Ziegel and Eirich.⁷ These data were apparently all measured using equivalent polymer samples with an upper bound for λ equal to 0.61. The theory thus predicts that there will be a step change in E_D as the glass transition is traversed. Stannett and Williams reported constant activation energies for eight gases in a temperature interval which included T_{g2} , whereas Ziegel and Eirich observed step changes in E_D for two penetrants. Zhurkov and Ryskin⁴ and Ryskin⁵ also reported step changes in E_D for poly(ethyl methacrylate)-penetrant systems. These investigations give results which do not appear to be consistent, but it can be shown that the data of Stannett and Williams are not necessarily in disagreement with the predictions of the free-volume theory. With the aid of the data reported by Meares² and by Stannett and Williams, curves depicting the temperature dependence of D can be constructed for the poly(vinyl acetate)-krypton and poly(ethyl methacrylate)-krypton systems. These curves are presented in Figures 5 and 6; the maximum value of λ was used in each case to construct the curve below T_{g2} .

It is evident from Figure 5 that a straight line will provide a good representation of the poly(ethyl methacrylate)-krypton data even though there is a step change in E_D at T_{g2} . Clearly, very accurate data are needed to detect this step change, and it is reasonable that Stannett and Williams concluded that the activation energy for diffusion was constant over the entire temperature range. On the

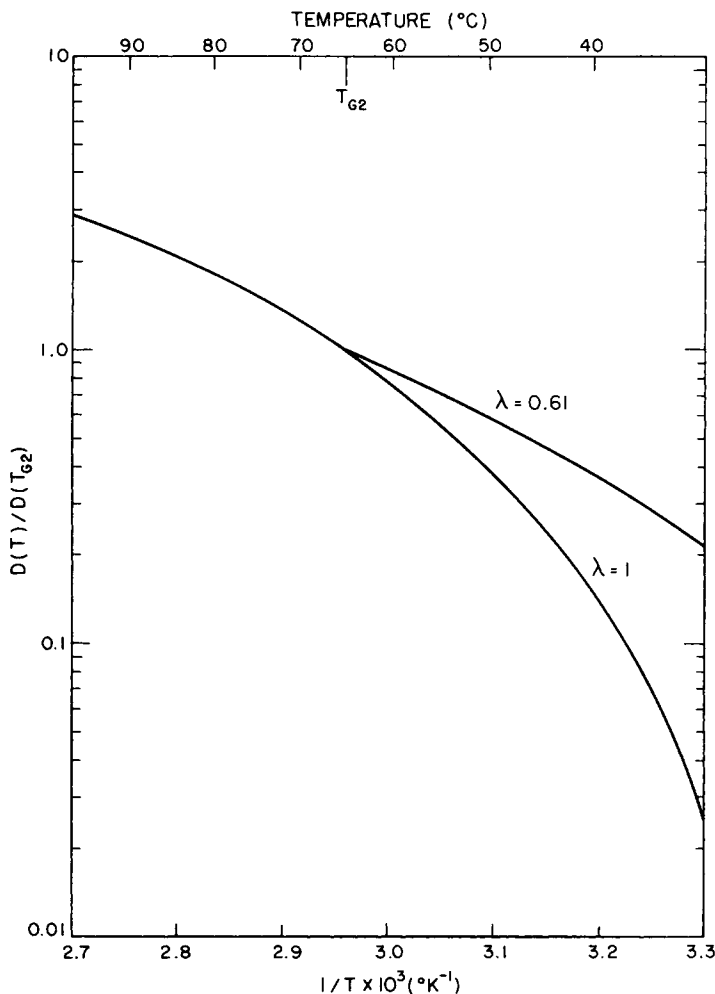


Fig. 5. Temperature dependence of D for poly(ethyl methacrylate)—krypton system.

other hand, it is quite clear from Figure 6 that there is a jump discontinuity at T_{g2} for the poly(vinyl acetate)—krypton system. This step change is much easier to detect than the previous one, and it would be expected that reasonably accurate data would show this phenomenon. Indeed, the diffusivity data of Meares and the poly(vinyl acetate) permeability data of Stannett and Williams both clearly indicate an effect of the glass transition on the mass transfer process.

It is fair to conclude from the above comparisons of data and theory that a free-volume description of the diffusion process around T_{g2} is a plausible alternative to previously proposed explanations. Both qualitative and quantitative agreement of theory and experiment were observed, and this suggests that consideration should be given to free-volume theory in the analysis of new diffusion data. A free-volume analysis of diffusion data would be considerably facilitated if viscosity and thermal data for the polymer were also obtained.

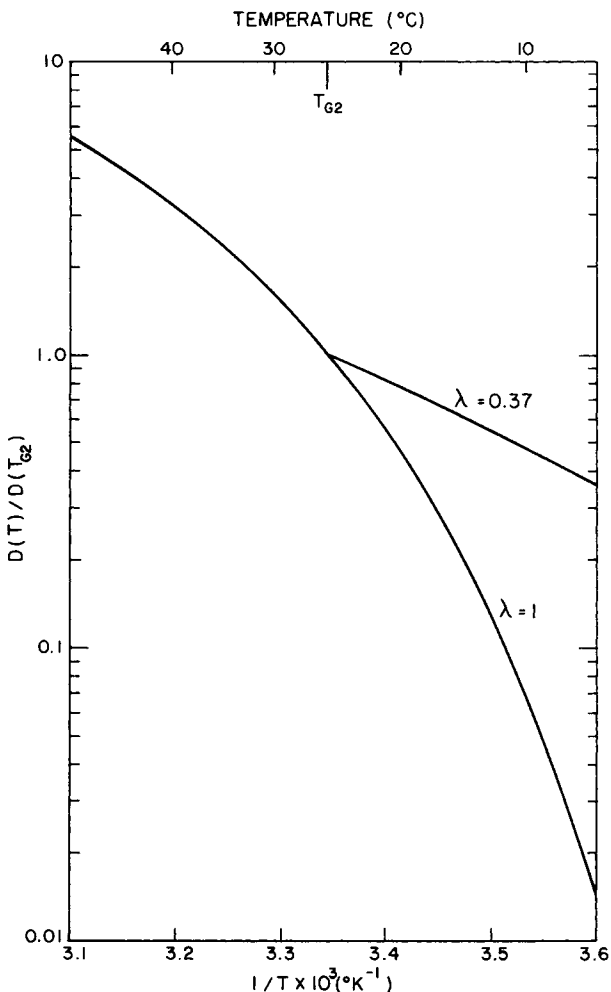


Fig. 6. Temperature dependence of D for poly(vinyl acetate)-krypton system.

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