

Solvent and Temperature Effects on Diffusion in Polymer-Solvent Systems

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Synopsis

The temperature dependence of the mutual diffusion coefficient at zero solvent concentration for a number of polystyrene-solvent systems is satisfactorily represented by an equation derived from a new version of the free-volume theory of molecular transport. The free-volume parameter which governs the temperature dependence of the diffusion rate is linearly related to the size of the solvent as estimated by its molar volume at 0K. Data taken on various polystyrene-solvent systems are used to deduce information on the mechanism of solvent transfer in polymeric systems.

INTRODUCTION

Diffusion in concentrated polymer solutions is usually described by application of the free-volume theory of molecular transport.¹ A new version of the free-volume theory^{2,3} has been developed to predict the temperature, concentration, and molecular weight dependence of mutual diffusion coefficients in amorphous polymer-solvent systems for wide molecular weight, temperature, and concentration ranges. The theory can be used in a predictive sense if the parameters of the free-volume theory are evaluated using data on the temperature dependence of self-diffusion coefficients of pure solvent, pure polymer, and of the solvent in a system consisting of a trace of solvent in the polymer. Hence, free-volume theory can be a viable predictive theory for mixtures only if the equations of the theory satisfactorily describe the temperature variation of self-diffusion coefficients (or, effectively, viscosities) of simple and polymeric liquids as well as the temperature variation of the self-diffusion coefficient of the solvent in the limit of zero solvent concentration. The latter quantity is equivalent to the mutual diffusion coefficient of the polymer-solvent mixture.

The applicability of the free-volume theory in describing the temperature dependence of the viscosity for both simple and polymeric liquids at temperatures above the glass transition temperature has been discussed elsewhere^{4,5,6} and is not the concern of the present investigation. It suffices to say that, in a recent study,³ we concluded that the equations of free-volume theory provided a satisfactory representation of viscosity data for both ethylbenzene and poly-

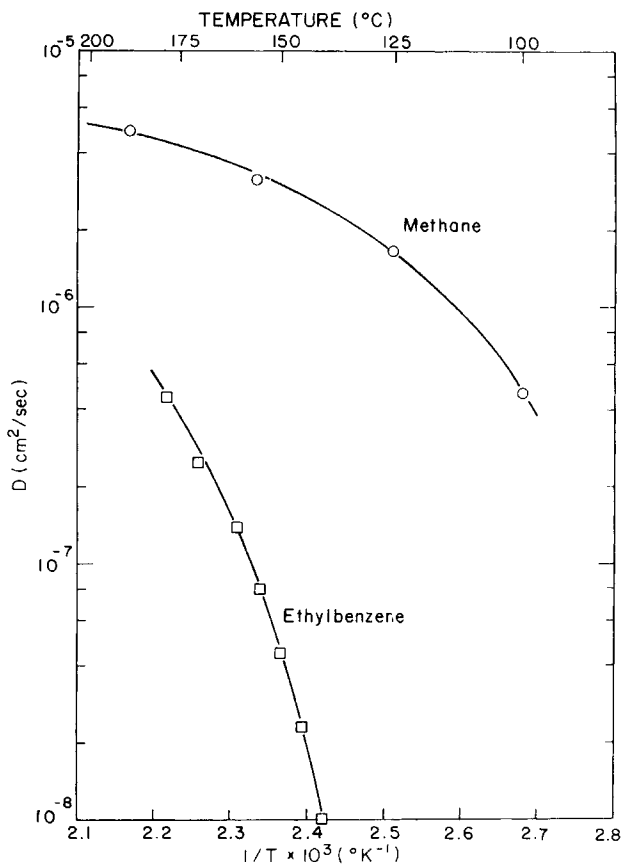


Fig. 1. Temperature variation of D for methane-polystyrene and ethylbenzene-polystyrene systems.

styrene for temperatures ranging as high as 300°C above the estimated glass transition temperature of the ethylbenzene. The purpose of the present investigation is to see how well the proposed free-volume theory correlates data for the mutual diffusion coefficient at zero solvent concentration over reasonably wide ranges in temperature and molecular size. Furthermore, it is of interest to deduce if there are any correlations among determined values of the free-volume parameters and molecular characteristics. In the remainder of this paper, we will confine our discussion to the investigation of the temperature and solvent dependence of mutual diffusion coefficients in polystyrene-solvent systems at zero weight fraction of the solvent.

There exists sufficient evidence^{7,8} that the temperature dependence of the mutual diffusion coefficient D for a polymer-solvent system cannot generally be described by an equation of the Arrhenius form at temperatures relatively close to the glass transition temperature of the polymer. The effective activation energy for diffusion, E_D , defined by the equation

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

decreases markedly with increasing temperature T . This point is clearly illustrated in Figure 1 where data are presented showing the temperature variation of diffusion coefficients for systems containing trace amounts of methane and ethylbenzene in polystyrene. The two plots of the logarithm of D versus $1/T$ are clearly nonlinear, and the temperature dependence cannot, of course, be described by an Arrhenius relationship. There is reason to believe, however, that the observed temperature dependence can be satisfactorily represented using an equation deduced from free-volume considerations, and the first objective of this paper is to examine how well such an equation describes the temperature dependence of D for diffusion of a variety of solvents in amorphous polystyrene. New data for the diffusion of ethylbenzene and toluene in polystyrene as well as data for six other solvents are used. In addition, the apparent failure⁹ of free-volume theory to describe n -pentane diffusion in polystyrene is examined.

It will be shown below that the variation of D with temperature can be correlated using three parameters which can be uniquely determined from the experimental data. One parameter is associated with the properties of the polymer, whereas the other two depend on the properties of the particular polymer-solvent system. A second objective of this paper is to determine whether there exists a relationship between each of the latter two parameters and the molecular characteristics of the polymer-solvent system.

A final objective of this investigation is to use data taken on various polystyrene-solvent systems to deduce some information on the mechanism of solvent transfer in a polymeric system. Free-volume theory is based on the determination of the probability that a fluctuation in the local density will produce a hole of sufficient size so that a diffusing molecule can perform a jump. Frenkel¹⁰ takes the point of view that fluctuations in local hole-free volume occur by a general recession of the molecules surrounding a particular molecule, and this molecule jumps to fill up the larger hole which is created, leaving a similar hole at its initial position. This hole is diminished in size by a process just opposite to that which increased the size of the initial hole. If this diffusion mechanism is accepted, the temperature dependence of the rate of diffusion of a trace of solvent in the polymer should depend only on the size of the solvent molecule and not on the size of the polymer jumping unit, regardless of whether the solvent molecule is larger or smaller than the jumping unit.

An alternative point of view, taken by Cohen and Turnbull,¹¹ is that the diffusion of a trace of a solvent in a polymer will be governed by the size of the jumping unit of the polymer if a molecule of the solvent is smaller than a polymeric jumping unit. In this picture of the diffusion process, it is assumed that the process of diffusional transport is completed only if a neighboring jumping unit of the polymer fills the void created by displacement of the solvent. Since diffusion data are available for polystyrene-solvent systems for a reasonably wide range of solvent size, we can conclude which of the above mechanisms better explains the effect of molecular size on the self-diffusion process.

THEORY

From the results of a new version of the free-volume theory for self-diffusion coefficients,² it can be shown that the self-diffusion coefficient of the solvent, D_1 , in the limit of zero mass fraction, is given by the expression

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

where the equality of D and D_1 is, in general, valid only for this limiting case. The parameter γ is an overlap factor (which should be between $\frac{1}{2}$ and 1) which is introduced because the same free volume is available to more than one molecule; \hat{V}_{FH2} is the average hole-free volume per gram of polymer; and \hat{V}_2^* is the minimum or critical local hole-free volume per gram of polymer required for displacement of a polymeric jumping unit. In addition, the parameter ξ is the ratio of the critical molar volume of the solvent to the critical molar volume of the polymeric jumping unit. Clearly, ξ provides a comparison of the size of the hole required for a solvent molecule to jump with the hole size needed for the movement of the jumping unit of the polymer chain. The preexponential factor, D_{01} , is a much weaker function of temperature than the exponential term and, hence, it can be treated as a constant.

In the proposed free-volume theory, the volume of the material is divided into occupied volume, interstitial free volume, and hole-free volume. The specific occupied volume of a pure liquid is defined to be the specific volume of the equilibrium liquid at 0°K which, for the polymer, is denoted by $\hat{V}_2^0(0)$. The specific interstitial free volume of the effectively pure polymer, \hat{V}_{FI2} , is the unoccupied volume which is distributed uniformly among the molecules of a given species because the energy for redistribution of this volume is large. The specific hole-free volume of the polymer, \hat{V}_{FH2} , is the volume associated with the discontinuous distribution of holes in the liquid, and it is assumed that this free volume can be redistributed with no increase in energy. The specific hole-free volume of the polymer can be calculated from the equation

$$\hat{V}_{FH2} = \hat{V}_2^0 - \hat{V}_{FI2} - \hat{V}_2^0(0) \quad (3)$$

if the specific volume of the polymer, \hat{V}_2^0 , is known and if an expression can be developed for the temperature dependence of \hat{V}_{FI2} . For the pure polymer, the thermal expansion coefficient for the sum of the specific occupied volume and the specific interstitial free volume is defined by the equation

$$\frac{1}{[\hat{V}_{FI2} + \hat{V}_2^0(0)]} \left\{ \frac{\partial [\hat{V}_{FI2} + \hat{V}_2^0(0)]}{\partial T} \right\}_p = \alpha_{c2} \quad (4)$$

and this equation yields the following result upon integration:

$$\hat{V}_{FI2} + \hat{V}_2^0(0) = [\hat{V}_{FI2}(T_{g2}) + \hat{V}_2^0(0)] \exp \left(\int_{T_{g2}}^T \alpha_{c2} dT \right) \quad (5)$$

where T_{g2} is the glass transition temperature of the polymer. For amorphous polymers like polystyrene and for the moderate temperature intervals utilized in this study, it is convenient to proceed by introducing the following assumptions:

1. The expansion coefficient for the polymer, α_{c2} , is independent of temperature and of polymer molecular weight.
2. The thermal expansion coefficient for the polymeric liquid, α_2 , defined in the usual way

$$\alpha_2 = \frac{1}{\hat{V}_2^0} \left(\frac{\partial \hat{V}_2^0}{\partial T} \right)_p \quad (6)$$

is approximated by an average value in the temperature range of interest.

3. For the two expansion coefficients, α_{c2} and α_2 , and for the temperature intervals of interest, approximations of the type

$$\exp [\alpha_2(T - T_{g2})] = 1 + \alpha_2(T - T_{g2}) \quad (7)$$

give satisfactory accuracy.

From eqs. (3), (5), and (6) and the three assumptions listed above, it follows that the specific hole-free volume of the polymer is given by

$$\hat{V}_{FH2} = K_{12}(K_{22} + T - T_{g2}) \quad (8)$$

$$K_{12} = \hat{V}_2^0(T_{g2})[\alpha_2 - (1 - f_{H2}^G)\alpha_{c2}] \quad (9)$$

$$K_{22} = \frac{f_{H2}^G}{\alpha_2 - (1 - f_{H2}^G)\alpha_{c2}} \quad (10)$$

$$f_{H2}^G = \frac{\hat{V}_{FH2}(T_{g2})}{\hat{V}_2^0(T_{g2})} \quad (11)$$

where α_2 and α_{c2} are appropriate average values of the expansion coefficients in the temperature interval of interest. Substitution of eq. (8) into eq. (2) gives the result

$$\ln D = \ln D_{01} - \frac{\gamma \hat{V}_2^* \xi}{K_{12}(K_{22} + T - T_{g2})} \quad (12)$$

and this expression will be the basic equation for investigating the temperature and solvent dependence of D . The quantities D_{01} and $\gamma \hat{V}_2^* \xi / K_{12}$ depend on the properties of the polymer-solvent system, whereas K_{22} depends on the polymer properties only. In this paper, we are concerned only with calculating these three quantities, and we do not deduce values for the parameters contained in these three groups. A method for evaluating the individual parameters is discussed elsewhere.³ Finally, by considering two temperatures, T and a reference temperature T_1 , it is easy to derive the following result:

TABLE I
Summary of Data for Polystyrene-Solvent Systems

Solvent	Temperature range, °C	Quality of data	Reference
Methane	100-188	good	7
n-Pentane	141-170	fair	9
Ethylbenzene	140-178	good	this investigation
Toluene	130-178	good	
Nitrogen	120-190	questionable	12
Hydrogen	108-191	questionable	
Carbon dioxide	165-186	questionable	
Ethylene	118-210	questionable	
Methanol	87-120	questionable	13
Ethanol	87-130	questionable	
Methylene chloride	87-115	questionable	
Ethyl bromide	87-120	questionable	
Pyridine	not known	questionable	
Chloroform	not known	questionable	
n-Propyl chloride	not known	questionable	
Benzene	not known	questionable	
Fluorobenzene	not known	questionable	

$$\frac{T - T_1}{\ln \left[\frac{D(T)}{D(T_1)} \right]} = \frac{K_{22}}{K_{32}} + \frac{T - T_{g2}}{K_{32}} \quad (13)$$

$$K_{32} = \frac{\gamma \hat{V}_2^* \xi}{K_{12}(K_{22} + T_1 - T_{g2})} \quad (14)$$

If the temperature variation of D is measured for a given polymer-solvent system, we can then determine D_{01} , $\gamma \hat{V}_2^* \xi / K_{12}$, and K_{22} using eqs. (12) and (13).

RESULTS AND DISCUSSION

The data which are analyzed in this paper using the results of the modified free-volume theory are summarized in Table I. The temperature range of reported diffusion coefficients for each polymer-solvent system is listed as well as an estimate of the quality of the data. The data for ethylbenzene and toluene are our unpublished results.

The experimental technique and data analysis procedures are described elsewhere,¹⁴ and extensive mutual diffusion coefficient data for these two solvents in polystyrene will be presented in later communications. Owing to the strong concentration dependence of D at small solvent concentrations and temperatures relatively close to the glass transition temperature, great care must be exercised in extrapolating diffusivity data to zero mass fraction. Since special attention was given to this problem and since good reproducibility of the data was attained, the quality of the toluene and ethylbenzene data is considered to be good. The *n*-pentane-polystyrene data⁹ were collected using an inferior version of the sorption apparatus used in the toluene and ethylbenzene studies. Less attention was given to the problem of deducing the value of D at zero mass fraction, and, hence, the quality of the data is judged to be fair.

Lundberg et al.⁷ measured the diffusivity for the methane-polystyrene system at high pressures, but the data were corrected to atmospheric pressure and effectively zero methane concentration. The free-volume equations presented above are valid only at low pressures since the effect of pressure on the free volume of the system was not considered. A careful experimental procedure and data analysis technique were utilized in the methane experiments, and the quality of the data is considered good. Newitt and Weale¹² measured the diffusion coefficients of carbon dioxide, ethylene, hydrogen, and nitrogen in polystyrene. Pressures up to 282 atmospheres were utilized, data were collected above and below the glass transition temperature, and no corrections for pressure and concentration effects were introduced. From the results of Lundberg et al.,⁷ we infer that pressure and concentration corrections for these gases will be relatively minor at temperatures above 120°C, and it is reasonable to assume that the majority of the reported data of Newitt and Weale above T_{g2} are relatively good approximations to the diffusivities at atmospheric pressure in the limit of zero solvent concentration. However, the experimental technique utilized by these investigators is questionable. The reliability of the solubility data presented by Newitt and Weale has also been questioned.^{15,16} Only the diffusivity data of Newitt and Weale above the glass transition temperature (100°C) are analyzed here.

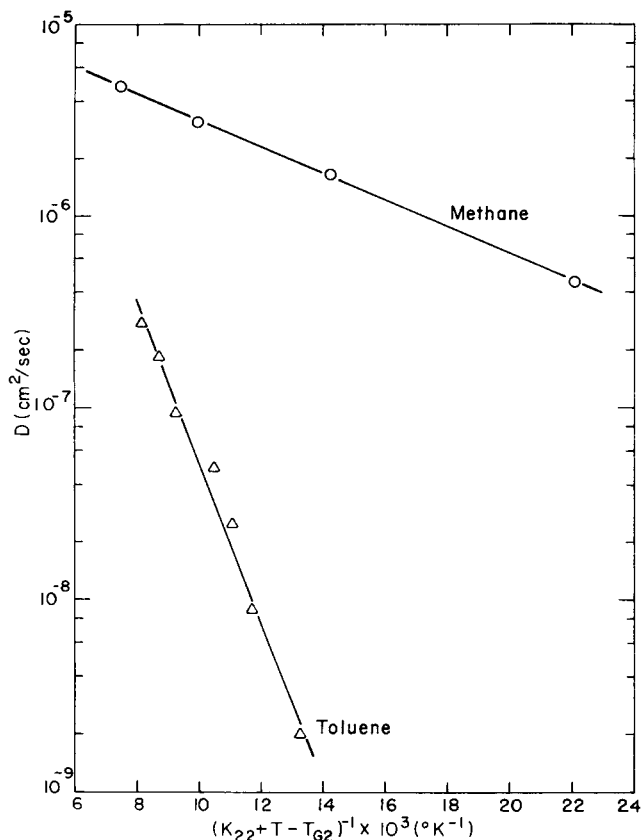


Fig. 2. Free-volume representation for methane and toluene diffusion data.

Zhurkov and Ryskin¹³ reported data for a number of polystyrene-solvent systems using a polymer sample with a measured glass transition temperature of 82°C. This temperature is significantly below the accepted value of 100°C for high molecular weight (>100,000) polystyrene with low volatile content. Zhurkov and Ryskin did not report the molecular weight of their polymer sample, but it does not seem likely that all of the depression in T_{g2} could be caused by the utilization of a low molecular weight polystyrene since this would require a polymer sample with a molecular weight¹⁷ of about 6000. Hence, it appears probable that volatile material was present in the polystyrene sample, and, without further information, it is not possible to properly analyze the diffusivity data of Zhurkov and Ryskin. Consequently, since the nature of the polymer that these investigators utilized is unknown and since the temperature range of their polystyrene experiments is relatively narrow, we felt that it was inappropriate to attempt to correlate the temperature dependence of their measured diffusion coefficients using free-volume theory. However, approximate values of free-volume parameters were derived from their data to see if there was any correlation of these values with the molecular characteristics of the polymer-solvent systems that were studied. Only the diffusivity data of Zhurkov and Ryskin above their measured glass transition temperature were considered.

As noted above, values of D_{01} , $\gamma \hat{V}_2^* \xi / K_{12}$, and K_{22} can be determined by using

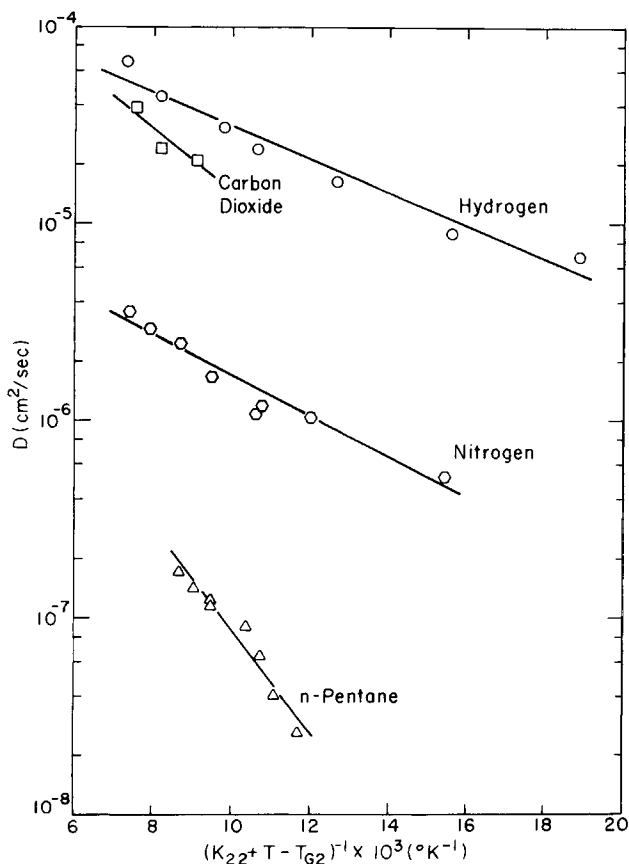


Fig. 3. Free-volume representation for carbon dioxide, hydrogen, nitrogen, and *n*-pentane diffusion data.

eqs. (12) and (13). If $(T - T_1)/\ln [D(T)/D(T_1)]$ is plotted versus $T - T_{g2}$, then, from eq. (13), it is evident that a straight line will result if free-volume theory is applicable, and K_{22} is equal to the ratio of the intercept to the slope that is determined from this straight line. This plot is sensitive to the quality of the data and, hence, it is preferable to determine K_{22} using only data of good quality taken over a reasonably wide temperature range. Of the data listed in Table I, only the methane, toluene, and ethylbenzene data are of sufficient quality, and furthermore, the data for the latter two solvents cover about one half of the temperature range used in the methane experiments. Hence, K_{22} was evaluated using the methane data of Lundberg et al.,⁷ and a value of 45.3°K was determined from the straight-line fit. Since K_{22} should be a property of the polymer only, it can also be determined by applying free-volume theory to viscosity data. A value of $K_{22} = 46.6^\circ\text{K}$ was determined previously,³ and Ferry¹⁸ reports values of 47.5°K and 50.0°K. These values are in good agreement with the value determined from the methane diffusion experiments of Lundberg et al.⁷

With K_{22} determined by the above procedure, we can then determine D_{01} and $\gamma \hat{V}_{22}^*/K_{12}$, the two parameters which are associated with the properties of both the polymer and the solvent, by plotting $\ln D$ versus $1/(K_{22} + T - T_{g2})$. If free-volume theory describes the data, then, from eq. (12), it is evident that a

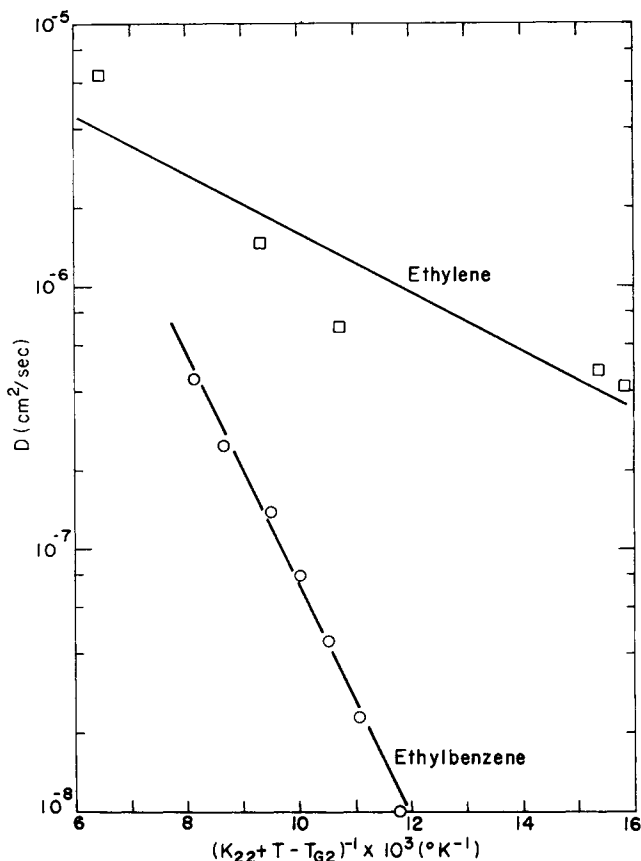


Fig. 4. Free-volume representation for ethylene and ethylbenzene diffusion data.

straight line will result with slope and intercept which are simply related to D_{01} and $\gamma \hat{V}_2^* \xi / K_{12}$. Graphs of the logarithm of D versus $1/(K_{22} + T - T_{g2})$ are presented in Figures 2-4 for eight of the solvents listed in Table I. The straight lines in these graphs represent least-squares fits to the experimental data. The correlations of the methane, toluene, and ethylbenzene data with the equation derived from free-volume theory are quite good. This can be considered strong support for the free-volume theory since this theory provides a good representation of the temperature dependence of the most reliable diffusivity data available for polystyrene-solvent systems. Furthermore, Lundberg et al.⁷ concluded that the zone theory and absolute reaction rate theory could not account for the magnitude of the observed decrease in the apparent or effective activation energy for polystyrene-methane diffusion with increasing temperature. However, free-volume theory appears to give an excellent representation of the temperature dependence of the mutual diffusion coefficient for the polystyrene-methane system.

It can also be concluded that free-volume theory provides a satisfactory representation of the temperature dependence of the diffusion coefficients of carbon dioxide, ethylene, hydrogen, and nitrogen. However, as is evident from Figures 3 and 4, there is significant scatter about the least-squares straight lines. Such scatter is, of course, to be expected because of the questionable experimental

procedure used by Newitt and Weale.¹² Furthermore, if experimental diffusivity data scatter sufficiently, it is, of course, nearly always possible to justify the construction of a straight line on a $\log D$ -versus- $1/T$ plot which adequately portrays the temperature dependence of the diffusivity. Clearly, data of this type cannot be used to differentiate between theories and cannot present conclusive evidence for either free-volume or Arrhenius-type relationships. This situation emphasizes the need for accurate data for the testing of theories.

Whereas the data of Newitt and Weale show a general scatter about the least-squares lines, the *n*-pentane data⁹ show a smaller scatter but with a subtle trend which could lead to the conclusion that the apparent activation energy undergoes a very significant change over a narrow temperature interval. This rapid decrease of the effective activation energy with increasing temperature over a narrow temperature range is more apparent on a plot of $\log D$ versus $1/T$.⁹ Such a temperature variation of the mutual diffusion coefficient cannot be described by the results of free-volume theory. In an earlier investigation,⁹ we tentatively associated this rapid variation in effective activation energy with a second-order transition point in atactic polystyrene. Other arguments¹⁹ have also been presented for the existence of a transition point 60–100°C above the glass transition. Although such a tentative conclusion appeared reasonable in light of the data available at that time, it now appears that there is sufficient evidence which argues against such a conclusion. In the first place, no excessively rapid change in the effective activation energy is observed for the methane, toluene, and ethylbenzene data, and the quality of these diffusion data is judged to be superior to that of the *n*-pentane-polystyrene data. Furthermore, free-volume theory provides a good representation of the temperature dependence of the diffusion coefficient for each of these three solvents. Second, since the

TABLE II
Free-Volume Parameters for Polystyrene-Solvent Systems

Solvent	$\hat{\gamma}V_{2c}^*/K_{12}$, °K	$\ln D_{01}$ (D_{01} , cm ² /sec) ^a	Molar volume of solvent at 0°K, cm ³ /g-mole
1. Hydrogen	196	-8.40	13.2
2. Methane	160	-11.1	27.2
3. Nitrogen	243	-10.9	21.1
4. Methanol	371	-9.50	34.0
5. Ethylene	257	-10.8	36.5
6. Carbon dioxide	398	-9.50	33.9
7. Ethanol	445	-11.3	48.1
8. Methylene chloride	509	-11.2	49.7
9. Ethyl bromide	551	-11.4	55.4
10. Pyridine	700	—	67.2
11. Chloroform	678	-10.2	60.9
12. <i>n</i> -Propyl chloride	725	—	66.6
13. Benzene	742	—	70.4
14. Fluorobenzene	763	—	75.0
15. <i>n</i> -Pentane	597	-10.3	83.6
16. Toluene	963	-7.05	84.4
17. Ethylbenzene	1030	-6.12	98.5

^a Values of D_{01} for solvents 10 and 12–14 could not be calculated because of insufficient data.

general quality of the *n*-pentane data is considered to be only fair, moderate scatter in the data is to be expected, and care must be exercised in drawing definitive conclusions from such data. Indeed, the conclusion that the effective activation energy changes significantly over a narrow temperature range depends on the accuracy of two data points near 150°C. Thus, it seems more reasonable to conclude that the *n*-pentane-polystyrene data are satisfactorily described by free-volume considerations, and any deviations are due to the moderate scatter that can be expected from data of this quality.

We can conclude from the above discussion that the most accurate polystyrene-solvent diffusion data suggest that free-volume theory provides a satisfactory representation of the temperature dependence of *D*. Hence, it seems worthwhile to obtain estimates of D_{01} and $\gamma \hat{V}_2^* \xi / K_{12}$ and attempt to correlate these parameters with molecular characteristics. With the exception of the data of Zhurkov and Ryskin,¹³ these two free-volume parameters follow from the slopes and intercepts of the straight lines presented in Figures 2-4. The data of Zhurkov and Ryskin were analyzed in an approximate manner by calculating $\gamma \hat{V}_2^* \xi / K_{12}$ using their reported activation energies at the average temperature of their experiments in conjunction with the following free-volume result:

$$E_D = \frac{RT^2 \left(\frac{\gamma \hat{V}_2^* \xi}{K_{12}} \right)}{(K_{22} + T - T_{g2})^2} \quad (15)$$

Values of D_{01} could be calculated for only five of the solvents used by Zhurkov and Ryskin since insufficient data were reported for the other solvents. Free-volume parameters for polystyrene-solvent pairs listed in Table I are reported in Table II.

There has been some previous success^{9,13,20} in correlating activation energies for diffusion in a particular polymer with the size of the solvent molecule, as estimated by its molar volume at some convenient temperature. Hence, in light of eq. (15), it seems appropriate to attempt to correlate $\gamma \hat{V}_2^* \xi / K_{12}$ with the molar volume of the solvent. A more convincing argument for constructing a plot of this type can be formulated by considering the nature of the group $\gamma \hat{V}_2^* \xi / K_{12}$. The quantity ξ can be expressed as

$$\xi = \frac{\tilde{V}_1^*}{\tilde{V}_2^*} \quad (16)$$

where \tilde{V}_1^* is the critical volume of solvent per mole of solvent, and \tilde{V}_2^* is the critical volume of jumping units per mole of jumping units. It is reasonable to expect that the critical amount of local hole-free volume per mole necessary for a jump of a solvent molecule to take place is approximately equal to the occupied volume per mole of the liquid; and, as noted above, this can be defined to be the molar volume of the liquid solvent at 0°K, $\tilde{V}_1^0(0)$. Hence, from eq. (16) it is evident that

$$\frac{\gamma \hat{V}_2^* \xi}{K_{12}} = \left(\frac{\gamma \tilde{V}_2^*}{K_{12} \tilde{V}_2^*} \right) \tilde{V}_1^0(0) \quad (17)$$

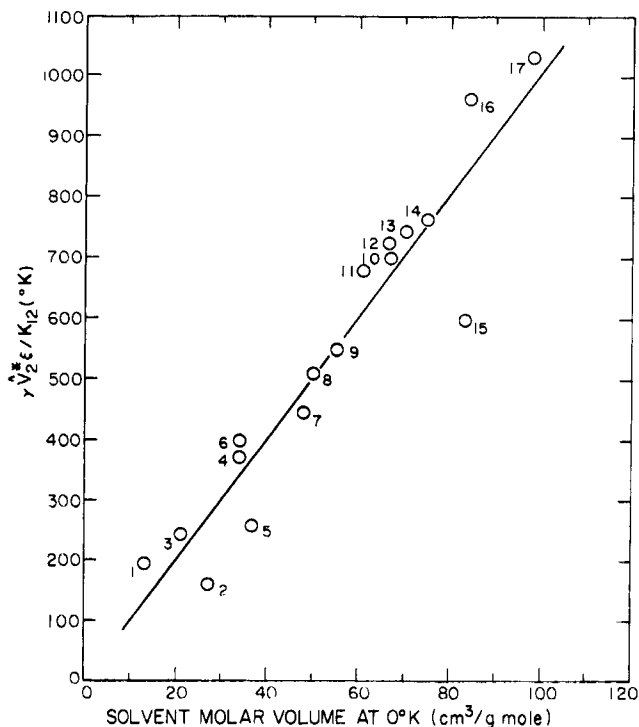


Fig. 5. Variation of $\gamma \hat{V}_2^* \xi / K_{12}$ with molar volume of the solvent at 0°K . Numbers of solvents correspond to those in Table II.

And, since γ , \hat{V}_2^* , \bar{V}_2^* , and K_{12} are the same for any solvent and a particular polymer, it follows that $\gamma \hat{V}_2^* \xi / K_{12}$ should be a linear function of the molar volume of the solvent at 0°K .

A graph of $\gamma \hat{V}_2^* \xi / K_{12}$ versus the solvent molar volume at 0°K is presented in Figure 5. The molar volumes at 0°K listed in Table II and used in Figure 5 were calculated by averaging values determined using the methods of Sugden²¹ and Biltz²² as summarized by Haward.²³ The data are adequately represented by a linear relationship, particularly since the quality of some of the data is suspect. The maximum deviations from the least-squares line occur for *n*-pentane, ethylene, and methane, the significant deviation of the methane being somewhat surprising. However, it is fair to conclude that a linear equation adequately describes the relationship between $\gamma \hat{V}_2^* \xi / K_{12}$ and the size of the solvent as estimated by its molar volume at 0°K ; and, hence, solvent molecular size dictates the temperature dependence of the diffusion rate. Graphs presented in Figure 6 illustrate the variation of E_D with temperature and molecular size.

In previous investigations,^{9,13,20} evidence was presented for a correlation between D_{01} and molecular size. However, as can easily be deduced from the data presented in Table II, no systematic relationship exists between D_{01} and the solvent molar volume at 0°K . This result appears reasonable, since the preexponential factor must absorb a term which depends on the energy a solvent molecule must obtain to overcome the attractive forces holding it to its neighbors. It is unlikely that the energetics of these attractive forces can, in general, be correlated with molecular size; and, hence, D_{01} must presumably be described

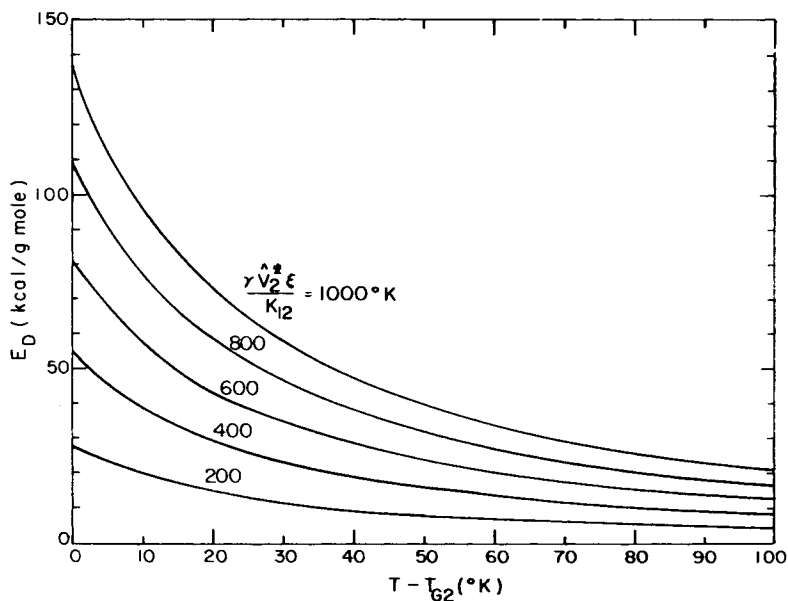


Fig. 6. Effect of temperature and solvent size on the effective activation energy for polystyrene-solvent diffusion.

by a different measure of the molecular characteristics of the solvent. However, one of the two parameters involving both solvent and polymer correlates well with molecular size, and this group can be estimated for the diffusion of any solvent in polystyrene using Figure 5.

From Table II, it is evident that $\gamma \hat{V}_2^* \xi / K_{12}$ ranges from 160°K to 1030°K , whereas, from the analysis of polystyrene viscosity data,³ it has been determined that $\gamma \hat{V}_2^* / K_{12}$ is equal to 1460°K . Consequently, $\xi < 1$ for all solvents considered in this study; and, hence, these solvents need a smaller hole to complete a jump than does a polymeric jumping unit. Therefore, the temperature dependence of the rate of diffusion of a trace of a solvent of any size in a polymer is primarily dependent on the size of the solvent molecule and not on the size of a polymeric jumping unit. Hence, it would appear that the effect of molecular size on diffusional transport is better explained by Frenkel's picture of the self-diffusion process¹⁰ rather than that of Cohen and Turnbull.¹¹

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