

Free Volume Theory of Diffusion: Method of Predicting Activation Energies of Diffusion for Gases in Elastomers

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Synopsis

It is well established that diffusion and relaxation processes in polymers above T_g are closely related in that they are both governed by the polymer segmental motions, which are believed to be determined by the free volume present in the system. The diffusion coefficients of gases in elastomers can be accounted for by the WLF equation using the "universal values" of constants A and B . The parameter $K = B_D/B_\eta$ of Frisch and Rogers is used as a correction factor. An analysis has been made of the diffusion of five gases in nine elastomers, from data found in the literature. K and $\log D_g$ are shown to vary with the penetrant but not with the polymer. Therefore, once the values of K and $\log D_g$ of gases are determined, their diffusion coefficients in any elastomers of known T_g at a variety of temperatures can be estimated. From the Arrhenius and the WLF relationships, an equation is derived to predict the activation energy of diffusion directly from the temperature of diffusion, the glass transition temperature of the amorphous polymer, the predetermined value of K , and the universal constants A and B . In the systems studied, the predictions agree on the average to within 11–17% of the values calculated from the experimental data.

INTRODUCTION

The diffusion and relaxation processes in polymers above T_g are governed by the segmental mobility of the polymer chains, which is in turn considered to be affected by the total free volume and its distribution in the polymer system.¹ A quantitative relation between the viscous flow and the free volume of a polymer can be based on an expression similar to that introduced by Doolittle² as shown in eq. (1):

$$\eta = A_\eta \exp(B_\eta/f) \quad (1)$$

where η is the viscosity coefficient of the polymer, A_η and B_η are constants depending on the geometry of the chain and independent of temperature, and f is the fractional free volume in the polymer system.

Diffusion depends on the mobility of penetrants within the polymer and also on the free volume in the polymer. According to Fujita,³

$$M_D = A_D \exp(-B_D/f) \quad (2)$$

where M_D is the mobility of the penetrant in the polymer, and A_D and B_D are constants depending on the geometry of the penetrant, i.e., molecular shape and size, but not on temperature.

From Doolittle's equation, Williams, Landel, and Ferry⁴ deduced an equation, known as the WLF equation, which describes the temperature dependence of viscous flow:

$$\log a_T = \log \frac{\eta}{\eta_g} = \frac{A(T - T_g)}{B + (T - T_g)} \quad (3)$$

where $\log a_T$ is the shift factor in the time-temperature superposition principle; η and η_g are the viscosity at T and T_g , respectively; T and T_g are the temperature of the flow and the glass transition temperature of polymer, respectively; and A and B are the "universal constants" having the values of -17.44 and 51.6 K, respectively.

The WLF equation holds in the temperature range from T_g to $T_g + 100$ K. Equations (1) and (2) can be compared at T and at T_g ; the relationships can be written as follows:

$$\ln \frac{\eta}{\eta_g} = B_\eta \left[\frac{1}{f(T)} - \frac{1}{f(T_g)} \right] \quad (4)$$

$$\ln \frac{M_D(T)}{M_D(T_g)} = -B_D \left[\frac{1}{f(T)} - \frac{1}{f(T_g)} \right] \quad (5)$$

where $f(T)$ and $f(T_g)$ are the fractional free volumes at T and T_g , respectively; and $M_D(T)$ and $M_D(T_g)$ are mobilities of penetrant at T and T_g , respectively. That is,

$$\ln \frac{M_D(T)}{M_D(T_g)} = \frac{-B_D}{B_\eta} \ln \frac{\eta}{\eta_g} \quad (6)$$

Since the mobility M_D can be defined as

$$M_D = D_T/RT \quad (7)$$

where D_T is the thermodynamic diffusion coefficient and R is the gas constant, eq. (7) can be rewritten as

$$\log \frac{D_T/T}{D_g/T_g} = -K \log \frac{\eta}{\eta_g} \quad (8)$$

where

$$K = B_D/B_\eta \quad (9)$$

The parameter K was first introduced by Frisch and Rogers.⁵ It was interpreted as "a measure of the efficiency or inefficiency of utilization of free volume by a mass transport process compared to its utilization by a momentum transfer process in the same process."¹ The magnitude of the parameter K was expected to vary from very small to unity, depending on the penetrant molecule size and shape. According to Rogers et al., " K must be determined from diffusion and viscoelastic property measurement made on the same polymer sample to avoid random variations due to differences in sample preparation, molecular weight, morphology, impurity content, etc."¹ However, if the WLF equation is valid within the temperature range of T_g to $T_g + 100$ K, the following expression should hold:

$$\log \frac{D_T T_g}{T} = \frac{-KA(T - T_g)}{B + (T - T_g)} + \log D_g \quad (10)$$

where D_g is the thermodynamic diffusion coefficient at $T = T_g$.

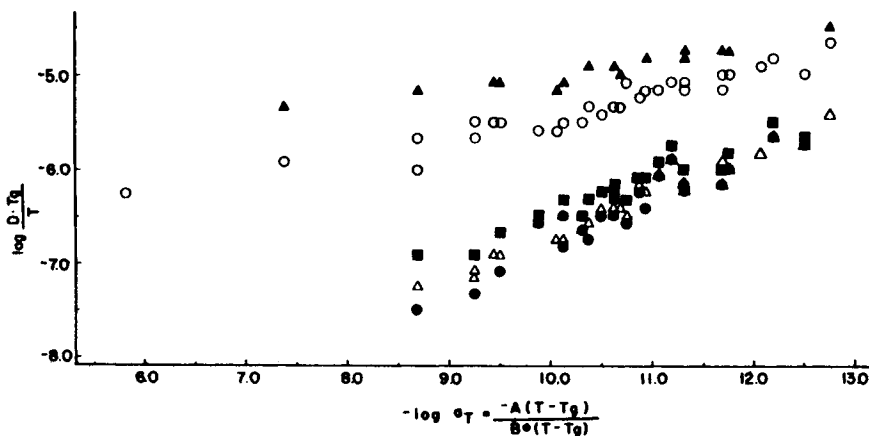


Fig. 1. Master plot of $\log(D \cdot T_g/T)$ vs. $\log a_T$ for five gases and nine polymers at various temperatures (Table I): (●) CO_2 ; (Δ) N_2 ; (■) O_2 ; (○) H_2 ; (\blacktriangle) He.

In the diffusion of ideal penetrants into amorphous polymers, which involves no specific interactions between the penetrants and the polymers, the thermodynamic diffusion coefficient in eq. (10) can be simply replaced by diffusion coefficients calculated from Fick's laws.

ACTIVATION ENERGY OF DIFFUSION

The diffusion coefficient can also be related to temperature using the Arrhenius equation:

$$D = D_0 \exp(-E_d/RT) \quad (11)$$

where D_0 is the preexponential factor and E_d is the activation energy of diffusion.

If the activation energy E_d does not vary too greatly over the temperature range of experiment (or if E_d varies linearly with temperature T), a plot of $\ln D$ vs. $1/T$ will give an apparent straight line of slope $-E_d/R$. However, from eq. (10) at any given temperature T , we have

$$\frac{d(\log D)}{d(1/T)} = T \left[\frac{KABT}{[B + (T - T_g)]^2} - 1 \right] \quad (12)$$

so that if eq. (11) is considered to refer to a narrow temperature range surrounding the temperature T ,

$$E_d = -2.303RT \left[\frac{KABT}{[B + (T - T_g)]^2} - 1 \right] \quad (13)$$

Gutta percha	7	-53	43	11.5	5.88	2.3	9.02	4.51	1.8	10.12	1.7	10.71
Poly(dimethylbutadiene)	8	-33	50	10.5	6.82	0.61	10.61	5.18	0.41	11.94	0.36	12.65
Natural rubber	8	-70	50	22.2	4.77	4.7	7.10	3.75	3.42	7.91	3.5	8.35
Polybutadiene	8	-80	50	18	4.41	3.7	6.49	3.51	2.9	7.22	2.8	7.62
80/20 Butadiene-acrylonitrile	8	-56	50	14.5	5.38	2.30	8.14	4.18	1.55	9.11	1.42	9.63
Perbunan	8	-46	50	11.1	5.92	1.44	9.07	4.56	0.98	10.17	0.77	10.77
68/32 Butadiene-acrylonitrile	8	-37	50	9.60	6.52	1.08	10.09	4.97	0.70	11.34	0.515	12.02
61/39 Butadiene-acrylonitrile	8	-26	50	6.56	7.43	0.565	11.64	5.60	0.34	13.11	0.221	13.91
Natural rubber	8	-70	18.5	1.3	6.82		10.83	5.08		12.23		12.99
Natural rubber	8	-70	0	3.7	7.1		9.24	4.49	0.22	10.40		11.03
Natural rubber	8	-70	12	6.2	6.7	5.53	8.52	4.23	0.52	10.7	9.57	10.14
Natural rubber	8	-70	35	14.2	6.0	5.00	7.54	3.90	1.82	8.8	8.43	8.92
Natural rubber	8	-70	70	37.1	4.54		6.65	3.63	6.63	6.6	7.39	7.79
Butadiene-acrylonitrile	8	-46	12	2.53	7.58		12.02	5.65	0.105	13.58		14.40
Butadiene-acrylonitrile	8	-46	35	6.70	6.42		9.96	4.88	0.46	10.6	11.21	11.88
Butadiene-acrylonitrile	8	-46	70	18.9	5.0	5.46	8.21	4.26	0.21	9.18		7.70
61/39 Butadiene-acrylonitrile	8	-26	0	0.665	12.74		20.87	9.20		23.73		25.27
61/39 Butadiene-acrylonitrile	8	-26	12	1.32	8.6	10.70	17.34	5.0		19.68		20.94
61/39 Butadiene-acrylonitrile	8	-26	35	3.74	7.7	8.35	13.27	10.7	5.5	13.1	15.00	15.93
61/39 Butadiene-acrylonitrile	8	-26	70	11.9	6.2	6.58	10.13	24.2	0.805	9.0	11.38	12.05

^a Blank spaces indicate that data are not available.

DISCUSSION

Significance of Frisch and Roger's Parameter $K = B_D/B_\eta$

Examining eq. (10), one would expect a plot of $\log (DT_g/T)$ vs. $[-A(T - T_g)]/[B + (T - T_g)]$ for a penetrant diffusing into an elastomer to be a straight line with slope K and an intercept of $\log D_g$ on the ordinate. Such plots have been made from literature data for small gases in various elastomers at different temperatures and are shown in Figure 1. The literature data and references are listed in Table I. The statistical analysis of the plots in Figure 1 is summarized in Table II.

It can be seen from Figure 1 and Table II that K and $\log D_g$ vary with the penetrant but not with the polymer. This suggests that the diffusion coefficient of any gas listed in Table II can be estimated, for any new elastomer, from the T_g of the elastomer. The temperature T of diffusion should be in the range $T_g + 100 \text{ K} \geq T \geq T_g$.

Relation between K , $\log D_g$, and Molecular Size of Penetrants

It is to be noted from Table II that the K values increase with the molecular size of the penetrant, whereas the $\log D_g$ values decrease. Although we examined plots of K and of $\log D_g$ against d , d^2 , and d^3 , where d is the molecular diameter of the gas (from viscosity data¹⁰), the best linear correlations were found using the linear diameter d (Fig. 2). The values of R^2 for the correlations are 0.9913 for K vs. d , and 0.9918 for $\log D_g$ vs. d . These results confirm the predictions made by Frisch, Rogers, and their co-workers^{1,5} that K will increase with the molecular size of the penetrant and will approach unity when the penetrant molecule becomes sufficiently large. Presumably, there is a critical size of the penetrant molecule, corresponding to the size of the preexisting holes in the polymer system, above which diffusion takes place only through the segmental motion of the polymer chains. The segmental mobility, in turn, is facilitated by an increase in the free volume of the polymer matrix. If the penetrant molecule is smaller than the critical size of the preformed cavity, the diffusion process below T_g may correspond to a rigid-pore diffusion mechanism and be insensitive to polymer chain mobility. Above the glass transition temperature of the polymer, it is possible that diffusion occurs due to both a pore mechanism and to the segmental mobility of the polymer chains.

TABLE II
Effect of Molecular Size of Gas on K and $\log D_g$ (Fig. 2)^a

Gas	K	$\log D_g$	Correlation coefficient	No. of observations	Molecular wt.	Molecular diameter, ^b Å
H ₂	0.2254 ($\pm 5.4\%$)	-7.694 ($\pm 1.7\%$)	0.916	33	2	2.40
He	0.1560 ($\pm 7.3\%$)	-6.566 ($\pm 1.8\%$)	0.930	15	4	1.90
N ₂	0.4410 ($\pm 4.7\%$)	-11.118 ($\pm 2.0\%$)	0.940	30	28	3.15
O ₂	0.3850 ($\pm 6.6\%$)	-10.331 ($\pm 2.6\%$)	0.920	21	32	2.98
CO ₂	0.4713 ($\pm 7.8\%$)	-11.492 ($\pm 3.4\%$)	0.893	21	44	3.34

^a Numbers in parentheses are the standard errors.

^b From viscosity measurements at 20°C.¹⁰

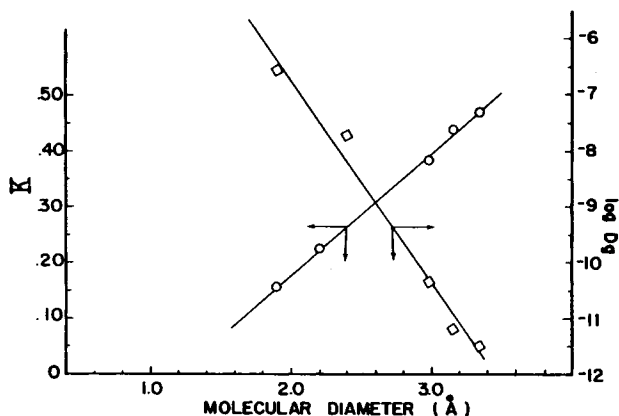


Fig. 2. Plots of K and of $\log D_g$ vs. molecular diameter of penetrant (Table II).

The behavior shown in Figure 2 implies a close relation between K and $\log D_g$. A plot of K vs. $\log D_g$ for the first five penetrant molecules gives a straight line with correlation coefficient $R^2 = 0.9988$ and a coefficient of variation of 1.62% about the regression line (Fig. 3). The statistical analysis is summarized in Table III. One cannot help but wonder if this excellent linear relation between the two parameters K and $\log D_g$ is spurious and arises merely because of random error, or because the ranges of data on both coordinates are small. Tests were made which are capable of revealing such a spurious linear correlation. A valid linear correlation between K and $\log D_g$ was confirmed. Details of these tests can be found in Appendix A. The approach used is essentially that introduced by Exner.^{12,13}

Predictions of Activation Energy of Diffusion from Proposed Equation

Using eq. (13), the predicted activation energy of diffusion ($E_{d,\text{pred}}$) of a gas listed in Table II, in any new elastomer, can be estimated from the temperature of diffusion T , the glass transition temperature T_g , and the tabulated value of K for the penetrant gas. This suggests that when a new elastomeric polymer or copolymer is synthesized, for example, only the T_g of the polymer needs to be found experimentally to obtain an estimate of the diffusion behavior of the different gases listed at different temperatures. Of course, the precise range of validity of this suggestion needs to be tested against new data, but our analysis of the literature data offers strong support for this approach.

A comparison of the values of the predicted and observed activation energies is also shown in Table I. The agreement of these two parameters is confirmed by the plot of $E_{d,\text{obs}}$ vs. $E_{d,\text{pred}}$ in Figure 4. The result of the statistical analysis of the linear regression is tabulated in Table IV.

TABLE III
Statistical Analysis of Linear Plot of K vs. $\log D_g$

Slope	= $-0.0631 (\pm 2.0\%)$
Intercept	= $-0.2602 (\pm 4.6\%)$
R^2	= 0.9988
Coefficient of variation about the regression line	= 1.62%

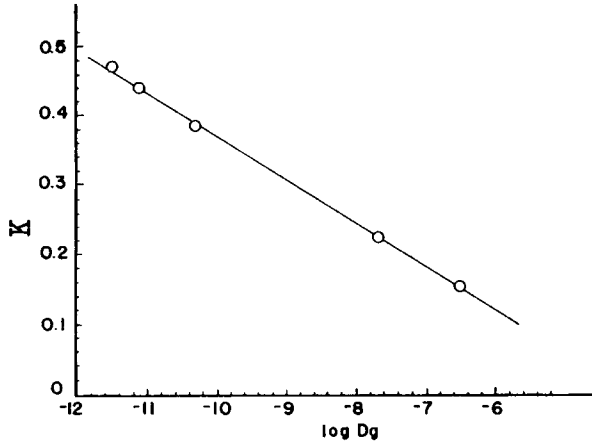


Fig. 3. Plot of K vs. $\log D_g$ for five penetrants (Tables I and II).

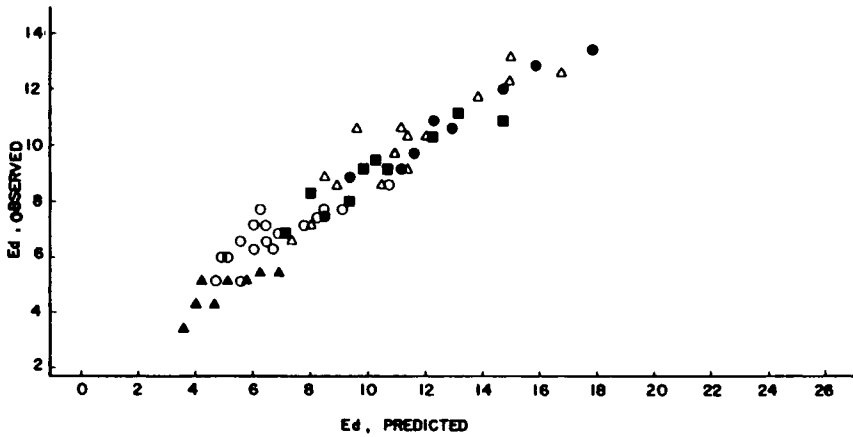


Fig. 4. Master plot of $E_{d,obs.}$ vs. $E_{d,pred.}$ (Table IV): (●) CO_2 ; (Δ) N_2 ; (■) O_2 ; (○) H_2 ; (\blacktriangle) He.

Relation between Activation Energy of Diffusion and Glass Transition Temperature

Frisch and his co-workers found that the activation energies for diffusion of small gases into polymers varied linearly with the glass transition temperatures

TABLE IV
Statistical Analysis: Linear Regression of E_d Observed vs. E_d Predicted (Figs. 4 and 5)

$$E_{d,pred} = -2.303RT \left[\frac{KABT}{[B + (T - T_g)]^2} - 1 \right]$$

Slope	= 0.6843 (± 0.0248)
Intercept	= 2.0008 (± 0.2428)
R^2	= 0.9302
Confidence limit	= 99.99%
No. of observations	= 58

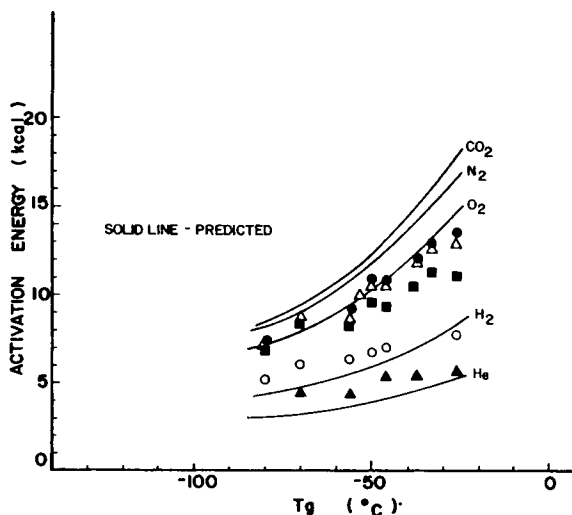


Fig. 5. Plot of predicted and observed activation energy of diffusion (at 25°C) vs. T_g of polymers (Table IV): (○) CO_2 ; (Δ) N_2 ; (■) O_2 ; (○) H_2 ; (\blacktriangle) He.

of the polymers.¹⁴ Figure 5 shows the literature data and the predictions from eq. (13) for diffusion temperatures of 25°C. The predicted curves are nonlinear, but the curvature is not great and would not be obvious experimentally if the data were subject to experimental errors. Equation (13) agrees in concept with Frisch's observation that the activation energies consist of two components: one is a function of the penetrant, the other of the polymer (T_g). According to eq. (13), for a given temperature T the parameter K , which depends on the molecular geometry of the penetrant, can be regarded as one component, while the second is a function of T_g and therefore characteristic of the polymer only. Frisch¹⁴ determined the parameter K to be proportional to the square of the diameter, or to the area of the gas molecules. In our investigation, we find that K varies directly with the linear diameter of the penetrant molecule.

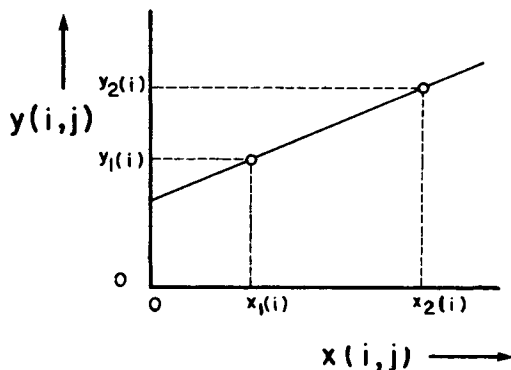
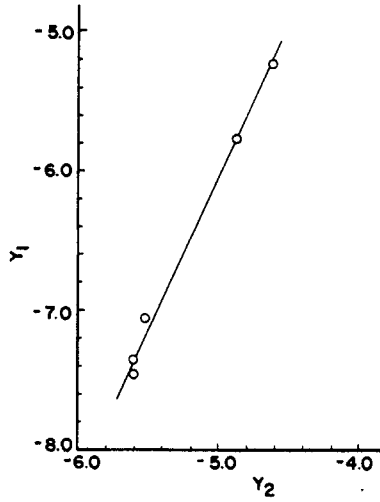
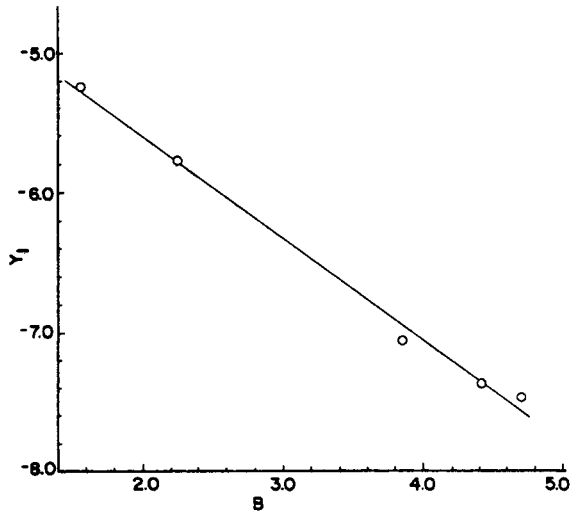


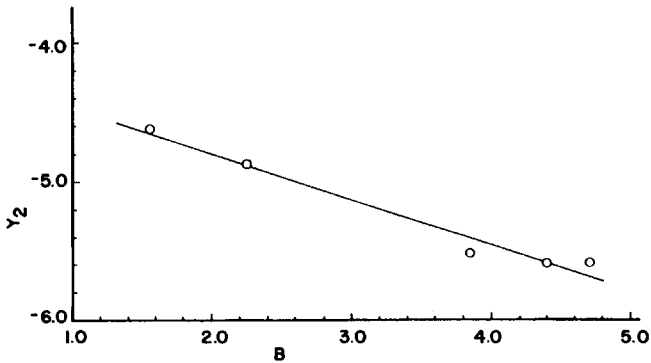
Fig. 6. Linear plot of $Y(i,j)$ vs. $X(i,j)$ for data set i (cf. Appendix A).



(a)



(b)



(c)

Fig. 7. (a) Test for spurious linear correlation (Table V). (b) Test for spurious linear correlation (Table V). (c) Test for spurious linear correlation (Table V). (d) Test for spurious linear correlation (Table V) (cf. Appendix A).

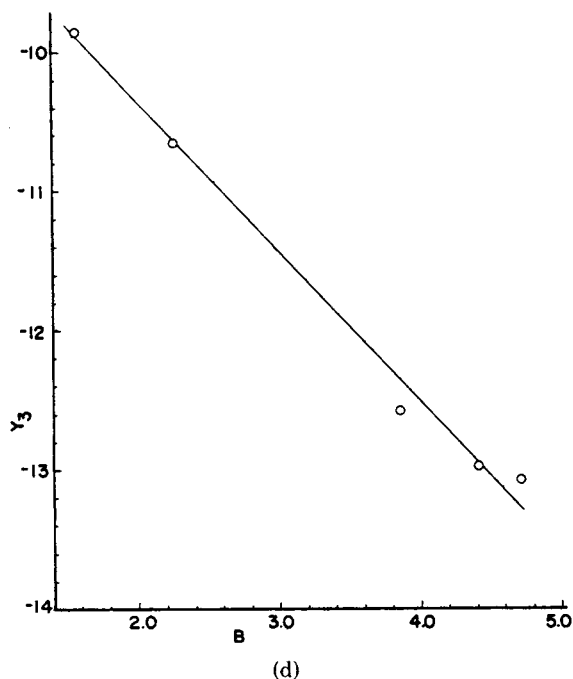


Fig. 7. (Continued from previous page.)

CONCLUSION

Using statistical analysis and a linear regression model, the diffusion parameters K and $\log D_g$ of an extended, free-volume diffusion model were found to be linearly correlated, to be independent of the polymer, and to vary linearly with the diameter of the penetrant gas molecules. Consequently, once the values of K and of $\log D_g$ for various gases are determined, the diffusion coefficients of those gases can be estimated directly from the temperature of diffusion T and the T_g of any new elastomer. Using the Arrhenius equation and the WLF equation, an equation was derived for predicting the activation energy of diffusion from the predetermined values of K , T , T_g , and the "universal constants" A and B . The predicted activation energies agreed on average to within 11% (H_2), 12% (He), 13% (N_2), 15% (O_2), and 17% (CO_2), respectively, with the experimental values. The maximum deviation observed was 35% for O_2 in 61/39 butadiene-acrylonitrile. The confidence level of the observed correlation is greater than 99%.

The extension of this approach to other polymers and to other penetrant types will be of considerable interest and is under current study. Our proposed approach should be valid for the gases of Table I diffusing in an elastomer which obeys the WLF equation with the "universal values" of A and B .

TABLE V
Statistical Analysis of Tests to Reveal Any Spurious Relations between K and $\log D_g$

Test	Plot shown in	R^2	Coefficient of Variation about the Regression Line (%)
$Y_1(i)^a$ vs. $Y_2(i)^b$	Fig. 7(a)	0.993	1.45
$Y_1(i)$ vs. $B(i)^c$	Fig. 7(b)	0.994	1.41
$Y_2(i)$ vs. $B(i)$	Fig. 7(c)	0.974	1.64
$Y_3(i)^d$ vs. $B(i)$	Fig. 7(d)	0.989	1.50

^a $Y_1(i)$ = the ordinate value calculated from the regression line at the abscissa value $X_1 = 8.50$ (Y_1 is a value of $\log D \cdot T_g/T$; X_1 is the corresponding value of $-\log a_T$), for a given gas (i).

^b $Y_2(i)$ = the ordinate value calculated from the regression line at the abscissa value $X_2 = 12.50$ (Y_2 is a value of $\log D \cdot T_g/T$; X_2 is the corresponding value of $-\log a_T$), for a given gas (i).

^c $B(i) = K$ value, or slope of the regression line: $\log D \cdot T_g/T$ vs. $-\log a_T$, for a given gas (i).

^d $Y_3(i) = Y_1(i) + Y_2(i)$, for a given gas (i).

APPENDIX A

Spurious Correlations between Slopes and Intercepts of Straight-Line Data Plots

Suppose we have m different data sets (i), each of which separately gives a straight-line plot in a given coordinate system:

$$Y(i,j) = A(i) \pm B(i) \cdot X(i,j) \quad \begin{array}{l} i = 1, 2, \dots, m \\ j = 1, 2, \dots, n_i \end{array} \quad (\text{A-1})$$

The data pair $[X(i,j), Y(i,j)]$ is the j th observation in data set i . The linear correlation found for data set i is concisely summarized in the two parameters $A(i)$ and $B(i)$, the intercept and slope, respectively, found for that straight-line plot of $Y(i,j)$ vs. $X(i,j)$.

If we can choose two common standard values X_1 and X_2 for the abscissae $X(i,j)$ for all data sets, then each data set (i) can also be characterized by the corresponding values $Y_1(i)$ and $Y_2(i)$ found for that data set (Fig. 6):

$$\begin{aligned} Y_1(i) &= A(i) + B(i) \cdot X_1 \\ Y_2(i) &= A(i) + B(i) \cdot X_2 \end{aligned} \quad i = 1, 2, \dots, m \quad (\text{A-2})$$

Suppose that a genuine linear relationship exists between the $A(i)$ and $B(i)$ values found for each of the m data sets $i = 1, 2, \dots, m$, i.e.,

$$A(i) = \alpha + \beta [B(i)] \quad i = 1, 2, \dots, m \quad (\text{A-3})$$

Let fixed values X_1 and X_2 be assigned to $X(i,j)$ for a comparison of all data sets. Then transformations of eqs. (A-1) through (A-3) can be made to produce the following expressions:

$$Y_1(i) = \alpha \left(\frac{X_2 - X_1}{\beta + X_1} \right) + \left(\frac{\beta + X_1}{\beta + X_2} \right) Y_2(i) \quad (\text{A-4})$$

$$Y_1(i) = \alpha + (\beta + X_1) \cdot B(i) \quad (\text{A-5})$$

$$Y_2(i) = \alpha + (\beta + X_2) \cdot B(i) \quad (\text{A-6})$$

$$Y_1(i) + Y_2(i) = 2\alpha + \{2\beta + X_1 + X_2\} \cdot B(i) \quad (\text{A-7})$$

Therefore, the plots of $Y_1(i)$ vs. $Y_2(i)$, $Y_1(i)$ vs. $B(i)$, $Y_2(i)$ vs. $B(i)$ and $Y_1(i) + Y_2(i)$ vs. $B(i)$ should give straight lines according to eqs. (A-4) through (A-7).

Figures 7(a)–7(d) show such plots of data with $A(i) = \log D_g$ and $B(i) = K$, determined for each of five gases (i). The results of the linear regression of the plots are tabulated in Table V. The linearity of all the plots in Figure 6 confirms that the linear relationship between the K and $\log D_g$ values obtained for each of the five gases is real and is not due to random error or a restricted measurement range.

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