

## Transient Permeation of Organic Vapors through Polymer Membranes

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### Synopsis

A method of analyzing permeation data has been developed which permits the diffusion coefficient  $D$ , its variation with concentration, and the solubility coefficient to be determined from a single experiment on the permeation of a vapor through a membrane when diffusion is known to be Fickian. There is evidence that in the range from the glass temperature  $T_g$  to  $(T_g + 20^\circ\text{C.})$  the diffusion of an organic vapor into a polymer is not always Fickian. In such a case a single permeation experiment gives the limiting value of  $D$  at zero vapor concentration. If the sorption isotherm is determined, two or three permeation experiments give sufficient information to characterize the concentration dependence of  $D$  and to predict a "Fickian time lag." The difference between the observed and the predicted time lag is the mean relaxation time of the time-dependent factors in the non-Fickian permeation. When there is a transient period of rapid permeation at the beginning of an experiment a plot of permeation rate against logarithmic time permits another relaxation time to be defined. By comparing these relaxation times with the mechanical characteristics of the polymer the time-dependent mechanisms of permeation may be identified.

The molecules of most organic vapors are comparable in size and chemical structure with the units of many polymer chains. Vapors are usually freely absorbed by polymers, and the sorbed molecules diffuse by a random exchange of places with polymer segments. The micro-Brownian motion of the chain segments is very retarded compared with that of the sorbed molecules. The diffusion coefficient  $D$  of the sorbate is therefore controlled by the frequency of the segmental motions.

The sorbed molecules increase the average free volume available to the chain segments and hence increase their jumping frequency.<sup>1</sup>  $D$  is found to increase more or less exponentially as the concentration  $c$  of sorbate increases.<sup>2</sup>

The absorption of vapor causes the polymer to swell and so changes the configurations of the polymer molecules. These configurational changes are not instantaneous; they are controlled by the retardation times of the chains. If these are long, stresses may be set up which relax slowly. Thus the absorption of a vapor is accompanied by time-dependent processes in the polymer which are slower than the micro-Brownian motion which promotes diffusion. These processes depend upon the nature of the polymer, the temperature, and the concentration of the sorbed substance.<sup>3</sup>

The factors discussed already explain why the diffusion of sorbed vapors in polymers is more complex than the diffusion of simple gases. The latter usually obey Fick's laws with a constant value of  $D$  at constant temperature. Fick's second law takes account of the dependence of  $D$  on the concentration  $c$  of the diffusate when it is written

$$\frac{dc}{dt} = \frac{d}{dc} \left( D \frac{dc}{dx} \right) \quad (1)$$

for diffusion in a single dimension  $x$ . Here  $t$  is time. The variation of  $D$  with time during the relaxation of stress in the polymer cannot be dealt with in this simple way. When  $D$  varies with  $t$  the diffusion is often called non-Fickian. A major objective in the study of diffusion of vapors in polymers is to assess the separate contributions of concentration dependence and time dependence to the observed behavior.

### KINETICS OF SORPTION

Many workers have studied the kinetics of the absorption and desorption of vapors by thin sheets of a polymer suspended in an atmosphere of the vapor kept at constant temperature and pressure.<sup>4</sup> Experimentally this is straight-forward, and the results are usually plotted as curves which show the ratio of the amount  $q_t$  absorbed or desorbed at time  $t$  to the amount  $q_\infty$  absorbed or desorbed at equilibrium versus  $t^{1/2}$ . Provided the diffusion is Fickian, i.e., eq. (1) is obeyed,  $D$  may be calculated as a function of  $c$  from such curves.<sup>5</sup>

To apply this procedure it is necessary to devise criteria which are sufficient to prove that the diffusion is Fickian. Many workers have accepted that this was so when  $q_t/q_\infty$  versus  $t^{1/2}$  was initially linear and later concave to the  $t^{1/2}$  axis and was never convex to this axis. This has led to the widely held view that diffusion is Fickian provided the polymer sample is above its glass transition throughout the whole sorption experiment. Evidence now available shows that this view is an oversimplification in the range from the glass temperature  $T_g$  up to about  $(T_g + 20^\circ\text{C})$ . The purpose of this paper is to draw attention to this and to indicate alternative methods for studying the concentration dependence of the diffusion coefficient and for analyzing the time-dependent factors.

A kinetic sorption experiment which commences with a uniform vapor concentration  $c_1$  in the polymer and ends with an equilibrium concentration  $c_2$  may be characterized by an integral diffusion coefficient  $\bar{D}$  defined by

$$\bar{D} = [1/(c_2 - c_1)] \int_{c_1}^{c_2} D dc \quad (2)$$

where  $D$  is the differential diffusion coefficient at concentration  $c$ .  $\bar{D}$  for Fickian diffusion is given by the initial slope of the graph of  $q_t/q_\infty$  versus  $t^{1/2}$ , since, for  $t \rightarrow 0$ ,

$$\frac{q_t}{q_\infty} = \left( \frac{16\bar{D}t}{\pi\delta^2} \right)^{1/2} \quad (3)$$

where  $\delta$  is the initial thickness of the sample. Evidently plots of  $q_t/q_\infty$  versus  $(t/\delta^2)^{1/2}$  for a series of samples of different thicknesses should all have the same slope.

Kishimoto and Matsumoto<sup>6</sup> have examined the sorption of allyl chloride vapor by poly(vinyl acetate) at 40°C., i.e., more than 10°C. above  $T_g$ . When they started with pure polymer ( $c_1 = 0$ ) and used a pressure of vapor for which  $c_2$  amounted to about 6% by volume, they found that  $q_t/q_\infty$  versus  $(t/\delta^2)^{1/2}$  was always concave to the abscissa, as required by Fickian diffusion. However the initial slope, and hence the apparent  $\bar{D}$ , increased as the thickness of the sample increased from  $2 \times 10^{-3}$  to  $6 \times 10^{-3}$  cm. When using a lower pressure of vapor, and hence a lower value of  $c_2$ , it was found that the only curves which were consistent in shape with Fickian diffusion were those for the thinnest ( $1.6 \times 10^{-3}$  cm.) and the thickest ( $8.9 \times 10^{-3}$  cm.) samples. The curves for the samples of thicknesses between these were obviously non-Fickian. They showed a short, steep initial period of extremely rapid sorption and were later convex toward the  $(t/\delta^2)^{1/2}$  axis before bending over toward the final equilibrium sorption. Similarly complicated behavior was noted during the sorption of methyl acetate vapor by poly(methyl acrylate) at 15°C. (10°C. above  $T_g$ ), but the sorption was truly Fickian at 35°C., since plots of  $q_t/q_\infty$  versus  $(t/\delta^2)^{1/2}$  were superposable over the initial period for all values of  $\delta$ .

Crank<sup>7</sup> has pointed out that this effect of thickness would be expected when diffusion was accompanied by a time-dependent relaxation even though the individual  $q_t/q_\infty$  versus  $t^{1/2}$  curves appeared to be Fickian. The true value of  $\bar{D}$  is obtained if the initial slopes found for a series of samples of different thicknesses are extrapolated to infinite thickness.

Kishimoto and Matsumoto therefore extrapolated plots of the apparent  $\bar{D}$  for each sample versus  $1/\delta^2$  to find the true  $\bar{D}$  for  $\delta = \infty$ . In the case of allyl chloride and poly(vinyl acetate), the values of  $\bar{D}$  at several concentrations  $c_2$  agreed very closely with those which had been obtained earlier from the steady-state method of studying permeation.<sup>8</sup> This agreement has resolved a long-standing discrepancy between the results of the sorption-kinetic and the steady-state investigations of this system.<sup>9,10</sup>

An important consequence of these findings is that, since the transport of relatively small organic molecules in polymers is frequently complicated by time-dependent processes in the temperature range from  $T_g$  to  $(T_g + 20^\circ\text{C})$ , it is necessary to carry out sorption-kinetic measurements on a series of samples of increasing thickness and to extrapolate to infinite thickness to obtain true values for the integral diffusion coefficient  $\bar{D}$ . Furthermore the analysis of complex  $q_t/q_\infty$  versus  $t^{1/2}$  curves is not yet a satisfactory way of studying time-dependent phenomena unless the relation between  $\bar{D}$  and  $c$  is known and has a simple form. With these difficulties in mind it is worthwhile reconsidering the information which can be obtained by studying the permeation of a vapor through a polymer membrane.

## PERMEATION OF VAPORS THROUGH MEMBRANES

The permeation method has always been the most favored way of studying the diffusion of gases in polymers.<sup>11</sup> The time lag which precedes the establishment of a steady state gives directly the diffusion coefficient  $D$ . Usually this is independent of the ingoing pressure of gas and hence of the concentration of diffusate in the polymer. The steady permeation rate gives the permeability  $P$ , from which the Henry's law solubility coefficient  $s$  may be obtained by using the relation

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

With vapors as diffusates,  $D$  varies with  $c$ , and frequently the sorption does not obey Henry's law. In such cases the interpretation of the time lag is less simple. It is further complicated when other time-dependent processes, such as the relaxation of stresses set up during swelling, are taking place.<sup>12</sup> The steady state of permeation is reached only after a time which is sufficiently long for all the time-dependent processes to be completed. The integral diffusion coefficient can be obtained from the final permeation rate if the concentration in the polymer at the ingoing face of the membrane is known. This usually requires the equilibrium curve of amount sorbed versus pressure of vapor to be determined. Even so, only a single value of  $\bar{D}$  is obtained from each steady-state experiment. To obtain the differential coefficient  $D(c)$  requires a series of runs at different values of the ingoing vapor pressure to establish  $\bar{D}$  as a function of  $c$ . The large amount of experimental work which this requires has discouraged most workers from using the membrane-permeation method to study the diffusion of vapors.

It now appears that in many cases much more information can be obtained from each experiment. Over the temperature range where time-dependent factors are important, a single permeation experiment may be more useful than a  $q_t/q_\infty$  versus  $t^{1/2}$  curve.

## TRANSIENT PERMEATION THROUGH MEMBRANES

From the instant when vapor is first admitted to one side of an outgassed membrane up to the time when a stationary state of dimensions and concentration distribution has been established, the rate at which vapor issues from the other side of the membrane varies with time. The behavior during this transient period is governed by the time and the concentration dependence of the diffusion coefficient. The diffusion equation cannot be completely solved when  $D$  varies with  $c$  and  $t$  for the boundary conditions which are appropriate to permeation through a membrane. Therefore a less general approach is required. One example of this is the determination of the time lag, i.e., the intercept on the time axis of the linear extrapolation of a trace of the total amount which has permeated versus time after all the transient processes have been completed. The time lag does not depend on the precise form of the permeation curve during the transient period.

Consequently, only a limited amount of information can be obtained in this way.

A convenient solution of the diffusion equation which gives the rate of permeation during the transient period was obtained by Holstein as a transformation of the more familiar expression which is given in eq. (5).

$$dp/dt = (Asp_i D/V\delta) \left[ 1 + \sum_{n=1}^{\infty} 2 \cos \pi n \exp \left\{ -n^2 \pi^2 D t / \delta^2 \right\} \right] \quad (5)$$

Holsteins' solution<sup>13</sup> when  $D$  is constant is

$$dp/dt = (2Asp_i/V)(D/\pi t)^{1/2} \sum_{m=0}^{\infty} \exp \left\{ -(\delta^2/4Dt)(2m+1)^2 \right\} \quad (6)$$

where  $dp/dt$  is the rate of increase of pressure in an initially evacuated vessel of volume  $V$  due to the gas issuing from a membrane of area  $A$  and thickness  $\delta$ .  $p_i$  is the constant pressure maintained from  $t = 0$  at the other side of the membrane;  $s$  and  $D$  are the solubility and diffusion coefficients, respectively, of the gas in the membrane.

In eq. (5) the series tends towards zero as  $t$  becomes larger. This is the form which is used to relate the time lag to  $D$ . In eq. (6) the dimensionless quantity  $Dt/\delta^2$  is inverted in the exponent. The series therefore tends toward zero as  $t$  tends towards zero. This equation was used by Rogers, Buritz, and Alpert<sup>13</sup> to obtain  $D$  for helium in glass from the rates of permeation determined after short times. When  $t$  is sufficiently small all the terms beyond the first in the series of eq. (6) may be neglected. It can be seen that eq. (6) may then be converted to

$$\ln (t^{1/2} dp/dt) = \ln [(2Asp_i/V)(D/\pi)^{1/2}] - (\delta^2/4Dt) \quad (7)$$

Hence a graph of  $\ln [t^{1/2}(dp/dt)]$  versus  $1/t$  should be a straight line of slope  $(-\delta^2/4D)$ . To obtain the true value of  $D$  from this plot it is necessary to obtain experimental data at values of  $t$  which are sufficiently small for the limiting slope to be reached.

The argument which led to eq. (7) assumed  $D$  to be independent of  $t$  and of concentration ( $sp_i = c$ ). In the case of a vapor diffusing in a polymer it is known that  $D$  always varies with  $c$  and often varies with  $t$ . However the permeation data have to be extrapolated towards  $t = 0$  (i.e.,  $1/t = \infty$ ) to find the limiting slope of  $\ln [t^{1/2}(dp/dt)]$  versus  $1/t$ . This extrapolation is towards the time when vapor has not penetrated beyond the ingoing face of the membrane. It has been demonstrated that in a polymer above  $T_g$  the equilibrium sorbed concentration is established at the ingoing face as soon as vapor is brought into contact with it.<sup>14</sup> Thus the limiting slope of a plot of eq. (7) gives  $(-\delta^2/4D_0)$ , where  $D_0$  is the limiting diffusion coefficient in the polymer at  $c = 0$ .

#### DETERMINATION OF $D_0$ FROM PERMEATION DATA

$D_0$  is a very important parameter in the study of variable diffusion coefficients. It has been determined from permeation data by extrapolating the

values of  $\bar{D}$  from a series of steady-state experiments to zero  $c$ . To be able to determine  $D_0$  from a single experiment by using eq. (7) would allow a great economy of effort. This section presents three experimental demonstrations that this is possible. In the first  $D$  is a constant, in the second  $D$  is a function of  $c$  only, and in the third  $D$  is a function of  $c$  and  $t$ .

### Diffusion of Hydrogen in Poly(vinyl Acetate)

A detailed study of hydrogen in poly(vinyl acetate) has been reported in an earlier paper.<sup>15</sup> An example of a plot of  $p$  versus  $t$  from a normal permeation experiment is shown in Figure 1. From this the time lag and the steady permeation rate may be obtained. The same data are replotted in Figure 2 in the form required for the short-time approximation of eq. (7).

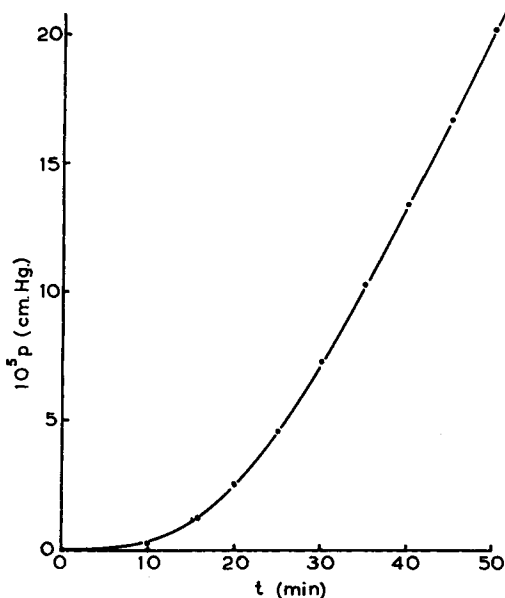


Fig. 1. Permeation plot of pressure vs. time for hydrogen through poly(vinyl acetate) at 24.1°C. Ingoing pressure 8.43 cm. Hg.

This graph gives an excellent straight line at the larger values of  $1/t$ . Table I compares the values of  $D$  obtained (a) from the time lag  $\theta$  in Figure 1 ( $D = \delta^2/6\theta$ ), (b) from the permeability coefficient  $P$ , obtained from

TABLE I  
Diffusion Coefficient  $D$  of Hydrogen in Poly(vinyl Acetate) at 24.1°C.

Method	$D \times 10^6$ , cm. <sup>2</sup> /sec.
Time lag	2.06
Steady state $P/s$	1.93
Slope of plot in Fig. 2	2.01

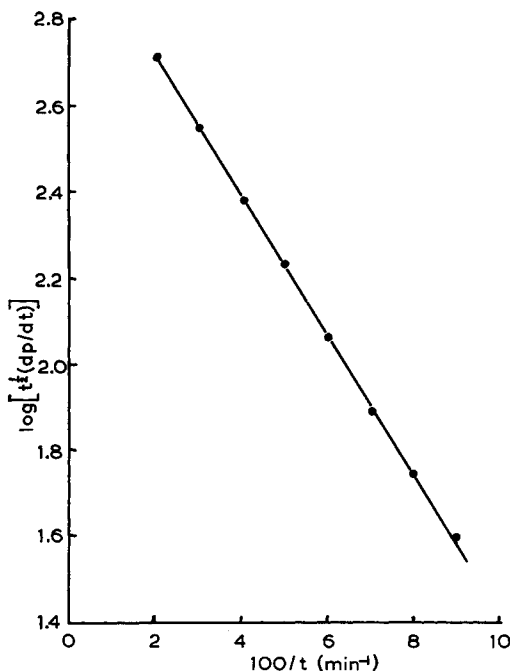


Fig. 2. Plot of  $\log [t^{1/2}(dp/dt)]$  vs.  $1/t$  drawn from Figure 1.

the limiting slope in Figure 1, divided by the Bunsen solubility coefficient  $s$ , determined separately by an equilibrium sorption method,<sup>16</sup> and (c) from the slope  $-\delta^2/4D$  of the plot in Figure 2. The three values of  $D$  are seen to agree with the experimental error. The error is largest in  $b$  on account of the lower accuracy of the equilibrium sorption experiments.

### Diffusion of Hydrocarbons in Natural Rubber

Aitken and Barrer have studied the diffusion of several hydrocarbons in natural rubber between 20 and 50°C.<sup>17</sup> They determined the permeability coefficients  $P$  from the steady rates of flow at various ingoing pressures of vapor and they determined the solubility  $s$  of the hydrocarbon in the rubber by separate equilibrium sorption experiments. They used eq. (4) to obtain  $\bar{D}$  and found that the diffusion coefficients were mildly dependent on concentration. The differential diffusion coefficients could be represented within experimental error by either

$$D = D_0(1 + ac) \quad (8)$$

or

$$D = D_0 \exp\{bc\} \quad (9)$$

Equation (9) will be used here, as it is the more suitable in cases where the diffusion coefficient is more strongly concentration-dependent. Because

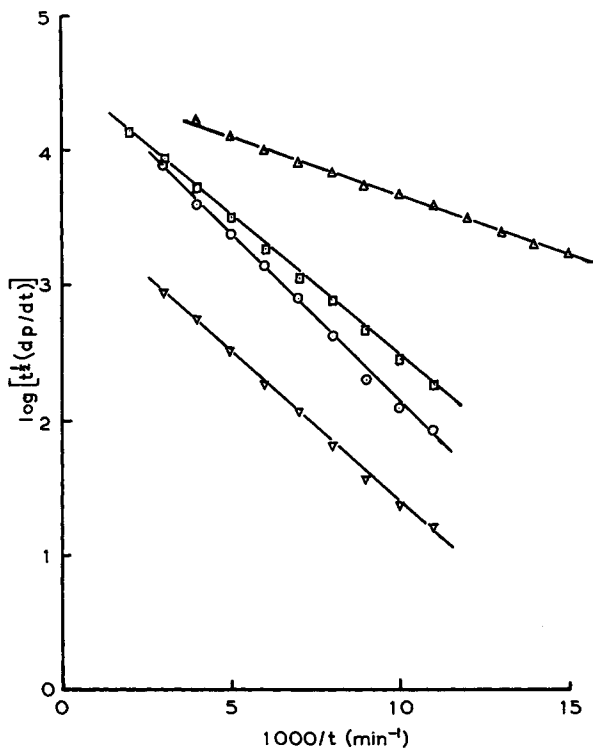


Fig. 3. Plots of  $\log [t^{1/2}(dp/dt)]$  vs.  $1/t$  for *n*-butane through natural rubber A: ( $\Delta$ ) 41.4°C.; ( $\square$ ) 27.4°C.; ( $\circ$ ) 24.9°C.; ( $\nabla$ ) 26.0°C. (add 1 to ordinate scale). Ingoing pressures about 6 cm. Hg.

no satisfactory theory of time lags in concentration-dependent permeation existed when their measurements were being made, Aitken and Barrer did not study the transient permeation stage systematically. Some data were obtained, however, and these permit several significant tests of the procedure suggested by eq. (7). (The author is greatly indebted to Dr. Angus Aitken for producing all his laboratory note books and records for examination. All the data for the tests described below have been taken from these, hitherto unpublished, results of Dr. Aitken and Professor Barrer.)

Figure 3 shows several plots of  $\ln [t^{1/2}(dp/dt)]$  versus  $1/t$  for *n*-butane in natural rubber determined at about the same ingoing pressure and at several different temperatures. Figure 4 shows similar plots for two similar ingoing pressures at the same temperature. Each example gave a long straight line from which the limiting slope was obtained with precision.

The integral diffusion coefficient  $\bar{D}$  over the concentration interval from zero to that of equilibrium sorption at the ingoing face, the differential diffusion coefficient  $D$  at this ingoing concentration and the diffusion coefficient  $D_0$  at  $c = 0$ , obtained by extrapolating a series of steady-state permeabilities to zero ingoing pressure, have all been given by Aitken and



Barrer. They are compared in Table II with  $D$  calculated from the slopes in Figures 3 and 4 and with  $\delta^2/6\theta$  which would give  $D$  if it were independent of  $c$ . It can be seen from Table II that the values of  $D$  given by eq. (7) from the slopes of the plots in Figures 3 and 4 correspond closely with  $D_0$  from the steady-state experiments. Thus  $D_0$  may be obtained from a single experiment by using eq. (7), whereas several experiments are needed with the steady-state method. The effect of the rather gentle increase in  $D$  with  $c$  is to prolong the initial straight portion of a plot of  $\ln[t^{1/2}(dp/dt)]$  versus  $1/t$  to longer times.

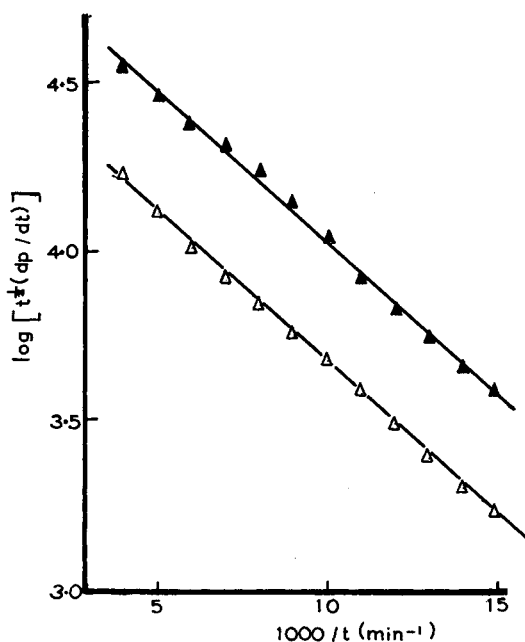


Fig. 4. Plots of  $\log [t^{1/2}(dp/dt)]$  vs.  $1/t$  for  $n$ -butane through natural rubber A at  $41.4^\circ\text{C}$ . at various ingoing pressures: ( $\Delta$ ) 5.40 cm. Hg; ( $\blacktriangle$ ) 11.80 cm. Hg.

The full analysis of a single curve giving the amount permeated versus time for a system in which it is known that the differential diffusion coefficient may be satisfactorily expressed by eq. (9) is set out below. A plot is prepared of the pressure of the total amount of gas which has permeated into a known volume  $V$  versus time (cf. Fig. 1). From this the steady permeation rate  $(dp/dt)_s$  and the time lag  $\theta$  are obtained. Tangents are drawn to this curve at a number of values of  $t$  up to about  $2.5\theta$  and their slopes  $(dp/dt)$  measured. A plot of  $\ln[t^{1/2}(dp/dt)]$  versus  $1/t$  is drawn, and its limiting slope for  $1/t$  tending to infinity is measured. This gives  $-\delta^2/4D_0$  and hence  $D_0$ . Frisch's theory of the time lag when eq. (9) is obeyed gives<sup>18,19</sup>

$$4D_0\theta/\delta^2 = [4e^{bc} - 1 + e^{2bc}(2bc - 3)]/(e^{bc} - 1)^3 \quad (10)$$

Thus a plot of the right-hand side of eq. (10) versus  $bc$  is drawn, and the value of  $bc$  which corresponds with the appropriate value of  $4D_0\theta/\delta^2$  is noted. Let this be  $bc_i$  where  $c_i$  is the concentration at the ingoing face.

The steady permeation rate through a membrane of area  $A$  is related to the diffusion coefficient by

$$(dp/dt)_s = (ART/V\delta) \int_0^{c_i} D_0 e^{bc} dc = (ARTD_0/V\delta b)(e^{bc_i} - 1) \quad (11)$$

Since  $D_0$  and  $bc_i$  have been determined already, eq. (11) permits  $b$  and hence  $c_i$  to be found. Thus a single permeation experiment has yielded all the parameters needed to express the differential diffusion coefficient as a function of concentration. It has also given the concentration sorbed at equilibrium with vapor at the ingoing pressure  $p_i$ . If Henry's law is known to be obeyed, this gives the solubility coefficient  $s$  which is equal to  $c_i/p_i$ .

A second experiment at a different ingoing pressure gives a second value of  $b$  and of  $c_i$ . If the two values of  $b$  agree, the validity of eq. (9) is demonstrated, and if  $c_i/p_i$  is constant, Henry's law is obeyed.

TABLE II  
Diffusion Coefficients of *n*-Butane in Natural Rubber A\*

Temp., °C.	Ingoing pressure, cm. Hg	Diffusion coefficients $\times 10^7$ , cm. <sup>2</sup> /sec.				
		Steady state			Slopes of Figs. 3 and 4	Time lag $\delta^2/6\theta$
		$\bar{D}$	$D$	$D_0$		
24.9	6.15	1.65	1.84	1.59	1.53	2.03
26.0	6.48	1.91	2.03	1.74	1.76	1.88
27.4	5.30	1.90	2.18	1.91	1.88	2.37
41.4	5.40	4.72	5.04	4.61	4.45	4.78
41.4	11.80	4.74	5.53	4.61	4.44	4.98

\* Data of Aitken and Barrer.<sup>17</sup>

It will be noted from eq. (7) that the intercept of  $\ln[t^{1/2}(dp/dt)]$  versus  $1/t$  on the  $\ln[t^{1/2}(dp/dt)]$  axis should give  $\ln[2Asp_i(D/\pi)^{1/2}/V]$ , from which the solubility coefficient  $s$  could be determined. This is a satisfactory procedure when  $D$  is constant, e.g., for hydrogen in poly(vinyl acetate), but it must not be applied when  $D$  varies with  $c$ .

The whole procedure has been illustrated by using the data from which Figure 4 was prepared. The results are shown in Table III. Highly accurate data are needed in the determination of  $4D_0\theta/\delta^2$ , as the value of  $bc_i$  is very sensitive to this. The two values of  $b$  and the two values of  $s$  in Table III agree as closely as can be expected from the precision of the data. The values of  $s$  also agree quite closely with the equilibrium solubility obtained by Aitken and Barrer, but the value of  $b$  is somewhat larger than the corresponding parameter obtained by the steady-state method. However, a higher degree of reproducibility and accuracy could undoubtedly be ob-

TABLE III

Analysis of Two Permeation Experiments for *n*-Butane in Natural Rubber A at 41.4°C.

Quantity	Run 1	Run 2	Data from steady-state analysis <sup>a</sup>
$p_t$ , cm. Hg	5.40	11.80	
$V$ , cm. <sup>3</sup>	352.7	352.7	
$(dp/dt)_s \times 10^3$ , cm. Hg./sec.	1.824	4.044	
$\theta$ , sec.	7755	7200	
$D_0 \times 10^7$ , cm. <sup>2</sup> /sec.	4.45	4.44	4.61
$4D_0 \theta/\delta^2$	0.6251	0.5791	
$bc_i$	0.244	0.505	
$b$ , cm. <sup>3</sup> /mole <sup>b</sup>	6850	7310	2200
$c_i \times 10^5$ , mole/cm. <sup>-3</sup>	3.56	6.91	
$c_i/p_i = s$ , cm. <sup>3</sup> at N.T.P./cm. <sup>3</sup> atm.	11.22	9.98	13.0

<sup>a</sup> Data of Aitken and Barrer.<sup>17</sup><sup>b</sup>  $b = ARTD_0(e^{bc_i} - 1)/[V\delta(dp/dt)]_s$ .

tained if experiments were specifically designed for the new method of analyzing the data.

### Diffusion of Allyl Chloride in Poly(vinyl Acetate)

The new procedure for finding  $D_0$  can be tested more severely by applying it to a case where  $D$  varies greatly with  $c$  and where time effects also are present. The only example for which sufficiently detailed data have been recorded over the whole of the transient region is the permeation of allyl chloride through poly(vinyl acetate) at 40°C.<sup>8,18</sup> This system behaved very differently from those described above. As soon as vapor was admitted to one side of the outgassed membrane, there was a copious permeation through the membrane. The highest rate of permeation appeared to be set up at zero time, and the rate decreased very rapidly thereafter. About 4 hr. later, permeation had virtually ceased, and subsequently the expected slow permeation began. Its rate increased to a steady state over several days. Vapor was continuously pumped away from the outgoing side of the membrane except for short periods during which the permeation rate  $(dp/dt)$  was determined.

A plot of  $\ln[t^{1/2}(dp/dt)]$  versus  $1/t$  is shown in Figure 5. The data obtained during the initial copious permeation have not been plotted on this graph. The plot is seen to be satisfactorily linear and from its slope,  $(-\delta^2/4D_0)$ ,  $D_0$  is found to be  $1 \times 10^{-11}$  cm.<sup>2</sup>/sec., i.e.,  $\log D_0(\text{cm.}^2/\text{sec.}) = -11.00$ .

The integral diffusion coefficients  $\bar{D}$  have been determined at several incoming concentrations by using the steady-state permeation method. The extrapolation of  $\bar{D}$  to zero concentration is somewhat uncertain, due to the curvature of the plot of  $\log \bar{D}$  versus  $c_i$ . However an examination of Figure 2 of reference 8 and of Figure 4 of reference 6 shows that  $\log D_0$

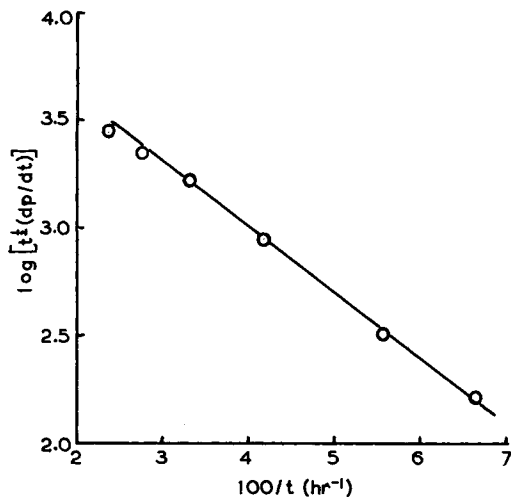


Fig. 5. Plot of  $\log [t^{1/2}(dp/dt)]$  vs.  $1/t$  for allyl chloride through poly(vinyl acetate) at 40°C. Ingoing pressure 4.34 cm. Hg.

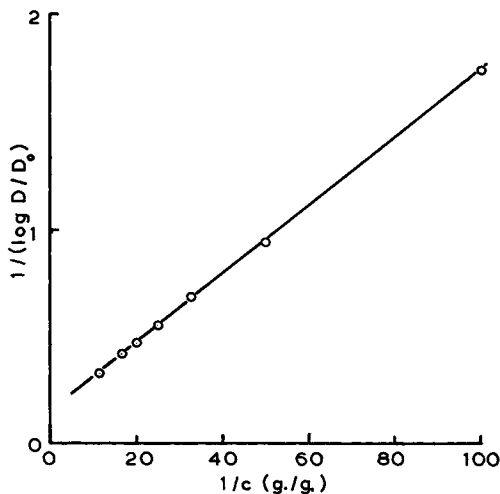


Fig. 6. Plot of  $1/(\log D/D_0)$  vs.  $1/c$  for allyl chloride in poly(vinyl acetate) at 40°C.

(cm.<sup>2</sup>/sec.) equals  $-11.04$  within the limits of precision of the extrapolation. This value is in excellent agreement with  $-11.00$  given above. Thus even in the presence of highly anomalous transient permeation behavior,  $D_0$  apparently may still be obtained from the slope of the plot of  $\ln [t^{1/2}(dp/dt)]$  versus  $1/t$ .

For two reasons it is not possible to proceed with a full analysis of diffusion and sorption from a single permeation curve as described for the hydrocarbons in rubber. The sorption of a vapor which is as soluble as allyl chloride is in poly(vinyl acetate) does not usually obey Henry's law.

Furthermore, eq. (9) does not represent the relation between  $D$  and  $c$  satisfactorily.

The free-volume treatment of diffusion in polymers<sup>20</sup> suggests that a more complete relation between  $D$  and  $c$  is

$$D = D_0 \exp[c/(f + gc)] \quad (12)$$

where  $f$  and  $g$  are constants at constant temperature. Figure 6 shows a plot of  $[1/\log(D/D_0)]$  versus  $1/c$  for allyl chloride in poly(vinyl acetate) drawn from the data of a previous study.<sup>8</sup> The linearity of this plot shows that eq. (12) is closely obeyed.  $f$  may be obtained from the slope and  $g$  from the intercept on the  $1/c$  axis of the graph in Figure 6. These parameters must be regarded as empirical, although in the complete free-volume theory (in which  $D$  and  $D_0$  are replaced by intrinsic diffusion coefficients corrected for the thermodynamic nonideality of the polymer + penetrant) the corresponding parameters have a clearly defined physical significance. To determine  $f$  and  $g$ , several steady-state values of  $\bar{D}$  are needed to obtain  $D$  as a function of  $c$  by a graphical method using the relation

$$D = d(\bar{D}c_i)/dc_i \quad (13)$$

The time lag may, in principle, be predicted by using Frisch's theory,<sup>12</sup> provided the  $D$  versus  $c$  relation is known. However the integral  $\int Ddc$ , where  $D$  is given by eq. (12), contains an infinite series, and the calculation of  $\theta$  becomes impossibly complicated.

As a result of these difficulties approximations have to be made in the analysis of the permeation data in order to obtain information about the time-dependent effects which operate. A treatment which is suitable for the experiment depicted in Figure 5 is described below.

By taking  $D_0$  as  $1 \times 10^{-11}$  cm.<sup>2</sup>/sec., as obtained from the slope of the line in Figure 5, the slope and intercept in Figure 6 give  $f = 0.00693$  g./g. polymer and  $g = 0.0634$ . In the run of Figure 5,  $c_i$  was 0.0145 g./g. polymer. Thus  $gc_i$  is about 0.14 $f$ . Over the range from 0 to  $c_i$ , therefore a good approximation to eq. (12) is

$$D = D_0 \exp\{c/(f + gc_i/2)\} \quad (14)$$

Thus  $\theta$  may be predicted by using eq. (10) and replacing  $b$  by  $1/(f + gc_i/2)$ . With this approximation  $\theta$  is predicted to be  $8.3 \times 10^4$  sec. The observed time lag was  $10.5 \times 10^4$  sec. According to Frisch, the difference between the observed and calculated time-lags  $\Delta\theta$ , in this case  $2.2 \times 10^4$  sec., defines the mean relaxation time of the time-dependent processes which, in addition to Fickian diffusion, control the approach to the steady state of permeation.

It was mentioned earlier that, at temperatures a few degrees above  $T_g$ , a rapid permeation begins as soon as vapor is admitted to one side of an out-gassed membrane and also that the rate of this rapid permeation soon falls almost to zero. This behavior has been confirmed in more recent observa-

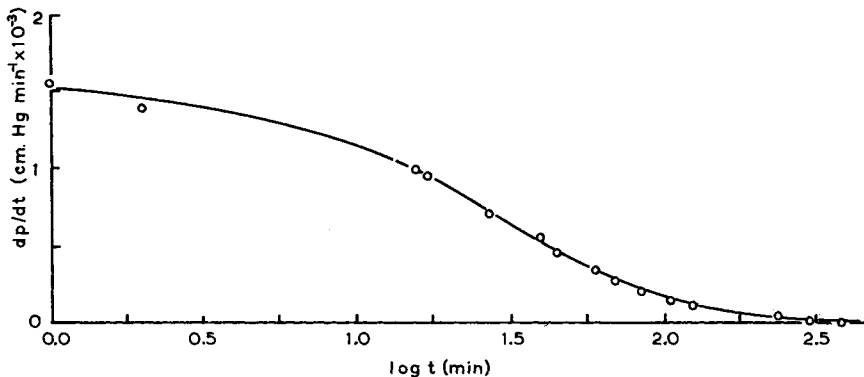


Fig. 7. Plot of  $dp/dt$  vs.  $\log t$  for initial rapid permeation of allyl chloride through poly(vinyl acetate) at  $40^\circ\text{C}$ . Ingoing pressure 4.34 cm. Hg.

tions of methanol permeating through poly(vinyl acetate).<sup>21</sup> The permeation rate of allyl chloride in poly(vinyl acetate) has been plotted against the logarithm of time in Figure 7 by using data obtained during the very early period of the experiment. The curve in Figure 7 resembles a retardation or relaxation curve obtained in the study of retarded elasticity. The characteristic time (i.e., the time for the permeation rate to fall to  $1/e$  of its initial value) in Figure 7 is about  $2.2 \times 10^3$  sec. That is just a tenth of the difference between the observed and calculated time lags  $\Delta\theta$ . It clearly suggests that there are two separate time-dependent processes which control the permeation.

The time-dependent mechanical behavior of poly(vinyl acetate) has been examined on several occasions.<sup>22-25</sup> The data at various temperatures may be converted to  $40^\circ\text{C}$ . by using the appropriate shifting factors according to the time-temperature superposition principle.<sup>26</sup> Thus the master stress relaxation curves of Ninomiya and Fujita<sup>23</sup> may be referred to  $40^\circ\text{C}$ . by multiplying their values of  $t$  at  $75^\circ\text{C}$ . by  $10^6$ . The relaxation curve so obtained, although similar in general shape to Figure 7, shows that the relaxation of stress occurs at least one hundred times more rapidly than the decrease in the initial permeation rate.

The relaxation and retardation-time spectra of Ferry and Williams<sup>22</sup> show that the principle retardation times are 100-1000 times greater than the principal relaxation times. This suggests that the initial rapid permeation may be strain-controlled by the response of the sample to an applied stress. This stress is unlikely to be the mechanical pressure of the vapor admitted to one side of the membrane as the membrane was well supported in the diffusion cell. It is more probable that the vapor instantly swells the surface layer with which it comes into contact.<sup>14</sup> This creates a stress which extends the underlying layers making them temporarily more permeable until the equilibrium density is restored by a redistribution of the polymer segments. A slow change in volume following a sudden change in temperature has also been noted in poly(vinyl acetate).<sup>24,25</sup> At  $40^\circ\text{C}$ . it

appeared that several minutes at least would be required for the volume to reach equilibrium after a rapid temperature change and this may well be parallel to the effect of time on the initial permeation rate.

The much longer times involved in the time-lag discrepancy  $\Delta\theta$  are possibly due to the need for relatively large changes in the dimensions of the membrane as it is swollen by the permeant. As swelling proceeds, the membrane becomes plasticized by the permeant, and  $\Delta\theta$  cannot be related to the mechanical characteristics of the pure polymer. It is easy to understand why at sufficiently large ingoing pressures of vapor the plasticizing effect so facilitates the flow which accompanies swelling that  $\Delta\theta$  falls almost to zero.<sup>8,21</sup>

While there is still much to be learned about the time-dependent phenomena in the diffusion of vapors through polymers, it may fairly be asserted that a thorough study of the transient states of permeation across membranes will yield more valuable information than has generally been realized.

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### Résumé

On a mis au point une méthode permettant d'analyser les résultats de pénétration par la mesure du coefficient de diffusion  $D$ , de sa variation en regard de la concentration et du coefficient de solubilité au départ d'une expérience unique de pénétration de la vapeur à travers une membrane lorsqu'il s'avère que la diffusion suit les lois de Fick. Il est évi-

dent que dans la gamme de température comprise entre la température vitreuse  $T_g$  et  $(T_g + 20^\circ)$  la diffusion d'une vapeur organique dans un polymère n'est pas toujours "Fickienne." Dans un tel cas, une simple expérience de pénétration fournit la valeur limite de  $D$  pour une concentration nulle en vapeur. Si l'on détermine l'isotherme d'adsorption, deux ou trois expériences de pénétration sont d'une information suffisante pour caractériser la dépendance de  $D$  vis-à-vis de la concentration et de prédire une diminution du comportement "Fickien" en fonction du temps. La différence entre la diminution en fonction du temps observée et celle qui est prédite est le temps de relaxation moyen des facteurs reliés au temps dans la pénétration non-Fickienne. Lorsqu'il existe une période transitoire de pénétration rapide au début d'une expérience, on peut définir un autre temps de relaxation en portant graphiquement la vitesse de pénétration en fonction du logarithme du temps. En comparant ces temps de relaxation aux caractéristiques mécaniques du polymère, on peut mettre en évidence les mécanismes de pénétration dépendant du temps.

### Zusammenfassung

Eine Methode zur Analyse von Permeationsdaten wurde entwickelt, welche die Bestimmung des Diffusionskoeffizienten  $D$ , seiner Abhängigkeit von der Konzentration und des Löslichkeitskoeffizienten aus einem einzigen Versuch über die Permeation von Dampf durch eine Membran gestattet, unter der Voraussetzung, dass es sich um eine Fick'sche Diffusion handelt. Es gibt Hinweise dafür, dass im Bereich von der Glas-temperatur  $T_g$  bis  $(T_g + 20^\circ)$  die Diffusion eines organischen Dampfes in ein Polymeres nicht immer dem Fick'schen Gesetz gehorcht. In einem solchen Fall liefert ein einziger Versuch den Grenzwert für  $D$  für die Dampfkonzentration Null. Bei Bestimmung der Sorptionsisothermen liefern zwei oder drei Permeationsversuche genügend Information zur Charakterisierung der Konzentrationsabhängigkeit von  $D$  und zur Voraussage einer "Fick'schen Verzögerungszeit." Der Unterschied zwischen der beobachteten und der vorhergesagten Verzögerungszeit ist die mittlere Relaxationsdauer der zeitabhängigen Faktoren bei der nicht-Fick'schen Permeation. Bei Vorhandensein einer Übergangsperiode mit schneller Permeation am Beginn eines Versuches erlaubt die Auftragung der Permeationsgeschwindigkeit gegen den Logarithmus der Zeit die Definition einer weiteren Relaxationszeit. Durch Vergleich dieser Relaxationszeiten mit der mechanischen Charakteristik des Polymeren kann der zeitabhängige Mechanismus der Permeation identifiziert werden.

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