NASA TECHNICAL MEMORANDUM

NASA TM X-64721

TRANSIENT PERMEATION OF ORGANIC VAPORS THROUGH ELASTOMERIC MEMBRANES

By James E. Curry
Astronautics Laboratory

January 22, 1973

NASA

George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama

TECHNICAL REPORT STANDARD TITLE PAGE

1. REPORT NO.
TM X- 64721

2. GOVERNMENT ACCESSION NO.

3. RECIPIENT'S CATALOG NO.

4. TITLE AND SUBTITLE
TRANSIENT PERMEATION OF ORGANIC VAPORS THROUGH ELASTOMERIC MEMBRANES

5. REPORT DATE
January 22, 1973

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
James E. Curry

8. PERFORMING ORGANIZATION REPORT #

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Marshall Space Flight Center
Marshall Space Flight Center, AL 35812

10. WORK UNIT NO.

11. CONTRACT OR GRANT NO.

13. TYPE OF REPORT & PERIOD COVERED
Technical Memorandum

12. SPONSORING AGENCY NAME AND ADDRESS

National Aeronautics and Space Administration
Washington, DC 20546

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

The permeation of benzene and acetone vapors through sulfur-cured natural rubber was studied by the time-lag method. The experimental results were analyzed by a method suggested by Meares. D_0, the zero concentration diffusion coefficient, was obtained by the early-time method. The Frisch time-lag equation was utilized to estimate both the solubility coefficient (s) and the additional parameter (b) required to define the concentration-dependence of the diffusion coefficient, $D(c) = D_0 \exp(bc)$. This form of concentration dependence was manifested by the corresponding permeability coefficient values. At low entering penetrant pressure where the transport coefficients are constant, indirect evidence was obtained that D_0 is the mechanistically correct diffusion coefficient. The solubility coefficient values calculated for benzene vapor in natural rubber are in reasonable agreement with published equilibrium sorption data for a similar rubber compound. At higher entering penetrant pressures, average diffusion coefficients obtained at steady state tended to be larger than the corresponding average diffusion coefficients derived from the time-lags. This has been attributed to slow relaxation effects in the swollen membrane which inject an element of time dependence into the transport process.

17. KEY WORDS

18. DISTRIBUTION STATEMENT

Unclassified - unlimited

James E. Curry

19. SECURITY CLASSIF. (of this report)	20. SECURITY CLASSIF. (of this page)	21. NO. OF PAGES	22. PRICE
U	U	29	NTIS

MSFC - Form 3292 (May 1969)

ACKNOWLEDGEMENT

Appreciation is expressed to J. W. Bransford of the Chemistry Branch, Materials Division (S&E-ASTN-M) for loan of the Baratron pressure measuring equipment. C. R. McIntosh and C. L. Reynolds of Brown Engineering Company provided valuable assistance in the design of the experimental equipment.

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NOTATION AND SYMBOLS

A. Primary Symbols

A	Effective area of membrane, cm^2
b	Exponential parameter for concentration-dependent diffusion coefficient
c	Penetrant concentration in membrane, g. mol/cc
D	Diffusion coefficient, cm^2/sec
$\bar{D}(c_i),\bar{D}(p_i)$	Concentration- and pressure-averaged diffusion coefficient, respectively
f(c)	A function of penetrant concentration
J	Penetrant flux, flow per unit membrane area per unit time
ℓ	Membrane thickness, cm
L	Time-lag
m	Summation index for series notation
P	Permeability coefficient, cc(STP)-cm/cm^2-sec-mm Hg.
$\bar{P}$	Average permeability coefficient
p	Penetrant pressure, mm Hg.
R	Universal gas constant
S	"Dimensionless" solubility coefficient, (pressure x volume product of dissolved gas) / (volume of membrane) x (inlet penetrant pressure)
s	Solubility coefficient, cc(STP)/cm^3-mm Hg.
T	Absolute temperature, degrees Kelvin
t	Time, seconds
u	Dummy concentration variable in Frisch time lag equation

NOTATION AND SYMBOLS

V	Downstream measuring volume, cm^3
x	Position coordinate, membrane thickness direction

B. Subscripts

c	Denotes a concentration-dependent parameter
i	Refers to inlet condition or surface at $x = o$
o	A parameter evaluated at $c = o$
p	Denotes a parameter dependent upon penetrant pressure
s	Steady state value
(STP)	A volumetric parameter referred to standard conditions of temperature and pressure, 0° C. and 760 mm Hg.
v	Denotes a parameter associated with the downstream measuring volume, V

TRANSIENT PERMEATION OF ORGANIC VAPORS THROUGH ELASTOMERIC MEMBRANES

SUMMARY

The permeation of benzene and acetone vapors through sulfur-cured natural rubber was studied by the time-lag method. The experimental results were analyzed by a method suggested by Meares. D_o, the zero concentration diffusion coefficient, was obtained by the early-time method. The Frisch time-lag equation was utilized to estimate both the solubility coefficient (s) and the additional parameter (b) required to define the concentration-dependence of the diffusion coefficient, $D(c) = D_o \exp(bc)$. This form of concentration dependence was manifested by the corresponding permeability coefficient values. At low entering penetrant pressure where the transport coefficients are constant, indirect evidence was obtained that D_o is the mechanistically correct diffusion coefficient. The solubility coefficient values calculated for benzene vapor in natural rubber are in reasonable agreement with published equilibrium sorption data for a similar rubber compound. At higher entering penetrant pressures, average diffusion coefficients obtained at steady state tended to be larger than the corresponding average diffusion coefficients derived from the time-lags. This has been attributed to slow relaxation effects in the swollen membrane which inject an element of time dependence into the transport process.

INTRODUCTION

The transport of organic molecules through polymeric membranes is a process frequently characterized by a variable diffusion coefficient, D(c), which is dependent upon the localized concentration of penetrant within the membrane[1]. A number of methods[2,3] have been employed to evaluate diffusion coefficients under these circumstances. There are several variations of the mass sorption techniques which can be utilized to obtain $\bar{D}(c)$, the concentration-averaged diffusion coefficient. The instantaneous or differential diffusion coefficient, D(c), may then be obtained by appropriate differentiation of $c\bar{D}(c)$ versus c data, or by various approximation methods.

The permeation approach is also useful for obtaining information on diffusion coefficients which vary with concentration. If independent knowledge of the solubility coefficient (s) is available, the average diffusion coefficient can be obtained from the equality

$$\bar{D}(c) = \frac{\bar{P}(c)}{s} \tag{1}$$

where $\bar{P}(c)$ is the measured average permeability coefficient. Repetitive experiments at different ingoing penetrant activities serve to define the dependence of $\bar{D}(c)$ upon c at membrane inlet conditions, and the differential diffusion coefficient, D(c), is extracted by the general approach advocated earlier for sorption data.

A somewhat different and more self-sufficient permeation method has been suggested by Meares[4] who pointed out that the Frisch time-lag theory for concentration-dependent diffusion and the early-time transform can be used advantageously to obtain information on the nature of concentration-dependent transport processes. Detailed independent knowledge of the solubility coefficient is not required for this approach. The objective of the work reported here is to further evaluate this method of analyzing permeation data in systems characterized by concentration dependence.

THEORY

The significance of the time-lag and early-time transform in concentration-dependent cases can best be understood by reference to the simpler case of a constant diffusion coefficient. For the usual type of permeation experiment:

$$\begin{aligned} c(x,o) &= o \quad \text{for all } x \\ c(o,t) &= c_i \\ c(\ell,t) &= o \quad \text{for all } t > o \end{aligned} \tag{2}$$

and a solution of Fick's second law equation valid for these conditions is given by[5,6]

$$c(x,t) = c_i \left[\frac{\ell - x}{\ell} - \frac{2}{\pi} \sum_{1}^{\infty} \frac{1}{m} \sin \frac{m\pi x}{\ell} \exp\left(- \frac{Dm^2\pi^2 t}{\ell} \right) \right] \tag{3}$$

Normally, the penetrant pressure (p_V) accumulated in a suitably calibrated downstream measuring volume (V_V) is monitored to follow the process. This pressure will increase progressively during the transient period and it will ultimately approach a steady rate of increase with time. Extrapolation of this steady state p_V versus t line back to the p_V = o axis yields the time-lag, L. When the diffusion coefficient is constant, the time-lag is a simple function of the membrane thickness, ℓ, and the diffusion coefficient:

$$L = \frac{\ell^2}{6D} \tag{4}$$

When the diffusion coefficient is a function of concentration, the p_v versus t curve again approaches linearity at large times, but the observed time-lag is affected by the concentration-dependence of the diffusion coefficient. The corresponding equation derived by Frisch[8] for the time-lag associated with a concentration-dependent diffusion process is

$$L(c_i) = \frac{\ell^2 \int_0^{c_i} cD(c) \left[\int_c^{c_i} D(u)du\right] dc}{\left[\int_0^{c_i} D(c)dc\right]^3} \tag{5}$$

Various functional forms have been proposed for D(c). In the common case where

$$D(c_i) = D_o \exp(bc_i) \tag{6}$$

equation 5 becomes[4]:

$$L(c_i) = \frac{\ell^2}{4D_o} \left(\frac{4 \exp(bc_i) - 1 + \exp(2bc_i)(2bc_i - 3)}{(\exp(bc_i) - 1)^3}\right) \tag{7}$$

The early-time transform derived using equation 3 is usually stated as follows, subject to the assumptions of a constant diffusion coefficient and the validity of Henry's Law[9-12]:

$$\ln\left(t^{\frac{1}{2}} \frac{dp_v}{dt}\right) = \ln\left(\frac{2Asp_v}{V_v}\left(\frac{D}{\pi}\right)^{\frac{1}{2}}\right) - \frac{\ell^2}{4Dt} \tag{8}$$

This version of the equation is obtained by truncating an exponential series after the first term. The early-time transform is applied only to data taken early in the process where the discarded series terms would tend toward insignificance. Under these conditions, a plot of $\ln\left(t^{\frac{1}{2}} \frac{dp_v}{dt}\right)$ versus 1/t should yield a straight line of slope $-\ell^2/4D$.

This approach, coupled with the traditional time-lag route, permits comparison of diffusion coefficients obtained at different time frames during the process. If the diffusion coefficient obtained by the early-time analysis agrees within experimental error with the diffusion coefficient calculated by equation 4 from data taken later in the experiment, it would then appear safe to assume that the process is "ideal" in the sense that it is not complicated by time-or concentration-dependent effects.

Meares[4] has pointed out that when concentration-dependent effects are present, the early-time diffusion coefficient is actually D_o. This "zero concentration" diffusion coefficient is a parameter in most equations of the type represented by equation 6 for depicting the concentration-dependence of the diffusion coefficient. After obtaining D_o, it should then be possible to use equation 5 to test various assummed functional forms of the type

$$D(c) = D_o\ f(c) \tag{9}$$

When f(c) is suspected to be the exponential form shown in equation 6, iterative solution of equation 7 will yield a value of the product (bc_i). The value of b is given by

$$b = \frac{ARTD_o}{V_v \ell \ (dp_v/dt)s} \ (\exp\ (bc_i) - 1) \tag{10}$$

where $(dp_v/dt)s$ is the steady state slope of the p_v versus t curve, normally a by-product of the measurements leading to $L(c_i)$ and $\bar{P}$. Further, the solubility coefficient, s, is obtained from

$$s = \frac{(bc_i)}{bp_i} \tag{11}$$

If the value of b remains constant within experimental error, the validity of equation 6 is indicated, and if s is constant, Henry's Law is obeyed. In any case, a value of s is obtained that corresponds to the prevailing inlet conditions at each time-lag measurement.

MATERIALS AND EQUIPMENT

Natural rubber membranes were used throughout this study. An attempt was made to duplicate the natural rubber formulation of Barrer and Fergusson[13]:

Smoked sheet	100.0	parts by weight
Stearic acid	0.5	
Zinc Oxide	3.0	
Sulfur	4.0	
Altax	1.5	

The final constituent was a substitute for Accelerator A. 3 in the original recipe. Flat sheets approximately 25 x 25 x 0.1 cm were molded from a single rubber master batch and cured for twenty minutes at 140°C. Benzene and acetone vapors were the penetrants investigated.

The permeation equipment was of standard design[1]. The permeation cell was sized to minimize radial permeation effects[14], and it incorporated a circumferential mercury seal which avoided undesireable contact between the rubber membrane and the water[15] of a surrounding constant temperature bath (± 0.2°C). A predetermined penetrant partial pressure was obtained from a few cubic centimeters of the corresponding organic liquid in a small capsule submerged in a separate bath maintained within ±0.1°C. The liquid penetrant was degassed by alternate freezing in liquid nitrogen and warming at the lower pressure limit of the vacuum system. For experiments using benzene as the penetrant, the reservoir was charged with ACS reagent grade benzene previously dried for at least 24 hours over metallic sodium. For the acetone vapor transport studies, reagent grade acetone was used without further attempts at purification.

The overall arrangement of the apparatus permitted imposition of the conditions specified in equation 2. At the start of an experiment, the inlet face of the previously evacuated rubber membrane was exposed to a constant penetrant vapor pressure fixed by the penetrant reservoir temperature as read by a thermometer calibrated at the ice point. Appropriate vapor pressure equations were used to calculate the corresponding benzene[16] or acetone[17] vapor pressure. Equations were chosen which appeared to represent the usual tabular vapor pressure data within three per cent over the ranges of interest. At low benzene reservoir temperatures where the vapor pressure equation was inaccurate, inlet pressures were interpolated graphically from a log p versus 1/T plot.

The rate of penetrant transport was monitored by reading the pressure (p_v) rise as a function of time in a known volume on the downstream side of the membrane. This pressure was read with a Baratron Type 90 Pressure Meter (MKS Instruments, Inc.) equipped with a type 90H-3E measuring head, 0 to 10.0000 mm Hg. range. Capacitance manometers of this type have been used successfully in the past for similar experimental work[18,19] and they appear free of the disadvantages associated with mercury-containing, compression-type vacuum gauges when applied to condensable vapors[20].

Two separate measuring volumes were used. During early-time experiments, a small 290.5 cc. measuring volume was used to magnify the initial transient portion of the p_V versus t curve. A much larger 34,733 cc volume was used for the longer-duration permeation measurements. The smaller volume was estimated from observed pressure changes on the Baratron gauge accompanying the introduction of known increments of dry air. The large volume was filled with water and measured directly.

EXPERIMENTAL AND ANALYTICAL

METHODS

Early-time experiments were conducted by recording p_V versus t data obtained at various membrane temperatures. The calculation of $\ln (t^{\frac{1}{2}} (dp_V(t)/dt))$ versus 1/t was programmed on an Olivetti-Underwood Programma 101 Computer with numerical differentiation of the pressure-time data as the first step. The time parameter in both quantities is the average of time readings corresponding to successive pressure measurements.

Initial data points invariably showed considerable scatter. However a strong trend toward linearity became apparent when the pressure rise rate increased to a level commensurate with the instrumentation capability. For each experiment, linear regression analysis was used to obtain the best slope of the $\ln (t^{\frac{1}{2}} (dp_V/dt))$ versus 1/t line for calculating D_o as follows:

$$D_o = \frac{\ell^2}{4\ (\text{Slope})} \qquad (12)$$

The intercept, $\ln (t^{\frac{1}{2}}\ dp_V/dt)$ at 1/t = o, was used to calculate the "dimensionless" solubility[10,12] when separate permeability evidence proved that the transport process was not concentration-dependent at the prevailing inlet pressure:

$$S = \left(\frac{\pi}{D}\right)^{\frac{1}{2}} \left(\frac{V_V}{2Ap_i}\right) \left[\left(t^{\frac{1}{2}}\ \frac{dp_V(t)}{dt}\right)_{1/t\ =\ o} \right] \qquad (13)$$

A typical early-time plot is shown in Figure 1.

The solubility S is related to s, in conventional cc(STP)/cm^3-mm

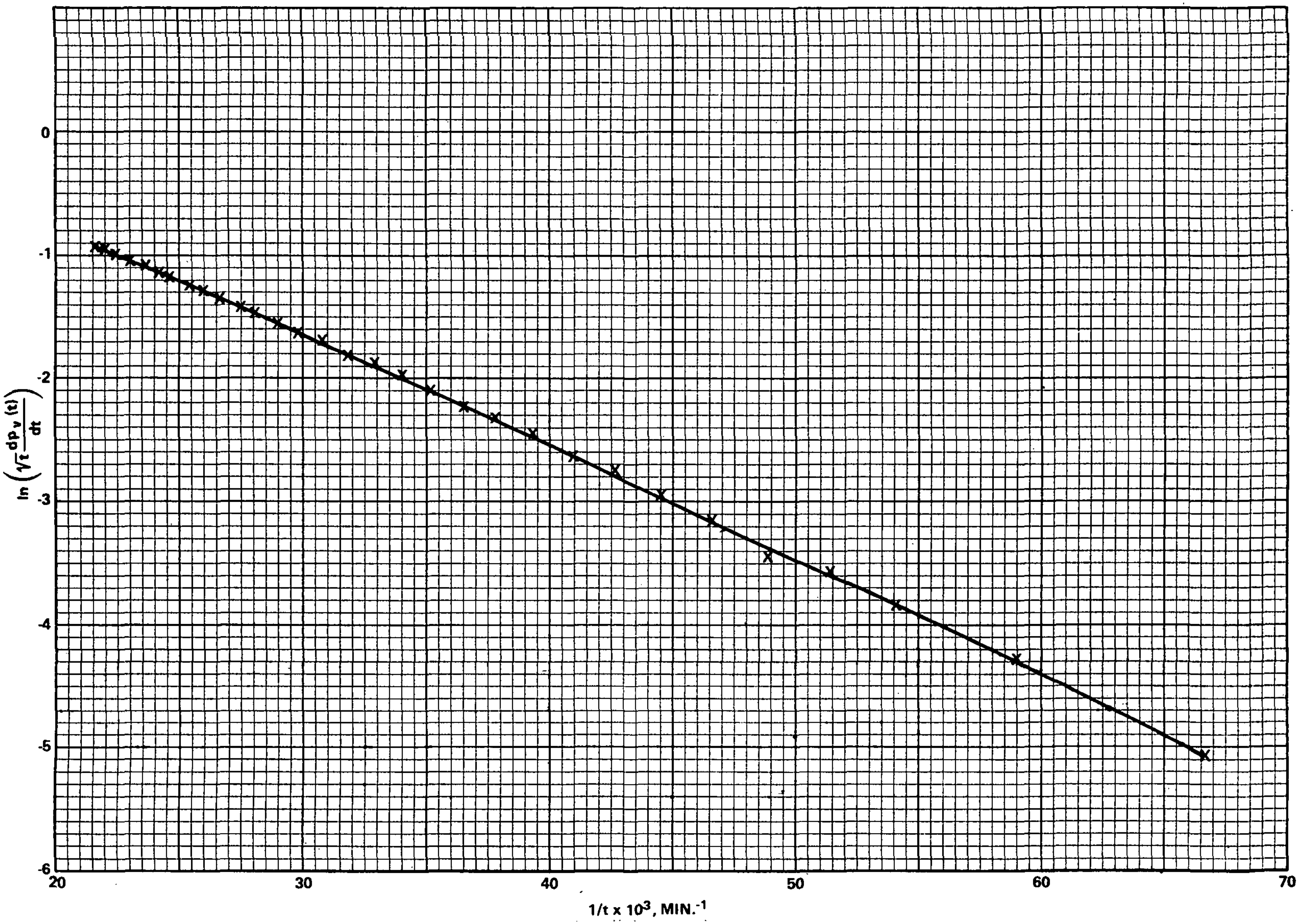

FIGURE 1. TYPICAL EARLY-TIME DATA PLOT FOR BENZENE VAPOR (26.75 mm Hg.) TRANSPORT THROUGH NATURAL RUBBER (0.0883 cm) AT 50.0°C.

Hg. units as follows[10]:

$$s = \frac{22,414S}{RT} \qquad (14)$$

During the longer-duration permeation experiments, the pressure (p_v) versus time plot was used to formulate a crude estimate of the time-lag and the experiment was continued for at least four apparent time-lags to insure a close approach to steady state. Linear regression analysis was then applied to a sequence of at least ten p_v versus t data points taken after at least four apparent time-lags. The true time-lag (L) was taken to be the value of t given by this linear regression equation when p_v was taken equal to the small initial pressure that existed at the start of the experiment. If the process is not concentration-dependent at the prevailing conditions, the p_v intercept at t = o, suitably corrected for the initial pressure, can also be used to calculate the "dimensionless" solubility[1,10]:

$$S = - \frac{6V_v \, (p_v)_{t=o}}{A\ell p_i} \qquad (15)$$

RESULTS AND DISCUSSION

a. Benzene Data

Benzene D_o versus 1/T plots are shown in Figure 2 for two natural rubber membrane materials examined during this study. They are compared with the mass sorption - derived D_o data of Hayes and Park[21] for uncured rubber. The lower line represents a series of measurements carried out during this investigation on an initial sample which ultimately developed a leak. Subsequent samples consistently yielded higher D_o results, typified by the center line of Figure 2. Equilibrium swelling measurements in benzene[22] confirmed that the first membrane had an anomalously higher cross-link density than subsequent samples used during this study. Attempts were made to numerically estimate cross-link densities from the swelling data using the Flory-Rehner equation and a value of $\chi = 0.58$ reported[13] for the polymer-solvent interaction parameter, χ. Although derived for a similar rubber compound, this value of χ yielded improbably low numerical cross link density values in the present case. However, the swelling data confirmed that all subsequent rubber samples used in this study had a uniform and significantly lower cross link density than did the anomalous first sample.

Average permeability coefficients ($\bar{P}$) at 50°C. as a function of benzene inlet pressure are shown in Figure 3. It appears that the

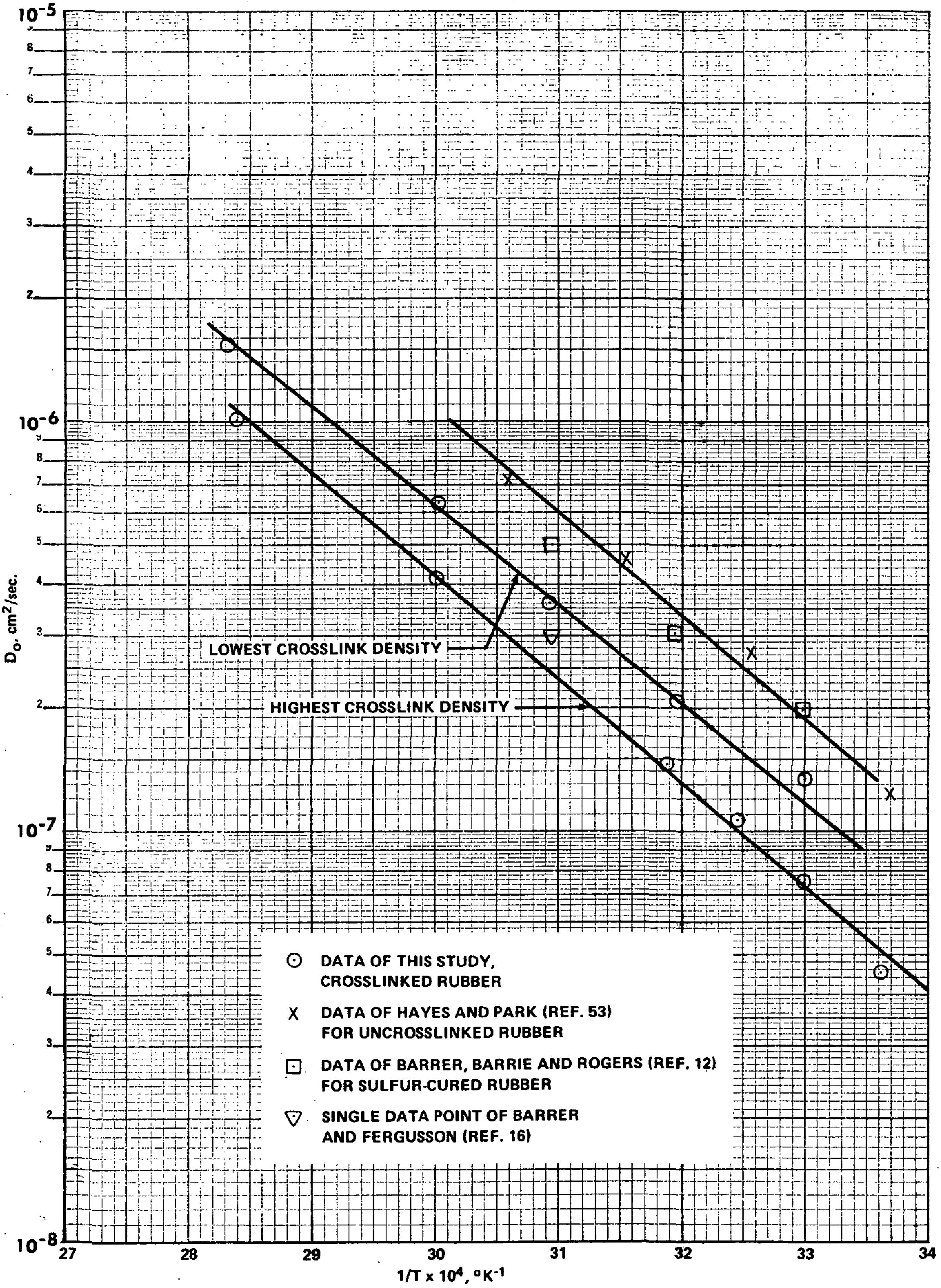

FIGURE 2. D_o DATA, BENZENE VAPOR DIFFUSION THROUGH NATURAL RUBBER.
TOP LINE - - DATA OF HAYES AND PARK[21]
CENTER LINE - - DATA OF THIS STUDY FOR TYPICAL SULFUR-CURED RUBBER
BOTTOM LINE - - DATA OF THIS STUDY FOR MORE HIGHLY CROSS-LINKED NATURAL RUBBER

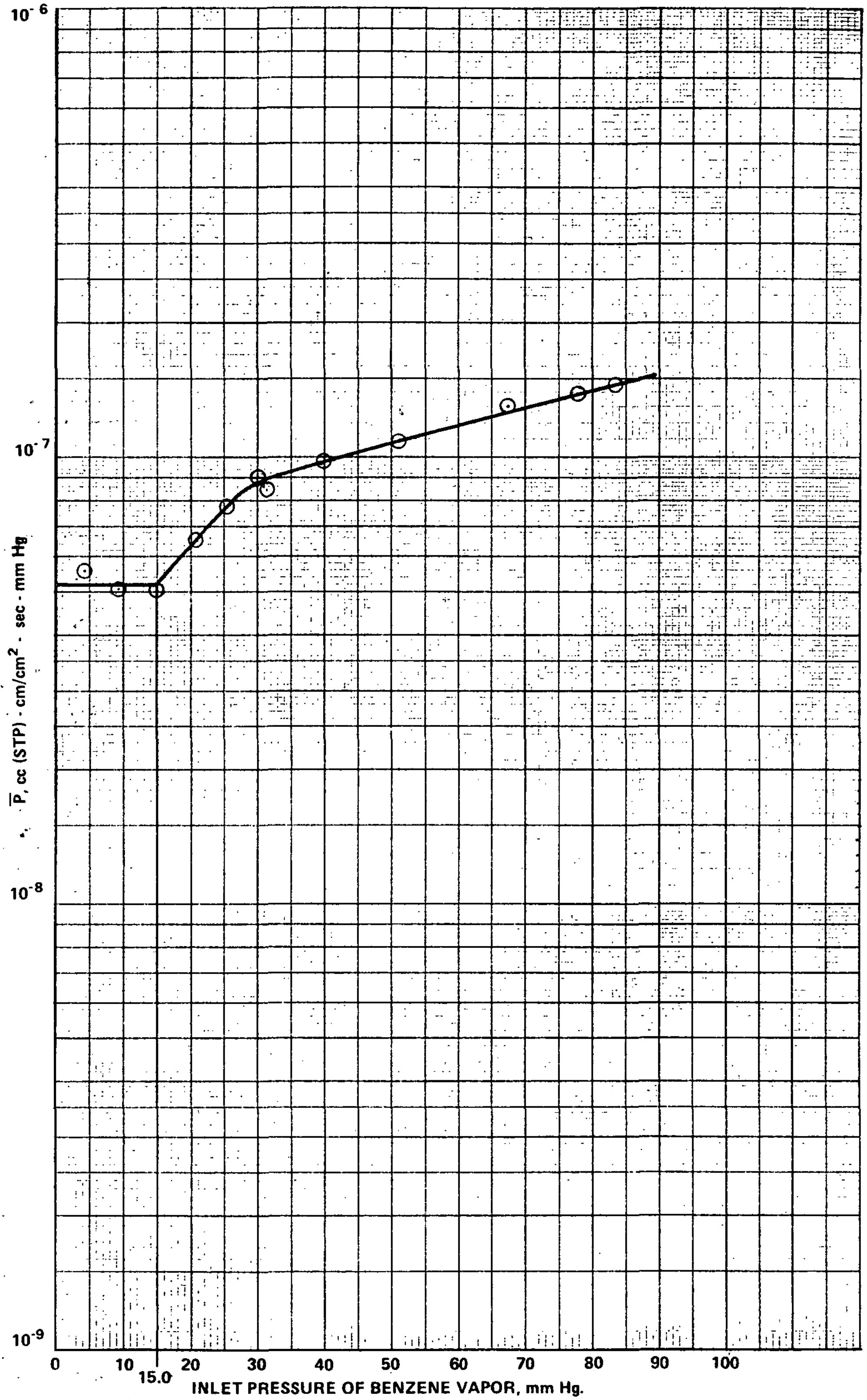

FIGURE 3. AVERAGE PERMEABILITY COEFFICIENTS FOR BENZENE VAPOR TRANSPORT THROUGH NATURAL RUBBER AT 50°C.

overall transport process is independent of inlet pressure or concentration until inlet pressures of 15-30 mm Hg. are attained. The development of a concentration-dependent transport process at higher inlet penetrant pressures is generally preceded by an "ideal" concentration-independent phase at lower penetrant activities[23]. The implication is that the diffusion coefficient is actually D_o in this regime. The measured values of D_o and P_o characteristic of this inlet range for benzene vapor were 3.63×10^{-7} cm^2/sec. and 5.28×10^{-8} cc(STP)-cm/cm^2-sec-mm Hg., respectively. Substituting these values into equation 1 yields a solubility coefficient (s) of 0.144 cc(STP)/cc-mm Hg. Applying the early-time intercept method of equations 13 and 14 to the data of Figure 1 taken at 26.75 mm Hg. gives an early-time estimate of 0.149 cc(STP)/cc-mm Hg. for s. A more direct evaluation of this data would theoretically be possible by comparing diffusion coefficients calculated by the early-time procedure with values obtained using the time-lag route of equation 4. However, in this case, the time-lags at low inlet benzene pressures were extremely erratic, despite reasonable agreement between the corresponding permeability values. It has been demonstrated analytically[24] that time-lags can be in error by a substantially greater margin than the corresponding permeability coefficients. Again, this solubility behavior is characteristic only of the "ideal" transport process that is restricted to low penetrant inlet pressures.

Following the transition zone, which spanned inlet benzene pressures between 15 and 30 mm Hg. for this rubber, the average permeability coefficient displayed the usual exponential dependence upon inlet pressure. There was considerably less scatter of the time-lag values over the zone of obvious concentration-dependence, so pointwise calculations were made to obtain s, the solubility coefficient and b, the exponential factor, by equations 7, 10 and 11. The results, summarized in Table I, suggest that over this range of inlet pressures, the solubility coefficient (s) of benzene vapor in natural rubber is essentially constant at 0.21 cc(STP)/cc-mm Hg. This value is in reasonable agreement with a solubility coefficient of 0.227 obtained by mass sorption methods on a similar rubber compound[25]. Despite the variations in b shown in Table I, it appears that the bulk of the concentration-dependence of $\bar{P}$ arises from a similar dependence of $\bar{D}$ (and hence D) upon concentration, while the solubility coefficient remains essentially constant over the range of inlet pressures studied here. Figure 4 shows that the relevant time-lag data are reasonably well correlated by equation 7 when the pressure-dependence of the diffusion coefficient of benzene is taken to be

$$D(p_i) = D_o \exp(0.0113 p_i) \qquad (16)$$

The factor 0.0113 mm Hg.$^{-1}$ was calculated from the average value of b in Table I.

TABLE I

Analysis of Time Lag Data for Benzene Vapor Transport through Natural Rubber at 50 °C.

p_i mm Hg.	$L(c_i)$ min.	$L(c_i)/{}^*L_o$	(bc_i)	b $cm^3/g.mol$	c_i $cc(STP)/cm^3$	s $cc(STP)/cm^3$-mm Hg.
31.98	54.0	0.6112	0.3233	1222	5.94	0.186
39.95	53.4	0.5966	0.4056	1114	8.16	0.204
52.16	50.3	0.5620	0.6001	1282	10.49	0.202
67.44	49.1	0.5486	0.6337	964	15.67	0.232
77.87	46.0	0.5140	0.8652	1127	17.21	0.221
83.20	42.3	1.0939	1.0939	1435	17.07	0.205

$^*L_o = \ell^2/4D_o$

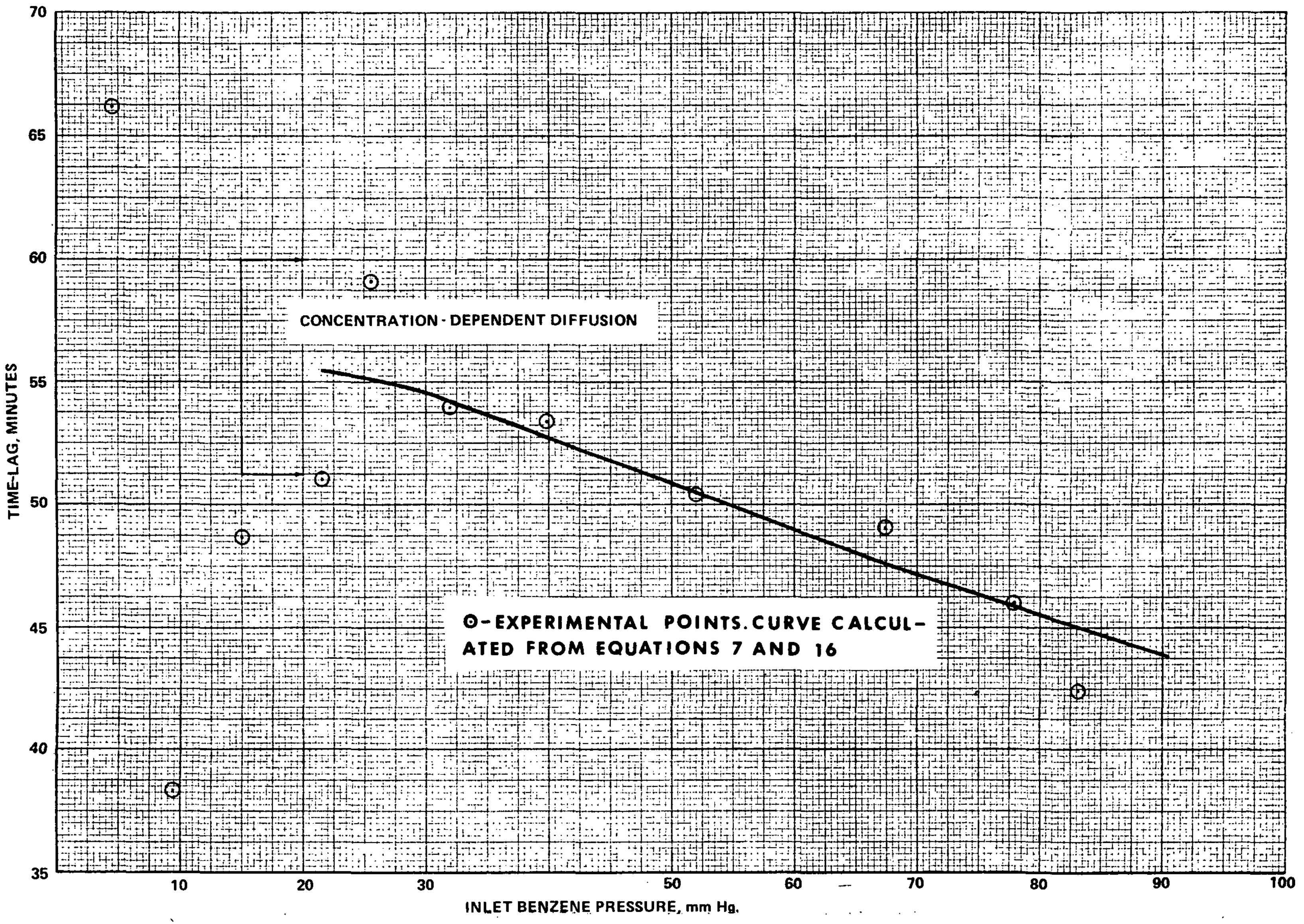

FIGURE 4. CALCULATED VERSUS OBSERVED TIME LAGS ASSOCIATED WITH BENZENE VAPOR PERMEATION THROUGH NATURAL RUBBER AT 50°C.

b. Acetone Data

D_o versus 1/T data for acetone vapor diffusion through natural rubber determined by the early-time method is shown in Figure 5. There is no known published information available for comparison.

Acetone vapor permeability coefficients were measured with the results shown in Figure 6. The data of this study at 24°C. ranges from ten to twenty percent lower than comparable data of Stannett and Yusuda[26], but this is believed explainable by differences in the rubber. At 24°C. and inlet acetone pressures below 40 mm Hg., the permeability coefficient appears constant at $P_o = 1.0 \times 10^{-8}$ cc(STP)-cm/cm^2-sec-mm Hg. The solubility coefficient calculated from a 24°C. early time experiment at 23.4 mm Hg. inlet acetone pressure was 0.092 cc(STP)/cc-mm Hg. With acetone vapor, consistent intercepts were obtained from the pressure (p_V)-time plots during these experiments at low inlet pressures, and the average of solubility coefficients calculated by equations 14 and 15 was 0.086 cc(STP)/cc-mm Hg. Finally, the observed D_o value, 1.039×10^{-7} cm^2/sec, and the corresponding value of P_o quoted earlier, yield by equation 1 a value of 0.096 for s. Again, the agreement between these various approaches vindicates the assumption of a concentration-independent mechanism with $D = D_o$ over this range of low inlet pressures.

The development of a concentration-dependent transport process at 24°C. in the case of acetone vapor was manifested by a smooth departure from the initial permeability (P_o) value on the log $\overline{P}$ versus p_i plot of Figure 6. This is in contrast to the behavior of benzene vapor, where development of the concentration-dependent transport process was presaged by a drastic increase in permeability over an appreciable transition zone of inlet penetrant pressure. This transition effect was also undetectable during acetone vapor permeation studies at the higher temperatures of 50 and 76°C. The degree of concentration-dependence of the acetone vapor transport process decreases with increasing temperature, a trend reported in other cases[27,28]. Replotting the acetone data in log $\overline{P}$ versus 1/T format at various inlet pressures, Figure 7, suggests a concentration-dependent transport mechanism similar to that noted for water vapor in several cases[1]. At high inlet acetone pressures, the apparent activation energy changes sign with increasing temperature. This type of anomalous increase in $\overline{P}$ with decreasing temperature has been attributed to drastic increases in both solubility coefficient and the degree of concentration-dependence of the diffusion coefficient as the temperature decreases. Both effects tend to override the normal tendency of $\overline{P}$ to decrease with decreasing temperature.

A recent study[19] of the transport of dimethylsulfoxide (DMSO) through polyethylene revealed that the observed permeability of DMSO vapor is a function of the surface area associated with the downstream

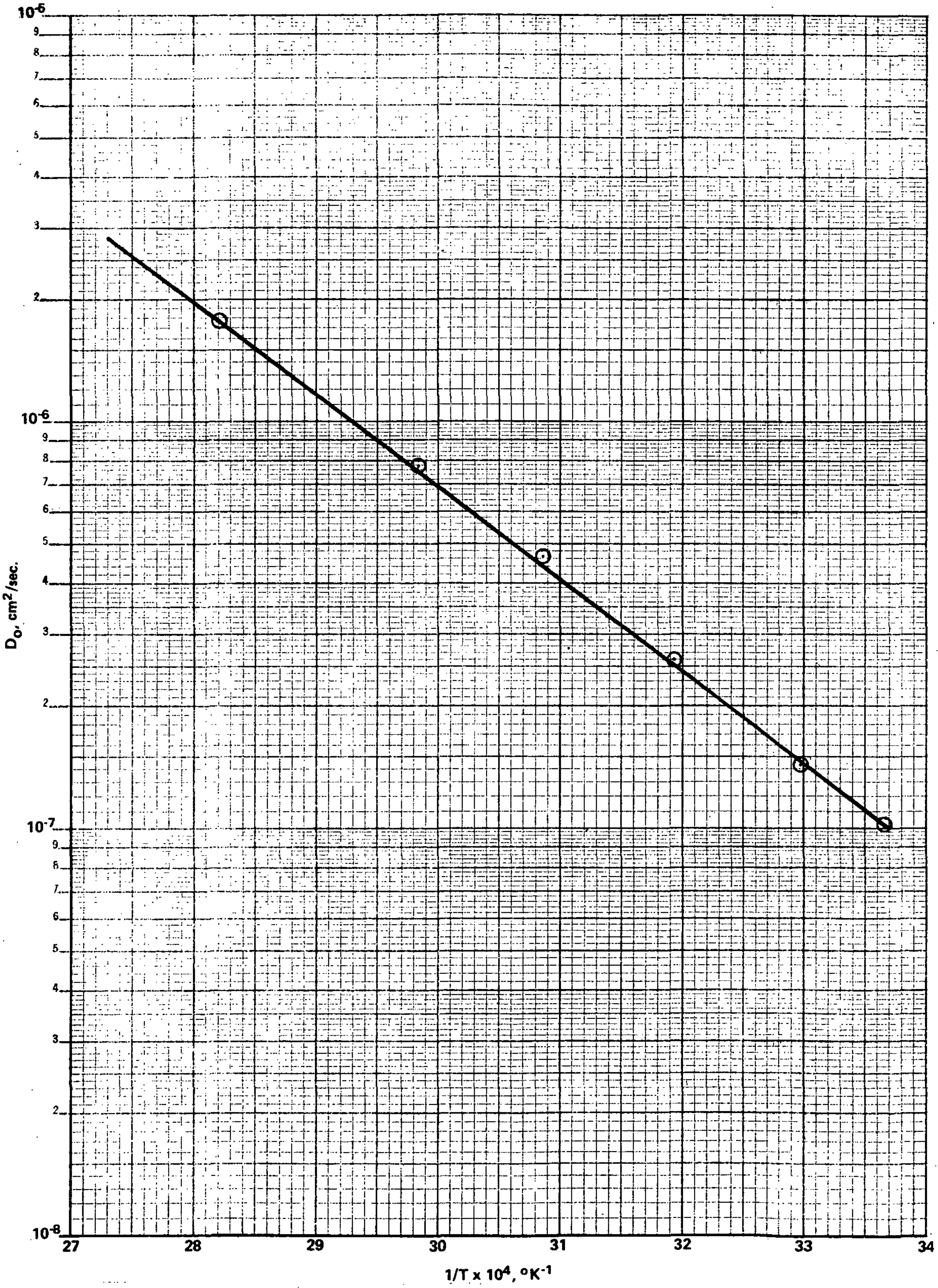

FIGURE 5. D_o DATA, ACETONE VAPOR DIFFUSION THROUGH NATURAL RUBBER.

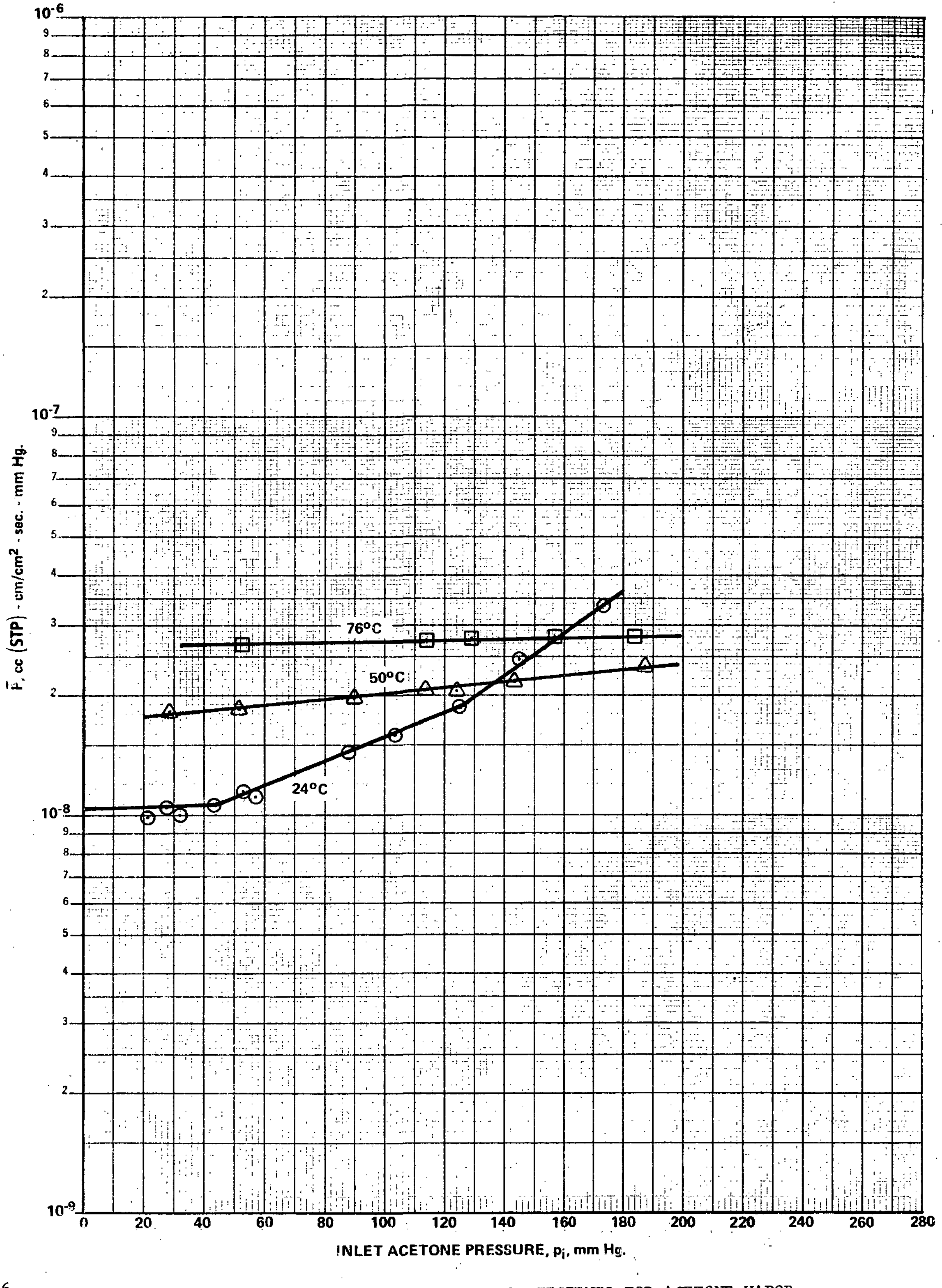

FIGURE 6. AVERAGE PERMEABILITY COEFFICIENTS FOR ACETONE VAPOR TRANSPORT THROUGH NATURAL RUBBER AT 24, 50 AND 76°C.

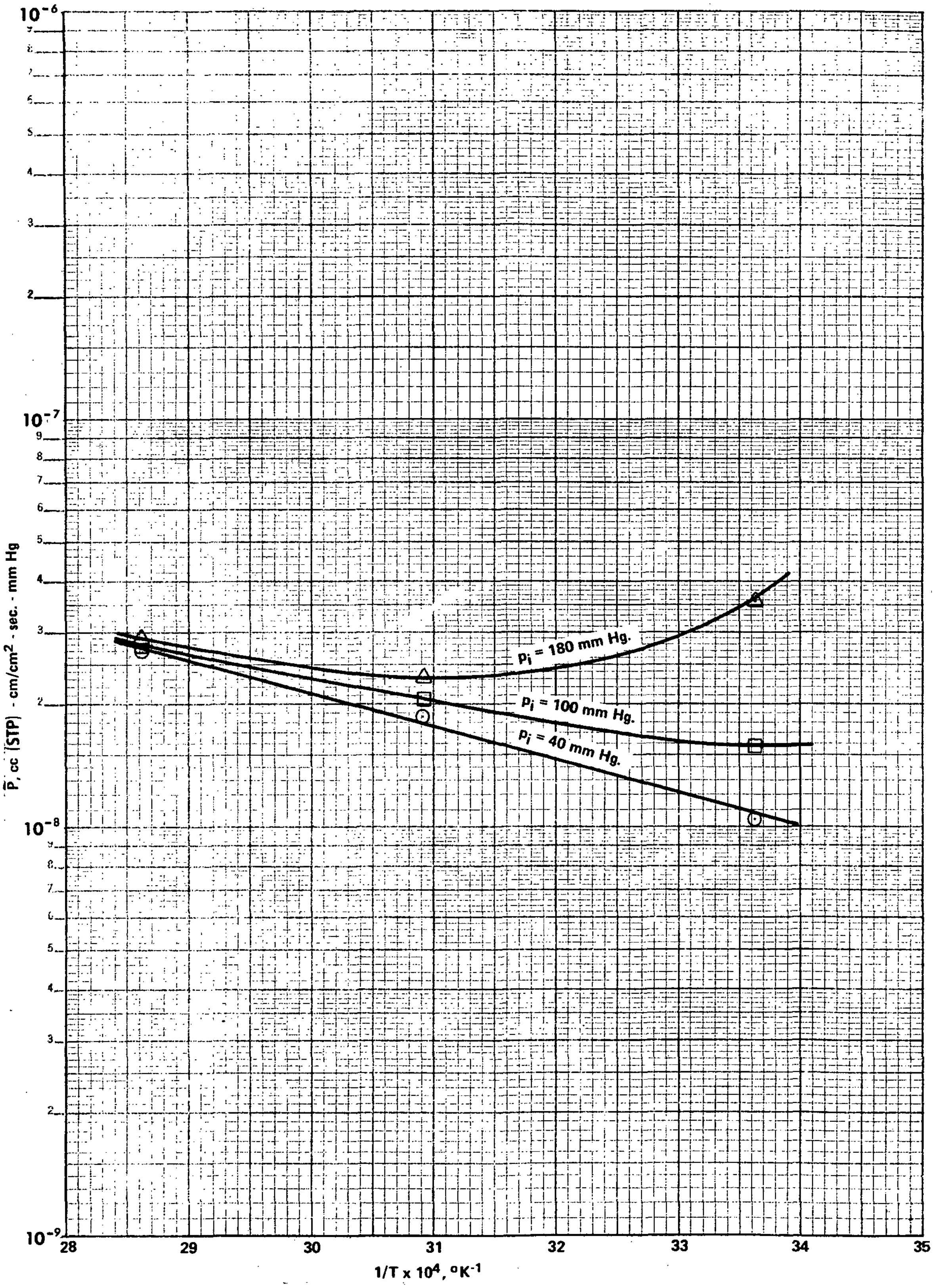

FIGURE 7. LOG $\overline{P}$ VERUS 1/T FOR ACETONE VAPOR PERMEATION AT VARIOUS INLET PRESSURES.

measuring volume. It was concluded that DMSO was being adsorbed on the walls of the low pressure side of the apparatus. Accordingly, several permeability experiments were conducted using each of the two volumes (34,733 and 290.5 cc) associated with the present equipment. The results were in reasonable agreement when data obtained using the smaller volume was adjusted to account for significant downstream pressures which developed during the experiment. For example, permeability experiments at 27.04 mm Hg. inlet acetone pressure and 50°C. yielded a $\bar{P}$ of 1.742×10^{-8} cc(STP)-cm/cm^2-sec-mm Hg. using the small volume, while an almost identical value of 1.813×10^{-8} in the same units was obtained with the larger volume. It was concluded that surface adsorption effects are negligible in the cases studied here.

Only the acetone data obtained at 24°C. appeared sufficiently concentration-dependent to justify pointwise calculations of b, the exponental factor, and s, the solubility coefficient, over the range of concentration-dependent behavior. The results of these calculations are shown in Table II. Again, there is considerable scatter in the values of b, but the solubility coefficients appear less erratic. As penetrant saturation conditions are approached, values of $\bar{P}$ deviate progressively and positively from the initial exponential dependence upon entering penetrant pressure. The data of Table II suggest a corresponding increase in s over the same inlet pressure range, 125-170 mm Hg. This indicates that the diffusion coefficient of acetone vapor at pressures greater than 40 mm Hg. can be represented by

$$D(p_i) = 1.039 \times 10^{-7} (\exp(0.00553 p_i)) \qquad (17)$$

The (bs) value of 0.00553 was obtained by averaging all such values calculated from the data of Table II within the 40 to 125 mm Hg. ranges, excepting the data point at $p_i = 43.6$ mm Hg. which had an associated solubility coefficient more typical of the low-pressure, concentration-independent range.

CONCLUSIONS

This general approach to the analysis of permeation data definitely appears capable of yielding more information and insight into the overall transport process than the older methods of analysis, particularly when added illumination is provided by corresponding permeability data. In principle, a comparison of diffusion coefficients calculated by the early-time method with values obtained using the Daynes time-lag relationship, equation 4, should indicate the presence of time-or concentration-dependent effects. In cases where such a comparison is compromised by unavoidable scatter in the time-lag data, recourse to the corresponding permeability data should indicate the extent of concentration-dependent effects. The cases studied here support the

TABLE II

Analysis of Time Lag Data for Acetone
Vapor Transport through Natural Rubber at 24 °C.

P_i mm Hg	$L(c_i)$ min.	$L(c_i)/L_o^*$	(bc_i)	b $cm^3/g.$ mol	c_i cc(STP/cm^3	s cc(STP)/cm^3-mm Hg.
43.6	265	0.6511	0.0924	502	4.13	0.0947
52.8	249	0.6118	0.3195	1458	9.40	0.178
89.2	242	0.5946	0.4172	941	9.94	0.1113
102.7	239	0.5896	0.4456	798	12.51	0.1218
124.9	209	0.5135	0.8678	1354	14.35	0.1148
144.8	214	0.5258	0.8000	822	21.82	0.1507
173.3	188	0.4619	1.1598	910	28.57	0.1647

$^*L_o = \ell^2/4D_o$

error analysis of Siegel and Coughlin[24] since the error-induced scatter in permeability data was considerably less than the scatter in corresponding time-lags.

The agreement of solubility coefficients calculated by the intercept formulas, equations 13 and 15, with the corresponding (P_0/D_0) values at low penetrant inlet pressures is evidence that D_0 calculated by the early-time procedure is the mechanistically correct diffusion coefficient in the concentration-independent domain.

The nature of the transition at ascending inlet penetrant pressures to a transport mechanism dependent upon concentration may be dictated by the swelling propensity of the penetrant toward the rubber. Benzene has the greater tendency to swell rubber, and the transition to a concentration-dependent vapor transport process in the case of benzene involves the more drastic effect of a sudden increase in permeability before emergence of the normal exponential dependence upon inlet pressure. Any transition effect that may be present, combined with an ideal transport mechanism that spans an appreciable range of lower penetrant inlet pressures, would compromise the estimation of true D_0 or P_0 values by extrapolation of data obtained at higher penetrant concentrations.

Inlet pressure-averaged diffusion coefficients were calculated from equations 16 and 17 for benzene and acetone, respectively. Allowance was made in each case for the appropriate initial pressure span wherein $D = D_0$. An estimate of the steady state average diffusion coefficient for each penetrant was obtained by dividing each measured permeability coefficient $(\bar{P})$ by the appropriate solubility coefficient. For these calculations, the s value of benzene vapor was taken to be 0.21 cc(STP)/cc-mm Hg. over the range of concentration-dependent behavior studied here. From Table II, an average value of $s = 0.124$ was used for acetone vapor at inlet pressures over the range $40 < p_i < 125$ mm Hg. At higher inlet acetone pressures where s appeared to increase progressively, individual solubility coefficient values from Table II were employed. At increasing penetrant inlet pressures, the steady state average diffusion coefficients grow progressively larger than the transient state diffusion coefficients as shown in Figure 8. This effect was noted in prior studies[13,14] of benzene vapor transport through sulfur-cured natural rubber. It was postulated that the transient state coefficients are lower because the slow relaxation of swelling-induced stresses injects an element of time-dependence into the transport process. The increasing severity of this effect with increasing penetrant concentration supports that postulate.

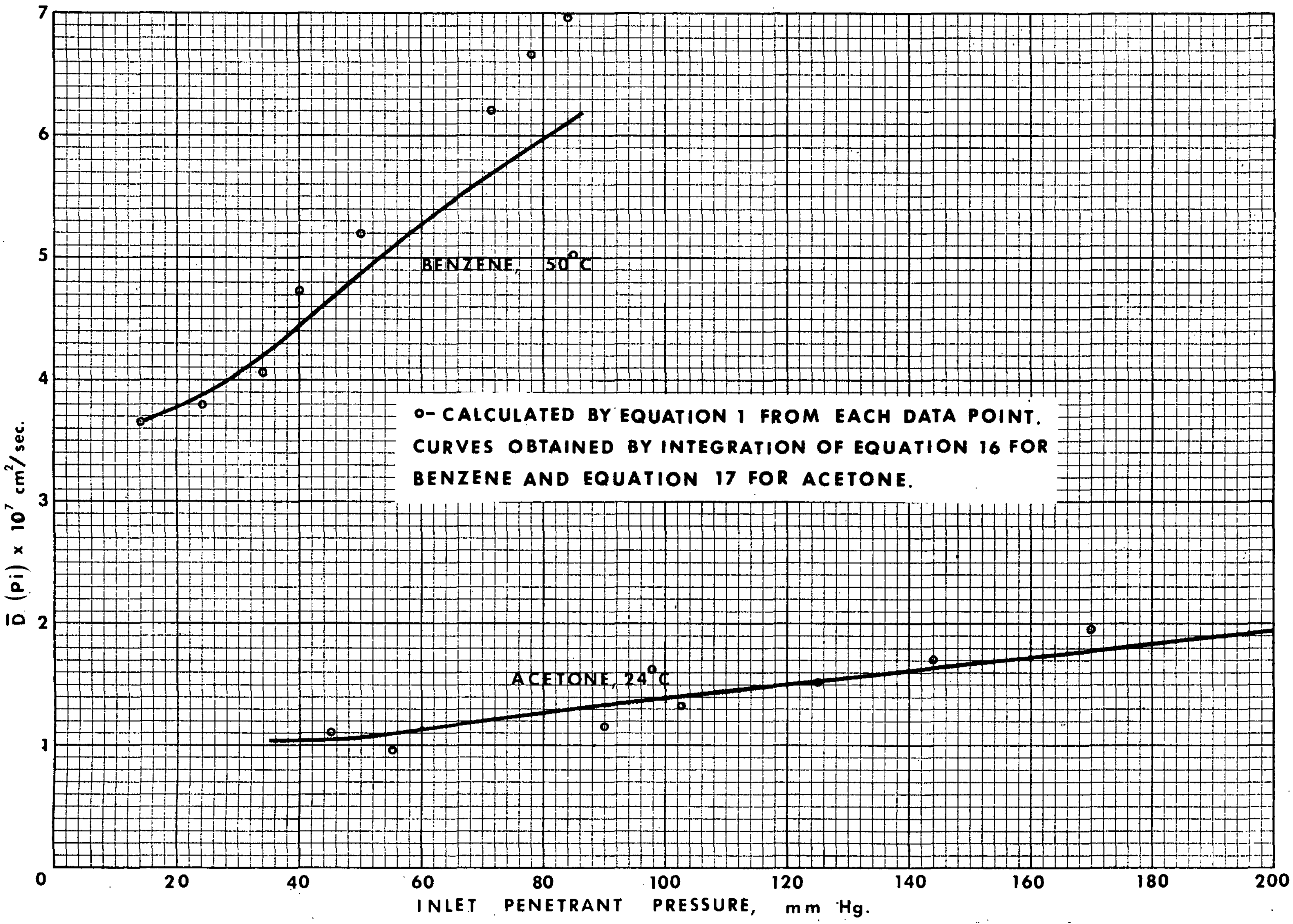

FIGURE 8. COMPARISON OF AVERAGE TIME-LAG DERIVED DIFFUSION COEFFICIENTS (SOLID CURVES) WITH ESTIMATED STEADY STATE ($\overline{P}$/s) VALUES (POINTS).

REFERENCES

1. J. Crank and G. S. Park (Editors), Diffusion in Polymers, Academic Press, London and New York, 1968.

2. G. J. van Amerongen, Rubber Chem. Technol., 37, 1065 (1964).

3. H. Fujita, Fortschr. Hochpolym.-Forsch., 3, 1 (1961).

4. P. Meares, J. Appl. Polym. Sci., 9, 912 (1965).

5. W. Jost, Diffusion in Solids, Liquids and Gases, Academic Press, New York (1961).

6. J. Crank, The Mathematics of Diffusion, Oxford University Press, New York (1957).

7. H. A. Daynes, Proc. Roy. Soc. (London), A97, 286 (1920).

8. H. L. Frisch, J. Phys. Chem., 61, 93 (1957).

9. T. Holstein, cited in reference 10.

10. W. A. Rogers, R. S. Buritz and D. Alpert, J. Appl. Phys., 25, 868 (1954).

11. R. M. Barrer and H. T. Chio, J. Polym. Sci. C, 10, 111 (1965).

12. R. M. Barrer, R. Mallinder and (in Part) P. S-L. Wong, Polymer, 8, 321 (1967).

13. R. M. Barrer and R. R. Fergusson, Trans. Faraday Soc., 54, 989 (1958).

14. R. M. Barrer, J. A. Barrie and M. G. Rogers, Trans. Faraday Soc., 58, 2473 (1962).

15. F. A. Long and L. J. Thompson, J. Poly. Sci., 14, 321 (1954).

16. Washburn, W. W. (Editor) International Critical Tables, III, McGraw-Hill, New York (1928).

17. Lange, N. A. (Editor), Handbook of Chemistry (Tenth Edition) McGraw-Hill, New York (1961).

18. T. Nakagawa, H. B. Hopfenberg and V. Stannett, J. Appl. Polym. Sci., 15, 231 (1971).

19. S. A. Stern and G. W. Britton, *J. Polym. Sci. A-2*, *10*, 295 (1972).

20. N. G. Utterbeck and T. Griffith, *Rev. Sci. Instr.*, *37*, 866 (1966).

21. M. J. Hayes and G. S. Park, *Trans. Faraday Soc.*, *51*, 1134 (1955); *ibid*, *52*, 949 (1956).

22. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953).

23. H. B. Hopfenberg and H. L. Frisch, *J. Polym. Sci. B*, *7*, 405 (1969).

24. R. D. Siegel and R. W. Coughlin, *J. Appl. Polym. Sci.*, *14*, 3145 (1970).

25. R. M. Barrer, J. A. Barrie and M. G. Rogers, *J. Polym. Sci. A*, *1*, 2565 (1963).

26. V. Stannett and H. Yasuda, *J. Polym. Sci. B*, *1*, 289 (1963).

27. J. L. Lundberg and E. J. Mooney, *J. Polym. Sci. A-2*, *7*, 947 (1969).

28. S. A. Stern, S-M. Fang and H. L. Frisch, *J. Polym. Sci. A-2*, *10*, 201 (1972).

APPROVAL

TRANSIENT PERMEATION OF ORGANIC VAPORS THROUGH ELASTOMERIC MEMBRANES

by

James E. Curry

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

R. J. Schwinghamer

R. J. Schwinghamer
Chief, Materials Division

Karl L. Heimburg

Karl L. Heimburg
Director, Astronautics Laboratory