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A Method for the Dynamic Measurement of Diffusivities of Gases in Polymers

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Synopsis

A method is presented for determining the diffusivity of a gas in a polymer from the response to a step concentration change in a continuous-flow permeation chamber. The outlined procedure has several advantages over techniques currently in use: it requires simple numerical integration rather than curve fitting; it utilizes the complete response, rather than a portion of the response which falls within the region of validity of a short-time asympotic solution of the diffusion equation; and it is applicable both to flat membranes and cylindrical tubes. An illustration of the method is provided by the measurement of the diffusivity of sulfur dioxide in a PTFE tube at several temperatures.

INTRODUCTION

The determination of the permeability or diffusivity of a gas in a polymer commonly involves measuring the amount of the gas which permeates through, into, or out of a sample of the polymer in a closed-volume system.[1] Several problems are associated with experiments of this type. Measuring the cumulative amount rather than the instantaneous rate of permeation or sorption limits the precision of the data; moreover, in batch permeation experiments, a pressure gradient is imposed across a membrane, and consequently elaborate membrane sealing and support provisions are required.[2,3]

An approach to permeation measurements in which a gas permeates through a membrane into a flowing stream avoids these problems. Steady-state operation can be achieved in such an experiment, thereby increasing the attainable precision, and equal pressures can be maintained in both compartments of the permeation chamber, minimizing the requirements for sealing and supporting the membrane.

The continuous permeation technique has been applied extensively to the measurement of permeabilities of gases in polymers.[2,4,5] Pasternak, Schimscheimer, and Heller[3] showed that the continuous technique may also be used to measure the diffusivity of a gas in a flat membrane. In the method proposed by Pasternak et al., a step change in the partial pressure of the penetrant is imposed on one side of the membrane, and the rate of permeation into the gas flowing past the other side is monitored continuously. The data are plotted such that a straight line is obtained for a portion of the response, with the slope of the line being a known function of the diffusivity. The method is effective, but being based on either a short-time or long-time asymptotic solution of the diffusion equation limits its applicability. When deviations from the anticipated straight line occur, it is difficult to determine whether they are due to experimental error or to a violation of the assumptions of the diffusion model, or simply to the invalidity of the asymptotic solution in the range of response times where the deviations occur.

This paper outlines an alternative method for determining the diffusivity of a gas in a polymer from step response data obtained in a continuous permeation chamber. The proposed method has several advantages over that of Pasternak et al.: it requires simple numerical integration of response data rather than curve fitting; it utilizes the complete response, rather than a portion of the response which falls within the region of validity of an asymptotic solution of the diffusion equation; and it is applicable to cylindrical tubes as well as flat membranes. The method is illustrated by the experimental determination of the diffusivity of sulfur dioxide in a PTFE tube.

THEORETICAL

A continuous-flow permeation chamber consists of two compartments separated by a membrane. At a time $t = 0$, a penetrant is introduced into one compartment (the upstream compartment) and permeates through the membrane into a stream flowing through the other (downstream) compartment. The concentration of the penetrant in the gas leaving the downstream compartment is monitored continuously until steady state is attained.

It is assumed that diffusion of the penetrant in the gas phase and absorption at the membrane surface are instantaneous processes, that diffusion in the membrane is Fickian with a constant diffusivity D (cm^2/s), and that the concentration of dissolved gas at the downstream surface of the membrane is always sufficiently low compared to the concentration at the upstream surface that it may be set equal to zero. The diffusion equation and boundary conditions for a flat membrane of thickness h, and for a cylindrical tube with inner radius a and outer radius b with the penetrant introduced on the outside of the tube, are given below:

$$\begin{array}{ccr} \underline{\text{Flat membrane}} & \underline{\text{Cylinder}} & \\ \dfrac{\partial C(t,x)}{\partial t} = D\dfrac{\partial^2 C(t,x)}{\partial x^2} & \dfrac{\partial C(t,r)}{\partial t} = \dfrac{D}{r}\dfrac{\partial}{\partial r}\left(r\dfrac{\partial C}{\partial r}\right) & (1) \\ C(0,x) = 0 & C(0,r) = 0 & (1a) \\ C(t,0) = C_1 & C(t,a) = 0 & (1b) \\ C(t,h) = 0 & C(t,b) = C_1 & (1c) \end{array}$$

The solutions of these equations may be obtained by simplifying solutions given by Crank[6] for more general boundary conditions, and the resulting expressions for $C(t,x)$ and $C(t,r)$ may in turn be used to derive expressions for the rate at which the gas permeates through the downstream membrane surface. For a flat membrane with a surface area A (cm^2),

$$\phi_{fm} = -DA\left(\frac{\partial C}{\partial x}\right)_{x=h}$$
$$= \frac{DAC_1}{h}\left\{1 + 2\sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{n^2\pi^2 Dt}{h^2}\right)\right\} \quad (2)$$

and for a cylinder of length L

$$\phi_c = 2\pi DL\left(r\frac{\partial C}{\partial r}\right)_{r=a}$$
$$= \frac{2\pi DLC_1}{\ln(b/a)}\left\{1 + 2\ln(b/a)\sum_{n=1}^{\infty} \frac{J_0(\alpha_n a)\, J_0(\alpha_n b)}{J_0^2(\alpha_n a) - J_0^2(\alpha_n b)} \exp(-\alpha_n^2 Dt)\right\} \quad (3)$$

where $\alpha_1, \alpha_2, \ldots$ are the real positive roots of the equation

$$J_0(\alpha_n a)\, Y_0(\alpha_n b) - J_0(\alpha_n b)\, Y_0(\alpha_n a) = 0 \quad (4)$$

and ϕ_c is defined to be positive for flow in the negative r direction. In eqs. (3) and (4), J_0 and Y_0 are the zero-order Bessel functions of the first and second kind. An expression for the permeation rate applicable to both geometries is

$$\phi(t) = \phi_{ss}\left[1 + K\sum_{n=1}^{\infty} b_n \exp(-\omega_n^2 Dt)\right] \quad (5)$$

where the steady-state permeation rate ϕ_{ss} is

$$\phi_{ss} = DAC_1/h \qquad \text{flat membrane} \quad (6a)$$
$$= 2\pi DLC_1/\ln(b/a) \qquad \text{cylinder} \quad (6b)$$

and the expressions for K, b_n, and ω_n^2 may be deduced by inspection of eqs. (2) and (3).

The total amount of the penetrant that has permeated through the membrane up to time t is

$$Q(t) = \int_0^t \phi(t)dt. \quad (7)$$

Substituting the expression of eq. (5) for $\phi(t)$ in eq. (7) yields

$$Q(t) = \phi_{ss}t + \frac{\phi_{ss}K}{D}\sum_{n=1}^{\infty}\frac{b_n}{\omega_n^2} - \frac{\phi_{ss}K}{D}\sum_{n=1}^{\infty}\frac{b_n}{\omega_n^2}\exp(-D\omega_n^2 t). \quad (8)$$

As t becomes large, the exponential terms become negligible, and a plot of $Q(t)$ versus t approaches a straight line. The intersection of this line with the time axis, the so-called time lag t_1, is obtained by setting the first two terms of eq. (8) equal to zero and solving for t, with the result

$$t_1 = -\frac{K}{D}\sum_{n=1}^{\infty}\frac{b_n}{\omega_n^2} \quad (9)$$

Expressions for the time lag for planar and cylindrical membranes are given by Crank and Park[1]:

$$(t_1)_{fm} = h^2/6D \tag{10}$$

$$(t_1)_c = \frac{a^2 - b^2 + (a^2 + b^2)\ln(b/a)^*}{4D\ln(b/a)}. \tag{11}$$

Equations (10) and (11) provide the basis for the determination of D from an experiment in which $Q(t)$ is measured in a closed-volume system and t_1 is determined graphically. If instead $\phi(t)$ is measured in a continuous permeation apparatus the following analysis is pertinent.

The quantity $(1 - \phi/\phi_{ss})$ may easily be calculated from experimental response data and integrated numerically from $t = 0$ to $t = \infty$. If the value of this integral is designated M_0, then from eq. (5)

$$M_0 = \int_0^\infty \left[1 - \frac{\phi(t)}{\phi_{ss}}\right] dt = -K \int_0^\infty \sum_{n=1}^{\infty} b_n \exp(-D\omega_n^2 t)\,dt. \tag{12}$$

Interchanging the order of summation and integration yields

$$M_0 = -\frac{K}{D} \sum_{n=1}^{\infty} \frac{b_n}{\omega_n^2} \tag{13}$$

which by comparison with eq. (9) is identical to the time lag, so that the expressions of eqs. (10) and (11) may be equated to M_0 as well as t_1. Thus, if

$$M_0 = \int_0^\infty \left[1 - \frac{\phi(t)}{\phi_{ss}}\right] dt \tag{14}$$

then for a flat membrane

$$D = h^2/6M_0 \tag{15}$$

and for a cylinder

$$D = \frac{a^2 - b^2 + (a^2 + b^2)\ln(b/a)}{4M_0\ln(b/a)}. \tag{16}$$

Experimental values of $\phi(t)$ or any measured quantity proportional to ϕ, such as the concentration of the penetrant in the gas stream flowing past the downstream side of the membrane, may be substituted into eq (14), and the value of M_0 may be obtained by numerical integration. The diffusivity D may then be calculated from eq. (15) or eq. (16). (In process dynamics terminology, M_0 is the zeroth moment of the negative unit step response of the membrane, and the technique of estimating D from the calculated value of M_0 is an example of the method of moments.)

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* The expression for the cylinder given by Crank and Park[1] erroneously omits the D in the denominator. The correct form is given in the original derivation by Jaeger.[7] A formula for this quantity given by Crank[6] is incorrect, although it yields results which are numerically quite close to the correct values.

EXPERIMENTAL PROCEDURE AND RESULTS

The diffusivity of sulfur dioxide in PTFE (Teflon) was determined at 100°C. A PTFE tube with an inner radius $a = 0.403$ cm and an outer radius $b = 0.480$ cm was mounted in a chamber in a thermostatically controlled oven. A stream of air containing less than 0.02 ppm SO_2—the carrier gas—passed through the inside of the tube. At a time $t = 0$, a gas containing 1.5% SO_2 by volume and the balance dry air—the chamber gas—was introduced into the chamber outside the polymer tube. SO_2 permeated through the tube wall into the carrier gas, which passed out to an electrochemical transducer SO_2 detector connected to a strip chart recorder. Additional details of the experimental apparatus are given by Rodes, Felder, and Ferrell.[4]

The total time lag due to the residence time of the chamber gas in the upstream compartment, the residence time of the carrier gas between the permeation chamber and the detector, and the 90% response time of the detector was estimated to be 17 sec. Since the 90% rise time of the measured response was of the order of 30 min, the precise dynamic characteristics of the chamber, the carrier gas lines, and the analyzer were not considered important, and the 17-sec lag was for simplicity assumed to be a pure time delay. The measured response was accordingly shifted horizontally by this amount to obtain the transient response of the polymer tube alone.

The corrected response $R(t)$ normalized by its asymptotic (steady state) value R_{ss} is shown in Figure 1 as a series of discrete points. The quantity M_0 was evaluated from eq. (14) by replacing ϕ/ϕ_{ss} with R/R_{ss} and using Simpson's rule with $\Delta t = 1$ min. The calculated value of M_0, 17.9 min, was substituted into eq (16) to obtain $D = 9.1 \times 10^{-7}$ cm^2/sec. This value was not highly dependent on the assumption of 17 sec for the time lag of the system components other than the membrane: using 0 sec or 34 sec instead of 17 sec made a difference of only 1.5% in the calculated diffusivity.

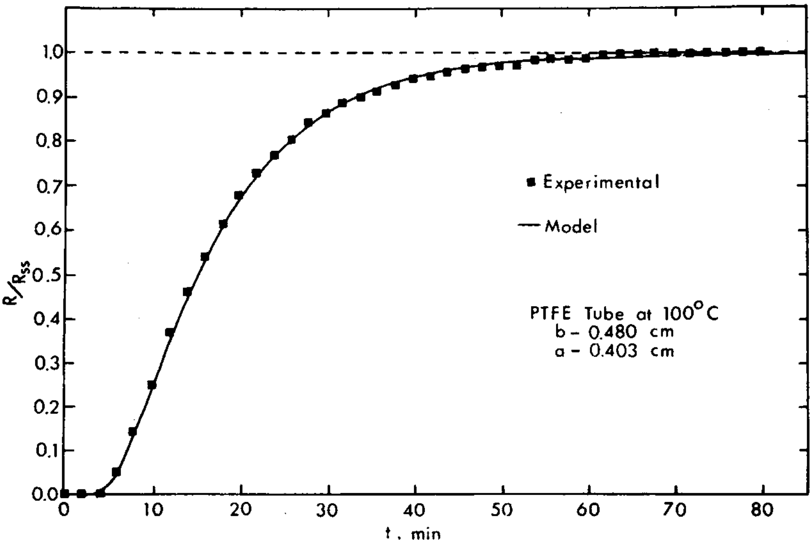

Fig. 1. Experimental and theoretical step responses of a PTFE tube.

The theoretical curve of $\phi(t)/\phi_{ss}$ ($= R(t)/R_{ss}$) versus t evaluated by substituting the tube dimensions and the calculated diffusivity into eq (3) is shown as the solid curve of Figure 1. The agreement between the experimental and theoretical responses is excellent, and confirms the validity of both the diffusion model and the technique used to estimate the diffusivity.

Diffusivities have been measured at several temperatures between 22°C and 121°C using this technique. Measurements were made using two PTFE tubes with different wall thicknesses and two upstream SO_2 concentrations for each tube. The measured diffusivities are shown in an Arrhenius plot in Figure 2; the SO_2 percentages shown in the legend on this figure are the molar percentages of SO_2 in the upstream chamber gas. Also shown in Figure 2 is an SO_2 diffusivity reported by Jordan[8] for PTFE at a temperature presumed to be in the range of 20°C to 30°C. Jordan used a sorption technique and calculated D as the quotient of a measured permeability and a measured solubility; the agreement between his value and the values obtained in the present study is reasonable, albeit not outstanding.

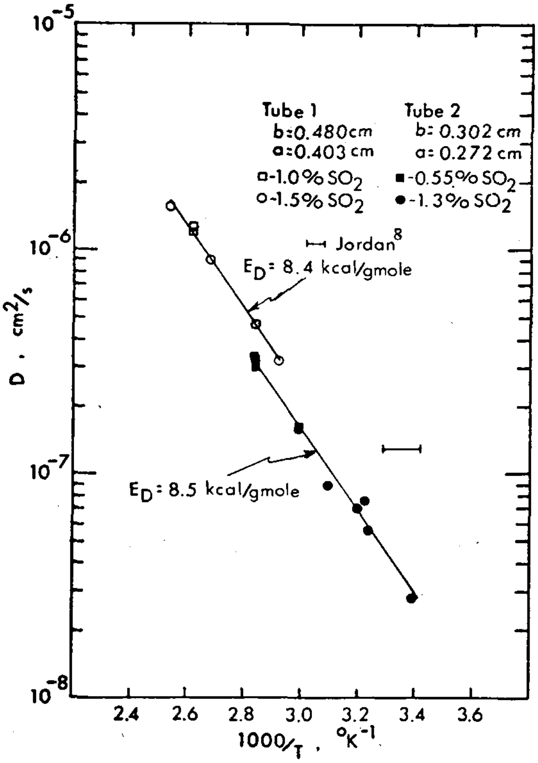

Fig. 2. Arrhenius plot of SO_2 diffusivities in PTFE tubes.

SO_2 diffusivities measured using thick and thin-walled PTFE tubes appear to differ by approximately 30–50%. The coincidence of data points obtained using two different upstream concentrations at a fixed temperature suggests the constancy of D under the prevailing experimental conditions. Least-squares fits to the data of Figure 2 yield an activation energy for diffusion of 8.45 ± 0.1 kcal/g-mole.

Future papers will report the results of diffusivity measurements for several penetrants and polymers and will outline applications of the continuous measurement technique to the monitoring of gaseous pollutant emissions from stationary sources, the project which provided the impetus for this study.

Nomenclature

A	surface area of a flat membrane, cm^2
a, b	inner and outer radii of a hollow cylindrical tube, cm
b_n	coefficient in eq. (5)
C	concentration of penetrant dissolved in a membrane, moles/cm^3
C_0, C_1	initial concentration and concentration at the upstream membrane surface, moles/cm^3
D	diffusivity, cm^2/sec
h	thickness of a flat membrane, cm
J_0	zero-order Bessel function of the first kind
K	coefficient in eq. (5)
L	length of cylindrical tube, cm
M_0	quantity defined by eq. (14)
$Q(t)$	cumulative permeation up to time t, moles
$R(t)$	measured variable proportional to $\phi(t)$
R_{ss}	asymptotic (steady state) value of R
r	radial position coordinate in a cylindrical tube, cm
t	time from imposition of a step change in penetrant partial pressure, sec
t_1	time lag, sec
x	position coordinate in a flat membrane, cm; $x = 0$ corresponds to the upstream surface of the membrane
Y_0	zero-order Bessel function of the second kind

Greek Letters

α_n	nth real positive root of eq. (4)
$\phi(t)$	rate of permeation into the gas downstream of the membrane, moles/sec
ϕ_{ss}	asymptotic (steady state) value of ϕ
ω_n	coefficient in eq. (5)

Subscripts

c	cylinder
fm	flat membrane

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References

1. J. Crank and G. S. Park, Eds., *Diffusion in Polymers,* Academic Press, New York, 1968.
2. T. L. Caskey, *Mod. Plast.,* **45,** 447 (1967).

3. R. A. Pasternak, J. F. Schimscheimer, and J. Heller, *J. Polym. Sci. A-2,* **8,** 467 (1970).
4. C. E. Rodes, R. M. Felder, and J. K. Ferrell, *Environ. Sci. Technol.,* **5,** 1121 (1971).
5. R. M. Felder, J. K. Ferrell, and J. J. Spivey, *Anal. Instrumentation,* **12,** 35 (1974).
6. J. Crank, *The Mathematics of Diffusion,* Clarendon Press, Oxford, 1956.
7. J. C. Jaeger, *Proc. Roy. Soc. N.S.W.,* **74,** 342 (1940).
8. S. Jordan, *Staub-Reinhalt Luft,* **33,** 36 (1973).

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