Determination of Diffusion Constants by Sorption of Solute from a Constant, Finite Volume

INTRODUCTION

Diffusion coefficients in a solute–sorbent system may be measured by following the concentration of the solute in a constant, finite volume as it is absorbed or desorbed by the sorbent. Carman and Haul[1] have provided solutions of the diffusion equation for parallel-plane sheet, cylindrical, and spherical sorbent geometries and applied them in sorption experiments. Crank[2] also summarizes the solutions. Despite the simplicity and diversity of the method, it has been used only infrequently to determine the diffusion constants of gases and vapors in polymers.[3–5]

Carman and Haul[1] formulated two solutions for the time t dependence of the pressure, one converging rapidly for large t and a second converging rapidly for small t. The objective of this note is, using the first solution, to introduce a time lag and provide another form of the solution which has the advantage that it may be applied to cases where it is difficult to measure accurately the values of the pressure or concentration at zero time.

SOLUTION FOR A PLANE SHEET SORBENT

Consider a parallel-plane sheet of thickness $2l$ exposed at both faces to a constant, finite volume of a gas. The sorbent, in equilibrium with the gas at pressure p_i, is exposed to pressure p_0 at $t = 0$, and the pressure p is determined as a function of t until equilibrium is established at the final pressure p_∞. The solution, obtained for D = constant, which converges rapidly at large t may be expressed as[1]

$$\frac{p - p_\infty}{p_0 - p_\infty} = \sum_{n=1}^{\infty} Z_n \exp\left(-DQ_n^2 t / l^2\right) \tag{1}$$

where

$$Z_n = \frac{2\lambda(1 + \lambda)}{1 + \lambda + \lambda^2 Q_n^2} = \frac{4 \sin^2 Q_n - 2Q_n \sin 2Q_n}{2Q_n^2 - Q_n \sin 2Q_n} \tag{2}$$

$$\lambda = \frac{V_g}{KA2l} = \frac{p_\infty - p_i}{p_0 - p_\infty} \tag{3}$$

where the Q_n are the nonzero, positive roots of

$$\tan Q = -\lambda Q \tag{4}$$

A is the area of one side of the parallel-plane sheet, D is the diffusion coefficient, V_g is the volume of the gas, and K is the partition coefficient defined by $K = C/C_g$ where C is the concentration of the penetrant in the polymer and C_g is its concentration in V_g. The expression describes both absorption, $p_0 > p_i$, and desorption, $p_i > p_0$.

For sufficiently large t, only the first term in eq. (1) is important. For a given D/l^2, the larger the value of λ, the shorter the time required to establish the simple-exponential dependence on t. Equation (1) reduces to

$$\ln\left[(p - p_\infty)/(p_0 - p_\infty)\right]_e = \ln Z_1 - DQ_1^2 t / l^2 \tag{5}$$

From a graph of $\ln\left[(p - p_\infty)/(p_0 - p_\infty)\right]$ versus t, the value of Z_1 is determined by extrapolating to $t = 0$ using eq. (5). Q_1 can be calculated from eq. (2) by iterative procedures without using λ, and D then follows from

$$D = Sl^2/Q_1^2 \tag{6}$$

where S is the slope of the semilogarithmic plot. The value of λ may then be obtained from eq. (2) or eq. (4). If the gas and sorbent volumes are measured, the partition coefficient K can be

calculated by eq. (3) and the permeability P, by $P = KD$. A single experiment provides the transport constants P and D and the equilibrium quantity K.

Alternatively, λ may be obtained directly from experimental quantities by $\lambda = (p_\infty - p_i)/(p_0 - p_\infty)$. Using this value of λ, Q_1 is calculated by eq. (2) and K, by eq. (3). Then D and P may be evaluated as described.

TIME LAG

Time lags θ have been used to calculate D in both traditional permeation experiments[6] and permeation experiments from a finite volume.[7] Equation (5) may be rewritten as follows to define a time lag for sorption from a constant, finite volume:

$$\ln\left[(p - p_\infty)/(p_0 - p_\infty)\right]_e = \frac{-DQ_1^2}{l^2}(t - \theta) \tag{7}$$

where

$$\theta \equiv \frac{l^2}{DQ_1^2}\ln Z_1 \tag{8}$$

The value of θ will depend on λ as well as on D and l:

$$\underset{\lambda \to \infty}{\text{Lim}}\,\theta = -0.0851 l^2/D \tag{9}$$

and

$$\underset{\lambda \to 0}{\text{Lim}}\,\theta = -\infty \tag{10}$$

However, for systems with large λ, eq. (9) provides an approximate method for determining D, i.e., $D \simeq -0.0851 l^2/\theta$. The error reaches 5% only when λ is reduced to 4.2, i.e., $(p_0 - p_\infty)/p_0$ becomes as large as 0.19.

ALTERNATE FORM OF THE SOLUTION

When D is large, it may be difficult to measure p_0 with sufficient accuracy.[3] A form of the solution which avoids the necessity of measuring p_0 is obtained from eqs. (1) and (3):

$$\frac{p - p_\infty}{p_\infty - p_i} = \sum_{n=1}^{\infty}\frac{Z_n}{\lambda}\exp\left(-DQ_n^2 t/l^2\right) \tag{11}$$

which for large t reduces to the simple-exponential form

$$\ln\left[(p - p_\infty)/(p_\infty - p_i)\right]_e = \ln(Z_1/\lambda) - DQ_1^2 t/l^2 \tag{12}$$

The slope is identical to that of eq. (5), but the line is displaced along the ordinate axis by $-\ln\lambda$. The intercept at $t = 0$ is $\ln(Z_1/\lambda)$, where

$$\frac{Z_1}{\lambda} = \frac{2(1 + \lambda)}{1 + \lambda + \lambda^2 Q_1^2} = \frac{4Q_1\cos^2 Q_1 - 2\sin 2Q_1}{2Q_1 - \sin 2Q_1} \tag{13}$$

The intercept at $t = 0$ is used in eq. (13) to determine Q_1, and P, D, and K may be calculated as before. The time lag defined by eq. (12),

$$\theta \equiv \frac{l^2}{DQ_1^2}\ln(Z_1/\lambda) \tag{14}$$

depends strongly on λ as well as on D and l, and no limiting form is suitable for estimating D.

EXAMPLE

Carman and Haul[1] provide data for the sorption of butane by a Linde silica plug at $-10°C$: $l = 0.75$ cm, $p_i = 436.5$ torr, $p_0 = 516$ torr, $p_\infty = 460$ torr, $Z_1 = 0.489$, and $\lambda = 0.42$. Using a graph of $\log(p - p_\infty)_e$ versus t, they calculated $D = 1.2 \times 10^{-4}$ cm²/s, using the slope, intercept, and appropriate equations. A plot of $\log[(p - p_\infty)/(p_0 - p_\infty)]$ versus t is given as curve a in Figure
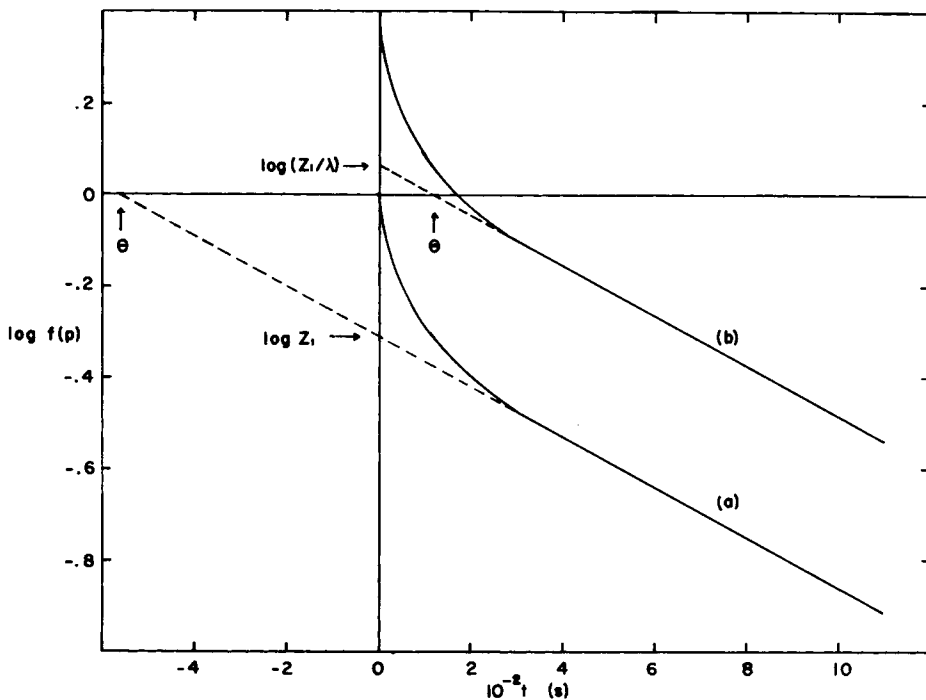
Fig. 1. Plot of log $f(p)$ vs. time: (a) $f(p) = [(p - p_\infty)/(p_0 - p_\infty)]$; (b) $f(p) = [(p - p_\infty)/(p_\infty - p_i)]$.

1. The limiting slope is 5.5×10^{-4} s^{-1} and $\theta = -5.6 \times 10^2$ s. Assuming that p_0 was not determined, we may plot log $[(p - p_\infty)/(p_\infty - p_i)]$ versus t (curve b in Fig. 1). In this case, the intercept yields $Z_1/\lambda = 1.16$ and $\theta = 1.2 \times 10^2$ s. Using eqs. (12) and (13), $\lambda = 0.41$ and $D = 1.2 \times 10^{-4}$ cm^2/s.

DISCUSSION

In comparison with the constant-pressure sorption procedure for determining diffusion coefficients of gases or vapors in polymers, the constant, finite-volume procedure provides a wider range of experimental conditions accessible in a simple apparatus.[1] The range extends to the use of high pressures when K is small.

The procedure also has apparent advantages over permeation methods. Fibers, spheres, softened or melted polymers, and fragile polymers may be employed, whereas a permeation procedure requires a strong membrane, hollow fiber, or tube.[3] The procedure may be used when D is small, i.e., when time lags are large, because θ is about half as large, at $\lambda \to \infty$, as for the permeation experiment.[5] In addition, the end effects and mounting problems in the permeation apparatus are avoided, and leaks may be minimized. Using a suitable value of λ, the procedure may also be used for systems with large D.

The procedure has the disadvantage that it is limited to systems with constant D. The introduction of the time lag opens the possibility of its use for systems with D a function of concentration, because it may be possible to obtain equations for the time lags without solving the differential equation.

References

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