Errors in Diffusivity as Deduced from Permeation Experiments Using the Time-Lag Technique

Transport through thin membranes is commonly described using diffusion theory as embodied in Fick's first and second laws:

$$J = -D \operatorname{grad} C \tag{1}$$

and

$$\operatorname{div}(\operatorname{grad} C) = \frac{\partial C}{\partial t} \tag{2}$$

where C is concentration, t is time, D is diffusivity, and J is flux. For the case of unidimensional flow of a penetrant through a finite solid with a concentration-independent diffusion coefficient, eq. (2) can be solved analytically[1] for the following boundary and initial conditions:

$$C(0,t) = C_1 \tag{3}$$

$$C(L,t) = C_2 \tag{4}$$

$$C(x,0) = C_0 \tag{5}$$

where x refers to position within a film of thickness L. That solution is

$$C = C_1 + (C_2 - C_1)\frac{x}{L} + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{C_2\cos n\pi - C_1}{n}\sin\frac{n\pi x}{L}\cdot\exp\left\{-Dn^2\pi^2\frac{t}{L^2}\right\}$$
$$+ 4\frac{C_0}{\pi}\sum_{m=0}^{\infty}\frac{1}{2m+1}\sin\frac{(2m+1)\pi x}{L}\cdot\exp\left\{-D(2m+1)^2\pi^2\frac{t}{L^2}\right\}. \tag{6}$$

The rate at which the diffusing substance emerges from a unit area of the membrane at face $x = 0$ is given by $D(\partial C/\partial x)\,x = 0$ and may be derived from eq. (6). Integrating that relationship with respect to time, one obtains Q_t, the amount of penetrant which has passed through a unit area of the membrane in time t:

$$Q_t = D(C_2 - C_1)\frac{t}{L} + \frac{2L}{\pi^2}\sum_{n=1}^{\infty}\frac{C_2\cos n\pi - C_1}{n^2}\left[1 - \exp\left\{-Dn^2\pi^2\frac{t}{L^2}\right\}\right]$$
$$+ 4\frac{C_0L}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\left(1 - \exp\left\{-D(2m+1)^2\pi^2\frac{t}{L^2}\right\}\right) \tag{7}$$

As $t \rightarrow \infty$, eq. (7) approaches a form linear in t:

$$Q_t = \frac{D}{L}\left[(C_2 - C_1)t + \frac{2L^2}{D\pi^2}\sum_{n=1}^{\infty}\left(\frac{C_2\cos n\pi - C_1}{n^2}\right) + \frac{4\,C_0L}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\right] \tag{8}$$

$$= \frac{D}{L}\left[(C_2 - C_1)t - \frac{C_2L^2}{6D} - \frac{C_1L^2}{3D} + \frac{C_0L^2}{2D}\right] \tag{9}$$

Therefore, if Q_t is plotted versus t, one obtains a curve that assumes straight line form at large t, as shown in Figure 1. This straight line has a slope $(D/L)(C_2 - C_1)$ and intersects the t-axis at

$$\theta_0 = \frac{1}{C_2 - C_1}\left[\frac{C_2L^2}{6D} + \frac{C_1L^2}{3D} - \frac{C_0L^2}{2D}\right]. \tag{10}$$

In many permeation experiments it is common to have $C_1 = C_0 = 0$, whereupon the asymptotic straight line can be defined by the t-axis intercept

$$\theta_0 = \frac{L^2}{6D} \tag{11}$$

and by the slope

$$d = \frac{DC_2}{L} \equiv \frac{P}{L} \tag{12}$$

where P is the permeability. Since in many cases it is rather difficult to measure C_2, eq. (11) provides a very convenient method for determining diffusivity from experimental data plotted as in Figure 1.

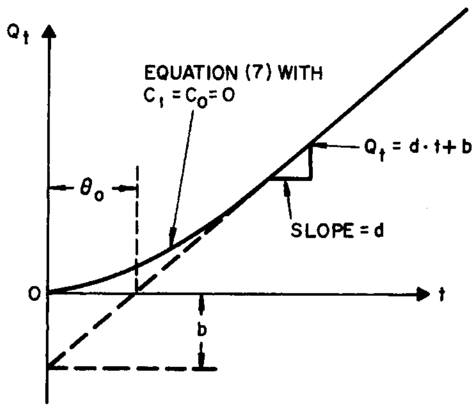

Fig. 1. Graphical representation of eq. (7) showing the amount of penetrant passing through a unit area of membrane surface in time t. For the case of $C_1 = C_0 = 0$, the asymptotic straight line of the figure is defined by the t-axis intercept, Θ_0, and by the slope, $d = P/L$, where P is permeability and L is film thickness.

The purpose of this communication is to point out that large errors in D can result from the application of this technique even though the experimental data exhibit a good fit to the straight line. Such a situation can lead to small errors in permeability P computed from the slope, but to much greater errors in D computed from the t-axis intercept.

The straight-line relationship between concentration and time shown in Figure 1 occurs only after t is sufficiently large that the exponential terms in eqs. (6) and (7) may be neglected:

$$\exp\left(-\frac{D\pi^2 t}{L^2}\right) \doteq 0. \tag{13}$$

This can be seen from eq. (7) plotted in dimensionless form in Figure 2 as $(\pi^2 Q_t)/(C_2 L)$ versus $(\pi^2 D_t)/L^2$ for the case $C_1 = C_0 = 0$. It is evident that experimental data will describe a straight line only for $t > t_0$, where t_0 is given by $(\pi^2 D t_0)/L^2 \doteq 3$. Since $\theta_0 = L^2/(6D)$, eq. (11), it follows that

$$t_0 \geq \frac{3L^2}{D\pi^2} = \frac{3}{\pi^2}\,6\theta_0 \doteq 2\theta_0, \tag{14}$$

that is, one should draw the straight line only through data taken after experimental times larger than about $2\theta_0$.

Assume then that the average time at which data are collected is about $4\theta_0$. Assume further that through these data is drawn the straight line

$$Q_t = (d \cdot t) + b. \tag{15}$$

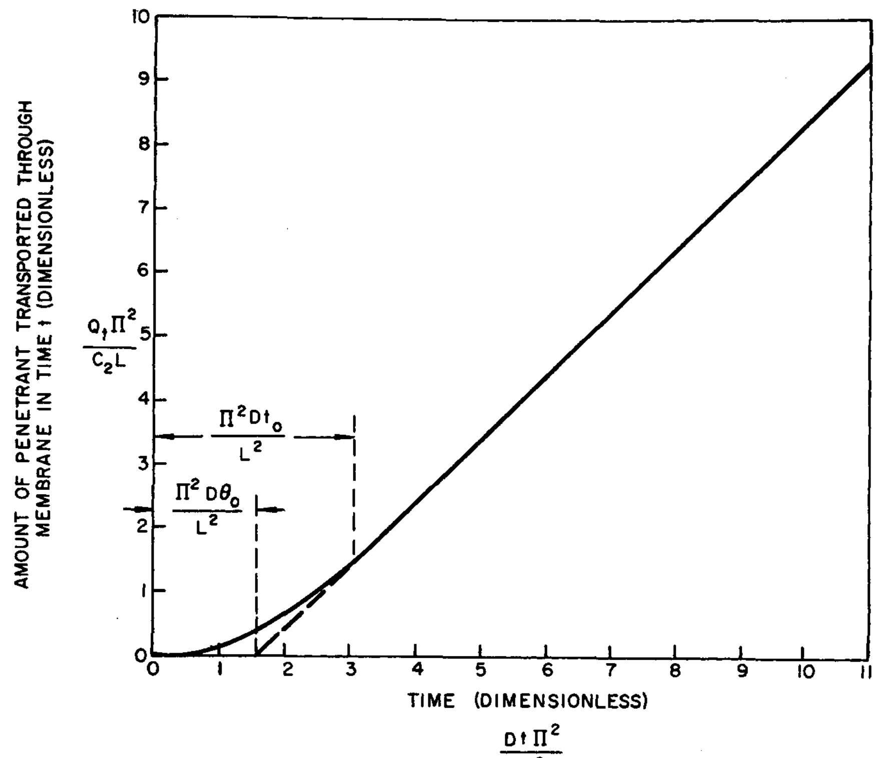

Fig. 2. Dimensionless plot of eq. (7) for the case $C_1 = C_0 = 0$. The figure is used to determine the time at which the exponential term of the equation is small enough that experimental data may be taken which describes the asymptotic straight line of Fig. 1.

Then, since the time lag, θ_0, is equal to $-b/d$, we have

$$\Delta\theta_0 = \left|\frac{\Delta b}{d}\right| + \left|\frac{b\Delta d}{d^2}\right| \tag{16}$$

or

$$\Delta\theta_0 = \left|\frac{\Delta b}{d}\right| + \left|\frac{\theta_0\Delta d}{d}\right| \tag{17}$$

A relationship between Δb and Δd can be developed by substituting $t = 4\theta_0$ in eq. (15) and differentiating with the assumption that $\Delta C = 0$, i.e., that errors in intercept arise only from errors in slope. The result is

$$\Delta b \doteq -4\theta_0\Delta d. \tag{18}$$

Substituting eq. (18) into eq. (17) and simplifying yields

$$\left|\frac{\Delta\theta_0}{\theta_0}\right| = 5\left|\frac{\Delta d}{d}\right|. \tag{19}$$

This means that the relative error in θ_0 is about five times larger than that in the slope; e.g., a 10% error in the slope will yield a 50% error in the delay time. Implicit in the development here is the assumption that the error in the t-axis intercept, $\Delta\theta_0$, results only from an error in slope of the straight line drawn through a data point at $4\theta_0$.

In experiments with thin membranes, data may, nevertheless, be taken at times much greater than $4\theta_0$. For example, the present authors[2-4] have made measurements with polyethylene films about 5 mils thick. Assuming for this case that $D \doteq 10^{-7}$ cm²/sec (an average of values taken from Long[5] and McCall[6]), one calculates a delay time for these films of about 5 min using eq. (11). A typical, convenient, average data collection time in these experiments was, however, about 2.5 hr. Thus, for those experiments, eq. (18) becomes

$$\Delta b = -30\theta_0 \Delta d \tag{18a}$$

and therefore

$$\left|\frac{\Delta\theta_0}{\theta_0}\right| = 31\left|\frac{\Delta d}{d}\right|. \tag{19a}$$

This order-of-magnitude relationship was confirmed by statistical analysis of the experimental data.[2] Errors in slope were about 3% at the 90 and 95% confidence levels whereas errors in intercept were between one and two orders of magnitude larger.

The mathematical and statistical problem of obtaining accurate time-lag values from permeation experiments appears to have received little attention in the literature. For example, negative time lags and anomalous time-lag behavior have been reported[7,8] with little further discussion of error.

Calculations based on the data extremes cited in one report,[7] i.e., a 1-min delay time for a 10-min experiment and an 8-hr delay time for a 48-hr experiment, indicate the relative error in the delay time to be about five times that of the slope. Assuming a modest error in these slopes of about 5%, an error of about 25% in the delay times, and therefore the diffusivities, might be expected based on the analysis given here.

It therefore appears that diffusivity data obtained from permeation experiments using the time-lag technique should be reexamined and used cautiously. The analysis developed here suggests that the error in D will always be several times larger than the error in P when such experiments are employed.

References

1. H. Daynes, *Proc. Roy. Soc. Ser. A*, **97**, 186 (1920).

2. R. D. Siegel, *Transport through Fully Swollen Polymer Membranes*, Ph.D. Thesis, Lehigh University, Bethlehem, Pennsylvania, October 1969.

3. R. D. Siegel and R. W. Coughlin, AIChE-PRIChE, (1970); *J. Appl. Polym. Sci.*, to be published.

4. R. D. Siegel and R. W. Coughlin, *Nature*, **226**, 938 (1970).

5. R. B. Long, *Ind. Eng. Chem., Fundam.*, **4**, 445 (1965).

6. D. W. McCall, *J. Polym. Sci.*, **26**, 151 (1957).

7. D. R. Paul and A. T. DiBenedetto, *J. Polym. Sci. C*, No. 10, 17 (1965).

8. V. Stannett, et al., *Permeability of Plastic Films and Coated Paper to Gases and Vapors*, TAPPI Monograph, Series No. 23, Technical Association of the Pulp and Paper Industry, New York, 1962.

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