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Review of Time Lag Permeation Technique as a Method for Characterisation of Porous Media and Membranes

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Abstract. The time lag permeation technique has proven to be an effective method for characterisation. Because of the simple nature of the permeation experiment, transport parameters can be directly obtained from experimental data hence avoiding the intensive mathematical treatment required by other techniques. The method has historically been applied to diffusion and adsorption in porous membranes and diffusion in polymer membranes. Since its origins in 1920, interest in the time lag method has expanded because of its value in characterising simple permeation processes and also complex systems of diffusion with simultaneous adsorption and surface diffusion. This review focuses on presenting the asymptotic solution of the mass balance diffusion equations and includes applications of time lag analysis, in order to give a critical and broad perspective of this method as a tool for characterisation. It includes much of the previously published literature in order to show that for most cases the asymptotic solution of the transport equations is simple, and for more complex cases that an analytical solution is possible hence avoiding cumbersome numerical techniques.

Keywords: time lag, porous media, membrane, Frisch's method, permeation

1. Introduction

There are several methods of characterisation employed for investigation of mass transport in solids. Among these are the 'integral permeation' methods, which are based on continuous monitoring of the amount of penetrant diffusing through a solid membrane into a closed vessel—similar to Fig. 1. These methods offer a simple, yet effective technique for determining the transport parameters characterising the solid-penetrant system.

The permeation process can be divided into its transient and steady state components. The transient or dynamic component can be represented by the 'time lag' parameter, obtained from the finite time difference observed between the time at which the penetrant enters the membrane and the time at which the flow rate of diffusing species into the closed volume reaches a steady state of permeation. This is shown in Fig. 2.

The time lag technique was originally conceived by Daynes, who in 1920, modelled the mass transport through a rubber membrane and obtained a solution for the observable time lag as a function of the diffusion coefficient. The mass balance and asymptotic solution was presented by Daynes only for slab geometry. Barrer (1939, 1940) modelled the mass balance to include slab, spherical and cylindrical geometries. Rogers et al. (1954) included a time lag expression for short times, useful for its application to relatively impermeable materials. The technique was further developed by Frisch (1957), who provided means for analytical evaluation of the asymptotic solution where numerical techniques would otherwise be required. Frisch's method is applicable to the mass balance for slab, spherical and cylindrical geometries. The work of Frisch coupled with that of Barrer, gives time lag analysis a great degree of flexibility and makes it favourable for a wide range of applications and currently the time lag permeation technique is being employed for

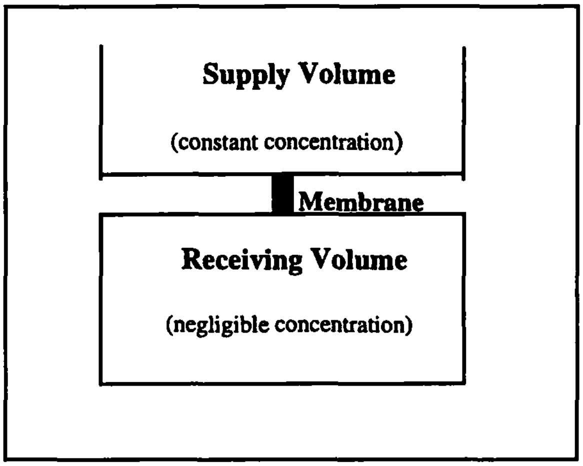


Figure 1. Schematic representation of 'time lag' apparatus.

characterisation of porous solids, polymers and metals (Table 1).

There are many variables which can affect the permeation process in solids, e.g., solid geometry and structure and the nature of the diffusant. For this reason, it is necessary to present the mass balance equations and corresponding asymptotic solutions for various diffusion mechanisms and also include simultaneous adsorption and surface diffusion. The texts by Barrer entitled "Diffusion In and Through Solids" and by Crank, "The Mathematics of Diffusion", provide the mass balance equations for several different cases together with the analytical solution for various boundary conditions and geometries. Due to the fact that diffusion of heat and mass are described by similar transport equations, heat conduction texts such as that of Carslaw and Jaeger (1947), serve to complement the previously mentioned texts.

2. Diffusion in Slab Porous Membrane

In order to model the permeation process through a porous membrane, we will firstly consider the slab porous medium of length L_c. Because the penetrating molecule is obstructed by the solid, the path is not straight along the medium coordinate, hence the diffusion path length will be greater than or at least equal to the length of the membrane. This gives rise to the tortuosity factor, τ, which has traditionally been defined as the ratio of length of the true molecular path (L) to the length of the displacement of the molecular path (L_c) along the medium coordinate.

$$\tau = \frac{L}{L_c} \tag{1}$$

The mass balance for the system relates the accumulation in the slab porous membrane to the change in flux at any time t, and at any point in the direction of diffusion, x:

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} \tag{2}$$

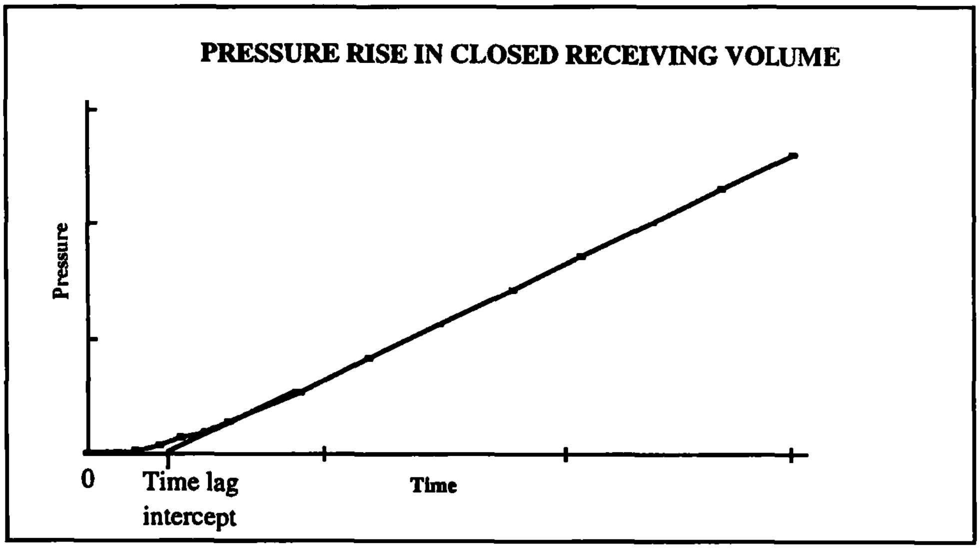


Figure 2. Pressure response indicating the 'time lag' before the establishment of steady state of flow into the receiving volume.

Table 1. Research conducted with time lag analysis.

Topic of investigation	Author
Origins of time lag analysis	Daynes (1920)
Time lag for permeation in cylindrical and spherical geometries	Barrer (1940, 1944)
Permeation behaviour at 'short times'	Rogers et al. (1954)
Permeation through porous adsorbents	Barrer and Grove (1951); Carman and Raal (1951); Barrer and Barrie (1952); Barrer (1953); Barrer and Strachan (1955); Ash and Grove (1960); Barrer and Gabor (1960); Ash et al. (1963); Aylmore and Barrer (1966); Ash et al. (1967, 1970, 1971, 1973, 1979); Barrie et al. (1975)
Permeation of gas mixtures	Barrer (1953); Ash et al. (1963, 1973, 1976); Barrer (1965); Aylmore and Barrer (1966);
Permeation through catalyst particles	Grachev et al. (1970); Gilbaro et al. (1970); Smith et al. (1975, 1976, 1979, 1983); Simon and Grzywna (1992); Moffat (1978)
Permeation with non Fickian diffusion	Frisch (1957, 1958, 1959, 1962); Pollack and Frisch (1959); Petropoulos and Roussis (1967, 1968, 1969); Tsimillis and Petropoulos (1972); Roussis and Petropoulos (1976, 1977)
Permeation through polymer membranes	Paul and DiBenedetto (1965); Crank and Park (1968); Paul (1969); Jenkins et al. (1970); Yasuda and Rosengren (1970); Tshudy and Von Frankenberg (1973); Vieth et al. (1975); Felder (1977); Barrer (1984); Alger et al. (1989); Nguyen et al. (1992,1994); Vasak and Broz (1993); Vieth (1991)
Permeation with serial and/or parallel paths	Chen and Rosenberger (1991)
Permeation with reaction	Ludolph et al. (1979)
Permeation in metallic solids	Refer to Barrer (1941)
Permeation through composite membranes	Jaeger (1950); Frisch (1957,1958,1959); Barrie et al. (1963); Ash et al. (1963,1965); Frisch et al. (1979)

where C is the concentration of diffusant in the membrane (mole/m^3 of membrane), J is the flux of diffusant (mole/m^2 of membrane.sec), and x is the coordinate along the porous medium. If Fick's Law applies to the diffusion process, the flux is linearly related to the concentration gradient.

$$J = -D\frac{\partial C}{\partial x} \quad \left[\frac{\text{mole}}{\text{m}^2 \text{ of membrane.sec}}\right] \tag{3}$$

where the constant D is defined as the diffusion coefficient. The value of the diffusion coefficient is specific for a defined fluid and material and is known to be concentration dependent if the adsorbed phase concentration is high. If this is the case, the solution of Eq. (2) for the concentration profile would require numerical methods. However, if the Knudsen mechanism alone is controlling, the diffusion coefficient is constant, denoted as D_K and Eq. (2) then becomes

$$\frac{\partial C}{\partial t} = D_K\frac{\partial^2 C}{\partial x^2} \tag{4}$$

The Knudsen diffusion mechanism applies at low pressures, hence the concentration of the penetrating species must be kept low in order to allow the simplifying assumption of constant diffusion coefficient to be made. In fact, for Knudsen diffusion in a porous solid with capillary channels of average radius r_p, the following criterion must be satisfied (Levenspiel, 1984):

$$P \cdot r_p < 0.005 \text{ Pa.m} \tag{5}$$

where P is the applied fluid pressure.

A porous solid of length L_c can be used as a means of separating two volumes having differing concentrations. The mass balance of Eq. (4) can be solved, subject to some specified boundary conditions, for the expected concentration rise along the diffusion path and into the outgoing volume as a function of the diffusion parameters. The outgoing concentration can be measured as a function of time, from which the diffusion parameters characterising the system can be derived.

2.1. Diffusion into a Medium Initially Purged of Diffusing Species

If the membrane is initially free of the diffusing species, the initial and boundary conditions for the system can be expressed by Eqs. (6):

$$C(x,0) = 0: \tag{6a}$$

$$C(0,t) = C_0; \tag{6b}$$

$$C(L,t) = C_L \approx 0; \tag{6c}$$

If the upstream concentration, C_0, remains constant during the course of the diffusion process and the downstream concentration is negligible compared to the upstream pressure (that is $C_L \approx 0$), the solution of Eq. (4) subject to the boundary conditions of (6), by either Laplace transform or separation of variables is given below (Barrer, 1939).

$$C = C_0\left(1 - \frac{x}{L}\right) + \frac{2C_0}{\pi} \times \sum_{n=1}^{\infty} \frac{1}{n}\sin\left(\frac{n\pi x}{L}\right)\exp\left(-\frac{D_K n^2 \pi^2 t}{L^2}\right) \tag{7}$$

The boundary conditions can be physically realised by using extremely large volumes on both upstream and downstream. In this case, the number of moles transmitted from upstream to downstream causes only very small changes in concentration (in the order of a few percent). With sensitive measurement these small changes can be easily measured with time.

The diffusive flux (J) can be obtained from the concentration profile of Eq. (7) by application of Fick's law (Eq. (3)). This is given as:

$$J(x,t) = \frac{D_K C_0}{L} + \frac{2D_K C_0}{L} \times \sum_{n=1}^{\infty} \cos\frac{n\pi x}{L}\exp\left(\frac{-n^2\pi^2 D_K t}{L^2}\right) \tag{8}$$

The second term in the flux equation represents the transient contribution and the first term is the steady state portion of the flux. It is a function of time and displacement in the direction of diffusion and hence can be solved for the fluxes entering and leaving the membrane ($x = 0$ and $x = L$, respectively).

2.1.1. *Dynamic Concentration Change at the Downstream Face of the Membrane.* The expression for flux at the end of the membrane can be obtained from Eq. (8) by setting $x = L$:

$$J_L(t) = \frac{D_K C_0}{L} + \frac{2D_K C_0}{L} \times \sum_{n=1}^{\infty} \cos(n\pi)\exp\left(\frac{-n^2\pi^2 D_K t}{L^2}\right) \tag{9}$$

yielding a time dependent flux equation and the convergence of the series is slow for 'short times' (low values of time). The short time solution obtained by Rogers et al. (1954) and presented below removes the problem of slow convergence for small values of time.

2.1.2. *Short Time Solution.* A solution to the mass balance of Eq. (4) was developed by Rogers et al. (1954) for the transient stage of diffusion, before the establishment of steady state of flow into the outgoing volume. This solution is useful for application to relatively impermeable materials, which require the short time solution because of the unreasonable length of time required for the diffusion process to reach steady state. By obtaining the Laplace transform solution of the mass balance Eq. (4), taking its Taylor series limit as $s \to \infty$, and then inverting the result back to the time domain yields the following solution for the flux at the exit face of the membrane

$$J_L(t) = 2C_0\sqrt{\frac{D_K}{\pi t}}\sum_{n=0}^{\infty}\exp\left(\frac{-(2n+1)^2L^2}{4D_K t}\right) \tag{10}$$

The terms of the series in Eq. (10) are small relative to the first term, hence by keeping only the first term, we have the following useful short time solution:

$$\lim_{t\to 0} J_L(t) = 2C_0\sqrt{\frac{D_K}{\pi t}}\exp\left(\frac{-L^2}{4D_K t}\right) \tag{11}$$

The flux at the exit can be readily measured experimentally. Thus, by plotting $\ln(J_L\sqrt{t})$ versus t^{-1} we would obtain a straight line having the following slope and intercept

$$S_{\text{short}} = \frac{-L^2}{4D_K} \tag{12a}$$

$$I_{\text{short}} = \ln\left(2C_0\sqrt{\frac{D_K}{\pi}}\right) \tag{12b}$$

which can be utilised to determine the tortuosity of the diffusion path and the diffusion coefficient. Rogers et al. (1954) suggested that the upper time limit for application of Eq. (11) should be 2.7 times the time lag (the definition of time lag is presented in 2.1.1.3).

We have established a pressure relation with time for the outgoing volume subject to the restrictions:

1) the pressure in this volume is always insignificant compared to that of the upstream.
2) the upstream pressure is constant throughout the experiment.
3) the time scale of the experiment is short (short time condition).

To remove the time scale restriction of the solution obtained by Rogers et al. (1954) we should examine the general solution.

*2.1.3. **General Solution.*** Integration of the general flux equation, Eq. (9), with respect to time, yields the amount permeating out of the pellet (Q_L):

$$\begin{aligned} Q_L(t) &= -A\int_0^t J_L(t)\,dt \\ &= \frac{AD_K C_0}{L}\left[t - \frac{L^2}{6D_K} + \frac{2L^2}{\pi^2 D_K}\right. \\ &\quad\left.\times\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n^2}\exp\left(-\frac{D_K n^2\pi^2 t}{L^2}\right)\right] \end{aligned} \quad (13)$$

The outgoing pressure then, subject only to the boundary condition restrictions, is obtained from the amount permeating through the end of the pellet (Eq. (13)):

$$\begin{aligned} P_L &= \frac{AD_K P_0}{VL}\left[t - \frac{L^2}{6D_K} + \frac{2L^2}{\pi^2 D_K}\right. \\ &\quad\left.\times\sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n^2}\exp\left(-\frac{D_K n^2\pi^2 t}{L^2}\right)\right] \end{aligned} \quad (14)$$

where A is the cross-sectional area available for gas phase penetration perpendicular to the direction of diffusion and V is the volume of the receiving reservoir. For the slab porous membrane, the cross-sectional area for diffusion is related to the measurable cross-sectional (A_c) through the porosity (ε), $A = \varepsilon A_c$.

The solution for downstream pressure with time given by Eq. (14) is not of useful form for analysis of experimental data. If we examine the asymptotic solution at large times a useful working relation will be revealed.

*2.1.4. **Steady State Solution.*** The steady state asymptote of Eq. (14) is found by taking the limit as $t \to \infty$, in which case the transient summation terms are reduced to zero and the downstream pressure rise is given by:

$$\lim_{t\to\infty} P_L(t) = \frac{AD_K P_0}{VL}\left(t - \frac{L^2}{6D_K}\right) \quad (15)$$

Hence the plot of pressure rise versus time will approach a linear asymptote, indicated in Fig. 2, if the downstream pressure remains negligible compared to the upstream pressure (boundary condition 6c). The linear asymptote has gradient denoted as S_∞, and the intercept on the time axis of such a plot is called hereafter the time lag and is denoted as t_{lag}:

$$S_\infty = \frac{AD_K P_0}{VL} \quad (16a)$$

$$t_{\text{lag}} = \frac{L^2}{6D_K} \quad (16b)$$

Membrane thickness (L_c) is known and can be related to the diffusion path length (L), through the tortuosity factor. From the 'time lag' diffusion experiment, we can obtain the gradient of the curve of outgoing pressure against time, S_∞ and the time lag intercept, t_{lag}. These can be used to evaluate the diffusion coefficient and tortuosity, noting that the product of the steady state slope and the time lag is independent of the diffusivity.

$$S_\infty \times t_{\text{lag}} = \frac{AP_0}{V}L \quad (17)$$

The Knudsen diffusion coefficient has been found to be related to the average pore size (r_p) through the Knudsen diffusion equation:

$$D_K = \frac{2r_p}{3}\sqrt{\frac{8RT}{\pi M}} \quad (18)$$

where T is the absolute temperature and M is the molecular weight of diffusant. Not only can we obtain information concerning the diffusion properties of a fluid through a particular solid (tortuosity), but we can also characterise the average pore size. Barrer (1953) used this approach to characterise porous glass.

We have noted in Section 2.1.2 that a plot of $\ln(J_L\sqrt{t})$ versus t^{-1} yields a straight line of slope and intercept given by (12a) and (12b). At steady state, we have shown that S_∞ and t_{lag} are given by Eqs. (16a) and (16b). If the diffusion coefficient is constant over the time period of approach to steady state, then

$$\frac{t_{\text{lag}}}{S_{\text{short}}} = -\frac{2}{3} \quad (19)$$

This becomes a convenient test for the presence of functional dependence of the diffusion coefficient with time.

Now that we have obtained an expression for the flowrate through the pellet, we can easily estimate the appropriate volume sizes needed in order to comply with the prescribed boundary conditions. Boundary condition (6b) requires the upstream concentration to be constant. If we assign the relative change in upstream concentration to be no greater than 1% and conduct the experiment for a period of 6 times the time lag, assuming for the worst case scenario that the steady state flowrate is reached instantly, then we find that the upstream volume (V_0) must be greater than 200 times the product of the cross-sectional area and length, i.e., $V_0 > 200$ AL. Similarly, the downstream volume (V) restriction is given by, $V > 100$ AL.

2.1.5. Concentration Change at the Upstream Face of the Membrane. In many instances it may be more convenient to measure the dynamic rate of the amount of diffusing species entering the pellet rather than the amount permeating and exiting the pellet. For example, to maintain the downstream boundary condition of 6c, the experimental rig must have the ability to hold static vacuum. Experimentally this is a difficult requirement to meet but holding dynamic vacuum by means of an operating vacuum pump can keep the pressure continually low. The disadvantage is that the ability to measure the amount exiting is lost. However if the amount entering is measured, characterisation can still be achieved through analysis of the inlet time lag and steady state slope.

To obtain the expression for the inlet time lag we must evaluate the flux given by Eq. (8) at $x = 0$ and then integrating the result with respect to time, we obtain the amount diffusing into the membrane:

$$\begin{aligned} Q_0(t) &= A\int_0^t J_0(t)\,dt \\ &= \frac{AD_K C_0}{L}\left[t + \frac{L^2}{3D_K} - \frac{2L^2}{\pi^2 D_K}\sum_{n=1}^{\infty}\frac{1}{n^2}\right. \\ &\qquad \left.\times \exp\left(-\frac{D_K n^2\pi^2 t}{L^2}\right)\right] \end{aligned} \tag{20}$$

The pressure variation in the upstream volume is obtained from the amount diffusing into the membrane and is given by Eq. (21).

$$\begin{aligned} &P_0(0) - p_0(t) \\ &\quad = \frac{AD_K P_0}{VL}\left[t + \frac{L^2}{3D_K} - \frac{2L^2}{\pi^2 D_K}\right. \\ &\qquad \left.\times \sum_{n=1}^{\infty}\frac{-1}{n^2}\exp\left(-\frac{D_K n^2\pi^2 t}{L^2}\right)\right] \end{aligned} \tag{21}$$

where $P_0(0)$ is the initial upstream pressure and $P_0(t)$ is the upstream pressure at time t. By taking the limit as time increases, the time lag and steady state slope are obtained from the asymptote.

$$S_\infty = \frac{AD_K P_0}{VL} \tag{22a}$$

$$t_{\text{lag}} = -\frac{L^2}{3D_K} \tag{22b}$$

as shown in Fig. 3.

2.2. *Diffusion into a Medium Initially Containing Diffusing Species*

To extend the analysis from Section 2.1 to the case where the membrane initially contains a known amount of diffusing species and its initial distribution across the membrane is uniform, we must alter the initial conditions.

2.2.1. Insignificant Downstream Concentration. The boundary conditions can be constructed to include a constant initial concentration in the membrane, exposed to a constant upstream concentration and negligible downstream concentration as indicated by Eqs. (23).

$C(x, 0) = C_i$; membrane initially has concentration C_i of diffusing species (23a)

$C(0, t) = C_0$; upstream pressure is constant (23b)

$C(L, t) \approx 0$; downstream pressure is negligible in comparison with the upstream (23c)

The solution of the mass balance Eq. (4), with these boundary conditions (23), is

$$\begin{aligned} C &= C_0\left(1 - \frac{x}{L}\right) - \frac{2C_0}{\pi} \\ &\quad \times \sum_{n=1}^{\infty}\frac{(1+\alpha)\cos(n\pi) - \alpha}{n} \\ &\quad \times \sin\left(\frac{n\pi x}{L}\right)\exp\left(-\frac{D_K n^2\pi^2 t}{L^2}\right) \end{aligned} \tag{24}$$

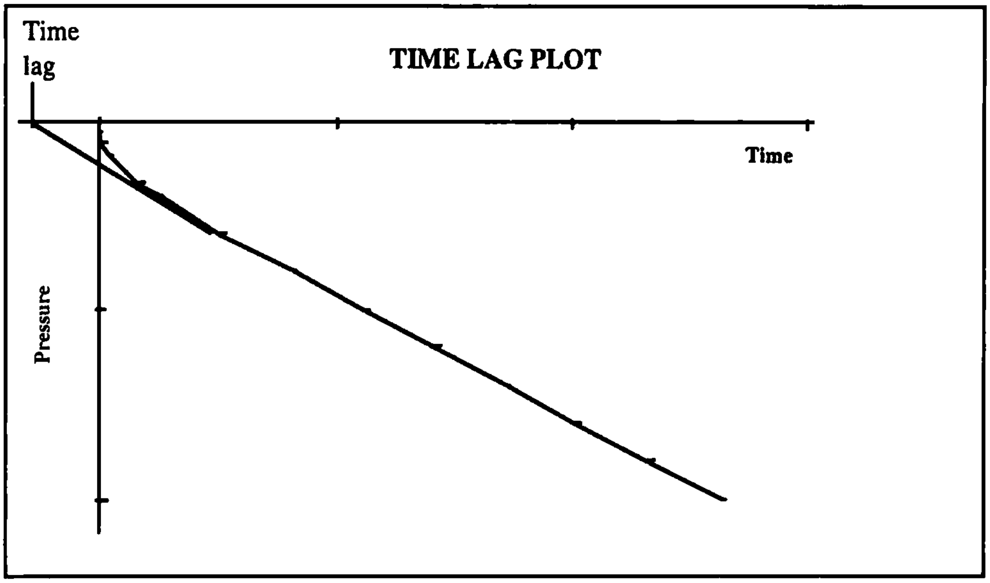


Figure 3. The pressure response in the upstream volume.

where α is defined as:

$$\alpha = \frac{C_i - C_0}{C_0} \tag{25}$$

The flux at any point along the axis of diffusion, is a function of time and displacement in the x direction and can be obtained by applying Fick's law.

$$\begin{aligned} J(x,t) = {} & \frac{D_K C_0}{L} + \frac{2D_K C_0}{L} \\ & \times \sum_{n=1}^{\infty} [(1+\alpha)\cos(n\pi) - \alpha] \\ & \times \cos\frac{n\pi x}{L} \exp\left(\frac{-n^2\pi^2 D_K t}{L^2}\right) \end{aligned} \tag{26}$$

We can obtain expressions for flux at the inlet and outlet, and by integrating with respect to time we can obtain the amounts entering and leaving the membrane as a function of time given as

$$\begin{aligned} Q_0(t) = {} & \frac{A D_K C_0}{L} \\ & \times \left[t - \alpha\frac{L^2}{3D_K} - (1+\alpha)\frac{L^2}{6D_K} - \frac{2L^2}{\pi^2 D_K}\right. \\ & \times \sum_{n=1}^{\infty} \frac{[(1+\alpha)\cos(n\pi) - \alpha]}{n^2} \\ & \left. \times \exp\left(-\frac{D_K n^2 \pi^2 t}{L^2}\right)\right] \end{aligned} \tag{27a}$$

$$\begin{aligned} Q_L(t) = {} & \frac{A D_K C_0}{L} \\ & \times \left[t + \alpha\frac{L^2}{6D_K} + (1+\alpha)\frac{L^2}{3D_K} - \frac{2L^2}{\pi^2 D_K}\right. \\ & \times \sum_{n=1}^{\infty} \frac{[(1+\alpha)\cos(n\pi) - \alpha]}{n^2} \\ & \left. \times \exp\left(-\frac{D_K n^2 \pi^2 t}{L^2}\right)\right] \end{aligned} \tag{27b}$$

respectively. The time lags obtained from taking the limit of Eqs. (27) as $t \to \infty$, are:

$$(t_{\text{lag}})_{\text{inlet}} = \alpha\frac{L^2}{3D_K} + (1+\alpha)\frac{L^2}{6D_K} \tag{28a}$$

$$(t_{\text{lag}})_{\text{exit}} = \alpha\frac{L^2}{6D_K} + (1+\alpha)\frac{L^2}{3D_K} \tag{28b}$$

If the membrane is initially clean (that is $C_i = 0$, hence $\alpha = -1$), Eqs. (28) will become:

$$(t_{\text{lag}})_{\text{inlet}} = -\frac{L^2}{3D_K} \tag{29a}$$

$$(t_{\text{lag}})_{\text{exit}} = \frac{L^2}{6D_K} \tag{29b}$$

If the membrane initially contains diffusant of concentration C_0 (that is $\alpha = 0$), we have

$$(t_{\text{lag}})_{\text{inlet}} = \frac{L^2}{6D_K} \tag{30a}$$

$$(t_{\text{lag}})_{\text{exit}} = -\frac{L^2}{3D_K} \tag{30b}$$

The analysis of Section 2.2.1 assumed that the downstream concentration was insignificant (boundary condition 23c). If the concentration rises to approach that of the upstream, the driving force for permeation reduces, we break the steady state linear pressure rise and approach an equilibrium concentration throughout the system. This is the case if the permeation rate is high relative to the downstream volume (see Section 2.1.4). In order to analyse data obtained from an experiment of this kind, we must find an asymptotic solution to the diffusion equations with general boundary conditions.

2.2.2. Significant Downstream Concentration. If the downstream concentration is held effectively constant with time (again by using a large volume), then the mass balance can be solved with the following boundary conditions:

$C(x,0) = C_i$; membrane initially contains concentration C_i of diffusant (31a)

$C(0,t) = C_0$; upstream pressure is constant (31b)

$C(L,t) = C_1$; downstream pressure is constant (31c)

The asymptotic solution of mass balance Eq. (4) with these boundary conditions (31) is given by Barrer (1940):

$$\begin{aligned} C &= C_0 + (C_1 - C_0)\left(\frac{x}{L}\right) - \frac{2}{\pi} \\ &\quad \times \sum_{n=1}^{\infty} \frac{C_1\cos(n\pi) - C_0}{n} \sin\left(\frac{n\pi x}{L}\right) \\ &\quad \times \exp\left(-\frac{D_K n^2\pi^2 t}{L^2}\right) + \frac{4C_i}{\pi} \\ &\quad \times \sum_{m=1}^{\infty} \frac{1}{(2m+1)} \sin\left[\frac{(2m+1)\pi x}{L}\right] \\ &\quad \times \exp\left[-\frac{D_K(2m+1)^2\pi^2 t}{L^2}\right] \end{aligned} \tag{32}$$

The flux at any point along the axis of diffusion, obtained from Fick's Law (Eq. (3)):

$$\begin{aligned} J(x,t) &= \frac{-D_K(C_1 - C_0)}{L} + \frac{2D_K C_0}{L} \\ &\quad \times \sum_{n=1}^{\infty} [C_1\cos(n\pi) - C_0] \\ &\quad \times \cos\left(\frac{n\pi x}{L}\right) \exp\left(\frac{-n^2\pi^2 D_K t}{L^2}\right) \\ &\quad + \frac{4D_K C_i}{L} \sum_{n=1}^{\infty} \cos\left(\frac{(2m+1)\pi x}{L}\right) \\ &\quad \times \exp\left[\frac{-(2m+1)^2\pi^2 D_K t}{L^2}\right] \end{aligned} \tag{33}$$

By integrating the flux equations at inlet and outlet with respect to time, we can obtain the amounts entering and leaving the membrane as a function of time. The time lag at the inlet and exit of the membrane, obtained from the time axis intercept of the long time asymptote is given by Eqs. (34) and (35):

$$(t_{\text{lag}})_{\text{inlet}} = \frac{L^2}{(C_1 - C_0)D_K}\left[\frac{C_1}{6} + \frac{C_0}{3} - \frac{C_i}{2}\right] \tag{34}$$

$$(t_{\text{lag}})_{\text{exit}} = \frac{L^2}{(C_1 - C_0)D_K}\left[\frac{C_1}{3} - \frac{C_0}{6} + \frac{C_i}{2}\right] \tag{35}$$

If downstream concentration is negligible ($C_1 = 0$) the time lag expressions reduce to:

$$(t_{\text{lag}})_{\text{inlet}} = \frac{L^2}{D_K}\left[\frac{C_i}{2C_0} - \frac{1}{3}\right] \tag{36}$$

$$(t_{\text{lag}})_{\text{exit}} = \frac{L^2}{D_K}\left[\frac{C_i}{2C_0} - \frac{1}{3}\right] \tag{37}$$

which are essentially the same as Eqs. (28) in Section 2.2.1. If the membrane is also initially clean ($C_i = 0$), then the time lag expressions simplify to:

$$(t_{\text{lag}})_{\text{inlet}} = -\frac{L^2}{3D_K} \tag{38}$$

$$(t_{\text{lag}})_{\text{exit}} = \frac{L^2}{6D_K} \tag{39}$$

as we have shown previously in Section 2.1.

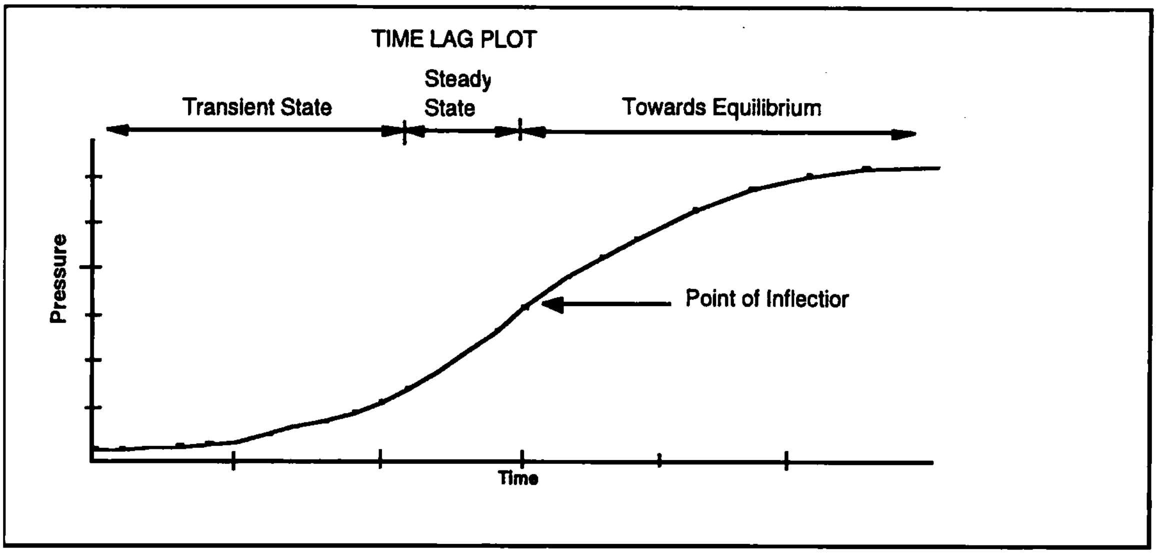


Figure 4. Pressure response in the downstream volume with approach to equilibrium.

*2.2.3. **Time Dependent Downstream Concentration.*** The boundary conditions of the previous section demand constant upstream and downstream concentrations during the experiment. The resulting solution for the amount permeated out of the pellet as a function of time requires identification of a linear asymptote. In order to ensure that the permeation has reached a constant rate, the experiment should be run for a long period of time and the slopes of the local asymptotes at large times compared. If the volume is too small to keep the concentration low over this period of time (in compliance with the previously presented boundary conditions) and hence maintain a constant permeation rate with time, then the pressure rise will approach that shown in Fig. 4. However, the diffusion coefficient can still be readily obtained from such data.

Nguyen et al. (1992) consider this problem and obtain an asymptotic solution based on the boundary conditions which allow the downstream concentration to be of significant value in comparison to the upstream and vary with time but the upstream must be held constant with time.

$$C(0,t) = C_0 \tag{40a}$$

$$C(L,t) = C(t) \tag{40b}$$

with the initial conditions

$$C_i = C_0 \tag{40c}$$

and a mass balance out of the pellet and into the downstream volume is needed to determine the downstream concentration

$$D_K \frac{\partial^2 C}{\partial x^2}\bigg|_L + \frac{V}{A}\frac{\partial C}{\partial t}\bigg|_L = 0 \tag{40d}$$

Nguyen et al. (1992) propose that the solution for the downstream concentration should take the following form:

$$C_L = C_0\left[1 - \sum_i a_i \exp(-\beta_i t)\right] \tag{41}$$

The asymptotic solution for this case differs from what we have seen previously. Instead of an eventual linear rise in pressure with time because of the constant driving force, we now have a non-linear asymptote because of the dynamic pressure changes. This asymptote is given by Nguyen et al. (1992) as

$$\lim_{t\to\infty} Q_L = AC_0 aL\left\{[1-\exp(-\beta t)] \times \left(\frac{D_K}{\beta L^2} - \frac{1}{3}\right) - \frac{1}{6}\right\} \tag{42}$$

where the parameter a is given by

$$a = 1 - \frac{P_L(0)}{P_0} \tag{43}$$

and the parameter β can be found graphically from the slope of the plot of $\ln(\Delta P)$ versus time,

$$\beta = \frac{\partial \ln(\Delta P)}{\partial t} \tag{44}$$

and hence the diffusion coefficient can be determined by the fit of Eq. (42) to the data. The procedure of Nguyen et al., is to extrapolate this asymptote back to the time axis ensuring that this line is tangential to the point of inflection marked in Fig. 4. The intercept is a function of the diffusion coefficient also and hence can be calculated from the transient data by using the relation

$$D_K = \beta L^2\left\{\frac{1}{6}+\frac{1}{3}[1-\exp(-\beta t_{\text{lag}})]\right\} \times [1-\exp(-\beta t_{\text{lag}})]^{-1} \qquad (45)$$

If the pressure difference is constant with time and the downstream pressure is negligible as we have assumed in our previous analysis then $\beta \to 0$, $\alpha = 1$ and the time lag reduces to the previously obtained relation of Eq. (16b).

2.3. *Permeation Time Lag by the Method of Frisch*

The analysis of Section 2 made the assumptions that the membrane had uniform properties throughout its cross-section and length and that the fluid phase diffusion was controlled by the Knudsen mechanism. This enabled the simplification of constant diffusion coefficient to be made. In some systems, these assumptions will not apply and the diffusion coefficient may be a function of concentration, displacement in the direction of diffusion, or time. Viscous diffusion mechanism, non-Henry law adsorption onto the membrane, the presence of blind pores or a structurally non-uniform membrane will all produce a variable observed diffusion coefficient. If this is the case, the mass balance must be solved numerically for the concentration profile through the membrane. In 1957 however, Frisch obtained an asymptotic solution without solving the diffusion equation explicitly for the concentration distribution.

2.3.1. Concentration Dependent Diffusion into Medium Initially Purged of Diffusing Species. Integration with respect to x, of the basic mass balance represented by Eq. (2) (subject to the boundary conditions given in Eqs. (6)), from any point x to L yields

$$\int_x^L \frac{\partial C(x,t)}{\partial t}dx = J(x,t) - J_L(t) \qquad (46)$$

Integrating again, with respect to x, from 0 to L and noting that $J_L(t)$ is not a function of x, we get

$$\int_0^L\int_x^L \frac{\partial C(z,t)}{\partial t}dzdx = \int_0^L J(x,t)dx - J_L(t)\cdot L \qquad (47)$$

Solving this equation for the flux at the exit $J_L(t)$, we have

$$J_L(t) = \frac{1}{L}\left[\int_0^L J(x,t)dx - \int_0^L\int_x^L \frac{\partial C(z,t)}{\partial t}dzdx\right] \qquad (48)$$

Integrating with respect to time up to time t gives

$$\int_0^t J_L(t)dt = \frac{1}{L}\left[\int_0^t\int_0^L J(x,t)dxdt - \int_0^L\int_x^L C(z,t)dzdx\right] \qquad (49)$$

in which we have used the initial condition (6a). Noting that $\int_0^t J_L dt = \frac{Q_L}{A}$ we can rearrange Eq. (49) to obtain an expression for the amount permeating at the exit (Q_L). If we take the limit as $t \to \infty$, we obtain

$$Q_{L,\infty} = \frac{A}{L}\left[t\cdot\int_0^L J_\infty(x)dx - \int_0^L\int_x^L C_\infty(z)dzdx\right] \qquad (50)$$

Integration of the double integral by parts and factorisation yields

$$Q_{L,\infty} = \frac{A}{L}\left[\int_0^L J_\infty(x)dx\right]\left(t - \frac{\int_0^L xC_\infty dx}{\int_0^L J_\infty dx}\right) \qquad (51)$$

Equation (51) represents a linear relation, the time intercept of which is represented by

$$t_{\text{lag}} = \frac{\int_0^L xC_\infty dx}{\int_0^L J_\infty dx} \qquad (52)$$

This is the most general time lag relation and assumes nothing about the diffusion coefficient. The only constraint for the validity of Eq. (52) is that the conditions given in Eqs. (6) are satisfied. A simplification can be made if we assume that the diffusion coefficient is a function of concentration only. Integration of Fick's Eq. (3) yields

$$\int_0^L J_\infty dx = \int_0^{C_0} D\,dC_\infty \qquad (53)$$

Substituting Eq. (53) into (52), allows the time lag to become

$$t_{\text{lag}} = \frac{\int_0^L xC_\infty dx}{\int_0^{C_0} D\,dC_\infty} \qquad (54)$$

The steady state concentration profile (C_∞) can be obtained as a function of x simply by solution of the diffusion equation at steady state (where the time dependent terms are removed). If the diffusion coefficient is independent of the upstream concentration (as it should be for Knudsen permeation alone or with Henry law adsorption) as we assumed in the previous analysis, then the steady state concentration profile is linear (Eq. (7) neglecting transient terms) and Eq. (54) reduces to our previously obtained Eq. (16b).

Further manipulation of Eq. (54) yields the final form of the time lag equation presented by Frisch (1957)

$$t_{\text{lag}} = \frac{L^2 \int_0^{C_0} wD(w) \int_w^{C_0} wD(u)du\,dw}{\left[\int_0^{C_0} D(u)du\right]^3} \qquad (55)$$

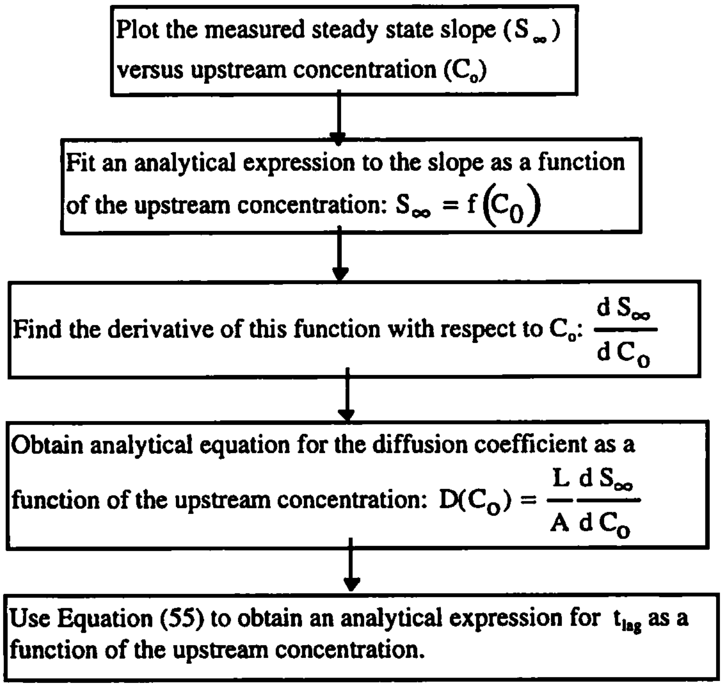
where we have removed the explicit dependence on x and u and w are simply dummy variables.

*2.3.2. **Practical Method for Application.*** Ash et al. (1963) have made practical use of Frisch's technique for investigating anomalies with the concentration dependence of the observed steady state slope and then predicting the corresponding dependence of the time lag. Figure 5 contains the procedure for this and involves a series of differentiation and integrations needed in order to convert the 'integral' diffusion coefficient obtained from the steady state slope measurement to a 'differential' one needed for evaluation of Eq. (55).

This procedure has the advantage of providing an analytical means for prediction of the time lag but gives little physical insight into the data as the method is empirical.

As stated earlier, the Frisch technique is useful for application to membranes containing 'dead end' pores or structurally heterogeneous solid, or for the cases of diffusion by viscous mechanism or with non linear adsorption. These factors are considered in the following sections.

*2.3.3. **Membrane Containing Blind Pores.*** 'Dead end' or 'blind' pores are small capillaries open to the main flow channel but closed at the opposite end. Diffusion into these capillaries can result in additional accumulation of diffusant within the membrane. To model such a system we could consider the blind pore volume as a transient sink for the permeating fluid as was considered by Goodknight and Fatt (1961). Ash et al. (1967) propose that for some solids the blind pore network is not truly a closed system, because it



Plot the measured steady state slope (S_∞) versus upstream concentration (C_0)

Fit an analytical expression to the slope as a function of the upstream concentration: $S_\infty = f(C_0)$

Find the derivative of this function with respect to C_0: $\frac{dS_\infty}{dC_0}$

Obtain analytical equation for the diffusion coefficient as a function of the upstream concentration: $D(C_0) = \frac{L}{A}\frac{dS_\infty}{dC_0}$

Use Equation (55) to obtain an analytical expression for t_{lag} as a function of the upstream concentration.

Figure 5. Algorithm for the prediction of the time lag as a function of upstream concentration requiring only the measurement of the steady state slope.

allows restricted passage of molecules to contribute to the steady state flux. The model of Goodknight and Fatt has received support from Roussis and Petropoulos (1977). The mass balance could be described by:

$$\frac{\partial C}{\partial t} + \frac{\varepsilon_B}{\varepsilon}\frac{\partial C_B}{\partial t} = D_k \frac{\partial^2 C}{\partial x^2} \tag{56a}$$

where C_B is the concentration of the fluid phase in the blind pore, ε_B is the porosity attributable to blind pores and ε is the porosity attributable to the void volume which forms the main flow channel.

To relate the concentration in the through flowing pores to the concentration in the blind pore we might assume that the filling obeys the following linear driving force model:

$$\frac{\partial C_B}{\partial t} = h(C - C_B) \tag{56b}$$

where h is a parameter representing the mass transfer resistance into the blind pore volume. An asymptotic solution is obtained by the method of Frisch and it is found that the time lag intercept is independent of the mass transfer resistance parameter (h) and is given simply by:

$$t_{\text{lag}} = \frac{(1 + \frac{\varepsilon_B}{\varepsilon})L^2}{6D_K} \tag{56c}$$

When the amount of blind porosity is negligible, the time lag is given as considered previously (Eq. (16b)). Also the macro pore size distribution, total porosity and average pore size can be obtained by various methods such as mercury porosimetry. The Knudsen diffusion coefficient can be determined from the average pore size and the total porosity is the sum of the through flowing and blind porosity. Hence we can obtain the magnitude of the blind pore volume from experiment. Ash et al. (1972) have shown that for a porous carbon membrane the relative magnitude of the blind pore volume is small. It should be noted that the small observed differences in the diffusion coefficient observed by Ash et al. (1967) and assumed to be attributed to the presence of blind pores has received criticism from Petropoulos and co-workers (1967, 1968, 1976, 1977), who have shown that for permeation through some membranes, it is the axial dependence of the diffusion coefficient which is controlling the observed anomalies. The time dependence inherent in the blind pore model, is believed to be insignificant in these systems. Even for membranes compressed in several increments, a procedure which reduces the change of porosity along the axis of diffusion, axial dependence of the diffusion coefficient is still observed in significant magnitude.

2.3.4. Viscous Diffusion of the Fluid Phase. The permeation experiment can be conducted at high pressures in which case the diffusion mechanism is controlled by collision of molecules instead of molecule-wall collisions along the diffusion path. In this case the fluid phase will diffuse as a bulk fluid. The mass balance must account for this viscous flux which can be described by the Hagen Poiseuille equation. The balance can be represented by:

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} - \frac{\partial J_V}{\partial x} \tag{57}$$

where

$$J = -D_K \frac{\partial C}{\partial x} \tag{58a}$$

and

$$J_V = -D_V \frac{\partial C}{\partial x} \tag{58b}$$

and D_V is the viscous diffusion coefficient and is a function of pressure. Using the Hagen Poiseuille equation we obtain an expression for the diffusion coefficient as a function of the viscosity of the permeating gas:

$$D_V = \frac{P r_p^2}{8\mu} = \frac{CRT r_p^2}{8\mu} \tag{59}$$

When the pore radius or upstream concentration is small, D_V is small and the Knudsen term dominates the mass balance. Likewise, when the pore radius or concentration is large the viscous term dominates the mass balance.

Because the viscous diffusion coefficient is a function of concentration we can not obtain a full analytical solution of the mass balance equation and must employ numerical techniques. However it is possible to obtain an asymptotic solution using the method of Frisch (1957) upon the mass balance. The steady state slope can be obtained by solution of the steady state mass balance equation resulting in

$$S_\infty = \frac{A}{L} D_K C_0 \left(\frac{C_0}{W} + 1\right) \tag{60a}$$

with the time lag given by

$$t_{\text{lag}} = \frac{\int_0^L \int_x^L C_\infty dz\, dx}{C_0 D_K (\frac{C_0}{W} + 1)} \tag{60b}$$

where $W = \frac{32\mu}{3r_p}\sqrt{\frac{8}{\text{RTM}\pi}}$ and C_∞ is the steady state concentration profile given by solution of the steady state mass balance. It is given by

$$C_\infty = \sqrt{C_0(C_0+W)\left(1-\frac{x}{L}\right)+\frac{W^2}{4}}-\frac{W}{2} \tag{61}$$

resulting in the time lag as a function of upstream concentration.

$$t_{\text{lag}} = \frac{L^2}{60D_K}\frac{\left[10+25\frac{C_0}{W}+\left(\frac{C_0}{W}\right)^2\right]}{\left(\frac{C_0}{W}+1\right)^3} \tag{62a}$$

When the Knudsen diffusion term dominates the mass balance, the parameter W becomes very large and the time lag approaches the common relation previously obtained. When the viscous term dominates the mass balance, the parameter W becomes very small and the time lag approaches that shown in Eq. (62b).

$$\underset{\lim C \text{ or } r_p \to 0}{t_{\text{lag}}} = \frac{L^2}{6D_K}; \quad \underset{\lim C \text{ or } r_p \to \infty}{t_{\text{lag}}} = \frac{L^2}{3D_V} \tag{62b}$$

In order to give a qualitative indication of the dependence of the time lag and steady state slope upon upstream pressure we will consider a permeation experiment at 303 K with Argon and a solid membrane with average pore radius 1×10^{-5} cm, effective cross-sectional area 0.1 cm^2 and length 10 cm. Figures 6 and 7 respectively show that the additional viscous flux reduces the time lag and increases the permeability (where we have defined the permeability as the observed steady state slope divided by the upstream concentration).

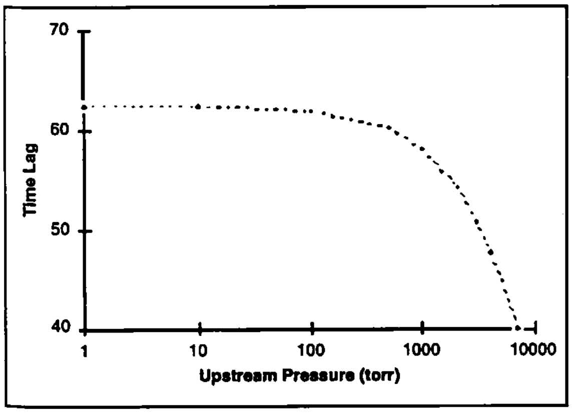


Figure 6. The effect of the viscous diffusion at higher pressures upon the time lag.

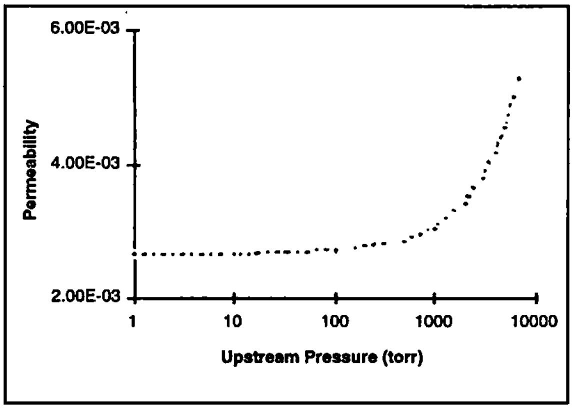


Figure 7. The effect of the viscous diffusion at higher pressures upon the permeability.

2.4. Dual Phase Flow in Membrane: Simultaneous Diffusion, Adsorption and Surface Diffusion

The previous analysis has considered only permeation of the fluid phase through the voids of the membrane. However, if adsorption occurs we must account for the additional accumulation of diffusing species within the material and also for the mobility of the adsorbed film by the mechanism of surface diffusion. With these considerations, we should rewrite the mass balance as:

$$\begin{aligned}\varepsilon\frac{\partial C}{\partial t}&+(1-\varepsilon)\frac{\partial C_\mu}{\partial t}\\ &=\varepsilon D_P\frac{\partial^2 C}{\partial x^2}+(1-\varepsilon)D_S\frac{\partial^2 C_\mu}{\partial x^2}\end{aligned} \tag{63}$$

where ε is the porosity of the membrane, C_μ is the concentration of the adsorbate on the solid surface of the membrane (mole/solid volume), D_S is the surface diffusion coefficient and D_P is the pore diffusion coefficient and is equivalent to the Knudsen diffusion coefficient if the Knudsen diffusion mechanism is controlling.

In order to derive the mass balance of Eq. (63), the assumption of constant diffusion coefficient has been made. In actual fact, the surface diffusion coefficient is well known to be highly concentration dependent at high pressures. However, if we conduct the experiment at low pressure corresponding to low adsorbed phase concentration, (Henry law) then this assumption is applicable.

2.4.1. Linear Isotherm. In order to solve the mass balance of Eq. (63) a relation between the gas phase and adsorbed phase concentrations is required. If local equilibrium is reached instantly and the relationship follows Henry law, then the mass balance is reduced to the form of Section 2 as we show next.

2.4.1.1. Instantaneous Adsorption. If the adsorption rate is much faster than the diffusion rate and if the concentration of sorbate in the fluid phase is relatively low, Henry law will apply. The adsorbed phase concentration will be linearly proportional to the concentration of the fluid phase as described by Eq. (64).

$$C_\mu(x,t) = K \cdot C(x,t) \tag{64}$$

With Henry law, the mass balance of Eq. (63) reduces to

$$\frac{\partial C}{\partial t} = D_{\text{app}} \frac{\partial^2 C}{\partial x^2} \tag{65}$$

where the apparent diffusivity, D_{app}, is defined as

$$D_{\text{app}} = \frac{\varepsilon D_P + (1-\varepsilon) K D_S}{\varepsilon + (1-\varepsilon)K} \tag{66}$$

If adsorption occurs instantly according to Henry law the analysis of Section 2 can be applied to the case of diffusion with simultaneous adsorption with the apparent diffusion coefficient (D_{app}) (which accounts for surface and fluid phase mobility) replacing the Knudsen diffusivity (D_K). Therefore, for the boundary conditions of Eq. (6), the time lag and steady state slope will be

$$t_{\text{lag}} = \frac{L^2}{6D_{\text{app}}} = \frac{L^2[\varepsilon + (1-\varepsilon)K]}{6[\varepsilon D_P + (1-\varepsilon) D_S K]} \tag{67a}$$

$$\begin{aligned} S_\infty &= [\varepsilon + (1-\varepsilon)K] \frac{A P_0 D_{\text{app}}}{VL} \\ &= [\varepsilon D_P + (1-\varepsilon) D_S K] \frac{A P_0}{VL} \end{aligned} \tag{67b}$$

When presenting the mass balance with adsorption and surface diffusion it is important that the units are stated. The mass balance presented by Barrer and Grove (1951) contained an adsorbed phase concentration expressed as an amount per surface area; in such a case, the Henry Law constant has units of length.

2.4.1.2. Determination of the Extent of Knudsen Flux. Introducing the surface mobility term into the mass balance of Eq. (63), introduces an additional variable in the form of the surface diffusion coefficient. If a time lag experiment is performed with a sorbing species, the apparent diffusion coefficient can be obtained. To divide the total flux into surface and pore diffusion components, we should perform a time lag run with a non sorbing species, to obtain the pore diffusion parameters. This can be done by using helium as the non-sorbing fluid. However, for some pellets, helium has been assumed to have a significant surface diffusion component (Hwang and Kammermeyer 1966) and hence we may require other means for determining the Knudsen diffusion parameters. Mercury porosimetry can be used to determine volume average pore size and hence Knudsen diffusion coefficient through Eq. (18). Schneider and Smith (1968) have performed experiments using higher temperatures where the amount adsorbed is small to reduce the contribution of surface flux to the total transport. Again this will only apply to some systems.

2.4.1.3. Helium Method. If helium permeation is controlled by Knudsen mechanism, then a conventional time lag plot with helium yields helium time lag and steady state slope. Due to the Knudsen diffusion condition, the diffusion coefficient for any species of molecular weight M can be related to that for helium as follows:

$$D_P = D_{P,\text{He}} \sqrt{\frac{M_{\text{He}}}{M}} \tag{68}$$

With the apparent or combined diffusion coefficient obtained from experiment with a sorbing fluid, and fluid phase pore diffusion coefficient obtainable through the helium method, the surface diffusion coefficient can be evaluated by means of Eq. (66). The difficulty with using this method, results from the fact that when using a sorbing species, membranes of short length are required to obtain a time lag on a reasonable time scale. However, when using a non sorbing species on the same membrane, a very short time lag results, leading to large relative error. Hence, the length of the membrane should be a matter for consideration.

2.4.1.4. Finite Time Delay for Adsorption. If the rate of adsorption is comparable to that of diffusion, the adsorption kinetics between the two phases must be considered. The adsorption kinetics may be considered to be described by the following equation:

$$\frac{dC_\mu}{dt} = k_a\left(C - \frac{C_\mu}{K}\right) \tag{69}$$

where k_a is the rate constant for the mass exchange between the two phases. If this rate is large, the adsorption process becomes instantaneous and we approach an equilibrium described by the Henry law relation.

If we consider the mass balance of Eq. (63) and consider the case of adsorption without surface diffusion as will be the case for slowly surface diffusing species, the mass balance should then be rewritten as:

$$\varepsilon\frac{\partial C}{\partial t} + (1-\varepsilon)\frac{\partial C_\mu}{\partial t} \approx \varepsilon D_P \frac{\partial^2 C}{\partial x^2} \tag{70}$$

The similarity between the case of time dependent adsorption and permeation with blind porosity is now evident by comparison between Eqs. (56) and (69) and (70).

Equations (69) and (70) can be solved for the case of initially clean medium with negligible downstream concentration:

$C(x,0) = C_\mu(x,0) = 0$; membrane initially clean (71a)

$C(0,t) = C_0$; upstream pressure is constant (71b)

$C(L,t) \approx 0$; downstream pressure is negligible (71c)

2.4.1.5. Steady State Solution. A steady state solution of Eqs. (69) to (71) will be:

$$C_{\mu\infty} = K C_\infty(x) \tag{72}$$

$$C_\infty(x) = C_0\left(1 - \frac{x}{L}\right) \tag{73}$$

2.4.1.6. Transient Solution. The full solution of Eqs. (69) to (71) can be obtained readily by employing the Laplace transform. Knowing the solution for the concentration distribution within the membrane, we can obtain the amount collected up to time t in the outgoing volume as:

$$Q_L(t) = \frac{A\varepsilon D_P C_0}{L}\left(t - \frac{L^2[\varepsilon + (1-\varepsilon)K]}{6\varepsilon D_P} + \sum_{n=1}^{\infty} \frac{\alpha(S_n)e^{S_n t}}{s \sinh \alpha(S_n)}\right) \tag{74}$$

where the coefficient α is defined as:

$$\alpha(S_n) = \frac{S_n}{D_P} + \frac{(1-\varepsilon)S_n k_a}{\varepsilon D_P\left(S_n - \frac{k_a}{K}\right)} \tag{75}$$

and S_n and u are given by:

$$S_n = -u + \sqrt{u^2 - n^2\pi^2\frac{\varepsilon D_P k_a}{\varepsilon K L^2}} \tag{76a}$$

$$u = \frac{1}{2}\left(\frac{k_a}{K} + \frac{(1-\varepsilon)k_a}{\varepsilon} + \frac{\varepsilon D_P n^2 \pi^2}{\varepsilon L^2}\right) \tag{76b}$$

The time lag derived from the intersection of the steady state asymptote of Eq. (74) with the time axis is:

$$t_{\text{lag}} = \frac{L^2}{6}\left[\frac{\varepsilon + (1-\varepsilon)K}{\varepsilon D_P}\right] \tag{77}$$

This time lag expression is equivalent to the one derived in Section 4.1.1 (Eq. (63) with the surface diffusion coefficient equal to zero). The method of Frisch could also be applied to the mass balance to yield the same time lag expression as is shown by Goodknight and Fatt (1961).

2.4.2. Permeation with Nonlinear Adsorption Isotherm in Glassy Polymers. If the time lag experiment with porous adsorbents is conducted at relatively high pressures, then the assumption of Henry law is not applicable. Adsorption on some polymers may follow non-linear isotherm also. Various isotherm equations have been used in the literature to describe equilibria outside the Henry law region. Here we shall consider the case of adsorption onto glassy polymers as considered by Paul (1969) and described by Langmuir isotherm. For adsorption onto porous adsorbents we will consider an example chosen to demonstrate the usefulness of the method of Frisch.

2.4.2.1. Mass Balance for Glassy Polymers. Permeation through 'glassy' polymer membranes have been investigated by Vieth and Sladek (1965) and Paul (1969). These glassy polymers are unique because of the presence of microvoids within the polymer network. The filling of these voids has been shown to exhibit Langmuir kinetics. The overall mass balance can be represented by the following: (Vieth and Sladek, 1965).

$$\left[1 + \frac{K}{(a + aC)^2}\right]\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{78}$$

where K and a are derived from the adsorption equilibrium constants. If we combine the mass balance with the initial and boundary conditions represented by Eqs. (31), we can numerically solve for concentration profile, the amount collected at the outgoing volume and for the time lag if desired. If the time lag is all that is desired, the method of Frisch can be employed.

2.4.2.2. Asymptotic Solution using the Method of Frisch. Considering the boundary conditions of Eqs. (31), we can integrate Eq. (78) with respect to x from x to L and then with respect to time from 0 to t. Rearranging and integrating the result with respect to x from 0 to L, yields

$$Q_L = \frac{D(C_0 - C_1)}{L}t + \frac{C_i L}{2} - \frac{1}{L}\int_0^L\int_z^L C\,dxdz - \frac{1-\varepsilon}{\varepsilon L} \times \int_0^L\int_z^L \frac{k(C - C_i)}{(1+aC_i)(1+aC)}dxdz \tag{80}$$

At steady state, the amount permeated approaches a linear asymptote, the intercept of which is a complex function of time as presented by Paul (1969).

$$t_{\text{lag}} = \frac{L^2}{6D} - \frac{L^2\delta}{2D} + \frac{L^2 K}{D} \times \left[\frac{(\delta+0.5)\varsigma^2 + \varsigma - [1 + (1+\delta)\varsigma + \delta\varsigma^2]\ln(1+\varsigma)}{(1+a\delta C_0)(1+aC_1)\varsigma^3}\right] \tag{81a}$$

where

$$\delta = \frac{C_i - C_0}{C_0 - C_1} \tag{81b}$$

and

$$\varsigma = \frac{a(C_0 - C_1)}{1 + aC_1} \tag{81c}$$

Hence the time lag can be predicted after the equilibrium experiment has been conducted to determine the parameters K and a. The diffusion coefficient can be determined from the steady state flow rate and hence the time lag predicted using (81).

2.4.3. *Permeation and Adsorption with Nonlinear Isotherm in Porous Adsorbents.* We should consider the case for porous adsorbents where the permeation is governed by diffusion in the gas phase and adsorption according to a non-linear isotherm. We will consider the case of non-linear adsorption according to the Unilan and Langmuir isotherms but with the limiting case where the surface flux is insignificant in comparison the fluid phase flux. These examples illustrate the usefulness of the method of Frisch.

Because the only contribution to the steady state flux is the permeation of the fluid phase, the steady state slope for this case is given previously as Eq. (16a).

If the surface flux is insignificant in comparison to the fluid phase flux and adsorption occurs simultaneously the mass balance can be represented by Eq. (71). If the permeating fluid has strong affinity for the solid the isotherm relation will generally be non-linear. As an example of the usefulness of the method of Frisch we will consider the asymptotic solution of the mass balance with three common isotherm relations: Langmuir, Freundlich and Unilan.

Integration of the mass balance with respect to x from z to L then with respect to t from 0 to t and finally with respect to z from 0 to L gives us the asymptotic solution of the mass balance.

The steady state concentration profile is required and can be obtained from solution of the steady state mass balance. It is given by Eq. (73). Hence at steady state the amount permeating is a linear function of time the intercept of which is:

$$t_{\text{lag}} = \frac{L^2}{6D_P} + \frac{(1-\varepsilon)}{\varepsilon L D_P C_0}\int_0^L\int_x^L C_\mu\,dzdx \tag{81}$$

The double integral can be evaluated for the two isotherms.

2.4.3.1. Langmuir Isotherm. If the adsorption equilibrium can be represented by the Langmuir isotherm

$$C_\mu = C_{\mu s}\frac{bC}{1+bC} \tag{82}$$

Then the double integral can be evaluated yielding the expression for time lag.

$$t_{\text{lag}} = \frac{L^2}{6\varepsilon D_P}[\varepsilon + (1-\varepsilon)C_{\mu s}bF(\lambda)] \tag{83}$$

where $F(\lambda)$ is given by

$$F(\lambda) = \frac{3}{\lambda} + \frac{6}{\lambda^3}[\lambda - (1+\lambda)\ln(1+\lambda)] \tag{84}$$

and λ measures the strength of the adsorption affinity

$$\lambda = bC_0 \tag{85}$$

If the adsorption affinity is small, the function $F(\lambda)$ will approach a limiting value.

$$\lim_{\lambda \to 0} F(\lambda) = 1 \tag{86}$$

and time lag will reduce to the familiar relation:

$$t_{\mathrm{lag}} = \frac{L^2}{6\varepsilon D_p}[\varepsilon + (1-\varepsilon)K] \tag{87}$$

which is the time lag derived earlier for Henry law isotherm, with an immobile surface layer. If adsorption affinity is large ($bC_0 \gg 1$),the isotherm becomes rectangular and the time lag of Eq. (83) will become

$$t_{\mathrm{lag}} = \frac{L^2}{6\varepsilon D_P}\left[\varepsilon + (1-\varepsilon)\frac{3C_{\mu s}}{C_0}\right] \tag{88}$$

2.4.3.2. Unilan and Freundlich Isotherms. The Langmuir isotherm is limited in its ability to fit some experimental data. Often a better fit of the data can be achieved through Unilan isotherm given in the form:

$$C_\mu = \frac{C_{\mu s}}{2s}\ln\left[\frac{1+\bar{b}e^{s}C}{1+\bar{b}e^{-s}C}\right] \tag{89}$$

where $\bar{b}$ and s are equilibrium adsorption constants. The time lag is more complex because of the complex equilibrium expression. Using the usual method of Frisch, the time lag is found to be:

$$\begin{aligned} t_{\mathrm{lag}} &= \frac{L^2}{6D_K} + \frac{(1-\varepsilon)C_{\mu s}L^2}{4\varepsilon D_K C_0^3 s \bar{b}^2} \\ &\quad \times [(\bar{b}C_0 + e^{-s})^2 \times \ln(1+\bar{b}e^{s}C_0) \\ &\quad - (\bar{b}C_0 + e^{s})^2 \times \ln(1+\bar{b}e^{-s}C_0) \\ &\quad + C_0\bar{b}(e^{s} - e^{-s})] \end{aligned} \tag{90}$$

Often a good fit to the isotherm data in the intermediate range of adsorption is the Freundlich isotherm given as:

$$C_\mu = kC^{1/n} \tag{91a}$$

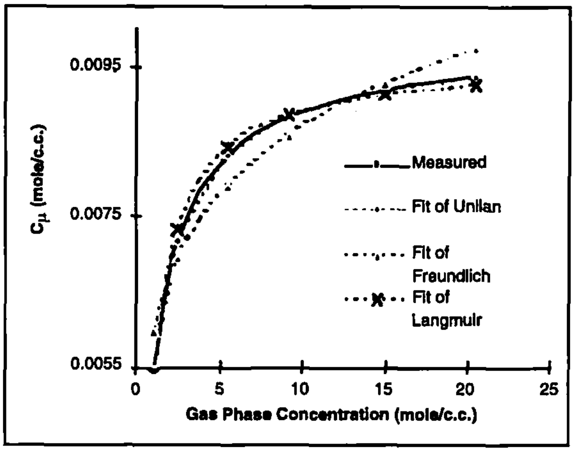


Figure 8. Equilibrium data fit by various isotherm equations.

This isotherm has no saturation limit nor does it reduce to Henry law at low concentrations and therefore there will be limits in the range of prediction. The time lag can be evaluated as was done for the Unilan isotherm with the result a function of upstream concentration given as:

$$t_{\mathrm{lag}} = \frac{L^2}{6D_K} + \frac{(1-\varepsilon)Ln^2kC_0^{1/n^{-1}}}{\varepsilon D_K(1+n)(1+2n)} \tag{91b}$$

To illustrate the differences between the prediction of the isotherms we can fit them to some adsorption data as is shown in Fig. 8. The fit is good for Unilan and Langmuir isotherms but not as good for Freundlich. To illustrate the dependence of the time lag upon the upstream concentration, we can calculate the time lag for permeation through a porous pellet whose length is 0.5 cm and whose porosity is 0.7 (loosely compacted) and where the Knudsen diffusion coefficient is 0.001 cm^2/s. As shown in Fig. 9, we see that the time lag is very sensitive to the isotherm fit and can result in significant differences in the predicted values.

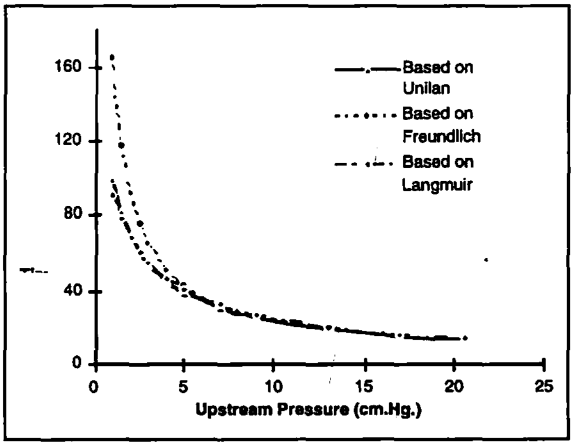


Figure 9. Predicted dependence of the time lag upon upstream pressure using various isotherm equations.

2.4.4. *Permeation with First Order Reaction.* Ludolph et al. (1979) have used a method similar to that of Frisch (1957) upon the mass balance to account for simple reaction or immobilisation of the penetrant. The mass balance can be represented by

$$(1+\xi)\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - kC \tag{92a}$$

where the term $k.C$ represents the amount of penetrant removed by first order reaction and ξ is the fraction of adsorbed molecules which are immobile and hence are unavailable for reaction. The time lag presented by Ludolph et al. (1979) is a complex function which is strongly dependent on the rate constant. A simple expression for the same time lag was found by Leypoldt and Gough (1980) and is given as

$$t_{\mathrm{lag}} = \frac{L^2(1+\xi)}{2D}\left[\frac{\coth\phi}{\phi} - \frac{1}{\phi^2}\right] \tag{92b}$$

where

$$\phi = \frac{kL^2}{D} \tag{92c}$$

Hence the permeation experiment in this case provides simple means for evaluating the reaction rate constant and immobilisation factor and hence characterising the physical mechanisms involved.

2.5. *Permeation with Serial and/or Parallel Paths*

Chen and Rosenberger (1991) have used the method of Frisch (1957) to obtain an expression for the time lag with permeation along 2 parallel paths which are in series with another path. Their analysis is useful for characterising permeation through body organs and in the process identifying various physical parameters characteristic of the organ.

2.5.1. *Combination of Upstream and Downstream Time Lag.* Simultaneous measurement of upstream pressure decay and downstream pressure rise during the time lag experiment has been recorded by Ash et al. (1979) and Petropoulos and Roussis (1967). This simultaneous measurement will yield the flux into and out of the membrane as a function of time. Using the asymptotic solution of the mass balance equations presented earlier we can determine the amount adsorbed and hence the isotherm in situ. This method provides a useful technique for investigation of permeation combined with time or displacement dependent adsorption.

2.5.2. *Permeation Through Composite Slabs.* If a slab porous membrane is formed from materials of differing permeabilities, the observed properties of the composite slab will be a function of the properties of the component materials. A slab of n layers, each layer characterised by its own diffusion coefficient and length can be used as a barrier for permeation. The asymptotic solution to the mass balance equation can be obtained using the method of Frisch once again. Ash et al. (1963,1965) uses the Frisch method to obtain a time lag expression for n laminates in series. Below we show the time lag for diffusion through 2 laminates in series

$$(t_{\mathrm{lag}})_{\mathrm{comp}} = \left[\frac{L_1}{D_1} + \frac{L_2}{D_2}\right]^{-1}\left[\frac{L_1^2}{D_1}\left(\frac{L_1}{6D_1} + \frac{L_2}{2D_2}\right) + \frac{L_2^2}{D_2}\left(\frac{L_2}{6D_2} + \frac{L_1}{2D_1}\right)\right] \tag{93}$$

This solution is particularly useful for application to polymer laminates. Another method to obtain this solution is to utilise the Laplace transform, in which case we can obtain a solution for the concentration profile also (Jaeger, 1950).

3. Permeation Through Spherical Membranes

Permeation experiments have been performed on objects of cylindrical and spherical geometry because of the practical importance in diffusion in organic (Crank and Park, 1968) and ionic solids and alloys (Barrer, 1941) and heat transfer in solids (Carslaw and Jaeger, 1947) in the form of rods, hollow fibres, wires and balls. The mass balance describing diffusion in spherical and cylindrical geometries can be reduced to the form of that describing slab geometry (considered previously) through suitable transformations. For the case of diffusion in spherical geometry, the mass balance of Eq. (4) can be rewritten as:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D\frac{\partial C}{\partial r}\right) \tag{94}$$

If diffusion is controlled by the Knudsen mechanism only, then the diffusion coefficient is constant, and a simplification can be made:

$$\frac{\partial C}{\partial t} = \frac{D_K}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) \tag{95}$$

If the diffusion coefficient is not constant with concentration, time or displacement in the direction of diffusion then Frisch analysis for spherical geometry (Section 5) could be applied or numerical methods used.

In spherical geometry we could consider the case of penetration of the solid sphere as presented by Barrer (1941), Crank (1975) and Carslaw and Jaeger (1947). However, the permeation process does not reach a steady state of flow but tends towards an equilibrium saturation of the solid sphere and cylinder. A more relevant case to consider is that of the hollow sphere.

3.1. *Hollow Spherical Shell*

Let us consider a hollow sphere of internal radius r_0, and external radius r_1. To account for the tortuosity of the diffusion path we must define the diffusion path outer radius r_c:

$$r_c = \tau \cdot r_1 \tag{96}$$

where r_1 is the measurable outer radius. The model for hollow sphere can be transformed into a slab by simple transformation

$$u = C \cdot r \tag{97}$$

and the mass balance of Eq. (95) will become

$$\frac{\partial u}{\partial t} = D_K \frac{\partial^2 u}{\partial r^2} \tag{98}$$

which can be solved by methods discussed previously and will depend upon the initial and boundary conditions.

3.1.1. *Hollow Spherical Membrane Initially Purged of Diffusing Species.* The boundary conditions for the case of an initially clean hollow sphere will be

$C(r_0, t) = C_0$; internal concentration is constant (99a)

$C(r_c, t) = 0$; external concentration is zero (99b)

$C(r, 0) = 0$; membrane is initially clean (99c)

The solution of the mass balance in spherical geometry with these boundary conditions, can be obtained in terms of the transformed variable u, and subsequent conversion will yield solution for concentration (Barrer, 1944).

$$C = \frac{r_0 C_0}{r} - \frac{r_0 C_0 (r - r_0)}{r(r_c - r_0)} - \frac{2 r_0 C_0}{\pi r} \times \sum_{n=1}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi(r - r_0)}{r_c - r_0}\right) \exp\left(-\frac{D_K n^2 \pi^2 t}{(r_c - r_0)^2}\right) \tag{100}$$

The amount of diffusing species leaving the membrane, obtained by integration of the flux equation with respect to time, is given by

$$Q_{r=r_c} = A \cdot D_K \int_0^t \left.\frac{\partial C}{\partial r}\right|_{r=r_c} dt \tag{101}$$

where A represents the surface area available for penetration perpendicular to the direction of diffusion as we defined earlier. In the case of radial diffusion, the area will be the surface area of the shell perpendicular to the direction of diffusion and will therefore depend upon the radial coordinate. For the case of the porous sphere of radius r_1 which we have considered, the outer area will be expressed in terms of r_1:

$$A = \varepsilon 4\pi r_1^2 \tag{102}$$

Using the concentration solution, we have the amount permeated expressed as:

$$Q_{r=r_c} = \frac{A D_K r_0 C_0}{(r_c - r_0) r_c} \left[t - \frac{(r_c - r_0)^2}{6 D_K} + \frac{2(r_c - r_0)^2}{\pi^2 D_K} \times \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \exp\left(-\frac{D_K n^2 \pi^2 t}{(r_c - r_0)^2}\right) \right] \tag{103}$$

At steady state the amount permeated approaches a linear asymptote given by:

$$Q_{r_c,\infty} = \frac{A D_K r_0 C_0}{(r_c - r_0) r_c} \left[t - \frac{(r_c - r_0)^2}{6 D_K} \right] \tag{104}$$

which has an intercept on the time axis given by

$$t_{\text{lag}} = \frac{(r_c - r_0)^2}{6 D_K} \tag{105a}$$

The steady state slope of the asymptote is

$$S_\infty = \frac{A D_K r_0 C_0}{(r_c - r_0) r_c} \tag{105b}$$

From experiment, we obtain two parameters—time lag and steady state slope. These will yield the unknown parameters which characterise the system—the Knudsen diffusion coefficient D_K and the outer diffusion radius r_c (hence tortuosity) through Eqs. (105).

3.1.2. Hollow Sphere Initially Containing Diffusing Species.

The boundary conditions for the case of hollow sphere initially equilibrated with fluid to a concentration C_i throughout, will be

$$C(r_0, t) = C_0; \quad \text{internal concentration is constant} \tag{106a}$$

$$C(r_c, t) = C_1; \quad \text{external concentration is constant} \tag{106b}$$

$$C(r, 0) = C_i; \quad \text{membrane is initially at constant concentration} \tag{106c}$$

The solution by the method presented in 7.1.1, with these boundary conditions is (Barrer, 1944)

$$\begin{aligned} C = {} & \frac{r_0 C_0}{r} + \frac{r_c C_1 - r_0 C_0}{(r_c - r_0)} \frac{r - r_0}{r} + \frac{2}{\pi r} \\ & \times \sum_{n=1}^{\infty} \frac{r_c C_1 \cos n\pi - r_0 C_0}{n} \sin\left(\frac{n\pi(r - r_0)}{r_c - r_0}\right) \\ & \times \exp\left(-\frac{D_K n^2 \pi^2 t}{(r_c - r_0)^2}\right) - \frac{2C_i}{\pi r} \\ & \times \sum_{n=1}^{\infty} \sin\left(\frac{n\pi(r - r_0)}{r_c - r_0}\right) \frac{r_c \cos n\pi - r_0}{n} \\ & \times \exp\left(-\frac{D_K n^2 \pi^2 t}{(r_c - r_0)^2}\right) \end{aligned} \tag{107}$$

The amount of diffusant leaving the membrane is given by integration of the flux equation with respect to time. As $t \to \infty$, the amount entering the receiving volume reaches a steady state asymptote, the intercept of which on the time axis is:

$$\begin{aligned} t_{\text{lag}} = {} & \frac{C_0 - C_i}{C_0 - C_1} \cdot \frac{(r_c - r_0)^2}{6 D_K} \\ & + \frac{C_1 - C_i}{C_0 - C_1} \cdot \frac{r_c}{r_0} \cdot \frac{(r_c - r_0)^2}{3 D_K} \end{aligned} \tag{108}$$

which reduces back to the expression given previously for initially clean membrane when $C_i = 0$ and $C_1 = 0$.

3.2. *Composite Spherical Shell*

Consider a spherical shell composed of n materials with their own distinct diffusion properties and with each layer in perfect contact with the neighbouring layers. The steady state parameters can be calculated for the composite shell along with the time lag for diffusional penetration. As stated in Section 6.2, the asymptotic solution of the mass balance for composite materials is complex. Only the solution for diffusion through a double laminate is presented below (Barrie et al. 1963).

$$\begin{aligned} (t_{\text{lag}})_{\text{comp}} & \\ = \frac{1}{6\phi_{\text{sph}}} \Bigg[& \frac{(r_1 - r_0)^3}{D_1^2 r_1 \cdot r_0} + \frac{(r_2 - r_1)^3}{D_2^2 r_1 \cdot r_2} + \frac{1}{D_1 D_2} \\ & \times \left(\frac{1}{r_1} - \frac{1}{r_c}\right) \frac{(r_1 - r_0)^2 (2r_1 + r_0)}{r_0} \\ & + \frac{1}{D_1 D_2} \left(\frac{1}{r_0} - \frac{1}{r_1}\right) \frac{(r_2 - r_1)^2 (2r_1 + r_2)}{r_2} \Bigg] \end{aligned} \tag{109}$$

where ϕ_{sph} is defined as

$$\phi_{\text{sph}} = \frac{1}{D_1}\left(\frac{1}{r_0} - \frac{1}{r_1}\right) + \frac{1}{D_2}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \tag{110}$$

The time lag in this case is useful for determination of transport properties of coated spherical shells.

4. Permeation in Cylindrical Geometry

The mass balance of Eq. (4) can be rewritten in cylindrical geometry as:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r}\left(D r \frac{\partial C}{\partial r}\right) \tag{111}$$

If diffusion of the fluid phase is controlled by the Knudsen mechanism, then the diffusion coefficient is constant and the mass balance of Eq. (111) reduces to the following relation:

$$\frac{\partial C}{\partial t} = \frac{D_K}{r} \frac{\partial}{\partial r}\left(r \frac{\partial C}{\partial r}\right) \tag{112}$$

If the diffusion coefficient is not constant, the method of Frisch can be applied to the mass balance to obtain the time lag (Section 9.0).

Of interest in permeation studies is the case of the hollow cylinder of internal radius r_0, external radius r_1. The tortuosity of the molecular path for diffusion through the cylinder must be accounted for as it was for slab geometry, hence we define the diffusion path length r_c as given by Eq. (96).

4.1. *Hollow Cylindrical Shell*

When considering permeation within a hollow cylinder, we should analyse the mass balance (Eq. (112)) by making a substitution $C = ue^{-D_K\alpha^2 t}$. The result is a Bessel equation of zero order,

$$\frac{\partial^2 u}{\partial r^2} + \frac{1}{r}\frac{\partial u}{\partial r} + \alpha^2 u = 0 \qquad (113)$$

The solution of the Bessel equation can be obtained in terms of Bessel functions, chosen to comply with the boundary and initial conditions.

*4.1.1. **Hollow Cylinder Initially Purged of Diffusing Species.*** When considering the hollow cylindrical membrane initially purged of diffusing species, we can obtain the solution of the mass balance of Eq. (112) by using the boundary conditions represented by Eqs. (99).

$$\begin{aligned} C ={}& \frac{C_0 \ln\left(\frac{r_c}{r}\right)}{\ln\left(\frac{r_c}{r_0}\right)} \\ &+ \pi \sum_{n=1}^{\infty} \frac{C_0 J_0(\alpha_n \cdot r_c) J_0(\alpha_n \cdot r_0) U_0(\alpha_n \cdot r)}{J_0^2(\alpha_n \cdot r_0) - J_0^2(\alpha_n \cdot r_c)} \\ &\cdot \exp\left(-D_K \alpha_n^2 t\right) \end{aligned} \qquad (114)$$

where U_0 is defined as $U_0(\alpha_n, r) = J_0(r\alpha_n)Y_0(r_c\alpha_n) - J_0(r_c\alpha_n)Y_0(r\alpha_n)$, J_0 and Y_0 are zero order Bessel functions of first and second kind respectively and α_n is defined as the positive root of $U_0(\alpha_n r_0) = 0$.

The amount of diffusing species leaving the outer face per unit length of cylinder is given by integration of the flux equation with respect to time.

$$Q_{r=r_c} = -AD_K \int_0^t \left(\frac{\partial C}{\partial r}\right)_{r=r_c} dt \qquad (115)$$

where the area A for the cylinder is $A = 2\pi r_1 \varepsilon$.The asymptotic solution has been found by Barrer (1940) and is a complicated function which has been simplified by Jaeger (1946) who employed Laplace transform technique for the solution.

$$\begin{aligned} Q_{r_c,\infty} ={}& \frac{AC_0D_K}{r_c \cdot \ln\left(\frac{r_c}{r_0}\right)} \\ &\times \left(t - \frac{r_0^2 - r_c^2 + \left(r_0^2 + r_c^2\right)^2 \ln\left(\frac{r_c}{r_0}\right)}{4D_K \ln\left(\frac{r_c}{r_0}\right)}\right) \end{aligned} \qquad (116)$$

The time lag intercept and steady state slope of the asymptote are given by:

$$t_{\text{lag}} = \frac{r_0^2 - r_c^2 + \left(r_0^2 + r_c^2\right)^2 \ln\left(\frac{r_c}{r_0}\right)}{4D_K \ln\left(\frac{r_c}{r_0}\right)} \qquad (117a)$$

$$S_\infty = \frac{AC_0D_K}{r_0 \cdot \ln\left(\frac{r_c}{r_0}\right)} \qquad (117b)$$

*4.1.2. **Cylindrical Membrane Initially Containing Diffusing Species.*** If the cylinder is initially equilibrated with penetrant to a significant concentration then the mass balance can be solved with the boundary conditions of Eq. (106) yielding a solution incorporating the Bessel function.

$$\begin{aligned} C ={}& \frac{C_0 \ln\left(\frac{r_c}{r}\right) + C_1 \ln\left(\frac{r}{r_0}\right)}{\ln\left(\frac{r_c}{r_0}\right)} \\ &+ \pi C_i \sum_{n=0}^{\infty} \frac{J_0(r_0\alpha_n)U_0(r\alpha_0)}{J_0(r_0\alpha_n) + J_0(r_c\alpha_n)} \\ &- \pi \sum_{n=1}^{\infty} \frac{[C_1 J_0(\alpha_n r_0) - C_0 J_0(\alpha_n r_c)] J_0(\alpha_n r_0) U_0(\alpha_n r)}{J_0^2(\alpha_n r_0) - J_0^2(\alpha_n r_c)} \\ &\cdot \exp(-D_K {\alpha_n}^2 t) \end{aligned} \qquad (118)$$

where the variables are defined in the previous section. By the usual procedure, we can obtain an expression for time lag, as the amount leaving the membrane approaches a steady state (Barrer 1940). The solution obtained by Jaeger (1946) with the Laplace transform technique is again of simpler form and is given as

$$\begin{aligned} t_{\text{lag}} ={}& \frac{C_1 - C_i}{C_1 - C_0} \frac{r_0^2 - r_c^2 + \left(r_c^2 + r_0^2\right) \ln\left(\frac{r_c}{r_0}\right)}{4D_k \ln\left(\frac{r_c}{r_0}\right)} \\ &+ \frac{C_0 - C_i}{C_1 - C_0} \frac{r_c - r_0^2 - 2r_0^2\left[1 + \ln\left(\frac{r_c}{r_0}\right)\right] \ln\left(\frac{r_c}{r_0}\right)}{4D_k \ln\left(\frac{r_c}{r_0}\right)} \end{aligned} \qquad (119)$$

4.2. *Composite Cylindrical Shell*

Permeation through a cylindrical shell constructed as stated in Section 3.2, yields an asymptotic solution of the mass balance which is complex. Only the solution for the double laminate is presented (Barrie et al., 1963)

$$\begin{aligned} &(t_{\text{lag}})_{\text{comp}} \\ &= \frac{1}{4\phi_{\text{cyl}}} \left\{ \frac{1}{D_1^2} \left[\left(r_1^2 + r_0^2\right) \ln \frac{r_1}{r_0} - \left(r_1^2 - r_0^2\right) \right] \cdot \right. \\ &\quad \left. + \frac{1}{D_2^2} \left[\left(r_1^2 + r_2^2\right) \ln \frac{r_2}{r_1} - \left(r_2^2 - r_1^2\right) \right] \right\} \\ &\quad + \frac{1}{4\phi_{\text{cyl}}} \left\{ \frac{1}{D_1 D_2} \left(\ln \frac{r_2}{r_1} \right) \left[2r_1^2 \ln \frac{r_1}{r_0} - \left(r_1^2 - r_0^2\right) \right] \right. \\ &\quad \left. + \frac{1}{D_1 D_2} \ln \frac{r_1}{r_0} \left[\left(r_2^2 + r_1^2\right) - 2r_1^2 \left(\ln \frac{r_2}{r_1} \right) \right] \right\} \end{aligned} \qquad (120)$$

ϕ_{cyl} is defined as

$$\phi_{\text{cyl}} = \frac{1}{D_1} \ln \frac{r_1}{r_0} + \frac{1}{D_2} \ln \frac{r_2}{r_1} \tag{121}$$

5. Method of Frisch Applied to Spherical and Cylindrical Geometries

If the measured diffusion coefficient is not constant over the time period of measurement, the pressure range tested, or along the axis of diffusion, then the asymptotic solution presented previously for cylindrical and spherical geometries is not applicable. The method of Frisch (1959) can be applied to the mass balance in spherical and cylindrical geometry to yield an expression for time lag as a function of the diffusion coefficient for this case. If we define a parameter φ as

$$\varphi = \int_0^{C(r,t)} D(C) dC \tag{122}$$

A general mass balance can be constructed to account for all three geometries:

$$\frac{\partial C}{\partial t} = \frac{1}{r^{n-1}} \frac{\partial}{\partial r} \left(r^{n-1} \frac{\partial \varphi}{\partial r} \right) \tag{123}$$

For $n = 1$, the equation reduces to the familiar mass balance expression for slab geometry, $n = 2$ corresponds to cylindrical and $n = 3$ corresponds to spherical geometry. For the general case of constant internal and external concentrations and constant initial concentration within the membrane, the boundary conditions become:

$C(r_0, t) = C_0$; $\varphi(C_0, r_0, t) = \varphi_0$; internal concentration is constant (124a)

$C(r_1, t) = C_1$; $\varphi(C_1, r_1, t) = \varphi_1$; external concentration is constant (124b)

$C(r, 0) = C_i$; membrane is initially at constant concentration (124c)

Using the boundary conditions of Eq. (124), we can integrate the mass balance (123) as described in Section 2.3. To obtain the expression for the amount permeated (as defined in Eq. (13)) an expression for the external area independent of geometry must be obtained and is presented as:

$$A = -\omega_n r^{n-1} \tag{125}$$

where ω_n is defined as:

$$\omega_n = \frac{2(\sqrt{\pi})^n}{\Gamma(n/2)} \tag{126}$$

Using this expression, the amount leaving the membrane at steady state is then given as

$$Q(r_1, \infty) = \frac{\omega_n(\varphi_{0,\infty} - \varphi_{1,\infty})}{\int_{r_0}^{r_1} \frac{dz}{z^{n-1}}} \times \left(t - \frac{\int_{r_0}^{r_1} \frac{dr}{r^{n-1}} \int_r^{r_1} (C_\infty - C_i) r^{n-1} dr}{\varphi_{0,\infty} - \varphi_{1,\infty}} + \frac{\int_0^\infty \varphi_0 - \varphi_1 - (\varphi_{0,\infty} - \varphi_{1,\infty}) dt}{\varphi_{0,\infty} - \varphi_{1,\infty}} \right) \tag{127}$$

where we have defined the integral diffusion coefficients as:

$$\varphi_{\infty,1} = \int_0^{C_1} D(C) dC, \quad \varphi_{\infty,0} = \int_0^{C_0} D(C) dC \tag{128}$$

The time lag intercept of the linear asymptote is:

$$t_{\text{lag}} = \frac{\int_{r_0}^{r_1} \frac{dr}{r^{n-1}} \int_r^{r_1} (C_\infty - C_i) r^{n-1} dr}{\varphi_{0,\infty} - \varphi_{1,\infty}} - \frac{\int_0^\infty \varphi_0 - \varphi_1 - (\varphi_{0,\infty} - \varphi_{1,\infty}) dt}{\varphi_{0,\infty} - \varphi_{1,\infty}} \tag{129}$$

This is the general expression for time lag, independent of the simplifying assumption of constant diffusion coefficient, for any of the three geometries considered. For slab geometry ($n = 1$) and for a constant diffusion coefficient, it can be shown that Eq. (129) reduces to the relation for Knudsen permeation only, given by Eq. (16).

6. Experimental Considerations

Permeation experiments have been performed on many types of solid membranes of differing structure. For porous solids, adsorption and surface diffusion occur in parallel. For non porous solids which contain a negligible amount of void volume (e.g., polymer, metal, or crystal) sorption is initiated on the outer face of the solid and subsequent diffusion through the solid in a single phase maintains the diffusive flux. Adsorption and diffusion are in series and hence the mass balance into and out of the volumes must include an adsorption/desorption relation between the face of the membrane and the fluid it is in contact with.

The book "Diffusion in Polymers" by Crank and Park (1968) can be used as a convenient reference for adsorption and diffusion data for common polymers. Attention has recently been given (see Section 2.4.2.1) to the 'glassy' polymer, because of the unique diffusion mechanism observed within these polymers. Accumulation and immobilisation of the penetrating species is assumed to occur in microvoids within the membrane. The monograph "Diffusion in and through Polymers" by Vieth (1991) provides a review of the topic.

6.1. *Experimental Configuration*

There are two possible configurations within which to conduct the permeation experiment. The first has been termed the 'Wicke-Kallenbach' diffusion cell experiment and involves an assumed inert carrier gas which is distributed on both sides of the pellet and keeps both sides at constant pressure. With the introduction of an adsorbate, a change in the molar concentration is observed and this provides the driving force. A step, pulse or wave change can be provided upstream and the moment of the response curve in this case can provide a simple means for analysis. Grachev et al. (1970), Gilbaro et al. (1986), Smith et al. (1975,1976,1983) and Moffat (1978) have used this technique for investigation of catalyst particles. The second configuration involves a single species with the pressure gradient providing the driving force. This has been the more popular form of the experiment and hence has been the focus of this review. Table 2 provides the relative advantages and disadvantages of both configurations. The essential disadvantage of the Wicke-Kallenbach configuration is the possible experimental complications resulting from the presence of the carrier gas e.g., unaccounted bulk movement leading to difficulties in analysis of results or the possibility of interference in the dynamic adsorption process (especially for weakly adsorbing gases). When the pressure difference is providing the driving force the obvious difficulty is the vacuum leak restriction.

The mass balances presented in this review included concentration as the measurable variable and hence applies to both configurations (concentration can be simply related to pressure at a known temperature and is directly measurable for the Wiçke-Kallenbach configuration). It should be noted that Section 2.3.4 on viscous permeation does not apply to the Wicke-Kallenbach configuration nor does the application of the helium method (Section 2.4.1.3). All other sections apply to both configurations.

6.2. *Pellet Formation*

Petropoulos and Roussis (1967) have shown that compression of the solid will have an effect on the observed permeability. Consistent compression and compression in several small increments has been suggested to be the best way to avoid permeation anomalies caused by change in porosity along the axis of diffusion.

There are 3 essential factors to consider in pellet design: length, diameter and consolidation pressure. Table 3 contains the limits and typical values for pellet formation.

Table 2. The relative advantages and disadvantages of both configurations.

Advantage	Disdvantage
Wicke-Kallenbach experiment	
Minimal leak restrictions	Carrier gas may interfere with dynamic equilibrium between adsorbate and solid
Multi-component permeation easily undertaken	Any pressure gradient will lead to bulk movement of carrier gas Need for chromatography, spectrometry, etc., equipment to determine concentration
Traditional pressure driven permeation experiment	
Simple monitoring using pressure transducer	Tight vacuum requirements
Single driving force	Variable system volume necessary
Fluid phase transport parameters easily determinable	High pressure differential places large stresses on the pellet Multicomponent analysis difficult

Table 3. Essential factors to consider in pellet design.

Length	Upper limit: Long pellets lead to inaccuracy in determination of time lag and flow rate from system leaks Lower limit: For short pellets, small error in time measurement may lead to significant error in time lag Typical measurement: Strongly consolidated pellets of fine powders: 3–5 cm. Crystal pellets with large macropore volume: ≈ 1m
Diameter	Upper limit: High permeate flow leads to fast pressure rise defying prescribed boundary conditions Lower limit: Low permeate flow results in inaccurate determination of flow rate Typical measurement: 0.5 – 1cm.
Level of compaction *	Upper limit: High pressure may lead to structural deformation Low limit: Low consolidation results in macropore diffusion control Typical measurement: 1000 kg/cm^2

*Pellets must be compressed in several increments to avoid inhomogeneities along the axis of penetration.

6.3. *Characterisation*

The permeation process in porous solids generally consists of Knudsen and surface diffusion in parallel. Monitoring the permeation of helium (only possible using pressure driven permeation) characterises the Knudsen permeation and reveals information regarding the mesopore network for tightly compressed pellets. All other gases have significant adsorption and surface diffusion combined with the gas phase permeation. The raw data obtained from the experiment must be treated and analysed appropriately to determine the surface diffusivity. Figure 10 provides the procedure for determining the diffusivity for the possible scenarios encountered in experiment. For each scenario the reader is directed to the relevant section of this review. This figure shows that the tortuosity, Knudsen and surface diffusivities and even the Henry law constant can be estimated from permeation data (using time lag and the steady state slope) with helium and an adsorbing species.

Table 4 contains the values for typical experimental variables together with the Knudsen and surface diffusivity values for material and adsorbate specified. All experiments were conducted using the pressure driven permeation method.

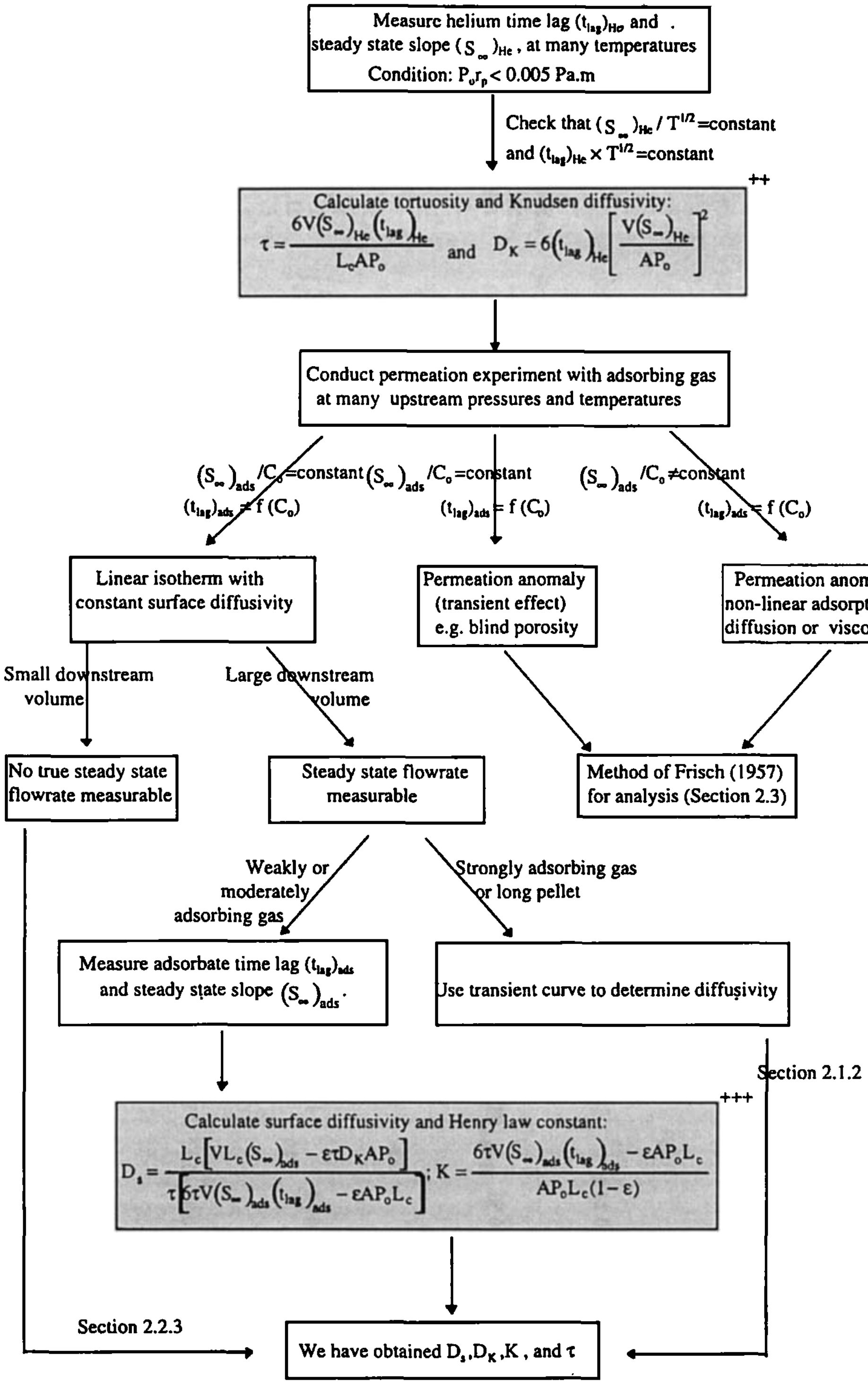
7. Conclusion

The time lag permeation method is a flexible technique for characterisation which can be applied to a variety of solids. Measurement of the amount of fluid penetrating the solid membrane provides the means for characterisation in the time lag technique. If the diffusion mechanism is one of simple Fickian diffusion with or without simultaneous adsorption, the asymptotic solution will reduce to a relatively simple relation with the diffusion coefficient. If the diffusion is of non-Fickian type, or the adsorption is nonlinear, the modelling equations should be solved by numerical methods for the concentration profile. However, an expression for the asymptotic solution can be obtained from the mass balance by the method of Frisch and used to evaluate the necessary parameters thus avoiding cumbersome numerical techniques. The complexity of the asymptotic solution is dependent upon the complexity of the kinetic processes occurring within the solid. A limitation of the time lag method which also applies to other techniques is the requirement of careful construction of the membrane in order for it to yield consistent data. The strict vacuum requirements for experimentation can also be considered a limitation.

Nomenclature

Symbol

A_c	Cross-sectional area of solid perpendicular to direction ofdiffusion
A	Area available for fluid phase penetration.
b	Adsorption affinity
C	Concentration of diffusant in the membrane
D	Diffusion coefficient
D_K	Ideal gas phase diffusion coefficient defined by the Knudsen equation
J	Flux
K	Henry law constant
l	Length of the membrane
L	Length of the diffusion path
L_c	Measurablel length of the pellet
P	Pressure
Q	Amount of permeating adsorbent measured



++ Equations obtained from simultaneous solution of (16a) and (16b).
+++ Equations obtained from simultaneous solution of (67a) and (67b).

Figure 10. Algorithm representing the procedure for determination of fluid phase and surface diffusivity, tortuosity and Henry law constant using Helium permeation and adsorbate permeation (in range of upstream concentrations corresponding to Henry law adsorption) for an initially clean slab pellet.

Table 4. Results of investigation of porous compacts by time lag method.

Author	Solid (B.E, T. area)	Membrane porosity ε	Membrane length (L)(cm)	Membrane cross-sectional area (A_c)(cm^2)	Diffusing species	T (°C)	Time lag (min)	$D_{\mathrm{app}}.10^3$ (cm^2/s)	$D_p.10^3$ (cm^2/s)#	$D_S.10^3$ (cm^2/s)#	$D_p.10^3$ (cm^2/s)##	$D_S.10^3$ (cm^2/s)##	K	$\frac{J_S}{J_p}$#	$\frac{J_S}{J_p}$##
1. Barrer and Grove (1951)	Analcite (350 cm^2/cm^3)	0.50	98	0.0962	Helium	25	4.9	5450							
					Nitrogen		11.0	2420							
					Oxygen		12.5	2130							
					Argon		14.7	1820	60						
					Neon		9.8	2730							
					Sulfur Dioxide		40.0	1470							
					Ammonia		100	2830							
2. Barrer and Barrie (1952)	Porous Glass (1.4E–6 cm^2/g)	0.2++	2.69	0.924	Helium	19	5.1	0.0258							
					Nitrogen		39.5	0.0033	9.4	1.53			3.5**	0.57	
					Methane		43.7	0.0030	12.4	1.24			5.3*	0.53*	
					Ethane		260	0.00057	9.0	0.26			36.3*	1.05	
3. Barrer (1953)	Analcite (350 cm^2/cm^3)	0.50	98	0.0962	Hydrogen	25	3.0	17.7							
					Helium		4.9	10.9							
					Neon		9.8	5.46							
					Nitrogen		11.0	4.84							
					Oxygen		12.5	4.26							
					Argon		14.7	3.64							
					Krypton		21.7	2.46							
4. Barrer and Strachan (1955)	Carbolac 1 (250 cm^2/g)	0.64	4.81	0.20	Helium	25	4.5		5.7	1.74			0.56	0.17	
					Neon		10.0		2.6	1.05			0.67	0.27	
					Hydrogen		3.6		8.3	2.86			0.84	0.29	
					Argon		33.5		1.9	0.16			7.4	0.62	
					Nitrogen		31.0		2.2	0.21			7.3	0.70	
	Carbolac 2 (250 cm^2/g)	0.37	3.31	0.20	Helium	25	7.7		15.4	2.7			1.54	0.27	
					Neon		17.3		6.6	1.6			2.1	0.51	
					Hydrogen		6.3		21	4.2			3.25	0.65	
					Argon		12.0		4.6	0.54			15.0	1.76	
					Nitrogen		9.0		5.5	0.61			16.0	1.77	

5. Barrer and Gabor (1960)	Catalyst 8 (N/A)	0.53	4.73	0.317	Nitrogen	30			16.43	2.35	14.44	0.49	1.54	0.22	0.05
					Methane	30	10.0	0.00621	21.67	1.57	19.1	0.32	3.33	5.22	1.07
					Ethane	100	16.8	0.00369	17.65	0.95	15.5	0.39	5.10	4.86	1.99
					Propane	180	16.2	0.00384	16.06	0.86	14.1	0.54	4.10	3.52	2.21
	Catalyst 4 (N/A)	0.40	3.71	0.317	Nitrogen	30		0.00057	2.94	0.49	2.51	0.17	2.25	0.37	0.15
					Methane	30	37.2	0.00057	3.91	0.44	3.31	0.18	4.88	2.15	0.88
					Ethane	100	63.8	0.00060	3.18	0.26	2.70	0.12	7.50	1.95	1.05
					Propane	180	62.0	0.00062	2.88	0.25	2.44	0.15	6.07	1.52	0.91
6. Ash and Grove (1960)	Ceramic (2.93 cm^2/cm^3)	0.30	46.7	0.315	Helium	25	3.1	1950	1950						
					Carbon Dioxide		9.75	620	706	91			0.159	0.02	
					Sulfur Dioxide		38	160	586				2.16		
7. Aylmore and Barrer (1966)	Carbolac (735 m^2/g)	0.497	3.11	0.180	Nitrogen	25	92		1.33	0.187	1.148	0.159	10.0	1.41	1.38
					Argon		98		1.110	0.182	0.961	0.137	9.27	1.52	1.32
					Krypton		430		0.771	0.0445	0.664	0.0452	40.2	2.32	2.74
8. Ash et al. (1967)	Carbon (200 m^2/g)	0.43	3.54	0.29	Argon	25	7.55		1.8	0.47		5.28	6.08	1.61	
	Graphon (79 m^2/g)	0.42	3.22	0.29	Argon		2.30		4.8	0.19		9.90	16.3	0.64	
9. Ash et al. (1972)	Graphon (89.8 m^2/g)	0.423	4.21	0.324	Helium	35	0.97		54		37.8				
					Nitrogen		2.68		20.4	15.3	14.3	10.8	0.68	0.51	
	Carbolac (1028 m^2/g)	0.48	4.1	0.32	Argon	35	220.7		0.95	0.120	0.64	0.122	8.65	1.09	
					Nitrogen		203.8		1.14	0.121	0.76	0.136	9.1	0.97	
	Carbolac (1052 m^2/g)	0.47	4.16	0.321	Methane	35	396		1.30	0.092	1.01	0.077	39.61	2.81	

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*Temperature at (21°C); **temperature at (17°C); ++cm^3/gram adsorbent; # determined from transient permeation data; ## determined from steady state permeation data.

Shah, D.B., S. Chokchai-acha, and D.T. Hayhurst, "Measurement of Transport Rates of C4 Hydrocarbons Across a Single Silicalite Membrane," *Trans. Faraday Soc.*, **89**(16), 3161 (1993).

Simon, A.M. and Z.J. Grzywna, "Time Lag Analysis of Mass Transport Through Catalytically Active Membranes," *Chem. Eng. Sci.*, **48**(6), 1051 (1993).

Tsimillis, K. and J.H. Petropoulos, "Experimental Study of a Simple Anomalous Diffusion System by Time Lag and Transient State Kinetics," *J. Phys. Chem.*, **81**, 2185 (1977).

Tshudy, T. and C. Von Frankenberg, "A Model Incorporating Reversible Immobilisation for Sorption and Diffusion in Glassy Polymers," *J. Polymer Sci. B*, **11**, 2027 (1989).

Van Amerongen, G.J., "The Permeability of Different Rubbers to Gases and its Relation to Diffusivity and Solubility," *Journal of Applied Physics*, **17**, 972 (1946).

Vieth, W.R., *Diffusion in and Through Polymers*, Hansen Publishers, New York, 1991.

Vieth, W.R., J.M. Howell, and J.H. Hsieh, "Dual Sorption Theory," *Journal of Membrane Science*, **1**, 177 (1976).

Vieth, W.R. and K.J. Sladek, *J. Colloid Sci.*, **20**, 1014 (1965).

Wang, C.T. and J.M. Smith, *Chem Eng. Sci.*, **34**, 267 (1979).

Wicke, E. and R. Kallenbach, *Kolloid-Z*, **17**, 135 (1941).

Yasuda, H. and K.J. Rosengren, "Gas Permeability of Polymers," *J. Appl. Polym. Sci.*, **14**, 2839 (1970).