Determination of small (<30 seconds) diffusional time lags in permeation experiments

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INTRODUCTION

Gas and vapour transport through polymeric films is studied in permeation cells. A thin film of the polymer separates two chambers, both of which are evacuated. One side of the membrane, the upstream side is suddenly exposed to a fixed pressure of the penetrant gas or vapour and the progress of the permeation is observed by measuring the rate of build up of pressure in the closed space on the downstream side. The rate of pressure build up on this side follows a curve similar to the one in *Figure 1*.

The line A–X shows background leakage into the downstream closed space. The penetrant is admitted to the upstream space at time, $t = 0$, corresponding to point A on the curve. There is then a short delay due to diffusion within the membrane before the penetrant begins to emerge at the downstream face of the membrane, at point B. The pressure then rises exponentially until at point C, steady-state flow through the membrane has been reached and the rate of pressure increase with time is linear. The portion of the curve C–D represents this steady-state flow through the membrane. From the gradient of this line the rate of pressure increase with time is found ($\mathrm{d}p/\mathrm{d}t$). From the known constant volume of the downstream chamber, the rate of gas transport across the membrane is calculated:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{273 \times V \times \mathrm{d}p/\mathrm{d}t}{760 \times T}$$

Then the permeability coefficient is given by:

$$P = \frac{\mathrm{d}V/\mathrm{d}t \times \text{Membrane thickness}}{\text{Membrane area} \times \Delta P}$$

The permeability coefficient is a phenomenological coefficient, not a property of the membrane in general, and bears no reference to the actual permeation mechanism which is now known to be a combination of solution and diffusion. The permeation coefficient is the product of the solubility and diffusion coefficients, $P = D \times S$, and it is possible to obtain a value for the diffusion coefficient indirectly from the data in a typical permeation/time curve. The technique, attributed to Daynes[1] is based on an extrapolation of the steady-state portion of the curve C–D back to the time-axis. Where this line intersects the time-axis, or more accurately the extrapolation of X–A which will allow for background leakage, is the value of the time lag (L), which is related to the diffusion coefficient (D):

$$D = \frac{l^2}{6L}$$

Amerongen[2] has reviewed possible sources of error in measuring the permeation coefficient, and permeation cells are designed bearing in mind the general principles Amerongen has laid down. The effect of cell design on accurate determination of the time lag has also to be taken into account, and the optimum permeation cell is a compromise between one that enables permeation to proceed so quickly that observation of the pressure–time curve is impossible, and one which is so slow that background leakage becomes more important than true gas permeation. Conventional permeation cells are designed to ensure that observation of the pressure–time curve, with for instance a Pirani gauge, can proceed for three to four times the time lag. In this way, confidence in the accuracy of the time lag is increased, since accurate extrapolation to the time lag demands knowledge that the steady state has been reached. Crank[3] has shown that the steady state has been reached when $Dt/l^2 = 0.45$, and Amerongen has shown that to obtain a time lag with an error less than 1% the steady state flow must be observed for at least three times the time lag. Cells are usually designed for an experimental time scale of the order of many minutes, and such long term experiments benefit from not having to determine the start time with undue precision, for instance a stopwatch started the moment penetrant is admitted to the upstream side of the membrane may be considered sufficient. However, any attempt to reduce the time scale of an experiment will encounter difficulties with measuring the start time, and, the shorter the time scale, the more critical does accurately defining the start time become.

An apparatus is described with which it was possible to measure time lags as small as 12.8 seconds, with steady state permeation confidence achieved at 2 min. The method is demonstrated for a thin silicone rubber membrane.

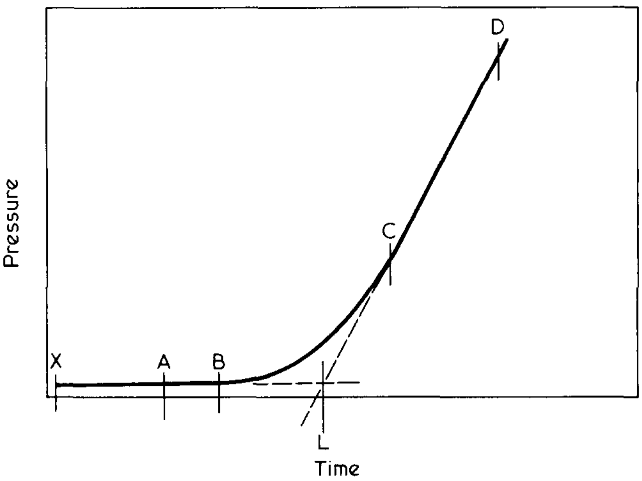

Figure 1 Typical curve showing the rate of pressure build-up in the downstream space in a permeation experiment

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Table 1 Values of the time lag broken down into temperature groups and a comparison of the values of the diffusion coefficient achieved by different methods

Penetrant	Mean Temperature °C (SD)	No. of expts	Range of pressure difference (mmHg)	Time Lag (s)				Diffusion coefficient x 10^6 ($cm^2 s^{-1}$)		
				Mean	Highest	Lowest	SD	$\bar{D}_L$	$\bar{D}_S$	D
n-Pentane	22.3 (0.3)	11	8–77	18.6	19.8	15.4	1.30	1.45	2.37	
	29.8 (0.2)	14	6–64	17.5	19.4	15.5	1.17	1.56	2.42	
	36.9 (0.5)	16	6–88	16.5	18.5	15.0	1.43	1.64	2.97	
	49.5 (0.38)	13	6–83	14.9	16.8	12.8	1.17	1.82	4.09	
Ethrane	22.5 (0.39)	8	11–39	25.4	27.8	20.6	2.54	1.07	1.23	1.24
	30.1 (0.09)	8	6–27	24.0	27.6	21.0	2.46	1.13	1.43	1.52
	40.1 (0.25)	8	11–24	21.1	22.7	19.0	1.24	1.28	1.90	1.96
	50.0 (0.17)	7	12–42	20.1	22.5	18.1	1.82	1.34	2.34	2.51
Halothane	22.3 (0.13)	14	4–52	22.4	28.0	19.9	2.20	1.21	1.34	1.44
	30.5 (0.25)	4	19–53	20.2	20.6	19.9	0.31	1.33	1.68	1.80
	35.3 (0.26)	5	21–39	19.7	19.9	19.4	0.24	1.37	1.90	2.00
	39.9 (0.23)	5	26–41	18.6	19.4	18.1	0.50	1.44	1.99	2.14
	49.4 (0.95)	4	20–75	17.3	18.8	16.0	1.15	1.55	2.34	2.46

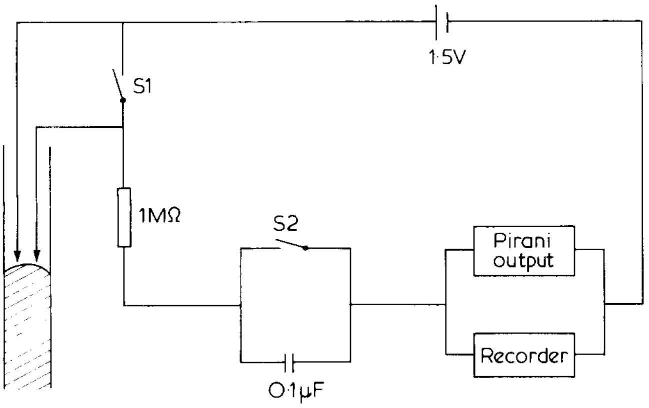

Figure 2 Permeation cell start time indicator. S1 and S2 are push on switches for manual event marking and discharging the capacitor for instant re-use

Apparatus

The permeation cell was a simple assembly produced by sandwiching the silicone rubber between two flange joints and sealing all around the edges with Apiezon wax. The downstream face of the membrane was supported on a grade 1 sintered glass disc. The assembly left 0.891 cm^2 of membrane face exposed to penetrant. The membrane was of 0.0127 cm thick silicone rubber, a copolymer of dimethoxysiloxane with a small amount of methyl vinyl siloxane for mechanical strength, vulcanized with 6% 2,4-dichlorobenzoyl peroxide and containing fume silica (0.02 μ) as an inert filler at approximately 25% loading. This chamber was wrapped with fine tubing, through which water from a thermostat was pumped, and insulated with cotton wool. The downstream side of the membrane was a closed space (120 cm^3) which contained an Edwards G5C2 Pirani gauge head to monitor pressure. Output from the Pirani 14 meter was recorded on a 10 mV chart recorder. This arrangement proved to be quite satisfactory in ensuring a rapid response to pressure change and has the added advantage of ensuring that ΔP remains essentially constant across the membrane since experiments were always complete before the pressure in the downstream space had risen above 1 mmHg.

The upstream side of the membrane was connected to a source of penetrant at constant pressure and an open ended U-tube mercury manometer. The mV output from the Pirani gauge was calibrated with a McLeod gauge for the vapours of interest. The final and novel part of the assembly was the device which indicated the start time. This was a pair of platinum wires which were placed marginally above the meniscus of the mercury in the limb of the U tube open to the atmosphere. These wires were part of the circuit shown in *Figure 2.*

With the chart recorder running, monitoring background leakage, the penetrant was suddenly admitted to the upstream side of the membrane. This caused a rapid movement of the mercury in the manometer, completing the circuit and putting a 1.5 mV spike on the recorder trace, effectively marking the start time at the instant penetrant entered the upstream space. The results of an experiment thus consisted of the mV *versus* time curve from the Pirani gauge with the start time conveniently marked. The mmHg *versus* time curve, akin to *Figure 1*, was constructed from the McLeod gauge calibration graphs for the Pirani gauge.

Results

Permeation experiments were conducted in the temperature range 20°–50°C, for transport of n-pentane, ethrane (2-chloro-1,1,2-trifluoroethyldifluoromethyl ether) and halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) through the silicone rubber at pressures rising to 90 mmHg. Halothane and ethrane are volatile anaesthetics and the method was devised to measure the transport properties of these agents in the silicone rubber. The full quantitative data of the measurements are reported elsewhere[4], the sole objective of this communication being to present the new method for measuring small time lags and to discuss the accuracy achieved.

Results are listed in *Table 1*, which shows the mean, range and standard deviation (δn-1) of each group of time lags measured. The range of pressure difference across the membrane is also shown as the maximum and minimum values.

DISCUSSION

There is no correlation between time lag and the pressure difference across the membrane, except for n-pentane which was found to have a diffusion coefficient which increases with concentration. Permeation of both ethrane and halothane occurred with a diffusion coefficient independent of concentration. Thus the analysis of the n-pentane data is complicated by a range in values of the time lag over and above that caused by the experimental error. The results show clearly that the diffusional time lag can be measured with good reproducibility even down to 12.8 seconds. To assess the accuracy of the method, the diffusion coefficient calculated from the mean time lag ($\bar{D}_L$) was calculated, and this is compared with $\bar{D}_S$ and D. $\bar{D}_S$ is the diffusion coefficient calculated as the mean of n diffusion coefficients, each calculated from the equation $P = D \times S$ for each experiment, where P was derived from the gradient of the C–D portion of the permeation curve, and the solubility, S, was extracted from the measurement of equilibrium solubility data with a quartz spring balance[4]. When the permeation rate or flux of gas across the membrane was plotted as a function of pressure difference across the membrane a line was produced showing the effect of concentration (pressure) on permeation. For ethrane and halothane the line was linear and the gradient of this line was used in conjunction with the equilibrium solubility data to calculate the diffusion coefficient D. The curving of this line was taken as an indicator of concentration-dependent diffusion for n-pentane. D and $\bar{D}_S$ are essentially the same, D being averaged graphically rather than numerically.

The diffusion coefficient measured by the time lag, $\bar{D}_L$, is consistently lower than that calculated from the steady state permeation region of each curve D_S. The percentage difference was calculated for each experiment.

$$\Delta D = \frac{D_S - D_L}{D_L} \times 100$$

and the mean percentage difference calculated

$$\overline{\Delta D} = \frac{\displaystyle\sum_{0}^{n} \frac{D_S - D_L}{D_L} \times 100}{n}$$

D_L was usually lower than D_S, only in one experiment out of each penetrant series was a D_L greater than D_S recorded.

Penetrant	No. of Expts	$\overline{\Delta D}$	Limits Max ΔD	 Min ΔD	SD (δn)
n-Pentane	54	83	243	−3	55
Ethrane	31	42	99	−9	55
Halothane	32	27	58	−7	17

Thus, on average, the diffusion coefficient measured by the short time time lag is 27 (halothane) to 42% (ethrane) lower than the diffusion coefficient measured by steady state permeation and equilibrium solubility measurements. The high value (83%) for n-pentane seems to be at least in part due to the effects of concentration dependance of the diffusion coefficient. Barrer *et al.*[5,6] who measured n-pentane diffusion in a similar rubber found that on average D_S was 5.2% greater than D_L. However, they operated over a pressure range (0–10 mmHg) that would not produce the same problems with concentration dependence of the diffusion coefficient. They also used a thicker membrane (0.2 cm) and consequently measured much longer time lags (~14 min). It is not unusual for D_S to exceed D_L, indeed it is only with very simple penetrants (i.e. the permanent gases) that the two diffusion coefficients are ever seen to be equal. Considering the bulk of the penetrant molecules (halothane and ethrane) it seems very likely that relaxation of the membrane will be involved in the solution process and relaxation has long been held responsible for differences between D_L and D_S in other penetrant/polymer systems.

Nomenclature

$\frac{dp}{dt}$ = rate of change of pressure in downstream side of permeation cell with time (mmHg s^{-1})
V = volume of downstream side of permeation cell (cm^3)
T = temperature of downstream side of permeation cell (K)
$\frac{dV}{dt}$ = rate of transfer of gas across the membrane surface (cm^3 (STP) s^{-1})
P = permeability coefficient $\frac{cm^3\,(STP).cm^2}{cm.mmHg.s}$
Δp = pressure differential across the membrane (mmHg)
D = diffusion coefficient ($cm^2.s^{-1}$)
S = solubility coefficient (cm^3(STP).$cm^{-3}mmHg^{-1}$)
l = membrane thickness (cm)
L = time lag (s)
D_L = diffusion coefficient from the time lag ($cm^2\ s^{-1}$)
D_S = diffusion coefficient from individual C–D line
$\bar{D}_L$ = mean diffusion coefficient from the time lag ($cm^2\ s^{-1}$)
$\bar{D}_S$ = mean diffusion coefficient from n(C–D) lines
ΔD = percentage difference between D_S and D_L
$\overline{\Delta D}$ = mean percentage difference between D_S and D_L

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