The Time Lag for the Diffusion of Gas Mixtures

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The diffusion of a gas mixture of several components through a polymer membrane is considered. An expression is obtained for the time lag L *assuming that the component flows are non-interacting and that the component diffusion and solubility coefficients are not functions of concentration. Measurements were made with a krypton–neon mixture and a silicone rubber membrane and good agreement obtained with the theoretical expressions. To establish the steady state of flow in a single component system requires a time of* ~3L. *For mixture diffusion it is shown that this criterion is not usually valid.*

THE solubilities of the rare gases in polymers are so small that for permeation of a mixture of such gases through a polymer membrane the component flows can be treated as non-interacting. The permeability constant P for the mixture is then simply related to the component permeabilities P_i(1). It is also of interest to consider the time lag L for a system of N components of which the flows are non-interacting and the diffusion coefficients are constants. It is assumed that Henry's law is obeyed for each component. Following Daynes[2] and Barrer[3] the solution of the diffusion equation for the i^{th} component with the initial and boundary conditions:

$$\begin{aligned} &C_i = 0,\ 0 < x < l,\ t = 0 \\ &C_i = C'_i, \quad x = 0,\ t > 0 \\ &C_i \sim 0, \quad x = l,\ t > 0 \end{aligned}$$

is

$$Q_i = \frac{tD_iC'_i}{l} - \frac{lC'_i}{6}\left\{1 + \sum_{n=1}^{\infty} \frac{12}{\pi^2} \frac{(-1)^n}{n^2} \exp\left(-\frac{n^2\pi^2}{l^2} D_i t\right)\right\} \tag{1}$$

Q_i is the amount of component i which has passed through unit area of the membrane of thickness l in time t and D_i is the diffusion constant of the component. For a mixture of N components the total amount Q which has permeated is

$$Q = \sum_{i=1}^{N} Q_i \tag{2}$$

and for $t \longrightarrow \infty$ the linear steady state relation

$$Q = (t/l) \sum D_iC'_i - (l/6) \sum C'_i \tag{3}$$

is obtained. The intercept of the straight line on the time axis gives the time lag L,

$$L = (l^2/6) \sum C'_i / \sum D_iC'_i = l^2/6D \tag{4}$$

so that

$$D = \sum D_iC'_i / \sum C'_i \tag{5}$$

The time lag L may also be expressed in terms of the time lags L_i of the pure components,

$$L = \sum C'_i / \sum (C'_i/L_i) \tag{6}$$

The steady state permeability is given by[1]

$$P=\frac{l}{\Sigma p_i}\left(\frac{\mathrm{d}Q}{\mathrm{d}t}\right)_{t\to\infty}=\frac{\Sigma D_i C'_i}{\Sigma p_i}=\frac{\Sigma P_i p_i}{\Sigma p_i} \tag{7}$$

where p_i is the partial pressure of the i^{th} component in the perfect gas mixture and P_i is the permeability coefficient of the i^{th} component. When Henry's law is obeyed for each component then $C'_i=\sigma_i p_i$ and the solubility coefficient for the mixture is

$$\sigma=\Sigma\, C'_i/\Sigma\, p_i=\Sigma\, \sigma_i p_i/\Sigma\, p_i \tag{8}$$

For a mixture of fixed composition it follows that P, D, L and σ are independent of the total ingoing pressure $\Sigma\, p_i$ and are constant. As for diffusion of a single component the relation $P=D\sigma$ is valid provided the composition of the mixture is kept constant.

To test equations (5) and (7) measurements were made at several temperatures with binary mixtures of krypton[1] and neon[3] using conventional permeation apparatus[4]. The membrane of thickness 1·06 (cm) was a polyphenylmethylsiloxane rubber (5·4 per cent phenyl content) lightly cured with 2,4-dichlorobenzoyl peroxide. Two gas mixtures were used for which the mole ratios of neon to krypton, n_2/n_1, were 1·01 and 2·73. The permeation rates of the components were not sufficiently large to cause any significant change in the composition of the ingoing gas phase by permselective fractionation during the relatively short period of a permeation experiment.

For both the pure components and the mixtures the diffusion coefficient was obtained from the relation $D=l^2/6L$ and the solubility coefficient from $P=D\sigma$. The relationships $D=D_0 \exp(-E_D/RT)$ and $\sigma=\sigma_0 \exp(-\Delta\bar{H}^0/$

Table 1. Values of P, D and σ for Kr(1) and Ne(2)

°K	$P\times10^7$ $\left(\frac{cm^3\, s.t.p.\, cm}{cm^2 .\, cmHg\, .\, sec}\right)$		$D\times10^4\,(cm^2\, sec^{-1})$		$\sigma\times10^3$ $\left(\frac{cm^3\, .\, s.t.p.}{cm^3\, .\, cmHg}\right)$	
	(1)	(2)	(1)	(2)	(1)	(2)
343·2	2·56	0·955	0·55	1·61	4·6	0·59
333·2	2·38	0·821	0·49	1·46	4·9	0·56
323·2	2·21	0·700	0·43	1·31	5·1	0·54
313·2	2·05	0·587	0·38	1·16	5·4	0·51

Table 2. P and D (measured values) and P^* and D^* (calculated values) for mixtures of Kr(1) and Ne(2)

		mole ratio $n_2/n_1=1·01$		
°K	$P\times10^7$	$P^*\times10^7$	$D\times10^5$	$D^*\times10^5$
343·2	1·86	1·75	6·5	6·7
333·2	1·70	1·60	5·8	5·9
323·2	1·51	1·45	5·1	5·2
313·2	1·37	1·32	4·5	4·5
		mole ratio $n_2/n_1=2·73$		
343·2	1·44	1·38	8·4	8·3
333·2	1·28	1·24	7·4	7·2
323·2	1·14	1·01	6·5	6·3
313·2	1·00	0·98	5·6	5·4

RT) were obeyed for all systems with D_0 and σ_0 effectively independent of the temperature over the range investigated. Smoothed values of P, D and σ for the pure gases are given in *Table 1*. In *Table 2* experimental values of P and D for the mixtures are compared with corresponding values calculated from equations (7), (5) and (8) using the results for the pure components. Values of E_D, D_0 and $\Delta\overline{H}^0$ for both the pure components and the mixtures are given in *Table 3*.

Table 3. Values of E_D, D_0 and $\Delta\overline{H}^0$

Gas	E_D (*kcal mole*$^{-1}$)	D_0 (*cm*^{2} *sec*$^{-1}$)	$\Delta\overline{H}^0$ (*kcal mole*$^{-1}$)
Kr	2·7	0·0027	−1·05
Ne	2·4	0·0049	1·13
Kr : Ne (1·01)	2·6	0·0030	−0·33
Kr : Ne (2·73)	2·8	0·0050	−0·30

The agreement between calculated and experimental values of P and D for the mixtures is within the limits of the experimental error so that the fluxes of neon and krypton can be considered to be virtually non-interacting. From equations (5) and (6) it is clear that the temperature dependence of both D and σ for mixtures is more complex than that for pure components. However, for the neon–krypton mixtures of this investigation any departure from linearity in the plots of $\log D$ and $\log \sigma$ versus $1/T$ was not sufficiently marked to be detected within the accuracy of the measurements.

Finally it is of interest to compare the time taken to establish the steady state of flow for a mixture with that for a pure component. For single component diffusion the term

$$\alpha_i = \sum_{n=1}^{\infty} \frac{12}{\pi^2} \frac{(-1)^n}{n^2} \exp\left(-\frac{n^2\pi^2}{l^2} D_i t\right)$$

of equation (1) has the values of $-0{\cdot}01$ and $-0{\cdot}001$ for $t/L = 2{\cdot}92$ and $4{\cdot}3$ respectively. Thus to establish a steady state of flow so as to yield a time lag with an error of less than one per cent would require a time greater than $2{\cdot}92\ L^5$. For mixture diffusion the corresponding term is $\alpha = \Sigma_i C'_i \alpha_i / \Sigma C'_i$. Values of t/L for which $\alpha = -0{\cdot}01$ were calculated for a binary mixture as a function of the fraction $F_i = C'_i / \Sigma_i C'_i$ for several values of the ratio $K = D_2/D_1$ and are shown in *Table 4*. For the binary mixture t/L is always greater than 2·92 and passes through a maximum located at relatively high mole fractions of the component with the larger value of D. For example, for $K = 100$, the maximum value of t/L is ~ 155 at $F_2 = 0{\cdot}80$. On the other hand the value of L for this composition will be close to the smaller value of the pure component time lags, namely $1{\cdot}24\ L_2$. For the neon–krypton mixtures $K \sim 3$ with $F_1 = 0{\cdot}1$ and $0{\cdot}2$ so that the departure from single component behaviour is not marked as was also observed experimentally.

Calculations were also made of the time required to establish a steady state of flow in which P is within one per cent of its equilibrium value ($t \longrightarrow \infty$). The flux ($\mathrm{d}Q/\mathrm{d}t$) follows from equations (2) and (1) and for single component diffusion the term

$$\beta = -\frac{2}{\sum_{i=1}^{N} D_i C'_i} \cdot \sum_{i=1}^{N} \sum_{n=1}^{\infty} D_i C'_i (-1)^{n+1} \exp \frac{(-n^2\pi^2 D_i t)}{l^2}$$

is $-0{\cdot}01$ for $t/L=3{\cdot}21$ (cf. 2·92 for $\alpha=-0{\cdot}01$). Thus for pure component diffusion the steady state flux is established within one per cent of its value $(\mathrm{d}Q/\mathrm{d}t)_{t\to\infty}$ after a time of 3·21 L. Values of t/L for binary mixtures with $\beta=-0{\cdot}01$ are also given in *Table 4* and its variation with composition is illustrated more clearly in *Figure 1*. Particularly for the higher D_2/D_1 ratios, the values of t/L for $\alpha=-0{\cdot}01$ are generally larger than for $\beta=-0{\cdot}01$ indicating that usually it takes longer to establish a steady state of flow so as to give L within one per cent of its equilibrium value than to give P within one per cent of its equilibrium value. It can also be shown that for

Table 4. Variation of t/L with composition of mixture for $\alpha=-0{\cdot}01$ and $\beta=-0{\cdot}01$ (in parentheses)

Composition F_2	t/L				
	$K=2$	$K=5$	$K=10$	$K=100$	$K=500$
0·0	2·92 (3·21)	2·92 (3·21)	2·92 (3·21)	2·92 (3·21)	2·92 (3·21)
0·1	3·41 (3·40)	3·99 (4·12)	5·42 (5·24)	31·08 (18·46)	145·1 (38·51)
0·2	3·34 (3·56)	5·00 (4·89)	7·78 (6·85)	57·82 (25·57)	280·2 (27·19)
0·3	3·51 (3·69)	5·94 (5·53)	9·99 (8·13)	82·85 (27·98)	406·7 (1·39)
0·4	3·65 (3·79)	6·77 (6·03)	11·98 (9·07)	105·8 (26·29)	522·6 (1·50)
0·5	3·76 (3·84)	7·48 (6·36)	13·72 (9·64)	126·0 (20·41)	624·8 (1·76)
0·6	3·80 (3·82)	8·02 (6·49)	15·09 (9·76)	142·5 (9·64)	708·5 (2·04)
0·7	3·77 (3·72)	8·30 (6·33)	15·94 (9·27)	153·3 (2·91)	764·9 (2·33)
0·8	3·63 (3·55)	8·14 (5·71)	15·88 (7·81)	155·4 (2·87)	775·2 (2·62)
0·9	3·35 (3·33)	6·97 (4·31)	13·79 (4·55)	136·6 (3·02)	682·3 (2·91)
1·0	2·92 (3·21)	2·92 (3·21)	2·92 (3·21)	2·92 (3·21)	2·92 (3·21)

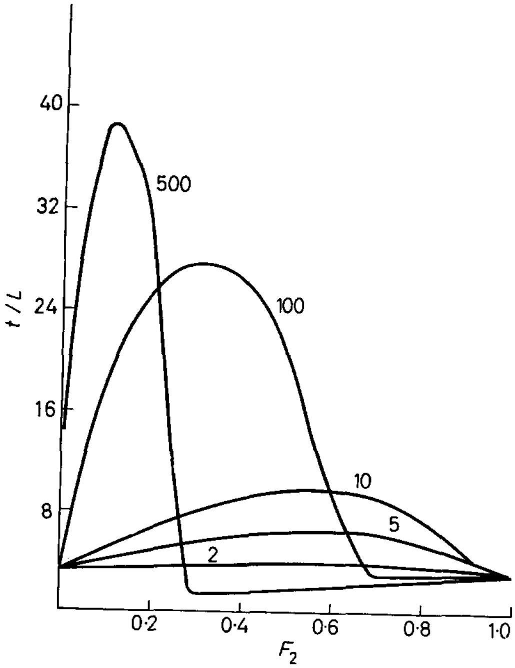

Figure 1—Variation of $t/L\,(\beta=-0{\cdot}01)$ with composition for a binary mixture with different K values

the binary mixture 2·92 (3·21) $L_2 < t < 2{\cdot}92\,(3{\cdot}21)\,L_1$ so that the time to establish the steady state such that either L or P is within one per cent of its equilibrium value is not longer than the corresponding time for the component with the largest time lag. In general it is clear that for mixture diffusion the criterion that the steady state of flow is established after a time $\sim 3L$ is not usually valid.

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