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The kinetics of volatilization from lead glasses

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The diffusion plus surface reaction theory first applied to glass melts by Terai and Ueno is examined and used to interpret several sets of data by Preston and Turner. First methods of evaluating the reaction rate constant and diffusivity are examined. A simple graphical method is shown to be capable of giving good results in some cases but a sophisticated computer program is needed in other cases.

The theory describes all the data reasonably and the dependence of reaction and diffusivity on temperature and melt composition are evaluated. Most sets of experiments give internally consistent sets of values of the parameters but diffusivity, especially, varies more between different experiments than is reasonable. The true meaning of the diffusivities and reaction rate constants is not clear.

Cinétique de la volatilisation à partir de verres au plomb

La théorie de la diffusion à laquelle se superpose une réaction en surface, qui avait été appliquée pour la première fois aux fontes de verres par Terai et Ueno, est examinée et utilisée pour interpréter plusieurs séries de données fournies par Preston et Turner. On examine en premier lieu les méthodes permettant d'évaluer la constante de vitesse de réaction et la diffusibilité. On montre qu'une méthode graphique simple est susceptible de donner de bons résultats dans certains cas mais qu'un programme élaboré de traitement sur ordinateur est requis dans d'autres cas.

La théorie décrit toutes les données de façon satisfaisante et les relations liant la réaction et la diffusibilité à la température et à la composition de la fonte sont évaluées. La plupart des séries expérimentales fournissent pour les paramètres des séries de valeurs répondant à une logique interne, bien que la diffusibilité, en particulier, varie de manière moins acceptable au cours des différents essais. La signification réelle des diffusibilités et des constantes de vitesse de réaction n'apparaît pas clairement.

Zur Kinetik der Verflüchtigung bei Bleigläsern

Die Theorie der Diffusion und Oberflächenreaktion, die zuerst von Terai und Ueno auf Glasschmelzen angewandt wurde, wird überprüft und zur Interpretation einer Reihe von Ergebnissen von Preston und Turner angewandt. Vor allem werden Methoden zur Berechnung der Reaktionsgeschwindigkeitskonstante und des Diffusionskoeffizienten untersucht. Es wird gezeigt, daß eine einfache grafische Methode in einigen Fällen gute Ergebnisse liefert und in anderen ein verfeinertes Rechenprogramm notwendig ist.

Die Theorie liefert eine plausible Erklärung für alle Literaturdaten sowie für die festgestellte Abhängigkeit der Reaktion und des Diffusionskoeffizienten von der Temperatur und der Zusammensetzung der Schmelze. Innerhalb der meisten Versuchsreihen ergaben sich jeweils übereinstimmende Werte für die Parameter; zwischen den einzelnen Versuchsreihen variiert aber besonders der Diffusionskoeffizient in einem Umfang, der nicht erklärt werden kann. Die genaue Bedeutung der Diffusionskoeffizienten und der Reaktionsgeschwindigkeitskonstanten ist ungeklärt.

Volatilization from glass melts has long been of interest to glass makers because such losses change the composition and the properties of the glass [1]. Volatilization losses may lead to serious problems with cord [2] and surface devitrification [3]. In recent years some other aspects have become very important; among these are corrosion of the furnace superstructure, pollution and corrosion of regenerators and pollution of the atmosphere. Many countries are introducing progressively stricter regulations about emissions from furnace chimneys and severe penalties for exceeding the legal limits. Atmospheric pollution has thus been the most discussed aspect in recent years.

There are more scientific reasons for studying volatilization. The chemical behaviour of glass melts is complex and far from being either ideal or regular but the high temperature chemistry of many vapours is known or, at least, predictable with reasonable accuracy. Detailed measurements of equilibria or the kinetics of exchange between glass melts and various vapour

species thus should lead to important advances in understanding the chemistry of glass melts.

1. Experimental Methods

The most widely used method has been to measure loss in weight for different times at constant temperature. Chemical analysis of the whole sample after suitable times indicates the composition of the volatile material which may also be determined by condensing and then analysing the volatile material itself. With many glasses the loss in weight may be attributed entirely to one species (allowance may have to be made for loss in weight of the sample container, usually platinum). The most volatile common constituents of glasses are alkali oxides, lead oxide and boric oxide but these may not be the species actually present in the vapour.

More information about the kinetics could be obtained by measuring concentration distributions in the

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melt. This is now possible though not always straightforward, by electron microprobe analysis and some data have been reported by Matoušek and Hlaváč [4]. Variation of refractive index with distance from the interface was measured by Dietzel and Merker [5] and also demonstrated (for water in silica) by Hetherington and Jack [6].

2. Interpretation

General knowledge of the properties of glass melts at high temperatures implies that volatilization is probably controlled by diffusion of the volatile species through the melt. The simplest plausible model therefore is to consider the sample as a semi-infinite slab with the concentration of volatile material suddenly reduced to zero at its upper surface. The total loss in weight (M) per unit surface area would then be:

$$M = \frac{2}{\sqrt{\pi}} C_0 (Dt)^{1/2}, \quad (1)$$

where C_0 is the initial uniform concentration of volatile material in the melt (g cm^{-3}), D is the effective diffusivity of this species through the melt ($\text{cm}^2 \text{s}^{-1}$) and t is time (s). Evaluation of C_0 requires that the density of the melt at the temperature of the experiment be known.

Rigorously this equation could only be said to describe fully the experimental results if four separate criteria were satisfied:

1. A plot of M vs $t^{1/2}$ was a straight line.
2. Backward extrapolation of this line gave $M=0$ at $t=0$.
3. The diffusivity (D) evaluated from the slope ($dM/d(t^{1/2})$) agreed with values expected from other types of experiment.
4. Weight loss was proportional to the surface area of the melt exposed to the atmosphere.

The first of these criteria has been confirmed by several authors, for example Oldfield and Wright [7], Matoušek and Hlaváč [4]. The second cannot be applied rigorously because of experimental errors which may include the time needed for the system to reach thermal equilibrium. For the latter reason one would often expect the intercept ($M=0$) at $t=5$ to 15 min rather than $t=0$. Some data show values of this intercept much greater than can be accounted for by likely experimental errors (see Matoušek and Hlaváč [4]).

The third criterion is almost impossible to satisfy. Most glasses are multi-component ones and the effective diffusivity depends very much on the type of experiment made [8]. Existing knowledge and data are rarely adequate for a rigorous test. Nevertheless the expected order of magnitude of D , its temperature dependence and composition dependence can often be estimated; such qualitative tests have to be accepted at present.

The last criterion was found correct for a soda-lime-silica glass [9] but only for four surface areas from 2,15 to 5,75 cm^2 and also for PbO-SiO_2 glass by Andersen [10]. Most other authors have assumed it valid without test.

Some data do not fit this simple model. Turner and his colleagues [11] were able to change M by almost a factor of two simply by varying the shape of the capsule containing the sample. Barlow [12] found that loss was

markedly dependent on the velocity of flow of gas over the sample.

Terai and Ueno [13] suggested an improved theoretical model capable of describing most of the deviations from equation (1). This model replaces the assumption that the interface concentration instantaneously becomes $C_i=0$ by the condition that the flux from the surface of the melt to the vapour is defined by

$$j_i = \alpha (C_i - C_2), \quad (2)$$

where C_2 is the uniform concentration in the vapour some distance from the interface (and is usually zero).

The first order surface reaction is linked to the diffusion process through the requirement

$$j_i = \alpha (C_i - C_2) = -D \left(\frac{\partial c}{\partial x} \right)_i, \quad (3)$$

where $(\partial c/\partial x)_i$ is the concentration gradient in the melt at the interface ($x=0$). The mathematics of this model is discussed below.

Terai and Ueno [13] showed that this model successfully described results for several glasses over a range of temperatures but did not discuss in detail how well theory and experiment agreed. Matoušek and Hlaváč [4] have also used this model. In view of these results it is desirable to see whether this theoretical model describes any other data that are available.

3. Surface reaction plus diffusion model

The melt is considered to be a semi-infinite slab ($0 < x < \infty$) with transport to the vapour phase across its upper surface ($x=0$). Transport within the melt is described by

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \quad (4)$$

thus D is assumed independent of c and no convective flow of any kind is allowed for, although the sample may be relatively fluid. The initial condition is

$$C = C_0, \quad 0 < x < \infty \quad (5)$$

and the boundary conditions for $t \geq 0$,

$$\begin{aligned} C &= C_i, \quad x = 0, \\ C_1 &= C_i, \quad t \rightarrow \infty, \\ C &= C_0, \quad x \rightarrow \infty, \\ j &= \alpha (C_i - C_1), \quad x = 0. \end{aligned} \quad (6)$$

The solution of this problem, for the heat transfer analogue, is given in detail by Carslaw and Jaeger [14]. The results of particular importance here are:

$$M = \frac{C_0 - C_1}{h} \left[\exp(h^2 Dt) \operatorname{erfc} h(Dt)^{1/2} - 1 + \frac{2}{\sqrt{\pi}} h(Dt)^{1/2} \right], \quad (7)$$

where $h = \alpha/D$ and

$$\frac{C - C_1}{C_0 - C_1} = \operatorname{erf} \frac{x}{2(Dt)^{1/2}} + \exp(hx + h^2 Dt) \operatorname{erfc} \left[\frac{x}{2(Dt)^{1/2}} + h(Dt)^{1/2} \right] \quad (8)$$

whence, putting $x=0$,

$$\hat{C}_i = \frac{C_i - C_1}{C_0 - C_1} = \exp(h^2 Dt) \operatorname{erfc} h(Dt)^{1/2}. \quad (9)$$

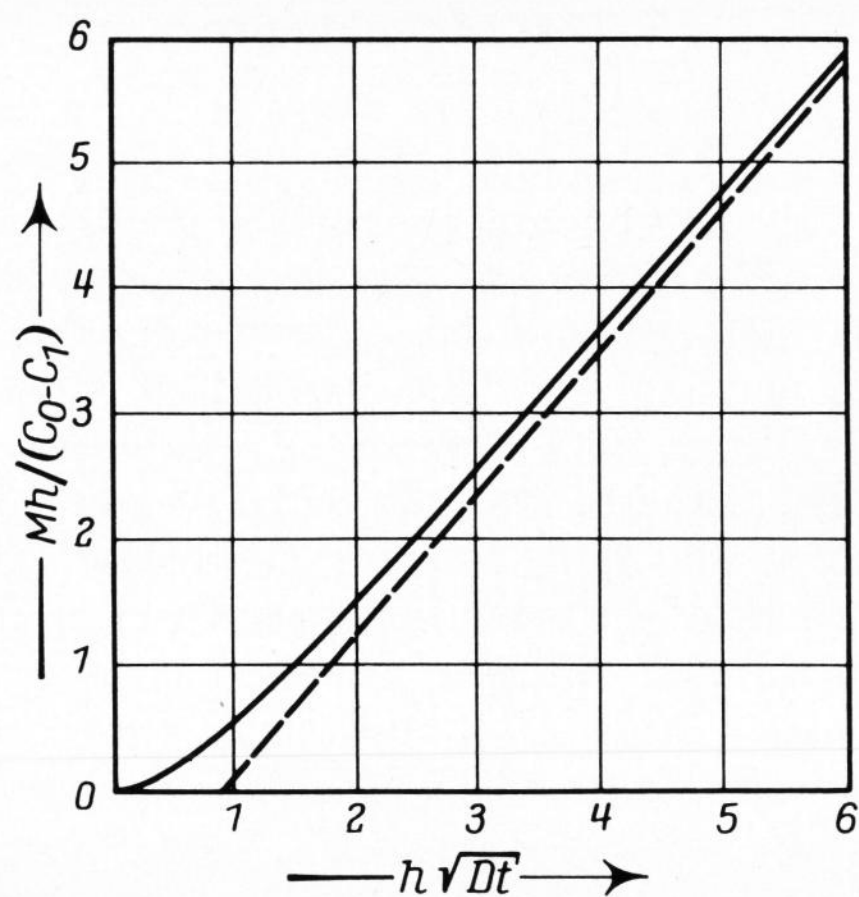


Figure 1. The theoretical relation (equation (7)) between weight loss (M) and time (t) plotted in dimensionless form. The dashed line shows the asymptote for which equations (10) and (12) give the correct values of α and D.

Equation (7) can be expressed in dimensionless form by plotting $Mh/(C_0 - C_1)$ against $h\sqrt{Dt}$ and is shown in figure 1. The interface concentration (equation (9)) is plotted in figure 2.

4. Evaluation of the Parameters

The main data available are a set of values of M at known times. It is also necessary to know $(C_0 - C_1)$. C_0 is obtained from the composition of the melt and its density at the temperature of experiment; this implies identification of the volatile component. The usual experimental conditions mean that both the initial and final equilibrium content of volatile material in the atmosphere (C_2) is zero and one may thus also write $C_1 = 0$.

4.1. Graphical solution

If the data are plotted as M vs $t^{1/2}$ they should correspond to a particular part of the curve shown in figure 1. At sufficiently long times the data lie on a straight line, $C_1 \rightarrow 0$, and the slope may be used to evaluate the diffusivity. In these conditions either equation (7) or equation (1) gives:

$$D = \left[\frac{\sqrt{\pi}}{2(C_0 - C_1)} \frac{dM}{d(t^{1/2})} \right]^2 \quad (10)$$

Backward extrapolation of the tangent to the curve at sufficiently long times gives the condition $M = 0$ when

$$\frac{2}{\sqrt{\pi}} h (Dt^*)^{1/2} = 1, \quad (11)$$

from which it follows that α may be evaluated from the intercept (t^*) on the time axis,

$$\alpha = hD = \frac{(\pi D)^{1/2}}{2 t^{*1/2}} \quad (12)$$

The asymptote to the curve, (equation (7)), which rigorously satisfies these conditions, is shown in figure 1. It is seen that drawing a tangent to the curve and using equation (10) will usually give a value of D which is rather low whilst the intercept and equation (12) will give a value of α which is too high. It takes a surprisingly long time for C_1 to become effectively zero, for example

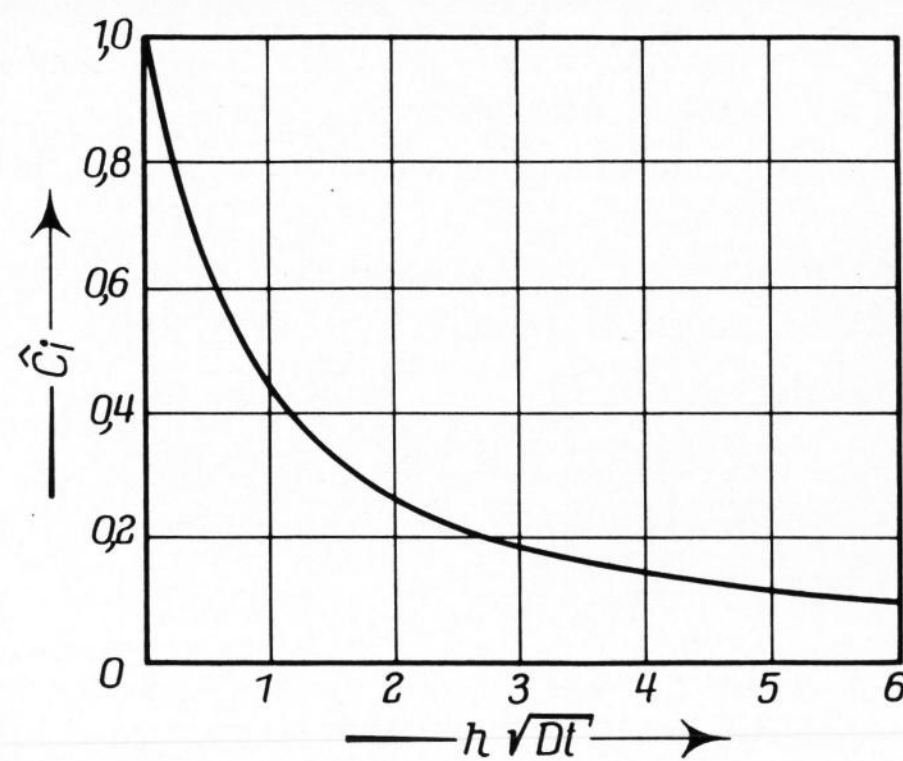


Figure 2. The theoretical dependence of surface concentration on time according to equation (9).

$\hat{C}_1 = 0,01$ at $h\sqrt{Dt} = 56$. The error in α will be larger than the error in D but should be less than a factor of 2. The existence of these systematic errors can be detected by calculating M for the relevant times and comparing with the actual data points.

The above arguments refer to data extending to fairly high values of $h\sqrt{Dt}$. If data are available only for small values of $h\sqrt{Dt}$ an alternative method may be used to evaluate α ; from equation (2),

$$M = \int_0^t j dt = \int_0^t \alpha(C_1 - C_2) dt, \quad (13)$$

and, in typical experimental conditions one assumes $C_2 = 0$ so that this becomes

$$M = \alpha \int_0^t C_1 dt. \quad (14)$$

As $C_1 = C_0$ at $t = 0$ and has fallen only to $0,90 C_0$ at $h\sqrt{Dt} = 0,10$, one may write:

$$\alpha \approx \frac{1}{C_0} \frac{dM}{dt}, \quad (t < 0,01 D/\alpha^2). \quad (15)$$

The slope dM/dt calculated from the first set of data points will, at 'short' times, give a reasonable estimate of α but the value is likely to be rather low: when the theoretical relation shown in figure 1 is replotted in the form M vs t, instead of $t^{1/2}$ the slope decreases with increasing time. The correct values of α and D would then have to be found by trial and error, which could be tedious, if the first estimate of α was poor.

4.2. Computer Solution

The simplest mathematical form for equation (7) is:

$$M = \frac{C_0 - C_1}{h} \left[\exp X^2 \operatorname{erfc} X - 1 + \frac{2}{\sqrt{\pi}} X \right], \quad (16)$$

where $X = h\sqrt{Dt} = A\sqrt{t}$. As a set of values of M (M_1, M_2, \dots, M_y) is known for times t_1, t_2, \dots, t_y , a solution to find the two unknowns h and A should be possible for $y \geq 2$ so long as $(C_0 - C_1)$ is known.

The obvious approach is to find some method of search by which the values of h and A best fitting the data are rapidly obtained even if the first values tried are seriously in error. Two different methods differing considerably in detail have been used.

4.2.1. First program

The first method operates on equation (7) and uses h and D as the variables. The outline of the procedure is:

1. choose h ;
2. calculate D_n from M_n and h , for every value of t ;
3. fit a straight line to $D_n, t_n^{1/2}$. Calculate $dD/d(t^{1/2})$;
4. repeat the cycle for a different value of h ;
5. find the h and D which give the value of $dD/d(t^{1/2})$ closest to zero.

The program uses a Fibonacci [15] search of 40th degree in the range $0,1 < h < 1000$ to make $dD/d(t^{1/2})$ as close to zero as possible. Numerous tests were made to show that the program gave good results. Besides the values of h and D the program also prints the calculated values of M for each given time and the differences between these and the data supplied. Examination of these differences is the most satisfactory way of seeing how well the theory fits the data.

4.2.2. Second program

This method uses equation (7) in the form

$$h_n = \frac{C_0 - C_1}{M_n} \left[\exp(A^2 t_n) \operatorname{erfc}(A\sqrt{t_n}) - 1 + \frac{2}{\sqrt{\pi}} (A\sqrt{t_n}) \right] \quad (17)$$

The outline of the method is:

1. select an arbitrary value of A ;
2. calculate h_n from equation (17) for all pairs of M_n, t_n ;
3. fit a straight line to h_n vs $\sqrt{t_n}$ and calculate $dh/d(t^{1/2})$;
4. repeat the cycle for a new value of A ;
5. find the value of A and hence h for which $dh/d(t^{1/2})$ is sufficiently close to zero.

This program uses the Rosenbrock [16] technique with $\alpha = 3,0$, $\beta = -0,5$ to iterate on A until $dh/d(t^{1/2}) < 1 \times 10^{-9}$. Again it prints out the values of M_n calculated for the given times (t_n).

4.3. Theoretical solution for a finite body

The samples might not be deep enough to act as a semi-infinite body throughout a series of experiments. The theoretical solution for a finite body would be useful to confirm this. A static melt of depth l with no transfer across the bottom surface ($x = 0$) is mathematically equivalent the body $-l < x < l$ with the same boundary conditions at l and $-l$. When all the conditions, except the finite depth of melt (l), are the same as for equations (4) to (7), the required result is:

$$\frac{M}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2L^2}{\beta_n^2(\beta_n^2 + L^2 + L)} \exp - \beta_n^2 Dt/l^2, \quad (18)$$

where M_∞ is the total possible loss (per unit area of surface), $L = lx/D$ and β_n are the positive roots of

$$\beta_n \tan \beta_n = L. \quad (19)$$

This result is derived and discussed (for the heat conduction analogue) by Carslaw and Jaeger [17]. In the conditions of particular interest the series converges quite rapidly.

5. Test of the theory

Fairly extensive data are available for a range of PbO-SiO₂ melts, one PbO-Al₂O₃-SiO₂ melt containing only 2,1 wt% Al₂O₃ and a lead crystal glass. One set of data for another lead crystal glass has already been interpreted by Matoušek and Hlaváč [4] using this model. Glasses containing PbO are particularly suitable for testing the theory. PbO is one of the most volatile oxides used in glasses and of high molecular weight; measurement of M is thus quite a sensitive indicator of its loss and the density of the remaining melt is decreased as lead is lost, consequently the melt is stable and convection not likely to occur. Absence of appreciable convection in a lead glass was confirmed by Kruithof, La Grouw and de Groot [2].

The high rate of volatilization also makes it easy to obtain data for fairly large values of h/\sqrt{Dt} (see figure 1) without requiring very long times for the experiments.

Preston and Turner [18] measured losses from a lead crystal glass containing 29,83 wt% PbO. The samples usually weighed 3,000 g and were heated in platinum capsules with somewhat curved sloping sides which were of 25 mm internal diameter at the top and 10 mm deep. Analysis of 12 samples showed that it was reasonable to assume that only PbO was lost. A graph of M vs t for times up to almost 200 h at temperatures from 900 to 1400 °C appears in the paper and a much larger version of the same graph and a table permitting accurate recovery of the actual M, t data appear in Preston's Ph. D. thesis [19].

A subsequent paper by Preston and Turner [20] reported results for a series of PbO-SiO₂ melts with 53,9 to 99,8 wt% (23,9 to 99,3 mole %) PbO. Losses in 1 h were measured for all compositions at 1000, 1100 and 1200 °C and for 12 out of the 14 compositions at 900 °C. Detailed studies of M vs t were reported only for six compositions at 1200 °C. Chemical analysis again confirmed that the loss could be attributed to PbO alone.

Preston's thesis [19] also contains some data for a glass of composition (in wt%): 65,0 PbO; 32,7 SiO₂; 2,1 Al₂O₃ (+ Fe₂O₃) at 1000, 1100 and 1300 °C.

These data have been analysed graphically and by both computer programs. In every case the graphical evaluation was made before any of the computed results was available. Every set of data was plotted as M vs \sqrt{t} . The slope $dM/d(t^{1/2})$ should not decrease as t increases. Sometimes the last few points showed a decrease in slope and were neglected; there are several reasons why this decrease might happen. First, the sample might not be deep enough to still act as a semi-infinite body; second if D varies with concentration this might cause such an effect, so might surface devitrification and so might the tapered shape of the container. The first possibility can be checked from equations (8) and (18) once α and D have been obtained.

The experimental conditions allow one to assume $C_1 = 0$ but evaluation of C_0 (g·cm⁻³) requires the density of the melt at the temperature of the experiment. Density at room temperature was measured by Weiller [21] for a series of PbO-SiO₂ glasses. Some results quoted by Morey [22] show that replacing up to about 6% SiO₂ by alkali has very little effect on density at room temperature. No data for high temperatures appear

to have been published. The high temperature densities were therefore estimated using the expansion coefficients up to the annealing range and the behaviour of those melts (mainly R_2O-SiO_2) for which high temperature data do exist. A 1% error in density may be considered equivalent to a 1% error in M and, because of the accuracy with which density can be measured, a 1% error in density would be rather large. The errors in the densities assumed are thus not likely to lead to important errors in the values of α and D obtained. The densities used are given in table 1.

The entire body of data is difficult to set out concisely and table 2 gives only a summary including the number of sets of M and t data used (y), M and t for the shortest time (M_1, t_1) and for the longest time (M_y, t_y). Figure 3 shows the data for the lead crystal glass in the form used for the graphical evaluation or to decide whether to truncate the total set of data. A vertical bar is drawn where a set of data has been truncated. Table 3 gives the values of α and D obtained by different methods.

Neither of the two programs gave reasonable values of D for lead crystal at 1400 °C. The values appearing in brackets for this glass at 1400 °C were obtained by fitting the finite slab model to 5 data points as discussed later.

6. Discussion

6.1. Fit of individual sets of data

The first condition for acceptance of the theoretical model is that a good fit to the data can be obtained by suitable choice of α and D . The curves drawn on figure 3 show the theoretical curves according to program 2 and are a reasonable good fit to the data, except at the longest times in some cases. The discrepancies between data and theoretical values (M calculated for given α, D and t) are usually small enough to appear unimportant on such a plot. Figures 4 and 5 therefore show the discrepancies as $M_{calc} - M_{data}$, expressed as a percentage of M_{data} plotted against $h(Dt)^{1/2}$ for lead crystal and the $PbO-SiO_2$ glasses at 1200 °C.

Only a few discrepancies exceed $\pm 5\%$ and several of the largest errors relate to relatively small values of M where a discrepancy of up to 10% is not outside possible experimental errors. Although the errors do not appear

Table 1. Densities at room temperatures and high temperatures in $g \cdot cm^{-3}$

glass in wt%	temperature in °C						
	20 to 25	900	1000	1100	1200	1300	1400
crystal (29,8 PbO)	3,080	2,958	2,941	2,926	2,910	2,895	2,880
90,05 PbO, 9,95 SiO ₂	7,71	—	—	—	7,24	—	—
87,4 PbO, 12,6 SiO ₂	7,23	—	—	—	6,72	—	—
84,8 PbO, 15,2 SiO ₂	6,85	—	—	—	6,35	—	—
82,5 PbO, 17,5 SiO ₂	6,48	—	—	—	6,00	—	—
79,4 PbO, 20,6 SiO ₂	6,14	—	—	—	5,70	—	—
75,6 PbO, 24,4 SiO ₂	5,67	—	—	—	5,29	—	—
65,0 PbO, 2,1 R ₂ O ₃	4,66	—	4,35	4,32	—	4,26	—

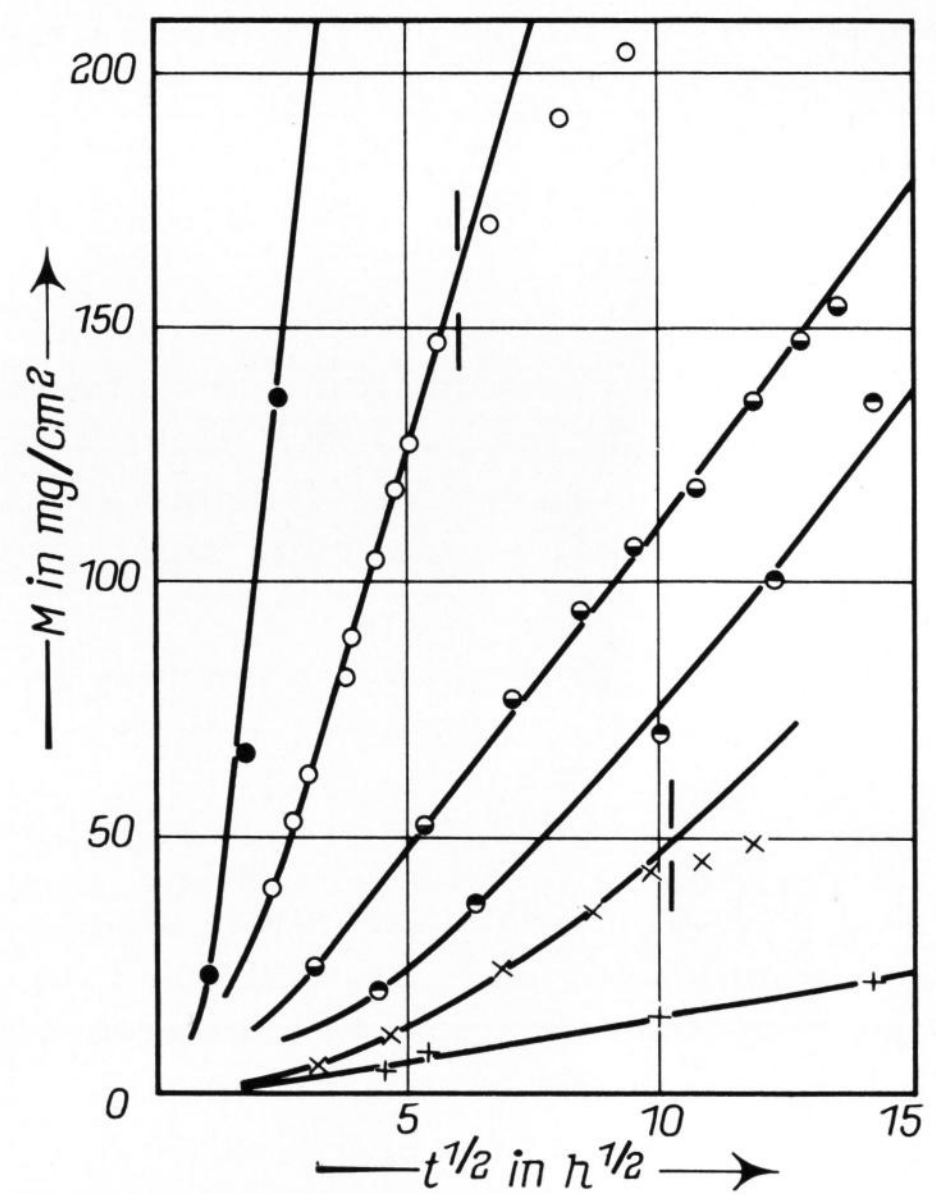


Figure 3. The experimental data for lead crystal compared with the computed theoretical results. Vertical bars show where sets of data were truncated when using the semi-infinite model. The scale of M is expanded $\times 10$ for 1000 and 900 °C.

- 1 $\hat{=}$ 1400 °C; 2 $\hat{=}$ 1300 °C;
- 3 $\hat{=}$ 1200 °C; 4 $\hat{=}$ 1100 °C;
- 5 $\hat{=}$ 1000 °C; 6 $\hat{=}$ 900 °C.

Table 2. Summary of data available

glass in wt %	temperature in °C	C_0 in gcm^{-3}	y	M_1 in $mgcm^{-2}$	t_1 in h	M_y in $mgcm^{-2}$	t_y in h
crystal (29,8 PbO)	900	0,881	4	0,4	20,0	2,2	200
	1000	0,877	5	2,0	20,0	13,5	200,0
	1100	0,873	5	5,0	10,0	43	96,0
	1200	0,868	6	24,0	10,0	118	114,0
	1300	0,864	9	40,0	5,0	147	31,0
	1400	0,860	3	23,0	1,0	136	6,0
90,05 PbO	1200	6,52	5	90,0	1,0	249	8,0
87,4 PbO	1200	5,87	6	56,0	1,0	207	10,0
84,8 PbO	1200	5,38	8	39,0	1,0	200	14,0
82,5 PbO	1200	4,94	8	23,0	1,0	130	14,0
79,4 PbO	1200	4,52	8	10,0	1,0	80	14,0
75,6 PbO	1200	4,00	8	7,0	1,0	67	14,0
65,0 PbO; 2,1 R ₂ O ₃	1000	2,83	5	8,2	20	40,4	108,0
	1100	2,81	3	28,6	10	123	54,0
	1300	2,77	7	33,2	0,584	449	17,58

Table 3. The reaction rate constants and diffusivities evaluated by different methods

glass in wt %	temp. in °C	graphical		eq. 15 α in cm s ⁻¹	program 1		program 2		h in cm ⁻¹
		α in cm s ⁻¹	D in cm ² s ⁻¹		α in cm s ⁻¹	D in cm ² s ⁻¹	α in cm s ⁻¹	D in cm ² s ⁻¹	
crystal (29,8 % PbO)	900	—	—	$6,3 \cdot 10^{-9}$	$1,4 \cdot 10^{-8}$	$1,4 \cdot 10^{-11}$	$8,5 \cdot 10^{-9}$	$3,2 \cdot 10^{-11}$	266
	1000	$6,4 \cdot 10^{-8}$	$7,2 \cdot 10^{-10}$	$1,9 \cdot 10^{-8}$	$3,8 \cdot 10^{-8}$	$8,7 \cdot 10^{-10}$	$4,2 \cdot 10^{-8}$	$7,3 \cdot 10^{-10}$	57,5
	1100	$4,8 \cdot 10^{-7}$	$1,2 \cdot 10^{-8}$	$1,6 \cdot 10^{-7}$	$2,1 \cdot 10^{-6}$	$3,8 \cdot 10^{-9}$	$1,8 \cdot 10^{-7}$	$1,8 \cdot 10^{-8}$	10,0
	1200	$2,5 \cdot 10^{-6}$	$5,1 \cdot 10^{-8}$	$7,7 \cdot 10^{-7}$	$1,7 \cdot 10^{-6}$	$5,5 \cdot 10^{-8}$	$1,6 \cdot 10^{-6}$	$5,7 \cdot 10^{-8}$	28,1
	1300	$6,2 \cdot 10^{-6}$	$3,6 \cdot 10^{-7}$	$2,6 \cdot 10^{-6}$	$4,5 \cdot 10^{-6}$	$4,0 \cdot 10^{-7}$	$4,6 \cdot 10^{-6}$	$3,9 \cdot 10^{-7}$	11,8
	1400	$2,4 \cdot 10^{-5}$	$2,5 \cdot 10^{-6}$	$7,3 \cdot 10^{-6}$	—	—	$(1,9 \cdot 10^{-5})$	$(2,8 \cdot 10^{-6})$	(6,78)
90,05 % PbO	1200	$6,2 \cdot 10^{-5}$	$4,4 \cdot 10^{-8}$	$3,8 \cdot 10^{-6}$	$6,5 \cdot 10^{-5}$	$4,4 \cdot 10^{-8}$	$2,6 \cdot 10^{-5}$	$5,4 \cdot 10^{-8}$	481
87,4 % PbO	1200	$1,4 \cdot 10^{-5}$	$3,1 \cdot 10^{-8}$	$2,6 \cdot 10^{-6}$	$1,1 \cdot 10^{-5}$	$3,2 \cdot 10^{-8}$	$1,1 \cdot 10^{-5}$	$3,2 \cdot 10^{-8}$	344
84,8 % PbO	1200	$6,5 \cdot 10^{-6}$	$3,1 \cdot 10^{-8}$	$2,0 \cdot 10^{-6}$	$5,6 \cdot 10^{-6}$	$3,0 \cdot 10^{-8}$	$5,1 \cdot 10^{-6}$	$3,2 \cdot 10^{-8}$	159
82,5 % PbO	1200	$3,9 \cdot 10^{-6}$	$1,4 \cdot 10^{-8}$	$1,3 \cdot 10^{-6}$	$2,9 \cdot 10^{-6}$	$1,5 \cdot 10^{-8}$	$2,8 \cdot 10^{-6}$	$1,6 \cdot 10^{-8}$	175
79,4 % PbO	1200	$2,0 \cdot 10^{-6}$	$7,6 \cdot 10^{-9}$	$6,1 \cdot 10^{-7}$	$9,0 \cdot 10^{-7}$	$1,3 \cdot 10^{-8}$	$8,6 \cdot 10^{-7}$	$1,5 \cdot 10^{-8}$	57,3
75,6 % PbO	1200	$1,6 \cdot 10^{-6}$	$6,4 \cdot 10^{-9}$	$4,9 \cdot 10^{-7}$	$6,6 \cdot 10^{-7}$	$1,5 \cdot 10^{-8}$	$6,5 \cdot 10^{-7}$	$1,7 \cdot 10^{-8}$	38,2
65,0 % PbO; 2,1 % R ₂ O ₃	1000	—	—	$4,0 \cdot 10^{-8}$	$1,3 \cdot 10^{-7}$	$4,4 \cdot 10^{-10}$	$4,6 \cdot 10^{-8}$	$9,2 \cdot 10^{-9}$	5,00
	1100	$7,2 \cdot 10^{-7}$	$2,1 \cdot 10^{-8}$	$2,8 \cdot 10^{-7}$	$3,4 \cdot 10^{-7}$	$4,9 \cdot 10^{-8}$	$3,4 \cdot 10^{-7}$	$4,5 \cdot 10^{-8}$	7,55
	1300	$1,6 \cdot 10^{-5}$	$4,6 \cdot 10^{-7}$	$1,6 \cdot 10^{-5}$	$1,0 \cdot 10^{-5}$	$5,6 \cdot 10^{-7}$	$9,6 \cdot 10^{-6}$	$6,3 \cdot 10^{-7}$	15,2

to be random with increasing time in some series of experiments, especially the PbO-SiO₂ melts, this is not sufficiently consistent to be clearly demonstrated. The data for the 65% PbO glass do not show any other notable features.

The theoretical model can be accepted as an appropriate description of the data to which it has been applied.

6.2. Values of α and D determined by different methods

As the functions involved are quite complex and the procedures significantly different between programs 1 and 2, they sometimes give somewhat different values of α and D for the same set of data. When both programs give very similar values of α and D there can be little doubt that these values are correct. When the two programs differ it is sensible to accept the result giving the smaller discrepancies between data points and the equivalent calculated values of M. Thus a simple criterion is to accept the program giving the smaller value of $\sum (M_{\text{calc}} - M_{\text{data}})^2$.

The results for lead crystal show good agreement of the two programs at 1300 and 1200 °C but distinct differences at lower temperatures the maximum difference being, rather unexpectedly, at 1100 °C not 900 °C. Table 4 lists the sum of the squares of the deviations

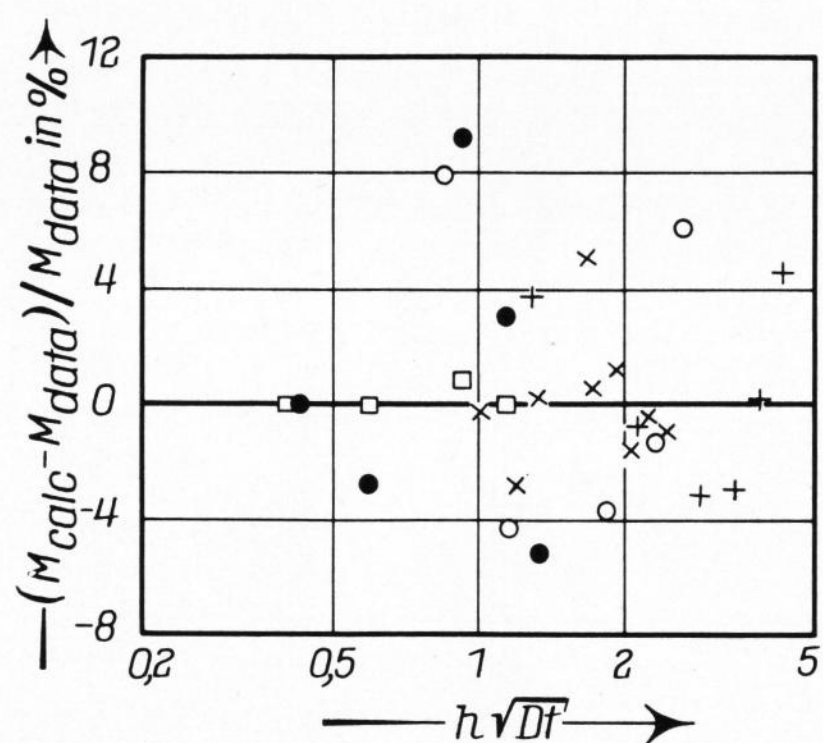


Figure 4. Discrepancies between data points and theory for lead crystal. The ordinate is $(M_{\text{calc}} - M_{\text{data}})/M_{\text{data}}$ expressed as a percentage.

×: 1300 °C; +: 1200 °C; ○: 1100 °C; ●: 1000 °C; □: 900 °C.

$(M_{\text{calc}} - M_{\text{data}})^2$ for these data. In three cases program 1 gives a very slightly better fit than program 2 but in one case (1100 °C) program 2 gives a much better fit.

A similar conclusion may be drawn from the other data. When the results of the two programs are very similar, program 1 is often slightly better: when there is a significant difference program 2 is the better choice. If only one program is to be used it should be program 2 using the Rosenbrock method. Subsequent discussion uses the results given by program 2.

In discussing evaluation of α and D graphically it was pointed out that D would generally be too low and α too high. Examination of the data in table 3 confirms this in all cases. Values of α calculated from equation (15) are likewise consistently low, as expected. In many cases the graphical values are not greatly different from the computed best fit results and would provide a good starting point for further trial and error solutions if the computer were not available. A graphical evaluation was

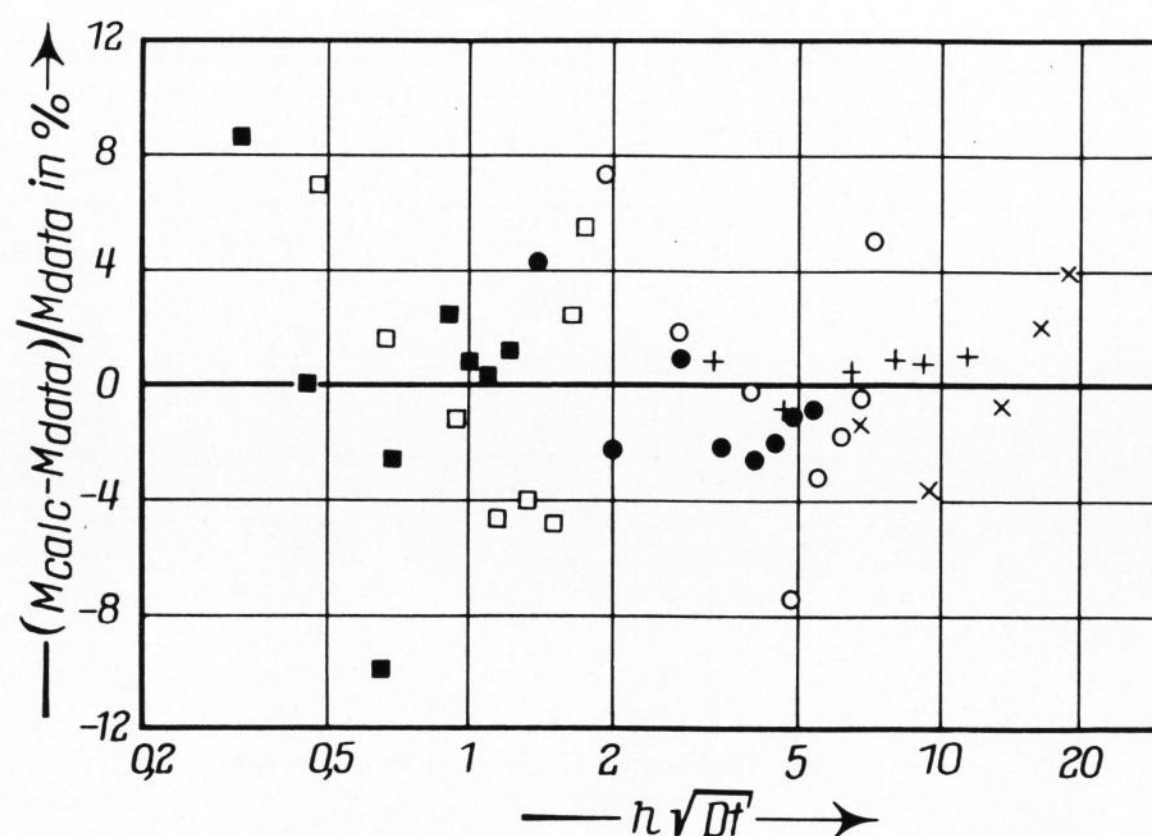


Figure 5. Discrepancies between data points and theory for the PbO-SiO₂ melts. The ordinate is $(M_{\text{calc}} - M_{\text{data}})/M_{\text{data}}$ expressed as a percentage.

×: 90,05 wt % PbO (70,9 mole %);
+ : 87,4 wt % PbO (65,1 mole %);
○ : 84,8 wt % PbO (59,0 mole %);
● : 82,5 wt % PbO (55,9 mole %);
□ : 79,4 wt % PbO (50,9 mole %);
■ : 75,6 wt % PbO (45,5 mole %).

Table 4. Comparison of discrepancies between data and computed results for programs 1 and 2

glass	temperature in °C	$\Sigma (M_{calc} - M_{data})^2$ in $mg^2 cm^{-4}$		y	better result	$h/\sqrt{Dt_1}$	$h/\sqrt{Dt_y}$
		program 1	program 2				
lead crystal	1300	25,55	26,38	9	1	0,987	2,46
	1200	39,89	44,8	6	1	1,29	4,34
	1100	160,5	8,23	5	2	0,085	0,264
	1000	0,88	0,95	5	1	0,413	1,31
	900	0,06	0,01	4	2	0,408	1,12
65 % PbO	1000	66,7	0,55	5	2	0,128	0,297
	1100	9,85	10,8	3	1	0,308	0,716
	1300	729	1339	7	1	0,561	3,08
90,05 % PbO	1200	200,6	237	5	1	6,71	53,7
87,4 % PbO	1200	10,75	10,33	6	2	3,26	9,23
84,4 % PbO	1200	266,5	295,5	8	1	1,28	4,06
82,5 % PbO	1200	15,23	17,34	8	1	1,21	3,83
79,4 % PbO	1200	45,62	53,36	8	1	0,309	0,977
75,6 % PbO	1200	9,96	13,57	8	1	0,274	0,865

not attempted for lead crystal at 900 °C or 65% PbO glass at 1000 °C, because the data do not extend to long enough times.

6.3. The significance of α and D

It has been demonstrated that the theory can describe the relation between M and t to an acceptable standard of accuracy. However, the theory cannot be claimed to be correct unless other ways of confirming the values of α and D can be found. Two different criteria can be applied; first internal consistency, second quantitative comparison with results obtained by other workers or in other ways.

6.3.1. Internal consistency

Two tests of internal consistency can be applied. It is reasonable to expect the relation between D and temperature to be of the form

$$D = D_0 \exp(-E_D/RT)$$

and by analogy with viscosity, electrical conductivity or other diffusion processes, it is possible to specify a likely range of values for the activation energy E. This test can be applied to the data for lead crystal and the 65% PbO glass.

It is rather unlikely that D is truly independent of glass composition, even though the model assumes this. If so the relation between D and original glass composition, at constant temperature, ought to be a smooth curve with no discontinuities, probably showing D to increase with increasing PbO content.

The true meaning of α is less clear than that of D but similar tests may reasonably be applied.

Figure 6 shows $\log \alpha$ and $\log D$ plotted against $1/T$ for both glasses. On examining the data the result for lead crystal seems the more reliable at 1300 °C but the

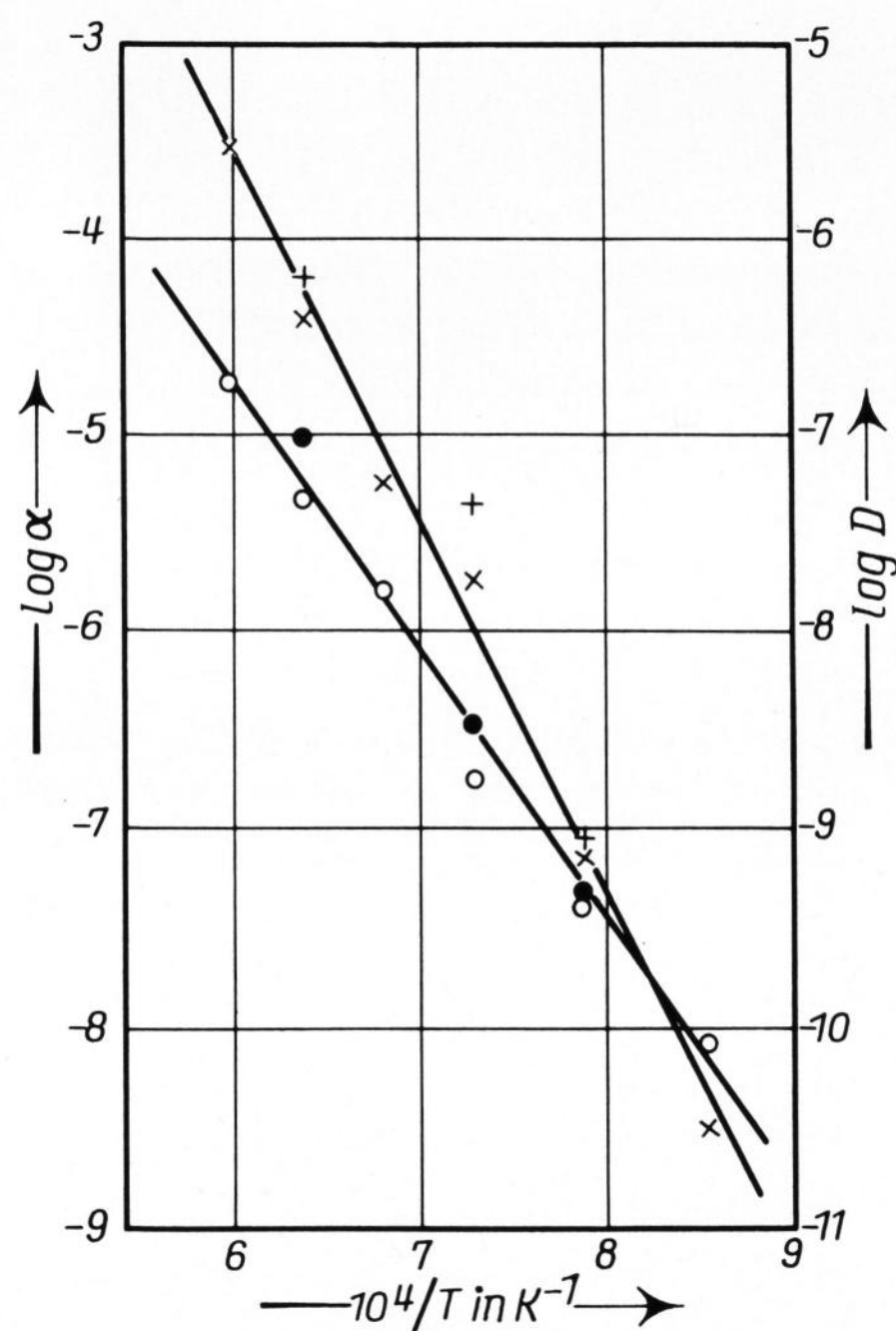


Figure 6. Plots of $\log \alpha$ and $\log D$ against reciprocal of temperature for lead crystal and the 65 % PbO glass.

○: α - lead crystal; ×: D - lead crystal;
 ■: α - 65 % PbO; +: D - 65 % PbO.

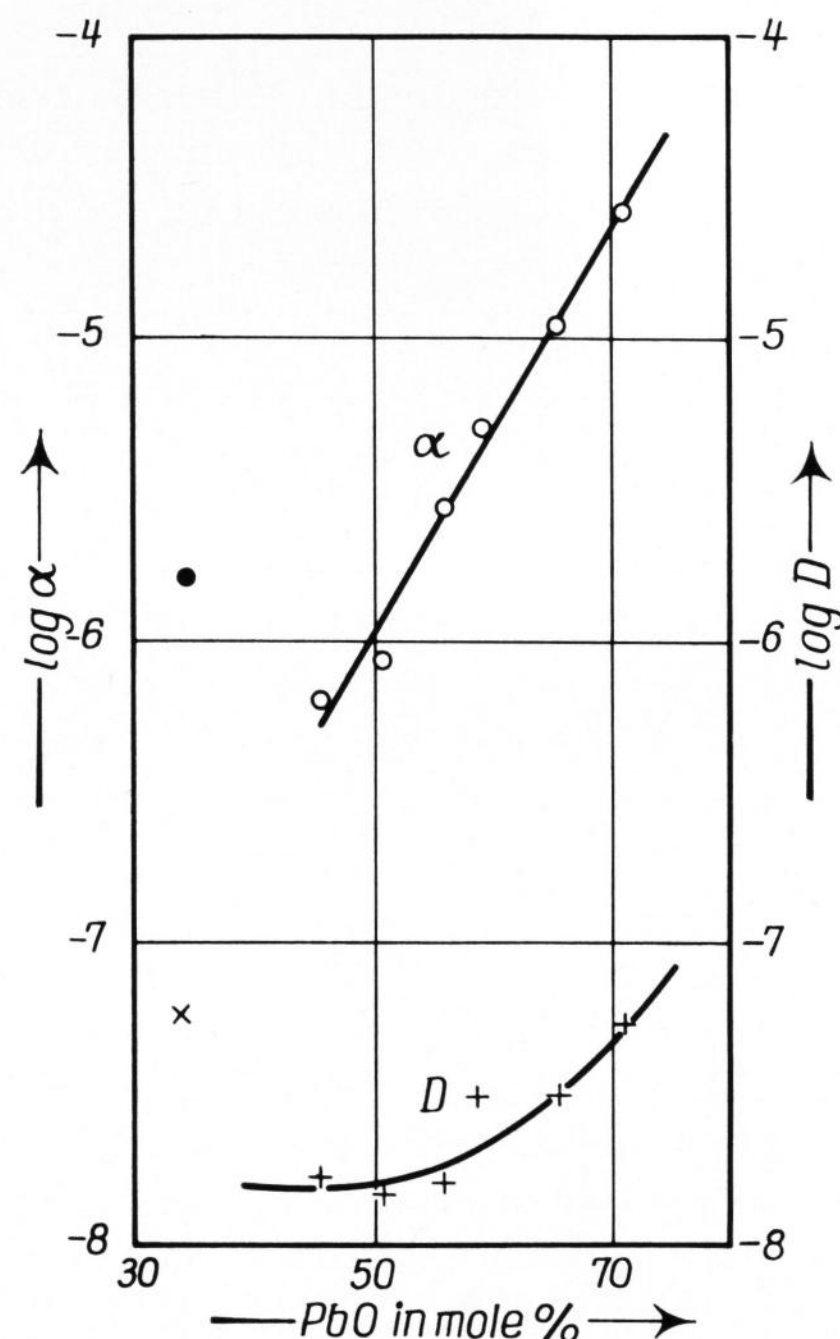


Figure 7. The relations between α or D and composition at 1200 °C for PbO-SiO₂ glasses. The odd points (●, ×) are the values for the 65 wt % PbO glass, read off figure 6.

Table 5. Comparison of α and D given by Terai and Ueno with values obtained graphically

glass	tempera- ture in °C	graphical		Terai and Ueno	
		α in cm s ⁻¹	D in cm ² s ⁻¹	α in cm s ⁻¹	D in cm ² s ⁻¹
SFS 1-1	1200	$1,1 \cdot 10^{-6}$	$3,0 \cdot 10^{-8}$	$1,0 \cdot 10^{-6}$	$7,8 \cdot 10^{-7}$
	1240	$3,3 \cdot 10^{-6}$	$1,1 \cdot 10^{-7}$	$3,3 \cdot 10^{-6}$	$1,4 \cdot 10^{-6}$
	1320	$1,4 \cdot 10^{-5}$	$9,3 \cdot 10^{-7}$	$1,1 \cdot 10^{-5}$	$2,7 \cdot 10^{-6}$
	1420	$4,8 \cdot 10^{-5}$	$2,3 \cdot 10^{-6}$	$2,8 \cdot 10^{-5}$	$4,3 \cdot 10^{-6}$
SFS 1-3	1125	$3,4 \cdot 10^{-6}$	$1,3 \cdot 10^{-7}$	$5,3 \cdot 10^{-6}$	$5,6 \cdot 10^{-7}$
	1240	$2,5 \cdot 10^{-5}$	$1,0 \cdot 10^{-6}$	$2,1 \cdot 10^{-5}$	$1,7 \cdot 10^{-6}$
	1320	$6,1 \cdot 10^{-5}$	$2,6 \cdot 10^{-6}$	$7,2 \cdot 10^{-5}$	$2,9 \cdot 10^{-6}$

opposite is true at 1100 °C. Bearing this in mind it seems best to assume that the relation between α and T is given by the line drawn for both glasses. The slope of this line is equivalent to $E_\alpha = 62$ kcal/mole. The data for D are not so well represented by a single straight line, both points for 1100 °C lying rather high, but the line drawn is a reasonable fit to the rest of the data for both glasses.

The slope of the line shown gives $E_D = 85$ kcal/mole. Both activation energies are rather high, values about half as big would have caused no comment, but this is a subjective judgement. Otherwise the temperature dependence confirms the acceptability of the model.

The dependence of α and D on composition at 1200 °C is shown in figure 7. As in figure 6 the results for D show the greater scatter and it should be noted that the value for 59,0 mole% PbO (84,8 wt%) was derived from data showing distinctly greater than average scatter. The qualitative forms of the relations are as expected and this graph also supports the plausibility of the theory. However, the values for the 65% PbO (33,9 mole%) glass are a factor of about 5 higher than expected from extrapolation of the other data and this as referred to again below.

6.3.2. Comparison with other data

Values of α and D obtained by other workers would be valuable confirmation, as would values of D obtained for similar processes such as dissolution of silica in lead silicate glasses.

A reasonably detailed set of volatilization measurements on lead silicates has been reported by Terai and Ueno [13] for six glasses with (in wt%) 45,2 to 77,0 PbO; 18,8 to 45,5 SiO₂ and 0 to 9,8 of other constituents, chiefly K₂O + Na₂O. They used a flow of 500 cm³ min⁻¹ but experimental conditions seem otherwise to have been fairly similar.

Their method of fitting the theory to the data used the same principle as program 2, finding values of h and D which made dh/dt as close to zero as possible by inspection of graphs. However they limited their search to the ranges $h = 1$ to 50 and $D = 1 \cdot 10^{-8}$ to $9 \cdot 10^{-5}$ cm² s⁻¹. Their experiments covered temperatures from 1125 to 1455 °C and reference to table 3 suggests that the ranges of both h and D may have been too narrow to obtain the best possible fit in some cases. Since Terai and Ueno gave plots of M vs $t^{1/2}$ data for SFS 1-1 (77 wt% PbO) and SFS 1-3 (72,1 wt% PbO, 7,2% K₂O) at several temperatures, the values of α and D were evaluated graphically and the results are given in table 5. The graphical values of α agree reasonably well

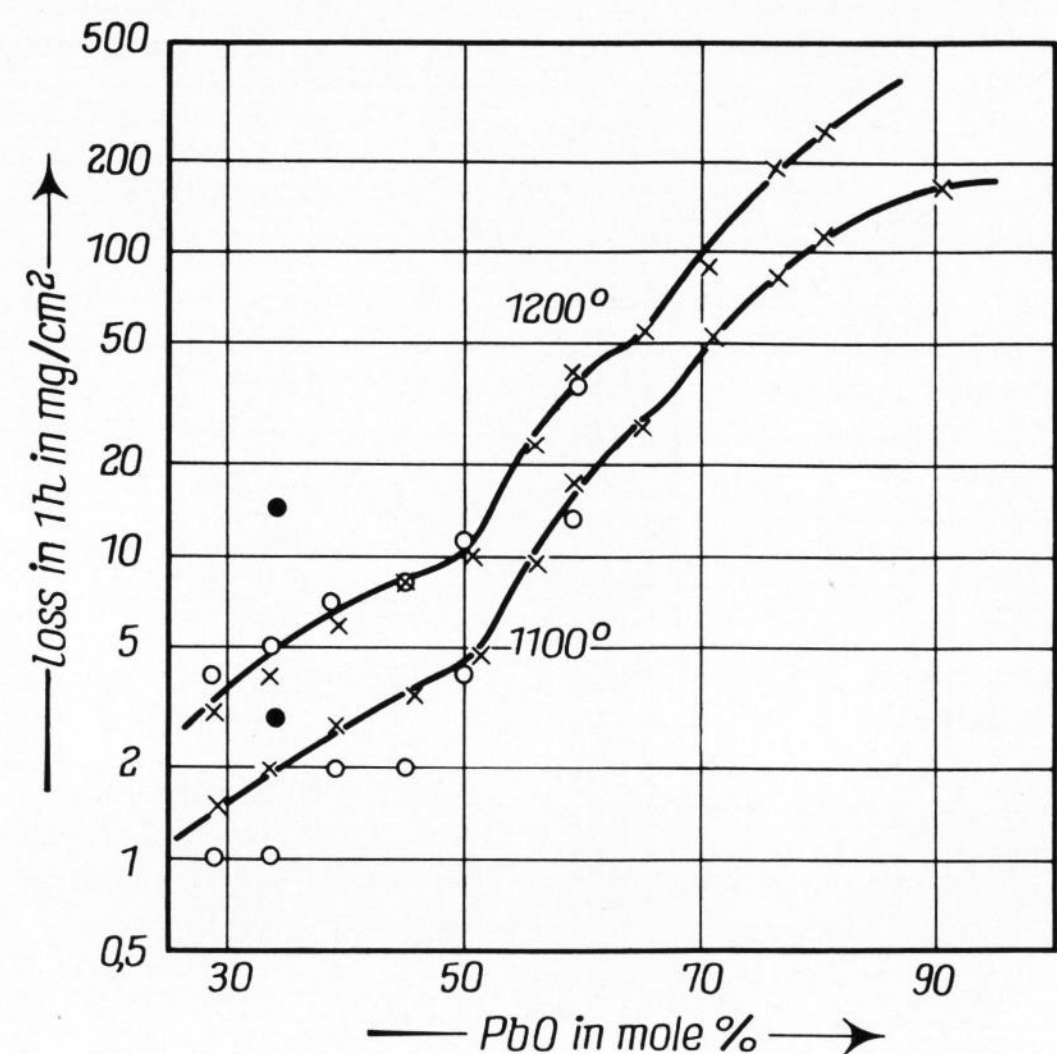


Figure 8. Weight loss per cm² in 1 h for PbO-SiO₂ glasses according to Preston and Turner (x) and Anderson (o). Preston and Turner's data for the 65% PbO glass are shown by ●.

with those given by Terai and Ueno, but the graphical values of D are lower and show a steeper temperature dependence. The graphical results for both α and D are somewhat greater than the data in figure 7 suggest (SFS 1-1 has 48,5 mole% PbO). If Terai and Ueno's results are correct, there is a serious discrepancy in D. The activation energies for the graphical values of α and D are very similar to those for the data in figure 6; Terai and Ueno's value of $E_D = 41$ kcal/mole is distinctly lower. A more detailed examination of the matter would require analysis of the actual data points of Terai and Ueno which are not given in their paper. Comparison of the two sets of results thus is, unfortunately, inconclusive.

Matoušek and Hlaváč [4] made a study of volatilization from a lead crystal with 24,8% PbO (8,86 mole%) at 1300 °C. From interpretation of their M vs t data they obtained $\alpha = 2,6 \cdot 10^{-5}$ cm s⁻¹ and $D = 1,3 \cdot 10^{-6}$ cm² s⁻¹ but a concentration profile determined by electron micro-probe analysis gave $\alpha = 2,2 \cdot 10^{-6}$, $D = 1,5 \cdot 10^{-6}$; these two values of α bracket those shown in figure 6 for 1300 °C but D is 2,0 to 2,5 times higher than indicated by figure 6.

These data suggest that different workers using different experimental conditions may obtain significantly different values of α and D. Although the exact significance of α is not clear, it could easily be influenced by factors such as the volume of the furnace and the flow of gas over the sample. On the other hand D should be an intrinsic property of the melt. Consequently one would expect values of D by different workers, or in different experimental conditions, to agree reasonably well whilst the values of α might show considerably greater divergence. The converse seems nearer the truth and there are usually bigger discrepancies in D than in α .

Accurate evaluation of α can be obtained from data for 'short' times ($h/\sqrt{Dt} \rightarrow 0$) whilst accurate values of D depend on data for 'long' times ($h/\sqrt{Dt} > 1$). There is thus a tendency for α to be more reliable than D. Despite this there are enough sets of data for which the longest

Table 6. Parameters used to evaluate M from finite slab model (lead crystal)

tempera- ture in °C	wt. of glass in g	α in $\text{cm}^2 \text{s}^{-1}$	D in $\text{cm}^2 \text{s}^{-1}$	l in cm	L	M_∞ in mg cm^{-2}
1400	3,000	$1,9 \cdot 10^{-5}$	$2,8 \cdot 10^{-6}$	0,350	2,375	270
1300	3,000	$4,6 \cdot 10^{-6}$	$3,9 \cdot 10^{-7}$	0,330	3,892	280
1300	2,500	$4,6 \cdot 10^{-6}$	$3,9 \cdot 10^{-7}$	0,310	3,656	230

time (t_y) gives $h/\sqrt{Dt_y} > 1$ to doubt that this alone accounts for the differences.

The most obvious discrepancy is between Preston and Turner's six PbO-SiO₂ melts at 1200 °C and their other two compositions at the same temperature. Figure 6 suggests $\alpha = (1,5 \pm 0,5) \cdot 10^{-5} \text{ cm s}^{-1}$ and $D = (8 \pm 2) \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 1200 °C for both lead crystal and the 65% PbO glass. Both of these glasses were studied in the same furnace over a relatively short period of time. However the data in figure 7 suggest $\alpha = 6 \cdot 10^{-7} \text{ cm s}^{-1}$, $D = 1,5 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for 65 wt% (33,9 mole%) PbO. This series of melts was studied about 3 years later and the furnace, even if nominally the same, had probably been rebuilt more than once. Here the values of α differ distinctly more than the values of D yet the difference in D is still large.

Although Preston and Turner reported M vs t data for only six compositions at 1200 °C, they reported losses in 1 h at both 1100 °C and 1200 °C for 12 compositions. A more restricted range of similar data was reported much earlier by Anderson [10]. Figure 8 shows remarkably close agreement between these two sets of data and implies that Preston's results for the '65% PbO' glass are the 'anomalous' ones. Anderson gave no details of his experimental procedure.

Preston and Turner themselves showed that sealing in the stopper at one end of the horizontal furnace tube instead of leaving it loose could change M by about 40% and Barlow [12] demonstrated a large effect (up to a factor of 5) of gas flow rate on M . The differences might thus be attributable to different conditions above the sample but should not affect D if D is the true effective diffusivity of PbO in the melt.

There seem to be no other reliable high temperature data from which diffusivities can be obtained to compare with the values shown in tables 3 and 5.

6.4. The finite slab model

The most obvious defect of the theory used so far is that it assumes the sample to be semi-infinite in depth. This theory may reasonably be used until M reaches approximately half its maximum value. For any sample of finite depth $dM/d(t^{1/2})$ decreases at longer times and approaches zero as $M \rightarrow M_\infty$. This was the main justification for truncating some of the sets of data before evaluating α and D either graphically or by computer. It is time to examine the correctness of doing so.

To evaluate M/M_∞ from equations (18) and (19) it is necessary to know l and M_∞ but difficulties at once arise because of the tapered shape of the capsule (25 mm internal diameter at the top, 15 mm at the base). The model can describe accurately only results for a parallel sided capsule. After some thought and several trials it was decided to use the actual depth of the melt and the value

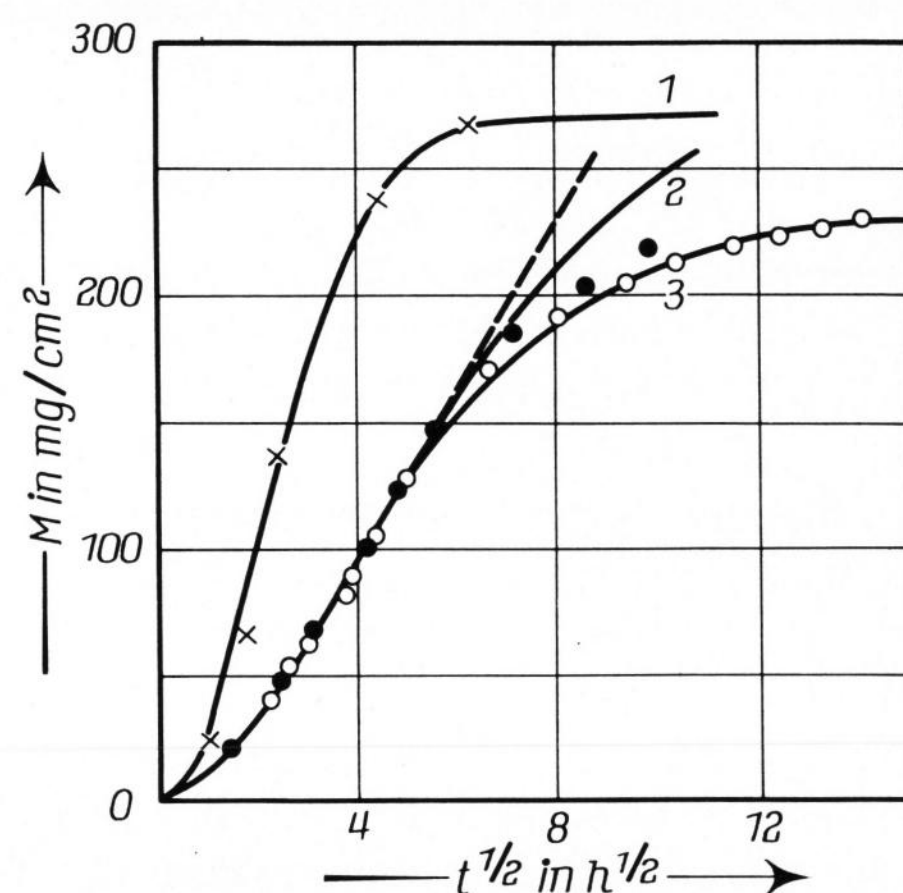


Figure 9. Predictions of the finite slab model compared with data for lead crystal at 1400 and 1300 °C. Curve 1 is for a 3,00 g sample at 1400 °C and the data are marked \times . Curve 2 is the predicted relation for a 3,00 g sample at 1300 °C and curve 3 for a 2,50 g sample at 1300 °C. The data \circ and \bullet are for 1300 °C. The prediction of the semi-infinite model for 1300 °C is shown dashed.

of M_∞ obtained from the area of the top surface. Calculations were made for several of the sets of data including those most likely to be influenced by the finite depth of the sample. The only two cases where the finite depth affected the observations were lead crystal at 1400 °C and 1300 °C. Table 6 gives the parameters used and the results are plotted in figure 9. It should be noted that solutions for the semi-infinite model, both graphical and computed, used only the first three data points at 1400 °C and the first nine points at 1300 °C.

The predictions of the finite slab theory fit the complete set of data for 1400 °C very well. The results for 1300 °C justify the truncation of the data after about 36 h when using the semi-infinite model, but show one curious feature. According to Preston's thesis [19] 3,00 g samples were used for all experiments except one at 1300 °C; thus one experiment at 1300 °C was said to have used 3,00 g whilst another used 2,5 g. Both sets of these are plotted in figure 9 and, surprisingly, the losses were slightly higher for the 2,5 g sample. Neither set of data fits the predicted relation for a 3,00 g sample but both sets are close to that predicted for the 2,50 g sample. Perhaps a mistake was made in transcribing some of the data. The data shown in figure 3 are those fitting curve 3 very closely.

If 2,5 g samples were used for both experiments at 1300 °C, agreement between theory and results is good at 1400 °C and 1300 °C. If this is accepted, the observed deviations from the semi-infinite model can be attributed entirely to the finite depth of the melt and these results also support the validity of the theory.

The rest of the results show only one case where the data were truncated but the discrepancy cannot be attributed to the finite depth of the melt. This is lead crystal at 1000 °C (see figure 3); no plausible explanation can be offered other than experimental error.

7. Conclusion

The theoretical model proposed by Terai and Ueno describes reasonably accurately 15 sets of data for glasses from which PbO is the major or only volatile constituent.

The data cover the temperatures from 900 to 1400 °C and initial lead contents from 29,8 to 90,05 wt% PbO. Despite some shortcomings of the data such as lack of data points at $h/\sqrt{Dt} \gg 1$ and lack of accurate high temperature densities, the model can be accepted as a description of the relation between M and t . The true significance of the parameters α and D is, however, not clear.

The diffusivity D should be an intrinsic property of the melt and different experimenters ought to obtain close agreement, say within $\pm 20\%$, for any particular glass in equivalent conditions.

Considerably bigger differences exist between sets of experiments by Preston and Turner (see figure 7) and also between very similar compositions studied by different workers eg. lead crystal glasses (Preston and Turner [18], Matoušek and Hlaváč [4]); 77 wt% PbO (Preston and Turner [20], Terai and Ueno [13]).

The most fundamental assumption made in using equation (4) is that the melt does not flow. Considering the distance that a particle will diffuse in a given time to be \sqrt{Dt} , quite slow flows could easily contribute more to transport than simple diffusion when values of D lie in the range 10^{-11} to 10^{-6} cm² s⁻¹ (table 3). Fortunately the density of PbO-SiO₂ melts decreases rapidly as PbO is lost and this provides a powerful stabilizing influence against buoyancy or thermal convection, as demonstrated by Kruithof et al [2]. However there might be some convection in the surface layers induced by surface tension gradients (see Hrma [23]). Slow convection does not seem likely to be the cause of the discrepancies but would deserve attention in any further studies. Significant convection would affect the form of the relation between M and t .

The theoretical model assumes that diffusivity is independent of composition yet figure 7 demonstrates this postulate to be untrue. Fortunately experience shows such constant diffusivity models often describe quite well integrated quantities such as M vs t even when the variation of D with c must be taken into account in analyzing concentration profiles. In such cases the average diffusivity may often be taken to be the mean of true

diffusivity over the concentration range concerned (Crank and Henry [24 and 25]):

$$D_{av} = \frac{1}{C_2 - C_1} \int_{C_1}^{C_2} D dc.$$

In the present work the appropriate range would be between $C_i(t=0) = C_0$ and $C_i(t_y)$. Deducing the true relation between D and C requires more information than is available in the present work.

The lack of other high temperature diffusion data in lead silicates inhibits further useful discussion of the values of D obtained here. Fortunately fairly extensive volatilization data and other diffusion results exist for alkali silicates and it is proposed to evaluate and discuss these in another paper.

The true meaning of the reaction constant α is less clear. It is unlikely that it genuinely represents a relatively slow reaction at the melt-gas interface. It is more likely that it describes the process by which the volatile constituent is transported away from the samples and may be proportional to the vapour pressure of PbO over the melt. The activation energy of α may thus represent the heat of evaporation of PbO. As in the case of D further discussion is better deferred until all the available data have been examined.

In any future work it would be possible to determine concentration profiles by electron microprobe (see Matoušek and Hlaváč [4]), C_i by a similar technique, or deduce concentration profiles from refractive index profiles (see Dietzel and Merker [5] or Hetherington and Jack [6]). Such measurements would help establish the true significance of the diffusivities obtained from M vs t data. Understanding the significance of α should be aided by obtaining data for different velocities of gas over the sample (see Barlow [12]) or at different pressures in a static atmosphere.

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