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The kinetics of volatilization of soda from sodium silicate melts

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Data on volatilization loss from 21 compositions in the range 11,8 to 54,8 % Na_2O at temperatures from 1100 to 1400 °C and for times up to 200 h are discussed. The data can be successfully described by a theoretical model which includes diffusion in the melt and a first order reaction at the surface. Values of reaction rate constant (α) are internally consistent in terms of composition and temperature dependence and fall in the range $\alpha = 2 \cdot 10^{-9}$ to $2 \cdot 10^{-4}$ cm·s^{-1}.

Diffusivity (D) values show considerable scatter and some anomalies in composition and temperature dependence. Many of the anomalous results can be explained by allowing for the strong dependence of D on composition but some results remain difficult to interpret. Values fall in the range $D = 4 \cdot 10^{-10}$ to $2 \cdot 10^{-8}$ cm^2·s^{-1}. Even after allowing for composition dependence, diffusivities for silica dissolution are about twenty times higher than for volatilization. The true significance of α and D for volatilization remains unclear.

Cinétique de la volatilisation d'oxyde de sodium à partir de la fonte de silicate de sodium

Les données concernant les pertes par volatilisation obtenues à partir de 21 compositions renfermant de 11,8 à 54,8 % de Na_2O à des températures comprises entre 1100 et 1400 °C et pendant des durées allant jusqu'à 200 h sont discutées. Les données peuvent être décrites de manière satisfaisante en utilisant un modèle théorique qui tient compte de la diffusion dans la fonte et d'une réaction du premier ordre en surface. Les valeurs de la constante de vitesse de réaction α s'accordent bien entre elles en fonction du rapport entre la composition et la température et elles se situent dans le domaine compris entre $\alpha = 2 \cdot 10^{-9}$ et $\alpha = 2 \cdot 10^{-4}$ cm·s^{-1}.

Les valeurs de la diffusibilité D témoignent d'une dispersion importante et de certaines anomalies de la relation température/composition. Bon nombre de ces anomalies peuvent s'expliquer par l'étroite dépendance de D par rapport à la composition; certains résultats restent cependant difficiles à expliquer. Les valeurs se situent entre $D = 4 \cdot 10^{-10}$ et $D = 2 \cdot 10^{-8}$ cm^2·s^{-1}. Même en tenant compte de la dépendance vis-à-vis de la composition, les diffusibilités correspondant à la dissolution de la silice sont environ vingt fois plus élevées que celles correspondant à la volatilisation. La signification réelle de α et de D dans le cas de la volatilisation reste obscure.

Zur Kinetik der Verflüchtigung von Natriumoxid bei Natriumsilicatschmelzen

An 21 Natriumsilicatzusammensetzungen mit Na_2O-Gehalten zwischen 11,8 und 54,8 % werden die Verflüchtigungsraten bei Temperaturen zwischen 1100 und 1400 °C und Versuchszeiten bis zu 200 h untersucht. Die Ergebnisse können mit einem theoretischen Modell, das die Diffusion in der Schmelze und eine Reaktion ersten Grades an der Oberfläche berücksichtigt, gut beschrieben werden. Die Werte für die Reaktionsgeschwindigkeitskonstante α sind in Abhängigkeit von der Zusammensetzung und der Temperatur in sich konstant und liegen zwischen $2 \cdot 10^{-9}$ und $2 \cdot 10^{-4}$ cm·s^{-1}.

Die Werte für den Diffusionskoeffizienten D weisen eine beträchtliche Streuung sowie einige Anomalitäten in Abhängigkeit von der Zusammensetzung und der Temperatur auf. Viele der anomalen Ergebnisse können mit der großen Abhängigkeit von D von der Zusammensetzung erklärt werden; einige lassen sich eben nur schwer interpretieren. Die Werte für D liegen zwischen $4 \cdot 10^{-10}$ und $2 \cdot 10^{-8}$ cm^2·s^{-1}. Selbst wenn man die Abhängigkeit von der Zusammensetzung berücksichtigt, sind die Diffusionskoeffizienten der SiO_2-Auflösung etwa 20mal größer als die bei der Verflüchtigung. Die genaue Bedeutung von α und D für den Vorgang der Verflüchtigung bleibt ungeklärt.

The properties of glass melts lead one to expect that diffusion in the melt will govern volatilization. If equilibrium between the surface of the melt and the atmosphere were established very rapidly, the relation between loss M (g cm^{-2}) and time t should be described by

$$M = \frac{2}{\sqrt{\pi}} (C_0 - C_1) \sqrt{Dt} \qquad (1)$$

where C_0 = initial uniform concentration of volatile component in the melt,

C_1 = final equilibrium concentration of volatile species (usually zero),

D = diffusivity of volatile species through the melt.

Although some data are described by this model, many are not. Many data not fitting equation (1) can be described by a model combining diffusion in the melt with

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a first order reaction at the surface. Instead of assuming instantaneous equilibrium at the interface, the flux (j) into the atmosphere is defined by

$$j = \alpha\,(C_i - C_1) \qquad (2)$$

where α = reaction rate constant,

C_i = the concentration in the melt at the interface.

Unless α is very high, C_i attains its equilibrium value over a measurable time and the flux is initially much lower than predicted by equation (1). The relation between M and t is now given by

$$M = \frac{C_0 - C_1}{h}\left[\exp(h^2Dt)\operatorname{erfc} h\sqrt{Dt} - 1 + \frac{2}{\sqrt{\pi}} h\sqrt{Dt}\right] \qquad (3)$$

where $h = \alpha/D$ and the surface concentration in the melt is

$$\hat{C}_i = \frac{C_i - C_1}{C_0 - C_1} = \exp(h^2Dt)\operatorname{erfc} h\sqrt{Dt}\,. \qquad (4)$$

This theoretical model and various ways of fitting equation (3) to data have been discussed in a recent paper [1]. When data extend to sufficiently long times M vs. $\sqrt{t}$ becomes a straight line and the diffusivity can be evaluated from the slope of the straight portion

$$D = \left[\frac{\sqrt{\pi}}{2\,(C_0 - C_1)}\,\frac{dM}{d(t^{1/2})}\right]^2. \qquad (5)$$

The reaction constant α can then be obtained from the intercept of the asymptote to the curve on the time axis t*

$$\alpha = \left[\frac{\pi D}{4\,t^*}\right]^{1/2}. \qquad (6)$$

Alternatively α is given reasonably accurately by

$$\alpha = \frac{1}{C_0}\,\frac{M_1}{t_1} \qquad (7)$$

so long as $t < 0{,}01\,D/\alpha^2$, but there is no easy way to obtain D from data for short times only.

In general it is better to find the best fit of equation (3) to the data by computer. The most useful of several programs written [1 and 2] finds the best values of h and $h\sqrt{D}$ by making $dh/d(t^{1/2}) \to 0$ using the Rosenbrock technique.

This theory has been applied to data for lead glasses [1] and to results for soda-lime-silica glasses, in vacuum and at 1 atmosphere [2]. Nearly all sets of data could be closely fitted by equation (3) when h and $h\sqrt{D}$ were regarded as empirical parameters but plots of α and D against melt composition and temperature raised some doubts about their true physico-chemical significance. Internal consistency is valuable evidence supporting the theory but it cannot be accepted until the values of α and D are understood and confirmed by other types of experiment. The Na_2O–SiO_2 system has been the most widely studied and several kinds of diffusion data are available. There is consequently a special interest in the values of D obtained by analysis of volatilization data for Na_2O–SiO_2 melts.

1. Data

Preston and Turner [3] reported M vs. t measurements for seven Na_2O–SiO_2 glasses at 1100 to 1400 °C using samples weighing about 3,0 g in platinum capsules which were placed in a horizontal refractory tube about 44 mm I.D. and 370 mm long. The experiments were made in static air, the ends of the tube being closed by loosely fitting stoppers. Full details are given in the published papers. Very similar conditions were used by Lawton [4] to investigate 14 melts with 15,2 to 54,8% Na_2O at temperatures from 1100 to 1400 °C. Both sets of data have been analysed; Lawton's data have not been published.

Calculation of concentrations in g cm^{-3} requires density at the temperature of the experiment as well as composition. High temperature density measurements for Na_2O–SiO_2 have been reported by Heidtkamp and Endell [5], Shartsis, Spinner and Capps [6] and Bockris, Tomlinson and White [7]. The three sets of results differ by amounts that are significant in terms of the accuracy to which the density of glass is usually measured at room temperature but not large enough to affect the present

Table 1. Summary of data analyzed showing minimum and maximum values of M and t, also number of data points (y)

Na_2O in %	Author	1100 °C					1200 °C					1300 °C					1400 °C				
		M_1[1]	t_1[2]	M_y[1]	t_y[2]	y	M_1[1]	t_1[2]	M_y[1]	t_y[2]	y	M_1[1]	t_1[2]	M_y[1]	t_y[2]	y	M_1[1]	t_1[2]	M_y[1]	t_y[2]	y
11,0	Preston	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2,6	20	14,0	140	7
15,2	Lawton	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3,0	20	12,0	84	4
17,7	Preston	—	—	—	—	—	—	—	—	—	—	1,0	20	4,5	80	4	3,8	20	22,0	140	7
20,8	Lawton	—	—	—	—	—	0,56	20	3,6	156	7	1,3	20	12,5	196	9	3,8	20	26,8	128	8
22,7	Preston	0,07	20	0,35	80	4	—	—	—	—	—	1,3	20	5,5	80	4	5,1	20	28,0	140	7
25,6	Lawton	0,11	20	1,0	198	9	0,75	22	5,0	157	7	1,4	20	15,0	196	9	5,1	20	40,0	196	9
30,5	Lawton	0,21	20	1,7	175	8	0,78	19	8,3	196	9	2,3	20	22,3	196	9	6,3	20	47,8	196	9
32,9	Preston	0,20	20	0,8	80	4	—	—	—	—	—	2,4	20	9,0	80	4	7,0	20	43,5	140	7
34,2	Lawton	0,36	20	3,1	197	9	1,0	18	11,3	196	9	3,4	20	27,0	196	9	10,0	23	59,9	196	9
35,8	Lawton	0,48	20	3,7	174	8	1,4	19	13,6	195	9	5,0	20	35,3	193	9	11,8	20	64,2	170	9
39,0	Lawton	0,77	20	5,4	172	8	1,9	20	20	181	8	6,8	20	44,5	189	9	16,1	20	56,3	104	5
39,3	Preston	1,0	20	3,8	80	4	—	—	—	—	—	7,2	20	33,0	144	7	18,0	20	66	120	6
42,6	Lawton	1,2	20	6,0	172	8	3,4	20	27,5	196	9	11,0	20	78,3	188	9	26,6	20	93,0	104	5
44,6	Preston	1,8	20	8,0	100	5	5,0	20	19,3	100	5	13,0	20	46	104	5	30,0	20	105	120	6
46,0	Lawton	1,9	22	12,7	177	8	5,6	20	39	198	9	17,5	20	114	196	9	40,0	20	123	110	5
48,8	Preston	2,8	20	10,1	80	4	8,0	20	26,2	108	5	20,0	20	77,5	104	5	48,0	20	157	120	6
49,0	Lawton	2,9	22	18,2	175	8	6,5	20	50	174	8	24,0	20	159	196	9	51	20	155	110	5
50,2	Lawton	—	—	—	—	—	8,1	20	37,4	105	5	29,1	20	114	108	5	57,5	20	165	110	5
51,4	Lawton	3,4	20	24,6	180	8	10,8	20	67	199	8	31,6	20	186	193	9	72,5	20	159	88	4
53,2	Lawton	—	—	—	—	—	14,0	20	77,2	156	7	41,0	20	197	170	8	91	20	178	80	4
54,8	Lawton	—	—	—	—	—	20	20	87	108	5	58,0	20	204	128	6	112	20	200	80	4

[1]) M_1, M_y in mg cm^{-2} [2]) t_1, t_y in h

work very much. As Bockris et alia have the most detailed set of data their results have been used.

Table 1 summarizes the data available. The number of data points (M_n, t_n) is denoted by y; M_1, t_1 indicate the smallest value of M and shortest time of measurement, M_y, t_y show the largest M and longest time. M is given in mg cm^{-2} and t in hours. Preston and Turner [3] analyzed five samples heated for 180 to 220 h at 1400 °C. The results showed that it was reasonable to assume that only Na_2O was lost by evaporation. This was confirmed by Lawton [4]. Identification of the volatile species is needed to define C_0.

2. Results

All sets of data have been plotted as M vs. $\sqrt{t}$ to see that the general form fits the theoretical model. In many cases α and D have been determined graphically (equations (5) and (6)) and also estimated from equation (7). All the results have been analyzed by computer to find the values of α and D best fitting the data. Graphical estimates were always made before the computed results were known. Table 2 includes all the values determined by computer. Table 3 shows a representative selection of values determined from equations (5), (6) and (7).

Drawing a tangent to the M vs. $\sqrt{t}$ curve and using equations (5) and (6) tends to give too low a value of D and too high a value of α unless the data extend to $h/\sqrt{Dt} \rightarrow 5$. Equation (7) gives an accurate value of α only if $h/\sqrt{Dt} < 0{,}1$. As the general trends are for α and D to increase with temperature and soda content, one expects best agreement between graphical and computed values for the highest temperatures and highest soda contents but best agreement for α calculated from equation (7) at lowest temperatures and lowest soda contents. Examination of the data shows the discrepancies expected. The graphical method and equation (7) cannot often be relied on for accurate results.

3. Discussion

3.1. Relation between M and t

The first test of the theory is how closely it describes the relation between M and t. When drawn on suitable scales, the fit generally appears convincing (figure 1). To examine this matter more closely, the differences between the data points and the calculated values of M_n given by the computer analysis, for the same times, have been examined. Figures 2 and 3 show plots of the data for two representative compositions at all temperatures. At 1100 and 1200 °C the discrepancies rarely exceed what could be attributed to weighing errors ($\pm$ 0,5 mg). Although the differences are distinctly larger at 1300 and 1400 °C, M is so much bigger that these errors rarely ex-

Table 2. Values of α and D determined by computer

Na_2O in %	Author	1100 °C		1200 °C		1300 °C		1400 °C	
		$\alpha \cdot 10^9$ in cm s^{-1}	$D \cdot 10^{10}$ in cm^2 s^{-1}	$\alpha \cdot 10^8$ in cm s^{-1}	$D \cdot 10^9$ in cm^2 s^{-1}	$\alpha \cdot 10^8$ in cm s^{-1}	$D \cdot 10^8$ in cm^2 s^{-1}	$\alpha \cdot 10^7$ in cm s^{-1}	$D \cdot 10^8$ in cm^2 s^{-1}
11,8	Preston	—	—	—	—	—	—	1,53	2,69
15,2	Lawton	—	—	—	—	—	—	1,29	33,2
17,7	Preston	—	—	—	—	3,97	10,6	1,45	6,34
20,8	Lawton	—	—	1,76	0,89	4,04	10,9	1,36	3,25
22,7	Preston	2,56	4,52	—	—	3,88	10,2	1,81	2,13
25,6	Lawton	2,39	4,41	1,97	1,53	4.07	11,2	1,27	16,5
30,5	Lawton	4,17	5,44	2,31	1,88	5,47	3,59	1,54	4,10
32,9	Preston	3,91	5,53	—	—	4,86	2,39	1,58	9,9
34,2	Lawton	6,31	10,4	2,14	28,7	6,60	1,79	1,92	3,47
35,8	Lawton	8,91	5,54	2,89	10,7	9,20	1,96	2,81	2,37
39,0	Lawton	26,8	5,53	—	—	14,7	1,03	4,12	2,31
39,3	Preston	16,3	30,3	—	—	17,7	0,537	5,14	2,17
42,6	Lawton	35,4	10,7	5,15	14,7	19,6	5,97	6,20	5,08
44,6	Preston	27,8	29,5	—	—	26,2	1,30	8,57	4,08
46,0	Lawton	24,2	26,5	8,42	10,4	30,8	5,12	11,5	5,18
48,8	Preston	39,2	44,3	18,5	22,5	32,9	4,53	13,5	6,61
49,0	Lawton	36,3	28,1	8,97	58,7	39,7	8,42	16,1	6,67
50,2	Lawton	—	—	11,9	26,0	49,4	7,88	20,3	6,51
51,4	Lawton	44,4	65,6	17,6	10,6	54,6	8,10	136	5,22
53,2	Lawton	—	—	21,6	22,2	81,0	6,96	795	6,94
54,8	Lawton	—	—	28,3	66,1	138	8,12	1180	8,62

Table 3. Comparison of computed and other estimated values of α and D

Na_2O in %	Temperature in °C	Computed			Graphical		Equation (7) α in cm s^{-1}
		α in cm s^{-1}	D in cm^2 s^{-1}	$h/\sqrt{Dt}$ max.	α in cm s^{-1}	D in cm^2 s^{-1}	
25,6	1400	$1{,}27 \cdot 10^{-7}$	$1{,}65 \cdot 10^{-7}$	0,263	$2{,}63 \cdot 10^{-7}$	$8{,}10 \cdot 10^{-9}$	$1{,}25 \cdot 10^{-7}$
39,0	1400	$4{,}12 \cdot 10^{-7}$	$2{,}31 \cdot 10^{-8}$	1,66	$7{,}83 \cdot 10^{-7}$	$1{,}49 \cdot 10^{-8}$	$2{,}61 \cdot 10^{-7}$
46,0	1400	$1{,}15 \cdot 10^{-6}$	$5{,}18 \cdot 10^{-8}$	3,18	$1{,}81 \cdot 10^{-6}$	$4{,}19 \cdot 10^{-8}$	$5{,}50 \cdot 10^{-7}$
49,0	1400	$1{,}61 \cdot 10^{-6}$	$6{,}67 \cdot 10^{-8}$	3,93	$2{,}37 \cdot 10^{-6}$	$5{,}87 \cdot 10^{-8}$	$6{,}59 \cdot 10^{-7}$
51,4	1400	$1{,}36 \cdot 10^{-5}$	$5{,}22 \cdot 10^{-8}$	33,5	$1{,}15 \cdot 10^{-5}$	$5{,}42 \cdot 10^{-8}$	$8{,}94 \cdot 10^{-7}$
39,0	1100	$2{,}68 \cdot 10^{-8}$	$5{,}53 \cdot 10^{-10}$	0,897	$3{,}74 \cdot 10^{-8}$	$1{,}64 \cdot 10^{-10}$	$1{,}21 \cdot 10^{-8}$
46,0	1100	$2{,}42 \cdot 10^{-8}$	$2{,}65 \cdot 10^{-9}$	0,375	$5{,}98 \cdot 10^{-8}$	$6{,}00 \cdot 10^{-10}$	$2{,}27 \cdot 10^{-8}$
49,0	1100	$3{,}63 \cdot 10^{-8}$	$2{,}81 \cdot 10^{-9}$	0,543	$8{,}47 \cdot 10^{-8}$	$9{,}10 \cdot 10^{-10}$	$3{,}23 \cdot 10^{-8}$
51,4	1100	$4{,}44 \cdot 10^{-8}$	$6{,}56 \cdot 10^{-9}$	0,441	$1{,}15 \cdot 10^{-7}$	$1{,}19 \cdot 10^{-9}$	$4{,}03 \cdot 10^{-8}$

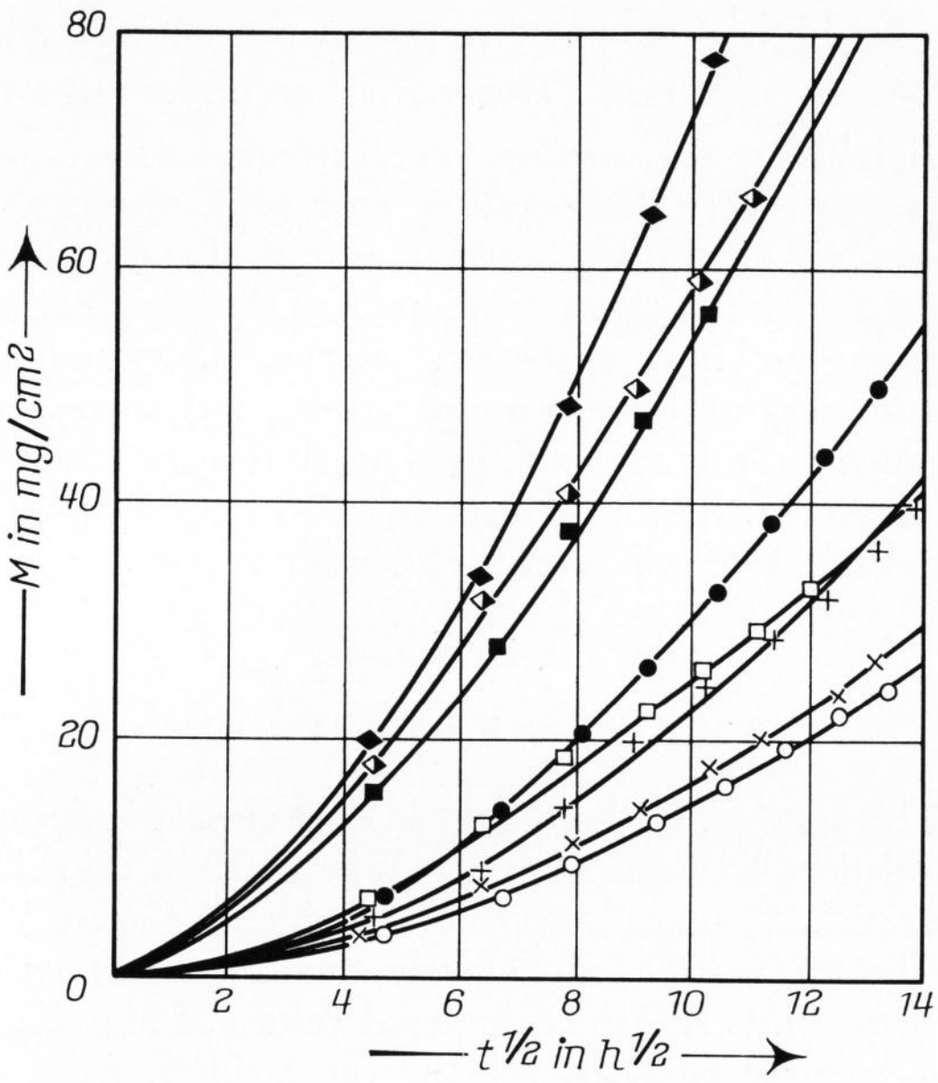

Figure 1. Examples of the fit of computer predicted relations (equation (3)) to the experimental data.

○ 1100 °C; 51,4% Na_2O (Lawton), × 1400 °C; 20,8% Na_2O (Lawton),
● 1200 °C; 49,0% Na_2O (Lawton), + 1400 °C; 25,6% Na_2O (Lawton),
□ 1300 °C; 39,3% Na_2O (Preston), ■ 1400 °C; 39,0% Na_2O (Lawton),
◆ 1300 °C; 48,9% Na_2O (Preston), ◇ 1400 °C; 39,3% Na_2O (Preston).

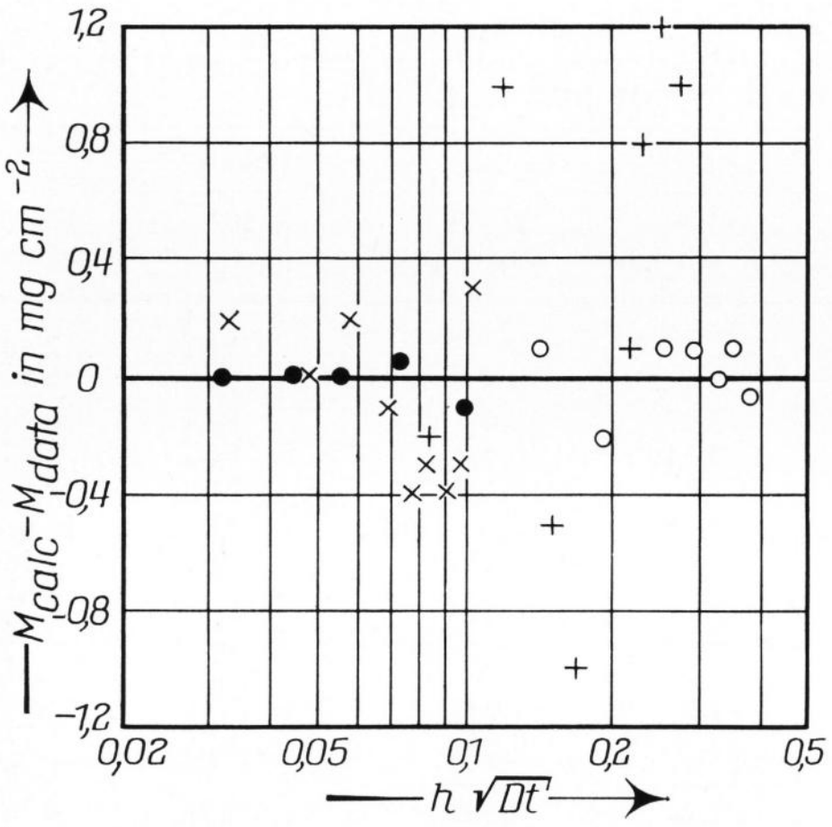

Figure 2. Discrepancies between theory and data for melts of initial soda content 25,6 wt %.

● 1100 °C, × 1300 °C,
○ 1200 °C, + 1400 °C.

ceed ± 5%. There seems to be some source of error which is more important at the higher temperatures and larger values of M. Although the differences do not always follow a random pattern, there is no consistent trend.

Examination of all the results shows that the model can provide a good description of all the data by suitable choice of α and D. Before the model can be accepted it must be shown that α and D are true physico-chemical parameters of the systems.

3.2. Internal consistency

Two tests of internal consistency may be applied to the values of α and D obtained by computer. Even though the exact form cannot be predicted, plots of α

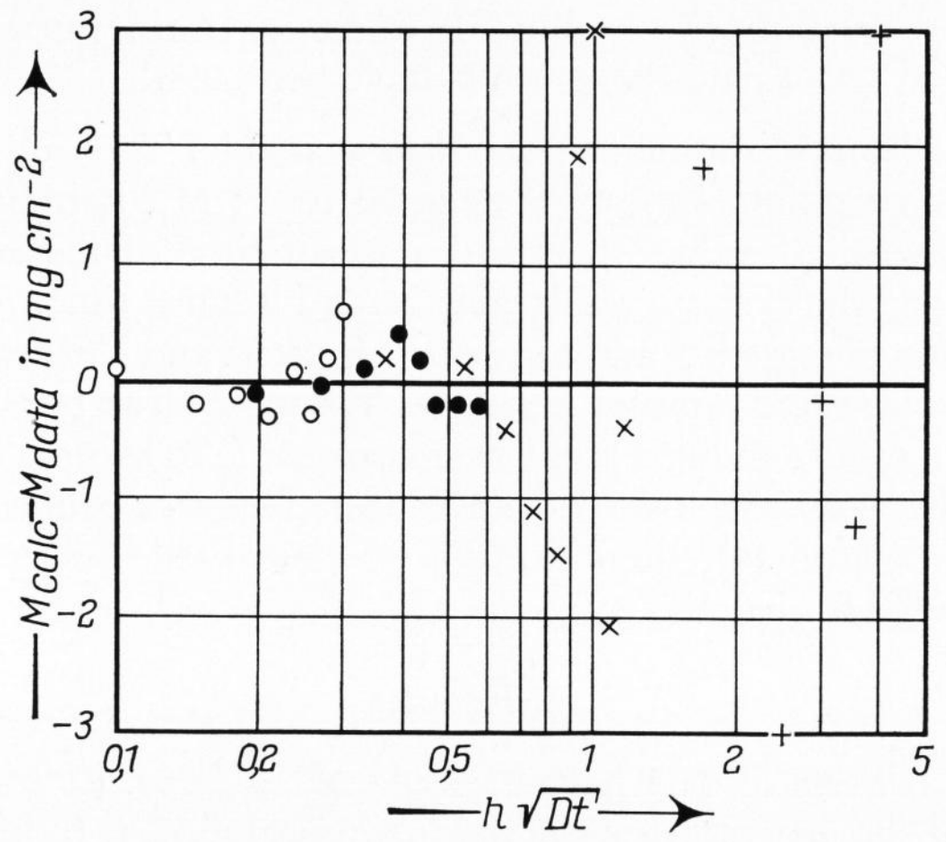

Figure 3. Discrepancies between theory and data for melts of initial soda content 49,0 wt %.

○ 1100 °C, × 1300 °C,
● 1200 °C, + 1400 °C.

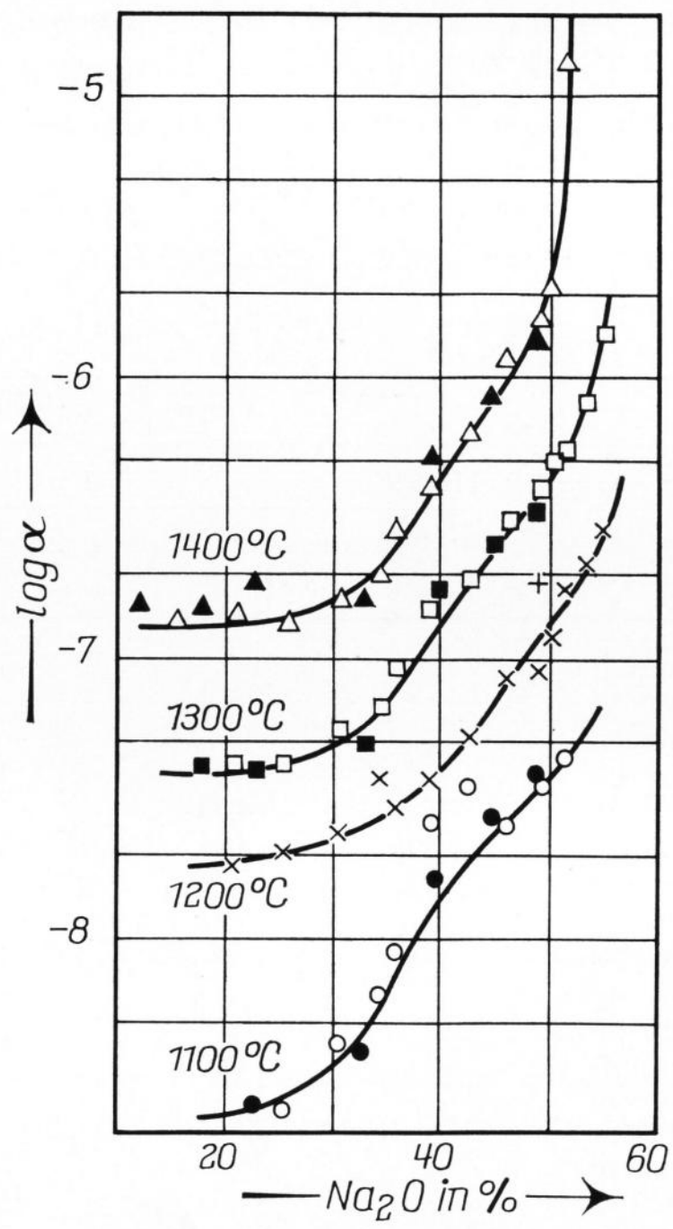

Figure 4. The relations between computed reaction rate constant (α) and initial composition at different temperatures.

○, ×, □, △: Lawton,
●, +, ■, ▲: Preston.

and D against composition or against temperature may be expected to be smooth curves. Figure 4 shows that the relation between α and composition to be similar at all four temperatures. The scatter of individual points is fairly small except at the lowest temperature where experimental errors are likely to be largest.

The results of the two different authors agree quite well. Even though no detailed theory has yet been developed to interpret the reaction rate constant α, it is reasonable that it increases as soda content increases. Plotting log α against 1/T for most compositions gives points reasonably well described by straight lines although smooth curves are sometimes a better fit. The increase

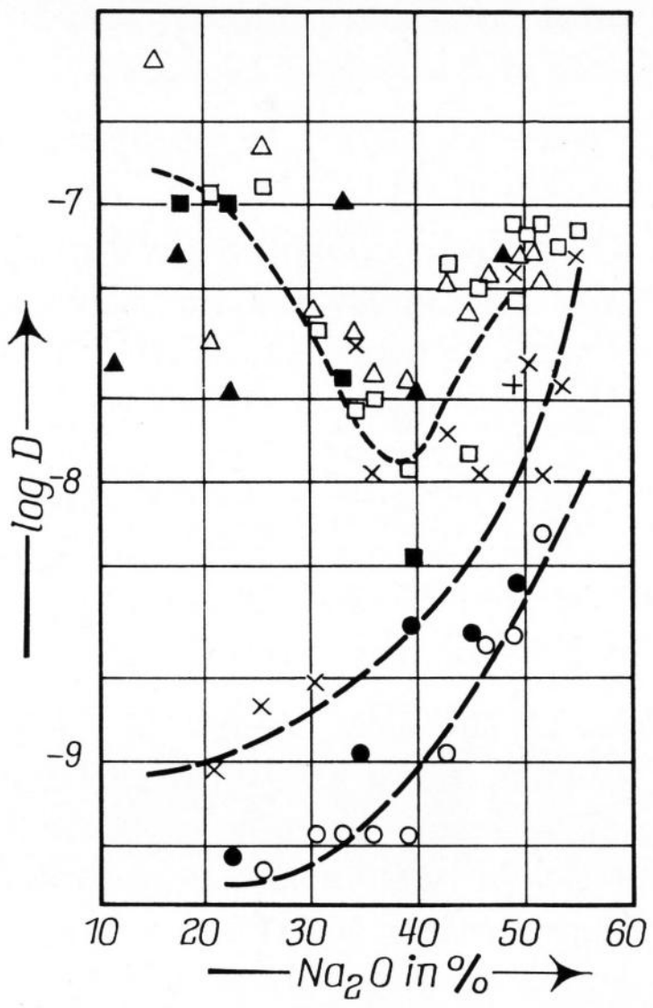

Figure 5. The relations between computed values of diffusivity for volatilization and initial composition at different temperatures. The symbols have the same significance as in figure 4.

of α with temperature is represented by activation energies in the range 46 to 63 kcal/mol.

Values of log D are plotted against melt composition in figure 5. From the form of the theory and the limitations of the data, D is expected to show greater scatter than α especially when the maximum value of $h\sqrt{Dt}$ is not very large. As very few sets of data at 1100 or 1200 °C have maximum values of $h\sqrt{Dt} > 1$, this may largely account for the scatter of points at these two temperatures. The relations between D and composition are similar at 1100 and 1200 °C and appear plausible.

At 1300 and 1400 °C several unexpected features are seen. First, there is a much wider scatter of points than can be accounted for by the range of data and method of determining D ($h\sqrt{Dt_y} > 1$ for more than half the sets of data); second, the shape of the D vs. composition curve is very different and appears to show a minimum at about 37% Na_2O; third, there are many cases where the calculated diffusivity is approximately the same at both 1300 and 1400 °C or else lower at the higher temperature. It is possible for the shape of a composition/property relation to change dramatically with change in temperature (one well known example is the viscosity of Na_2O–B_2O_3–SiO_2 glasses, see English [8]) but such effects are not common; it is also unusual to have a zero or negative temperature coefficient. The lack of internal consistency in the values of D describing the data, especially at 1300 and 1400 °C, also means that they cannot be accepted without closer examination.

3.3. Comparison with other data

Two kinds of comparison can be made; with the volatilization results of other workers for similar glass melts and with diffusivities obtained by different but comparable experiments.

Holá, Matoušek and Hlaváč [9] have reported a series of volatilization experiments for sodium disilicate (34,1% Na_2O) in flowing gas at 1300 °C. In dry nitrogen they obtained $\alpha = 6{,}7 \cdot 10^{-7}$ cm s^{-1} and $D = 2{,}1 \cdot 10^{-8}$

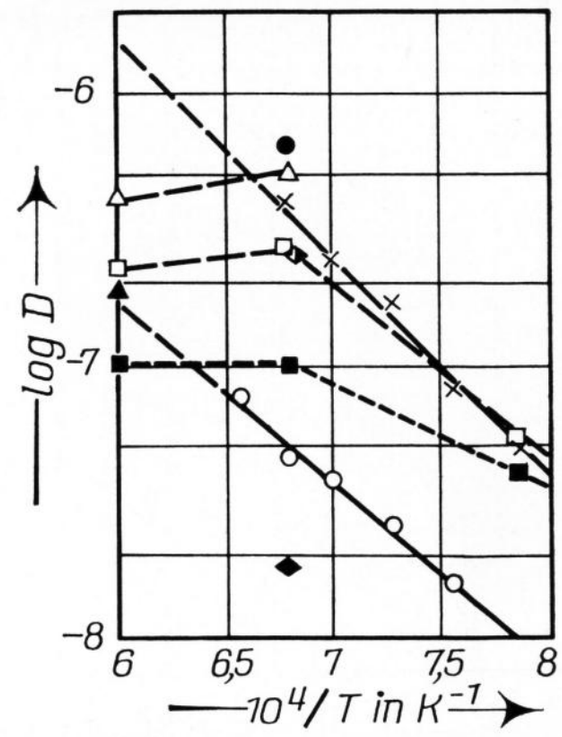

Figure 6. The temperature and composition dependence of effective diffusivity for dissolution of silica in sodium silicates.
Compositions are initial soda contents of the melts.

○ 34,1% Truhlářová and Vepřek, △ 50% Schwerdtfeger (static),
× 34,1% Hlaváč and Nademlýnská, ▲ 50% Schwerdtfeger (rotating),
● 50% Truhlářová and Vepřek, □ 40% Schwerdtfeger (static),
◇ 38% Truhlářová and Vepřek, ■ 30% Schwerdtfeger (static).
◆ 22,5% Truhlářová and Vepřek,

$cm^2\ s^{-1}$; this value of α is ten times higher than for the data of Preston or Lawton but the value of D agrees very well. The difference in α might be due to the use of flowing gas (13 cm s^{-1}) instead of a stationary atmosphere.

Cable and Chaudhry [2] have reported some results for soda-lime-silica melts having 16,0 to 20,7% Na_2O. Their results gave α between $2{,}4 \cdot 10^{-8}$ and $2{,}3 \cdot 10^{-7}$ cm s^{-1} and D between $3 \cdot 10^{-8}$ and $2{,}6 \cdot 10^{-6}$ $cm^2\ s^{-1}$ at 1400 °C. Preston's and Lawton's data suggest $\alpha \simeq 1{,}5 \cdot 10^{-7}$ cm s^{-1} and D in the range $3 \cdot 10^{-8}$ to $5 \cdot 10^{-7}$ $cm^2\ s^{-1}$ for such compositions at 1400 °C. The values of α agree reasonably but the spread of values of D is remarkable in both sets of results.

Fortunately some comparable diffusivities obtained from a different type of experiment are available. So far as diffusion within the melt is concerned, removing soda by volatilization should be equivalent to enrichment by dissolution of solid silica. Several sets of experiments on dissolution of silica in sodium silicates have been reported: Schwerdtfeger [10] made experiments at 1000, 1200 and 1400 °C with melts containing 30, 40 and 50% Na_2O; Truhlářová and Vepřek [11] studied dissolution in sodium disilicate from 1050 to 1250 °C and also four other compositions at 1200 °C; Hlaváč and Nademlýnská [12] also used sodium disilicate but from 900 to 1200 °C.

The results available are plotted in figure 6 and show considerable discrepancies. Careful examination of the experimental conditions and theoretical models used by the different authors shows possible sources of error in all cases. However it is not possible to evaluate the errors and determine the true values. A lengthy discussion of this point thus does not seem appropriate here. The correct values probably lie within the ranges indicated by figure 6. Diffusivity clearly depends on composition and appears to increase by a factor of from 10 to 30 between 20 and 50% Na_2O. At 1100 °C the relevant range is probably between $D = 1 \cdot 10^{-8}$ and $3 \cdot 10^{-7}$ $cm^2\ s^{-1}$; at 1400 °C the corresponding values are probably about $1 \cdot 10^{-7}$ to $2 \cdot 10^{-6}$ $cm^2\ s^{-1}$. Schwerdtfeger was able to offer a plausible reason for the anomalous temperature dependence between 1200 and 1400 °C: this is discussed below.

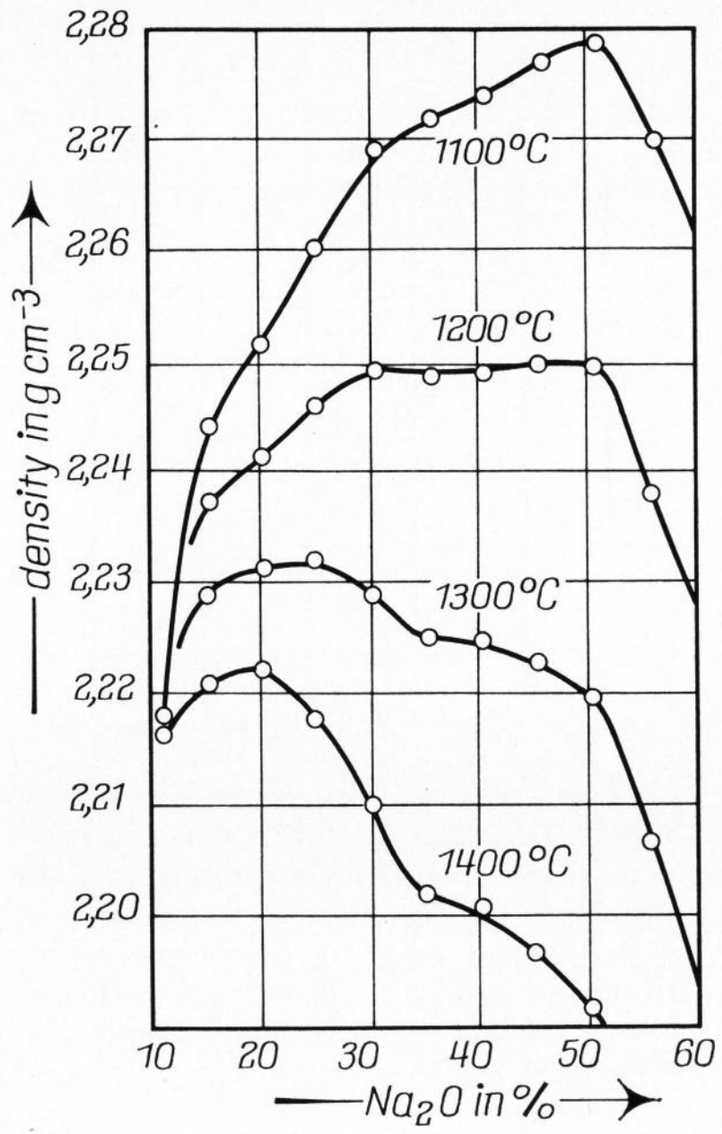

Figure 7. The relation between composition and density for sodium silicates at 1100, 1200, 1300 and 1400 °C, according to Bockris, Tomlinson and White [7].

The diffusivities describing volatilization (figure 5) are considerably lower than for silica dissolution at all temperatures. At 1100 and 1200 °C the two sets of results differ by factors of 20 to 40 and the discrepancies seen in figure 6 are small compared with these. At 1300 and 1400 °C the volatilization diffusivities appear only 3 to 10 times lower. The agreement hoped for between the two types of experiment does not appear to exist but some further discussion is useful.

3.4. Factors influencing diffusivity values

Transport through the melt by diffusion is so slow that any convection could easily be more important. Convection could be produced by growth and rise of gas bubbles, temperature gradients, change of density with composition as volatilization proceeds or surface tension gradients at the surface of the melt.

The first two are unlikely to be significant but the third might be important.

If loss of the volatile constituent reduces the density of the melt the system should be stable and this is evidently true with lead glasses, as shown by Kruithof et alia [13]. However the results of Kruithof and his colleagues show that this was not true with the soda-lime-silica and borosilicate glasses investigated by them. Quantitative evaluation of volatilization experiments in such conditions would undoubtedly give apparent diffusivities higher than the true values.

Figure 7 shows the most reliable of the density data for sodium silicates, those of Bockris, Tomlinson and White [7]. If these results are correct, all melts with up to 50% Na_2O should be hydrodynamically stable during volatilization experiments at 1100 and 1200 °C but this is not true at higher temperatures. At 1300 and 1400 °C there is a distinct maximum in the density around 20 to 25% Na_2O and hydrodynamic instability is expected in melts with higher soda contents because loss of soda will, initially, increase density. Melts with more than 51% Na_2O are likely to show such an effect at all temperatures. This effect could account for an unexpectedly large increase in apparent diffusivity between 1200 and 1300 °C for melts with between about 25 and 50% Na_2O. The major anomaly seen in figure 6 is a very large increase in D between 1200 and 1300 °C for melts with $< 35\%$ Na_2O; unfortunately the density data provide no grounds for attributing this to convection in the melt.

Figures 5 and 6 show that diffusivity is a function of melt composition and the assumption of constant diffusivity in equation (1) and the rest of theory is not valid.

Fortunately experience shows that it is not necessary to reject the theory but great care is needed in interpreting the effective diffusivity. The value of D should, in particular, be regarded as the average for the range C_0 to C_i rather than the value for C_0. By assigning the effec-

Table 4. Initial Na_2O concentrations, maximum values of $h\sqrt{Dt}$ with corresponding predicted interface and mean concentrations

Na_2O in %	1100 °C				1200 °C				1300 °C				1400 °C			
	C_0 in g cm^{-3}	$h\sqrt{Dt}$ max.	C_i in % Na_2O	$\overline{C}$	C_0 in g cm^{-3}	$h\sqrt{Dt}$ max.	C_i in % Na_2O	$\overline{C}$	C_0 in g cm^{-3}	$h\sqrt{Dt}$ max.	C_i in % Na_2O	$\overline{C}$	C_0 in g cm^{-3}	$h\sqrt{Dt}$ max.	C_i in % Na_2O	$\overline{C}$
11,8	—	—	—	—	—	—	—	—	—	—	—	—	0,262	0,663	6,38	9,09
15,2	—	—	—	—	—	—	—	—	—	—	—	—	0,338	0,124	13,3	14,2
17,7	—	—	—	—	—	—	—	—	0,393	0,065	16,5	17,1	0,392	0,408	11,8	14,8
20,8	—	—	—	—	0,466	0,441	13,5	17,1	0,464	0,103	18,6	19,7	0,462	0,596	11,9	16,3
22,7	0,512	0,0015	22,6	22,7	—	—	—	—	0,506	0,066	21,1	21,9	0,504	0,883	10,5	16,6
25,6	0,579	0,099	23,0	24,3	0,575	0,378	17,5	21,6	0,571	0,103	22,0	24,2	0,568	0,263	19,5	22,5
30,5	0,691	0,142	26,0	28,3	0,685	0,447	19,6	25,1	0,679	0,242	23,7	27,1	0,673	0,638	16,8	23,7
32,9	0,747	0,089	29,5	31,2	—	—	—	—	0,732	1,69	9,64	21,3	0,726	0,229	25,9	29,4
34,2	0,777	0,165	29,0	31,6	0,770	0,106	30,5	32,3	0,762	0,415	22,9	28,6	0,753	0,864	16,0	25,1
35,8	0,813	0,300	26,3	31,0	0,805	0,233	28,0	31,9	0,797	0,547	21,2	28,5	0,788	1,52	11,4	23,6
39,0	0,887	0,897	17,8	28,4	—	—	—	—	0,867	1,19	14,8	26,9	0,858	1,66	11,6	25,3
39,3	0,893	0,159	33,1	36,2	—	—	—	—	0,874	1,74	11,3	25,3	0,865	2,30	8,91	24,1
42,6	0,969	2,70	8,39	25,5	0,958	0,357	29,7	36,2	0,947	0,660	23,1	32,8	0,937	1,71	12,4	27,5
44,6	1,01	0,307	32,2	38,4	1,00	—	—	—	0,990	1,41	15,0	29,8	0,979	2,79	8,52	26,5
46,0	1,05	0,376	31,5	38,8	1,03	0,697	24,2	35,1	1,02	1,14	18,0	32,0	1,01	3,18	7,91	27,0
48,8	1,12	0,316	35,3	42,1	1,10	2,43	10,6	29,7	1,08	0,945	21,6	35,2	1,07	3,47	7,78	28,3
49,0	1,12	0,543	29,1	39,1	1,10	0,293	36,2	42,6	1,09	1,15	19,1	34,1	1,08	3,93	4,27	26,6
50,2	—	—	—	—	1,30	0,452	32,2	41,2	1,12	1,10	20,2	35,2	1,10	5,01	5,70	27,9
51,4	1,17	0,441	33,3	42,3	1,16	1,44	17,1	34,2	1,14	1,60	15,7	33,6	1,13	33,4	3,1	27,1
53,2	—	—	—	—	1,19	1,09	21,4	37,3	1,18	2,40	11,6	32,4	1,17	241	0,16	26,7
54,8	—	—	—	—	1,23	0,687	29,1	42,0	1,21	3,29	9,2	32,0	1,19	107	0,37	27,6

tive diffusivity to $\overline{C} = (C_0 + C_i)/2$ Schwerdtfeger [10] successfully accounted for his anomalous temperature dependence between 1200 and 1400 °C (figure 6).

When dissolving solid silica in the melt one may assume that C_i is constant at the value given by the phase diagram and this varies only between about 13,5 and 22% Na_2O for sodium silicates between 1100 and 1400 °C. In a volatilization experiment C_i varies more slowly with time starting at C_0 and eventually reaching zero. It is clear that examining the relations between D and C_0 is not the best way to compare results of the two types of experiment. The mean concentrations ($\overline{C}$) for volatilization experiments have therefore been determined using the values of C_i obtained from equation (4) and the computed values of α and D, see table 4.

Plotting D against the mean composition produces the results seen in figure 8. For 1100 and 1200 °C the scatter of the individual points is much reduced when compared with figure 5; in each set there are several pairs of values having very similar values of D and $\overline{C}$ although differing in C_0. As with Schwerdtfeger's results, this plot resolves the anomalous temperature dependence at 1300 and 1400 °C for many of the results. Two thirds of the results (for $\overline{C} > 24\%$ Na_2O) now fall into two groups showing relatively small scatter at both temperatures. Below $\overline{C} = 24\%$ the values are widely scattered and much higher than expected; this could be the result of convection caused by hydrodynamic instability.

Unfortunately the hypothesis of convection leading to high apparent diffusivities is not immediately acceptable. Low soda melts should be stable and those rich in soda unstable but figure 8 suggests the opposite. As surface tension decreases only a little as soda content is reduced, it should not make convection inevitable. Although the source of convective flow has not been identified it remains the most likely interpretation of the high and scattered values of both individual data points (figures 2 and 3) and D at 1300 and 1400 °C.

If unusually high diffusivities are disregarded as possibly influenced by convection, the relation between D and $\overline{C}$ appears to be of very similar shape at all four temperatures, see the curves drawn on figure 8. Plots of log D vs. 1/T are very close to straight lines for compositions from 20 to 40% Na_2O. The apparent activation energies range from 58 kcal·mol^{-1} for 20% Na_2O to about 88 kcal·mol^{-1} for 40% Na_2O.

The data shown in figure 6 allow the composition dependence of diffusivity for silica dissolution to be estimated at 1200 °C for the range $20 < \overline{C} < 35\%$ Na_2O. The relation appears very similar in shape to that seen in figure 8 but the silica dissolution values are about 20 times higher. Table 4 shows that values of C_i were quite similar to those in silica dissolution so that cannot account for the difference. As the volatilization values are the lower and some silica dissolution results were obtained by methods relying on convection, convection cannot be invoked to explain the discrepancy.

4. Conclusion

The theory proposed provides a good description of the kinetics of volatilization of soda from sodium silicate melts but the dependence of diffusivity on composition and temperature shows some anomalies. Melts with more than about 40% Na_2O appeared to show a lower diffu-

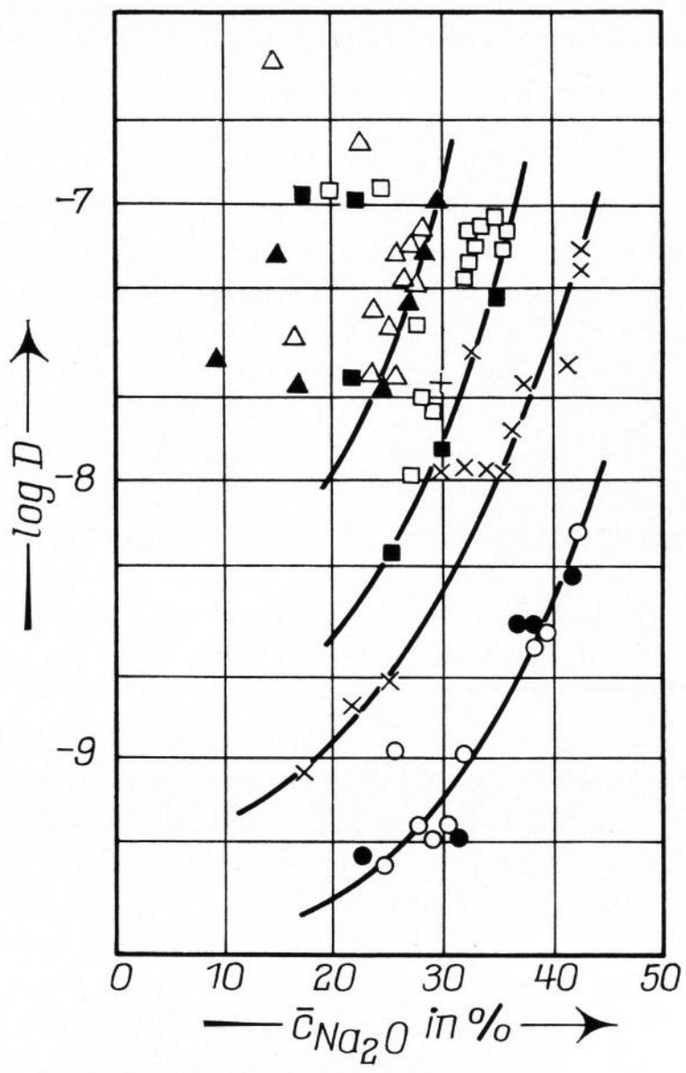

Figure 8. The dependence of diffusivity for volatilization on mean composition ($\overline{C} = C_0 + C_i)/2$). The symbols have the same significance as in figures 4 and 5.

sivity at 1400 than at 1300 °C. This anomaly can be successfully interpreted by considering the diffusivity to apply to the mean concentration $\overline{C} = (C_0 + C_i)/2$ rather than to the initial composition C_0. At 1300 and 1400 °C the diffusivities for low soda melts were higher and showed a much wider scatter than expected. Although the relation between composition and density showed that hydrodynamic instability could occur at these temperatures, this does not agree with the observed effect. According to the density data such instability should have occured with the compositions richest in soda.

The diffusion process in the melt should be similar for silica dissolution and for loss of soda by volatilization, but diffusivities for volatilization were a factor of twenty lower at 1200 °C. Both types of experiment need further study.

The dependence of reaction rate constant α on composition and temperature showed none of the anomalies seen with diffusivity but no theoretical interpretation of α has yet been proposed and its true meaning is not clear.

The theory provides a good description of the data but the uncertainties surrounding the values of α and D prevent its complete acceptance. More detailed study of volatilization is necessary. Samples should be examined for signs of convective flow during the experiment and concentration profiles in the melt or interface concentrations should be determined by experiment. The effects of composition, pressure and flow of the atmosphere on α should help to elucidate its significance.

The theory needs refinement to allow for the strong composition dependence of diffusivity; the simple method of assigning the apparent diffusivity to $\overline{C}$ is not very reliable when the effect is as large as it is in this case.

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