Influence of hydroxyl content on the diffusion of water in silica glass*

I. Burn† *& J. P. Roberts*

Department of Ceramics, Houldsworth School of Applied Science, University of Leeds, Leeds 2

The diffusion of 'water' following the reaction of HTO or D_2O vapour with silica glass containing various uniform concentrations of hydroxyl was studied between 600 and 1200° C. At temperatures above the transformation range, the penetration of the tracer was appreciably greater than that found previously in 'water'-free material, because of the dependence of the diffusion coefficient upon concentration. The concentration dependence of the diffusion coefficient as measured under isocompositional conditions was, however, slightly different from that which had been obtained from the experiments with initially 'water'-free glass. Below the transformation range, the sensitivity of the diffusion to initial hydroxyl content decreased with increasing fictive temperature, and the sensitivity of the diffusion to thermal history decreased with increasing hydroxyl content.

Previous work in this laboratory on the diffusion of 'water' in silica glass[1–6] was concerned mainly with diffusion into material initially free of 'water'. Water entering the glass was found to be accommodated principally as hydroxyl,[1, 5] and the diffusion coefficient was found to vary with concentration.[2, 4] The present work, on silica glass already containing 'water', was undertaken primarily to obtain further information about the concentration dependence of the diffusion coefficient, but it has, as was anticipated, at the same time contributed to knowledge about the mechanism of diffusion in this system.

Diffusion of the hydrogen of 'water' in the glass at temperatures above the transformation range (≥1000°C) was investigated at constant 'water' concentration, i.e. under isocompositional conditions, as far as was practicable. This was achieved by exposing the various specimens of glass to tritiated or deuterated water vapour at pressures appropriate for equilibrium with the 'water' inside the material. At temperatures below the transformation range, however, equilibrium conditions could not be predetermined, and here the sensitivity of the diffusion to initial hydroxyl content was investigated for an arbitrarily chosen vapour pressure as the thermal history of the glass was varied.

Whilst the use of tritiated water (T/H ratio $\sim 10^{-4}$) allowed, as before,[2, 6] determination of penetration profiles for 'water' entering the glass from the vapour with considerable precision, it was not possible by this method to obtain information about the mobility of the 'water' already in the glass. This information was obtained from experiments with D_2O, followed by infrared absorption measurements.

Materials and equilibrium vapour pressures

Attempts were made at the start to produce specimens of silica glass containing various uniform concentrations of 'water', i.e. hydroxyl, by equilibrating 'water'-free specimens with water vapour at suitable pressures. However, it was found that specimens of sufficient thickness could not be produced in this way because devitrification set in during the equilibration when the process was carried out at temperatures at which the saturation with 'water' could be accomplished in a practical time. The difficulty was circumvented by working with a series of silica glasses already containing 'water' at various concentrations, the result of differences in manufacturing method. The materials were either synthetic silica glass (Spectrosil‡) or flame fused quartz crystal (O.G. Vitreosil‡).

The hydroxyl content of the glasses was assessed in terms of their optical density at 2·7 μm: the optical density per mm at this wavelength is very nearly 10×wt% OH.[7] Although some of the hydroxyl in Spectrosil and O.G. Vitreosil is undoubtedly a consequence of reaction of hydrogen gas with the glass during manufacture,[8] it was assumed that the amount

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† Present address: Sprague Electric Company, Research and Development Laboratories, North Adams, Massachusetts.

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Table 1. *Equilibrium vapour pressures for the materials used in the experiments, for temperatures above the transformation range*

*Glass**	*Optical density per mm at 2·7 μm*	*Equilibrium water vapour pressure (1000–1200° C) (mm Hg)*
Spectrosil (I)	1·2	700
Spectrosil (II)	0·85	400
O.G. Vitreosil (I)	0·40	100
O.G. Vitreosil (II)	0·21	20

* The usual impurity content and other information about Spectrosil and O.G. Vitreosil are given in Reference 7.

of 'hydrogen' was small compared with the amount of 'water' because the solubility of hydrogen in silica glass is about 100 times less than that of water vapour.

In order to calculate the pressures of water vapour at the desired diffusion temperatures which would give equilibrium with the 'water' already in the glasses, it was necessary to know the dependence of the saturation concentration (the 'solubility') of 'water' in silica glass upon both temperature and water vapour pressure. Above the transformation range the solubility of water in silica glass is essentially invariant with temperature[1, 2] and is proportional to the square root of the water vapour pressure.[1, 7, 9] Equilibrium vapour pressures for the materials used in the present work at temperatures above the transformation range were interpolated from data obtained by Stephenson & Jack[7, 9] and are given in Table 1.

Below 1000° C the solubility depends not only upon the ambient water vapour pressure but also upon temperature and thermal history.[4] However, since few data on solubility dependence were available for temperatures below 1000° C, a vapour pressure of 450 mm Hg was chosen arbitrarily for use with all the materials. Because of the importance of controlling the thermal history of glasses in experiments below the transformation range, materials used at these temperatures were generally given prior stabilising heat treatments (i.e. fixing their 'fictive temperatures'), in air, at 1000, 1100, or 1200° C followed by quenching in cold water. Annealing times were based on those reported to be required for stabilisation of the density, viscosity, etc., of silica glass,[10–14] viz. 1000 h at 1000° C, 100 h at 1100° C, or 1 h at 1200° C. By annealing blocks of the materials and afterwards cutting specimens from their centres, it was hoped to minimise any change in 'water' content that might have occurred by diffusion into or out of the glass during the stabilisation.

Tritiated water experiments

Experimental

In the experiments with tritiated water at temperatures above the transformation range, specimens of Spectrosil I and of the two O.G. Vitreosil materials, in the form of polished plates (19×15×2 mm), were heated at constant temperature under their respective equilibrium water vapour pressures (Table 1) for a period of 5 h. A range of temperature from 1000 to 1200° C was covered at intervals of 50 deg C, experiments at higher temperatures being prevented by the onset of devitrification.

Diffusion below the transformation range was investigated mainly at 700° C with a diffusion time of 25 h. In these experiments specimens of the same materials, cut from blocks previously annealed at temperatures of 1000, 1100, and 1200° C as mentioned earlier, were exposed to tritiated water vapour (450 mm Hg pressure) together with similarly annealed specimens of 'water'-free glass (I.R. Vitreosil*). In addition, the diffusion of tritiated 'water' into 'as-received' specimens of Spectrosil I was investigated in the range 600–900° C, again with 450 mm Hg water vapour pressure, but with a diffusion time of 5 h.

The diffusion apparatus, the procedure, and the method of obtaining penetration profiles by sectioning and counting the specimens after exposure to the tritiated water vapour were essentially the same as described previously.[2, 4] Water vapour pressure was controlled by the temperature of a reservoir of tritiated water (about 2 ml; 200 mC/ml activity) immersed in a thermostatically regulated oil bath and checked by a suitably adapted Bourdon type pressure-gauge.[14] The diffusion time was accurately defined by making provision for moving the specimens into and out of the hot zone of the apparatus at the beginning and end of the heating period. After the exposure to tritiated water vapour, layers of glass (about 10 μm thick) were removed progressively from one face of the specimen (by grinding and repolishing) and the activity of each new surface counted by solid state assay in a 2 π gas flow proportional counter. Normally the same procedure was then repeated on the other face of the specimen, as a check.

Analysis of diffusion profiles

Solution of Fick's second equation for diffusion into a semi-infinite medium when the boundary is kept at a constant concentration, C_0, and the initial concentration in the medium is zero, shows that, if the diffusion coefficient is constant, the concentration, C–distance, x, profile after a time, t, can be expressed by the relation

$$C = C_0\left(1-\operatorname{erf}\frac{x}{2\sqrt{(D^*t)}}\right) \qquad (1)$$

$$= C_0 \operatorname{erf} c\,\frac{x}{2\sqrt{(D^*t)}}$$

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where erf $z=2/\sqrt{\pi}\int_0^z \exp(-\eta^2)\,d\eta$ is the error function and erfc z is the error function complement. For the present purposes, the symbol D^* represents the diffusion coefficient when isocompositional conditions are maintained, to distinguish it from that for diffusion into initially 'water'-free glass, which will be denoted hereafter simply as D.

Thus for a non-variable diffusion coefficient, an inverse error function complement plot, or more conveniently an arithmetical probability plot, of C/C_0 against x is a straight line and the diffusion coefficient can be evaluated from its slope. Alternatively the diffusion coefficient can be evaluated by graphical integration by the Matano method,[15] though there is normally little merit in this approach unless the coefficient varies.

Results

Diffusion above the transformation range

Tritium penetration profiles for diffusion of 'water' under isocompositional conditions obeyed Equation (1) at temperatures clearly above the transformation range, but some slight departures from theoretical behaviour were observed at 1000°C. Figure 1(a) shows probability plots of diffusion profiles in each of the materials at 1100°C, illustrating the error function complement dependence; Figure 1(b) shows the slight non-linearity of the probability plots at 1000°C. The deviations from theoretical behaviour are believed to be a consequence of entry into the transformation range because a similar and even more pronounced effect was observed at 900°C, Figure 5(b), and also because it is noticeable that the curvature of the probability plots for diffusion at 1000°C is the greater the lower the 'water' content of the glass, i.e. the higher the transformation range of the material.[12]

Values of the diffusion coefficient D^* evaluated from the probability plots are shown in Figure 2. As in the case of the non-linear probability plots, the apparent inconsistency of the values of D^* for 1000°C with those for the other temperatures is very likely also a transformation range effect. Because of the limited temperature range available for the isocompositional diffusion experiments, the 'activation energy' for diffusion could not be evaluated precisely but it appeared to decrease slightly with increasing water content from 17 kcal/mole for O.G. Vitreosil II, to 14 kcal/mole for Spectrosil I, approximately. For a given water concentration, values of D^* were broadly similar to values of the diffusion coefficient, D, obtained from work on initially 'water'-free glass,[2, 4] but there were some small yet significant differences, as will be discussed later. The penetration of tracer under isocompositional conditions was appreciably greater than that in initially 'water'-free glass under similar conditions of temperature and water vapour pressure (e.g. Figure 3), because at low tracer concentrations D^*

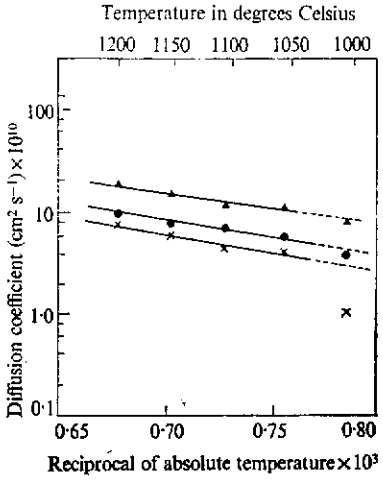

Figure 2. *Arrhenius plot of the diffusion coefficient for 'water' in silica glass under isocompositional conditions*

▲ Spectrosil I (o.d./mm 1·2)
● O.G. Vitreosil I (o.d./mm 0·4)
× O.G. Vitreosil II (o.d./mm 0·2)

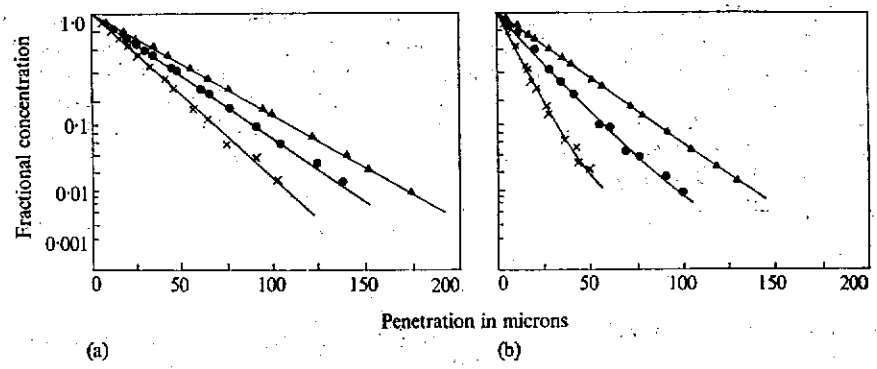

Figure 1. *Probability plots for diffusion of tritiated 'water' into silica glass under isocompositional conditions for 5 h*

(a) 1100°C
(b) 1000°C
▲ Spectrosil I (o.d./mm 1·2)
● O.G. Vitreosil I (o.d./mm 0·4)
× O.G. Vitreosil II (o.d./mm 0·2)

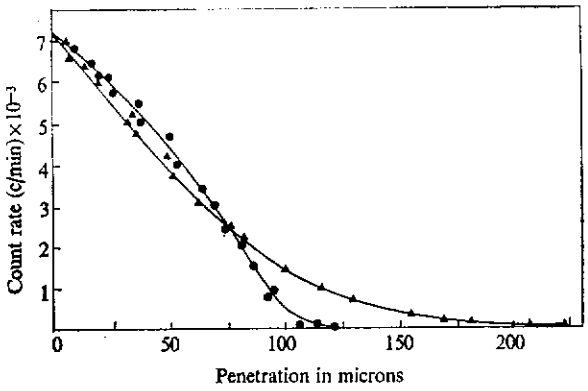

Figure 3. *Comparison of tritiated 'water' diffusion profiles in silica glass above the transformation range under isocompositional conditions and when the glass was initially 'water'-free (both at 1200° C, 700 mm Hg, for 5 h)*

▲ Spectrosil I (uniform initial 'water' content of 0·12 wt% OH, i.e. isocompositional conditions)
● I.R. Vitreosil ('water'-free)

retains a high value, being constant, whereas D gets smaller.[2, 4]

Diffusion below 1000° C

Diffusion profiles obtained from the 25 h experiments at 700° C are shown in Figures 4(a)–(c). It can be seen that when the temperature of pretreatment was high, e.g. 1200° C; Figure 4(a), the solubility (i.e. the extrapolated surface count rate[2]) and diffusion did not appear to be influenced by the initial 'water' content. When the materials were preheated at lower temperatures, 1100 and 1000° C; Figures 4(b) and (c), however, lower solubilities and greater penetrations were observed with decreasing initial 'water' content. Also, whereas the solubility and diffusion rate in Spectrosil I were little affected by thermal pretreatment, these parameters for the glasses with a low 'water' content were markedly dependent on thermal history, in accord with earlier work.[4]

Penetration profiles obtained from the 5 h diffusion experiments with as-received Spectrosil I (i.e. no stabilising heat treatment given) in the temperature range 600–900° C are shown in Figure 5(a), where the dashed line indicates the initial concentration of 'water' in the glass. In spite of large departures from isocompositional conditions, the probability plots, Figure 5(b), are linear within experimental error except for the 900° C plot which shows the systematic deviation from theoretical behaviour similar to that observed for diffusion at 1000° C, Figure 1(b). The curvature of the 900° C probability plot appeared not to be a consequence of departure from isocompositional conditions: with a vapour pressure of 700 mm Hg (which was found to be very close to the equilibrium water vapour pressure of the glass at that temperature), an almost identical plot was obtained, included in Figure 5(b). Values of the diffusion coefficient for Spectrosil I are given in Figure 6, together with those obtained with the same material at higher temperatures; a result from a preliminary experiment (at 765° C) is

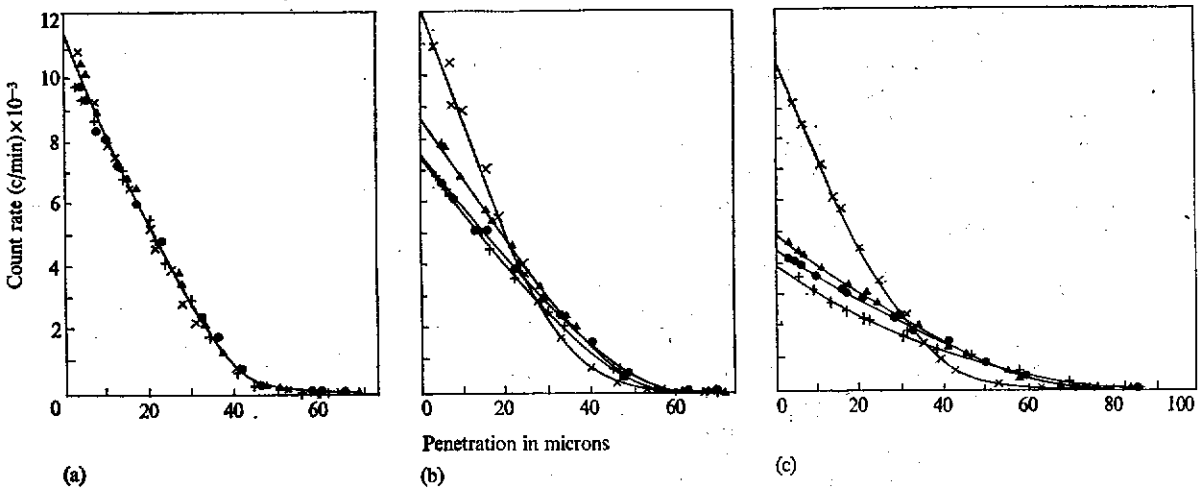

Figure 4. *Diffusion of tritiated 'water' at 700° C (450 mm Hg for 25 h) into silica glass stabilised at various temperatures*

(a) 1200° C for 25 h
(b) 1100° C for 100 h
(c) 1000° C for 1000 h
× Spectrosil I
▲ O.G. Vitreosil I
● O.G. Vitreosil II
+ I.R. Vitreosil

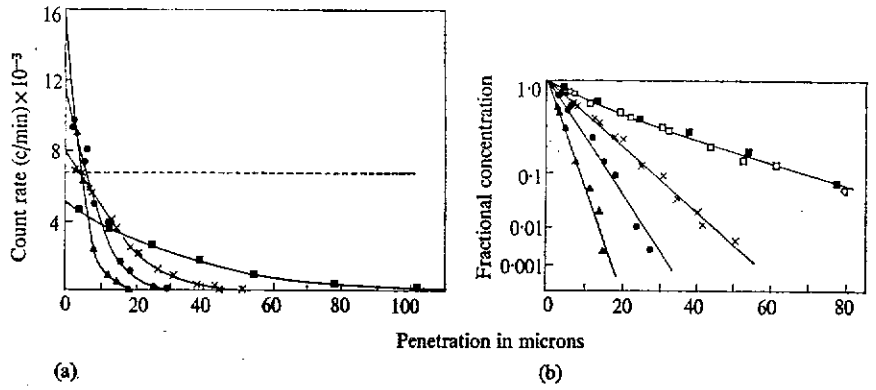

Figure 5. *Diffusion of tritiated 'water' into as-received Spectrosil I (450 mm Hg for 5 h)*
(a) Linear plot
(b) Probability plot
■ 900°C
× 800°C
● 700°C
▲ 600°C
□ 900°C (700 mm Hg)
– – – – Initial (untritiated) 'water' concentration

also included. The values shown for 1000 and 900°C, temperatures at which a variable diffusion coefficient was indicated by curved probability plots, are the maximum and minimum values obtained from analysis of the diffusion profiles by the Matano method. The results indicate an appreciable increase in the 'activation energy' for the diffusion of 'water' in Spectrosil from 14·0±0·5 kcal/mole at the higher temperatures to 25±1 kcal/mole at lower temperatures, with a transition in the transformation range.

Deuterated water experiments

Experimental

Basically these experiments involved heating specimens of the glasses containing 'water' for various times in deuterated water vapour (99·9(5)% D_2O, I.C.I. Ltd., Billingham), usually under isocompositional conditions. The rates of disappearance of OH and of appearance of OD groups were determined from measurements of the optical density of the glass at 2·7 and 3·7 μm respectively, made before and after each heat treatment. In some cases, specimens were heated in D_2O vapour for a single period only, but often, after infrared measurements had been made, they were reheated for further periods to obtain longer exposure times.

Most of the work was concerned with diffusion in Spectrosil I (0·12 wt% OH) at 750, 1000, 1100, and 1200°C, but a few experiments were also carried out at 1000°C on Spectrosil II (0·085 wt% OH) and O.G. Vitreosil I (0·04 wt% OH). Although 'thin' specimens (19×15×0·2 mm) were used in all the experiments, 'thick' plates (19×15×2 mm) were also used in the experiments on Spectrosil I at the higher temperatures.

The apparatus and method of heating the glass in D_2O vapour were similar to those for the tritiated water work. The deuterated water in the reservoir of the apparatus was changed several times during the course of the work in case it had become diluted by exchange with 'water' in the walls of the apparatus. Allowance was made for the fact that the vapour pressure of D_2O is slightly different from that of H_2O (e.g. pure D_2O boils at 101·4°C).

Evaluation of the infrared absorption data

One drawback of the infrared method for diffusion measurements is that it is difficult to determine a true diffusion coefficient, unless it is known not to vary with composition; if there is such a variation, only some average value of the coefficient can be obtained. However, for the present work with deuterated water, it appeared to be justified to assume that the diffusion coefficient for the 'deuterium', and for the 'hydrogen' it was replacing, would be constant in most of the experiments undertaken, because experiments (described above) with tritiated water under similar conditions had shown little variation of D^* (Spectrosil I, 1000–1200°C, 700 mm Hg; O.G. Vitreosil I, 1000°C, 100 mm Hg).

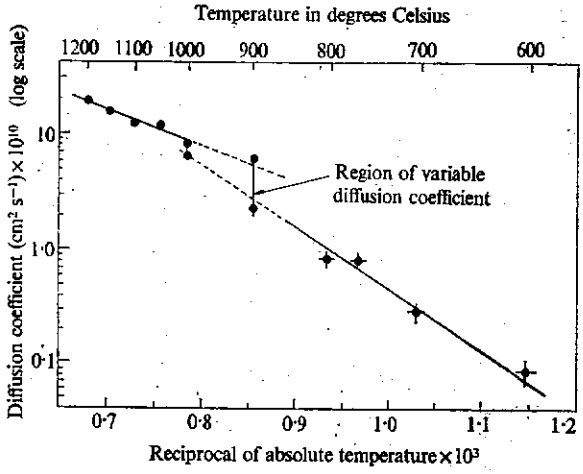

Figure 6. *Arrhenius plot of the diffusion coefficient for 'water' in as-received Spectrosil I*

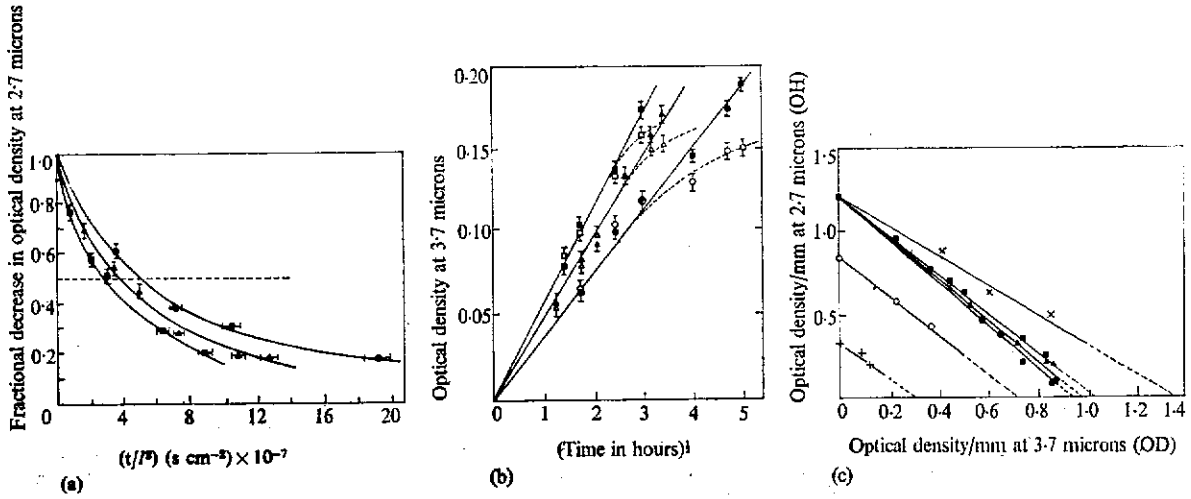

Figure 7. *Replacement of* (OH) *in 'water'-containing silica glass with* (OD) *when heated in D_2O vapour*

(a) Removal of (*OH*) from Spectrosil I (0·12 wt% *OH*) heated at 1000, 1100, or 1200°C in D_2O vapour at 700 mm Hg pressure (isocompositional conditions)
● 1000°C
▲ 1100°C
■ 1200°C

(b) Uptake of (*OD*) accompanying the removal of (*OH*) in Figure 7(a)
● 'thick' specimen, 1000°C
○ 'thin' specimen, 1000°C
▲ 'thick' specimen, 1100°C
△ 'thin' specimen, 1100°C
■ 'thick' specimen, 1200°C
□ 'thin' specimen, 1200°C

(c) (*OH*) removal plotted against (*OD*) uptake; various materials and conditions
● 1000°C, ▲ 1100°C, ■ 1200°C } Spectrosil I, 700 mm Hg (c.f. Figures 7(a) and (b))
× 750°C, Spectrosil I, 450 mm Hg
○ 1000°C, Spectrosil II, 400 mm Hg
\+ 1000°C, O.G. Vitreosil I, 100 mm Hg

The diffusion coefficient for the removal of OH groups was obtained using the relation[16]

$$D^*_{OH} = \frac{0{\cdot}049}{(t/l^2)_{\frac{1}{2}}} \qquad (2)$$

where t is the time which elapses before the number of OH groups in a plane sheet (i.e. a 'thin' specimen) of thickness l is reduced to half the original number, the number of OH groups in the glass at any instant of course being proportional to the optical density at 2·7 μm (Beer's Law).

For the entry of OD groups, the following relation[1] was used

$$D^*_{OD} = \frac{\pi}{16}\left(\frac{1}{n_\infty}\cdot\frac{N_t}{\sqrt{t}}\right)^2 \qquad (3)$$

where N_t is the number of *OD* groups which have entered a prism of unit cross-section extending from face to face of the specimen after a time, t, (entry from both sides of the specimen being allowed for) and n_∞ is the number of *OD* groups per cm³ of the glass at saturation, i.e. the solubility. As, however, this relation is valid only when there is no appreciable overlap of the diffusion from opposite faces of the specimen, 'thick' specimens were used as well as 'thin' ones in those experiments in which saturation was being approached in 'thin' specimens.

Results

Figure 7(a) shows the rate of decrease in hydroxyl concentration in Spectrosil I when this material was heated in D_2O vapour under isocompositional conditions. Figure 7(b) shows the accompanying increase in *OD* concentration; the departure of the *OD* absorption from the $t^{\frac{1}{2}}$ dependence in the case of the 'thin' specimens corresponds to approach to saturation. The *OH–OD* conversion as measured in the 'thin' specimens of Spectrosil I and the other glasses (Spectrosil II and O.G. Vitreosil I) is shown in Figure 7(c). Values of the *OD* absorption at saturation, n_∞, were obtained by extrapolation, Figure 7(c), since the accuracy of measurements of optical density per mm generally diminished as saturation was approached because of a small amount of warping of the specimens (especially at 1200°C). The magnitude of the *OD* absorption at saturation in Spectrosil I at 750°C indicates a definite increase in the total water content of the glass and so it follows that, as in the experiments with tritiated water below the transformation range, isocompositional conditions were not strictly maintained at this temperature.

Table 2 contains values of the diffusion coefficient calculated from the measurements of the removal of *OH* and uptake of *OD*; also included, for comparison, are values obtained from the tritiated water experiments under similar conditions, D^*_T.

It is clear from Table 2 that D^*_{OH} and D^*_{OD} are equal within experimental error and that their value depends on the total water content of the glass. Also, the measure of agreement between values of the

Table 2. *Comparison of the values of diffusion coefficient obtained for 'water', with various hydrogen isotopes, in silica glass*

Material	*Temperature* (°C)	$10^{10}.D^*_{OH}$ (cm^2/s)	$10^{10}.D^*_{OD}$ (cm^2/s)	$10^{10}.D^*_T$ (cm^2/s)
Spectrosil I	1200	17·5 ±1·1	17·9 ±1·3	18·7 ±0·8
Spectrosil I	1100	13·1 ±0·7	13·5 ±1·0	12·1 ±0·5
Spectrosil I	1000	9·6 ±0·4	8·8 ±0·6	7·8 ±0·4
Spectrosil I	750	0·79±0·08	0·71±0·09	0·78±0·04 (765°C)
Spectrosil II	1000	6·3 ±0·6	6·4 ±0·6	—
O.G. Vitreosil I	1000	3·6 ±0·7	4·1 ±0·8	3·8 ±0·3

diffusion coefficient obtained by the infrared absorption and tritiated water methods shows that there can be no appreciable isotope effect in the diffusion in this system. It is apparent from the *OH–OD* conversion data in Figure 7(c), however, that the extinction coefficient for the *OD* group in its fundamental stretching mode is lower than that of the *OH* group. For the experiments under isocompositional conditions the extinction coefficients for the *OH* and *OD* groups are proportional to the maximum values of the optical densities per mm at 2·7 and 3·7 μm respectively. The ratio of the extinction coefficients for the two groups, i.e. E_{OH}/E_{OD}, was found to be 1·25±0·05 and, taking E_{OH} as 85±7 *l* mol^{-1} cm^{-1},[1, 9] this gives E_{OD} as 68±8 *l* mol^{-1} cm^{-1}. A similar difference in extinction coefficients has been reported for the stretching modes of *OH* and *OD* groups in H_2O and D_2O (81 and 59 *l* mol^{-1} cm^{-1}).[17]

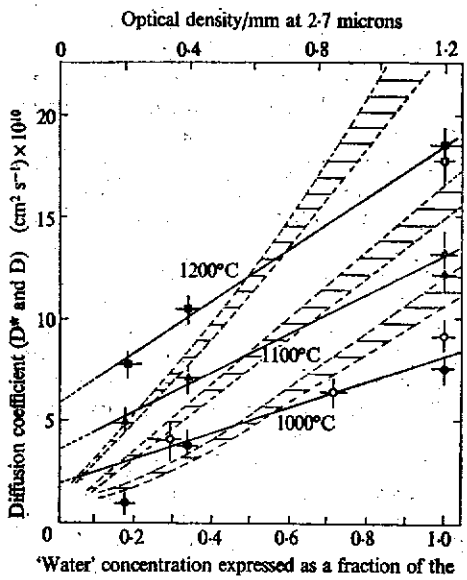

Figure 8. *Comparison of* D* *and* D

■ ▲ ● } *D**: isocompositional conditions (HTO)

□ △ ○ } *D**: isocompositional conditions (D_2O)

Shaded areas: *D*. Initially 'water'-free material (References 2 and 4)

General discussion

As mentioned earlier, values of the diffusion coefficient, *D**, obtained from the isocompositional experiments were similar to those, *D*, obtained, as a function of concentration, from earlier work with initially 'water'-free silica glass (I.R. Vitreosil), but there appeared to be some small but systematic differences which could not be accounted for in terms of experimental error. Although the reason for these differences has not been clearly established, some possible explanations can be advanced.

It is simpler to consider initially diffusion at temperatures above the transformation range, because of the complications arising from thermal history effects at lower temperatures. As can be seen from Figure 8, at 1000–1200°C, *D** appears to be smaller than *D* at high 'water' concentrations, but greater than *D* at low concentrations.

The relationship between *D** and viscosity in these glasses should first be considered, because it gives an indication of whether or not differences among the materials other than in 'water' content are likely to be influencing the value of *D**. Figure 9 shows *D** as measured in the present work plotted against viscosity, values of which were obtained by interpolation of viscosity data reported for the various glasses by Hetherington, Jack & Kennedy.[12] A log–log relationship is to be expected, since both *D** and the viscosity (stabilised glass) are exponential functions of temperature. It is noticeable, however, that, whilst the results for the two O.G. Vitreosil materials lie fairly well on a single straight line, the results for Spectrosil I fall on a distinctly different line. (The relationships between *D** (in cm^2 s^{-1}) and the viscosity (in poises) between 1000 and 1200°C are approximately $D^*\eta^{\frac{1}{4}}=2{\cdot}5\times10^{-8}$ for the Vitreosil materials, and $D^*\eta^{\frac{1}{4}}=4{\cdot}0\times10^{-8}$ for

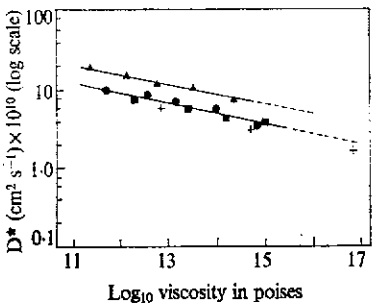

Figure 9. *The isocompositional diffusion coefficient for 'water' in silica glasses plotted against their viscosity (1000–1200° C)*

▲ Spectrosil I
● O.G. Vitreosil I
■ O.G. Vitreosil II
+ I.R. Vitreosil (extrapolated value of D^*)

Spectrosil I.) Spectrosil I has a greater viscosity than might be expected from its high water content.[12] Reasons could be that it has less metallic impurity than have the fused quartz materials or that it is the more homogeneous.[7] It is possible therefore that D^* is correspondingly lower in Spectrosil than it would be in fused quartz of the same 'water' content, and that it is this which accounts for the disagreement found between D^* and D at high water concentrations.

Values of D^* for zero 'water' concentration estimated by extrapolation in Figure 8 and plotted against the viscosity of I.R. Vitreosil lie quite close to the line for the other fused quartz materials (viz. O.G. Vitreosil I and II), Figure 9. On the other hand, extrapolated values of D for zero concentration when plotted in this way appear to give marked disagreement, and thus it is possible that the values of D at low concentrations are anomalous.

From considerations of chemical potential one might expect in principle that D^* would differ from D, according to the relationship[18]

$$D = D^* \left(1+\frac{C}{\gamma}\frac{d\gamma}{dC}\right)$$

where γ is the activity coefficient and C is the (molar) concentration of the diffusing species. However, this relation predicts that D^* should approach D at very low concentrations ($\gamma \to 1$) and this seems not to be the case in the present system. A possible reason for the observed difference between D and D^* at lower concentrations is that D depends upon the concentration gradient as well as upon the concentration, since Fick's law is an approximation that can be expected to be inaccurate in sufficiently steep chemical concentration gradients.[19] The values giving the shaded areas for D in Figure 8 were evaluated from diffusion profiles obtained for a single pressure of water vapour (700 mm Hg) and, because of the shape of these profiles[2, 4] (e.g. curve 2 in Figure 3), the values of D relate to gradually increasing concentration gradient with decreasing concentration over nearly all of the concentration range. Thus a discrepancy between D and D^* of the type observed would occur if D, whilst increasing with concentration, decreased with increasing concentration gradient. This can be described in a qualitative way by supposing that, on any given plane in the glass normal to the direction of diffusion, the mean displacement by random migration away from this plane is greater against the concentration gradient than with it, because up the gradient the diffusing species are moving into a region of higher concentration and greater mobility, i.e. back diffusion is favoured, the effect being the more pronounced the greater the chemical concentration gradient.

Whilst some or all of the above considerations may apply to diffusion at temperatures in and below the transformation range of the glass, the thermal pretreatment of the material exerts an overriding influence on values of D at these temperatures.[4] 'Water' initially present in the glass can modify the influence of thermal pretreatment in such a way that the diffusional penetration is reduced, cf. Figure 4(c). Also, except when annealing is carried out at about 1200° C or higher, the solubility of 'water' at temperatures below the transformation range increases with the initial 'water' content of the material, Figures 4(b) and (c). The reduced diffusion and increased solubility of 'water' with increasing concentration of initial 'water' therefore provide an apparent inverse correlation between diffusion and solubility. The same apparent correlation at temperatures below the transformation range has been seen before in this system, but previously the variable was fictive temperature and the glass was always initially 'water'-free.[4, 13, 20] It is possible that these two findings may be explained as follows.

Roberts & Roberts[4, 13, 20] postulated that 'water' in silica glass is accommodated at some kind of thermally produced reactive sites ('defects'), and suggested that the solubility of 'water' in the glass at temperatures below the transformation range depends on the defect concentration 'frozen in' from higher temperatures. If the 'defects' are broken or weakly bonded Si–O–Si bridges,[4, 13, 20] it would follow that when silica glass containing 'water' is annealed at a temperature lower than its original fictive temperature, removal of reactive sites by reformation of Si–O–Si bridges would be prevented in those sites that contain 'water', and this would lead to increased solubility with increasing initial water content.

It would be possible to explain the apparent inverse correlation between solubility and diffusivity in terms

of diffusing water molecules[21] participating in reversible reactions of the type:

$$H_2O + \underset{\text{(Weak or broken bridge)}}{\equiv Si-O-Si\equiv} \overset{\text{fast}}{\underset{\text{slow}}{\rightleftarrows}} 2(\equiv Si-OH)$$

The smaller the concentration of reactive sites, as determined by fictive temperature and initial water content, the greater would be the distance diffused by a molecule between its creation at one such site and its destruction at another (hence enhancement of diffusional penetration with decrease of solubility, and vice versa). If indeed this is the mechanism of diffusion at lower temperatures, one might expect that, at the higher temperatures at which structural rearrangement can take place in the glass, new reactive sites would be continually created and destroyed as a result of the thermal energy available, and that the 'jump' distance would eventually diminish to the extreme case of the distance between nearest-neighbour Si–O–Si bridges. Water molecules would then be virtually absent from the glass, and a change in the diffusion mechanism could be envisaged in which condensation reactions were superseded by direct transfer of the water components (H^+ and OH^-) to neighbouring sites.[3, 5] The model suggested above for diffusion at the lower temperatures is not of course inconsistent with the deduction that the concentration of water molecules must be small compared with the concentration of hydroxyl groups (cf., for example the half-power relation between solubility and water vapour pressure found at 1000–1200°C[1, 7, 9, 14, 20] and, with only small deviation, at 750°C[20]).

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