WATER IN SILICA GLASS

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Silica glass specimens were heated in water vapour and the resulting infra-red absorption at 2·7 μ was measured. Between 600° and 1200°C, the diffusion coefficient for entry of absorbing centres was

$$D = (1{\cdot}0 \pm 0{\cdot}2) \times 10^{-6} \exp\left(\frac{-18{,}300 \pm 500}{RT}\right) \text{cm}^2\ \text{sec}^{-1},$$

and for removal

$$D = (2{\cdot}7 \pm 1{\cdot}0) \times 10^{-7} \exp\left(\frac{-17{,}300 \pm 2{,}000}{RT}\right) \text{cm}^2\ \text{sec}^{-1}.$$

At 1000°C the saturation concentration of absorbing centres varied as the square root of the pressure of the surrounding water vapour, suggesting that the water molecule dissociates on entry, with the production of two hydroxyl groups in the atomic network of the glass. Using a value of extinction coefficient determined for the hydroxyl group in the molecule of triphenylsilanol, the solubility under 700 mm Hg water vapour pressure, expressed as the number of hydroxyl groups per SiO_2 " molecule ", was estimated to range from 6×10^{-3} at 600°C to 3×10^{-3} at 1200°C.

Some samples of silica glass absorb infra-red radiation of wavelength near 2·7 μ. Garino-Canina [1] found that the occurrence or absence of such absorption in his specimens depended upon whether or not water vapour had been present when the glass was made (by the fusion of quartz crystal). Following Harrison,[2] he attributed the absorption to the stretching vibration of hydroxyl groups in the glass. In the present work the solubility of these absorbing centres in, and their rate of diffusion through, silica glass have been determined.

EXPERIMENTAL

MATERIALS

Two grades of silica glass (Thermal Syndicate Ltd.) were used:

(*a*) ordinary optical grade (O.G.): impurity content less than 0·1 % by wt.;
(*b*) synthetic silica (O.S.): impurity content less than 0·001 % by wt.

The specimens took the form of:

(i) " Thick " slabs, of thickness approximately 2 mm, length and breadth approximately 20 mm and 10 mm respectively, in the ordinary grade material. No 2·7 μ absorption was detectable on delivery.

(ii) " Thin " slips, of thickness approximately 100-200 μ, in ordinary or synthetic grade material, either obtained as microscope cover slips or prepared by grinding down and repolishing " thick " slabs. Prior to treatment, the infra-red absorption characteristics of the " thin " specimens were as follows: the microscope cover slips in the ordinary grade material showed a weak absorption at 2·7 μ; the slips in the synthetic material showed a strong absorption band at 2·7 μ; and the slips prepared by grinding down " thick " slabs showed no absorption at 2·7 μ.

Silica glass tends to devitrify if maintained for long times above about 1000°C. The effect can be severe if the surface is contaminated, e.g. by handling with the fingers. In the present experiments the surfaces were cleaned by washing in Teepol, then immersing for 15 sec in 5 % hydrofluoric solution and finally washing in distilled water. The specimens were afterwards handled only with tweezers.

MEASUREMENT OF OPTICAL DENSITY

The infra-red absorption spectra were obtained with a Grubb-Parsons single-beam spectrometer (type S.3) having a sodium-chloride prism. The sample absorption was measured relative to the absorption of a water-free specimen of similar size and surface finish, in order to compensate for reflection losses.

APPARATUS FOR HEATING SPECIMENS UNDER CONTROLLED TEMPERATURE AND PRESSURE OF WATER VAPOUR

The specimens were heated in a closed-ended alumina tube enveloped by a vertical platinum muffle furnace. At its open end the alumina tube was joined with Araldite to a T-shaped glass system. This could, when desired, be evacuated through one of the horizontal limbs, which also contained an isolating tap. A vacuum stopper directly above the alumina tube allowed the insertion and removal of the specimens. A small bulb containing water (~3 ml) was situated in the other horizontal limb. When it was desired to maintain the water vapour pressure in the apparatus at some pre-determined value, the bulb was surrounded by an oil-bath controlled (±0·4°C) at the appropriate temperature, all the remainder of the closed system being kept at a temperature above that of the bulb (using, where necessary, externally-wound heating wires). Silicone grease was used in the tap and the stopper. The specimens were carried in a platinum foil cradle which could be lowered into, and lifted out of, the hot zone of the furnace on a platinum wire suspension.

At the start of an experiment to put water into a specimen, the water in the bulb was first frozen by surrounding it with liquid nitrogen. The apparatus was then evacuated, the isolating tap closed and the coolant replaced by the hot oil bath. With the platinum furnace at the temperature chosen for the experiment (control ±10°C), the specimen was then lowered into the furnace. At the end of the heating time selected, the specimen was raised from the hot zone and, after opening the apparatus to the atmosphere, removed for measurement. With the water reservoir empty, the same apparatus was used for vacuum experiments (approx. 10^{-4} mm Hg).

DETERMINATION OF SOLUBILITY

Solubility was calculated from the optical density and thickness of thin specimens that had reached equilibrium (i.e., were saturated) with the prevailing atmosphere of water vapour, assuming a value for the extinction coefficient. The extinction coefficient for the 2·7 μ absorption by the hydroxyl group in the molecule of triphenylsilanol was measured and taken as an estimate of the extinction coefficient for the absorbing centre in the silica specimens. (Evidence for the dissociation of the water molecule on its entry into the glass is given below.) To obtain the coefficient for triphenylsilanol, the absorption spectrum of solutions of this compound in carbon disulphide (~0·04 mole/l.) was measured between 2·0 and 4·0 μ, using a liquid cell of length 0·8 mm.

DETERMINATION OF DIFFUSION COEFFICIENTS

To determine the diffusion coefficient for entry of the centres into silica glass, a thick and a thin specimen were heated together under controlled temperature and water vapour pressure. Afterwards the optical density of the two specimens at 2·7 μ was measured. Heating of the thin specimen alone was then, if necessary, continued under the same conditions until its optical density reached a stationary value, indicating that it was saturated with centres. The assumption is made that the equilibrium concentration of centres is uniform throughout the saturated thin specimen and identical to that maintained in the surface of the thick specimen. The results of sectioning experiments (see below) suggested that this assumption is reasonable.

To determine the diffusion coefficient for the removal of centres, saturated thin specimens were heated *in vacuo* and the optical density at 2·7 μ was measured when from time to time the heating was interrupted.

SECTIONING EXPERIMENTS

For sectioning, specimens (thick) were mounted in a grinding jig consisting of a brass disc (2½ in. diam. × ¼ in. thick) in the centre of which had been cut a rectangular hole (⅞ in. × ½ in.). One surface of the jig was faced with glass so that it had a resistance to grinding similar to that of the silica glass. The specimen was glued into the jig with a

thermoplastic (Lakeside 70C) such that the surface to be ground lay flush with the glass-facing of the jig. The assembly was ground gently by hand on a plate glass surface with carborundum powder (600 grade) as the abrasive and water as lubricant. The relatively large diameter of the jig compared with the dimensions of the face of the specimen assured that the usual departure from planarity at edge regions was confined to the jig and did not encroach on the specimen. After each grinding the specimen was repolished on a lap carrying rouge, to eliminate the scattering around 2·7 μ which occurred with ground surfaces. The thickness (approx. 10 μ) of each section removed was determined, with an accuracy of $\pm 2\ \mu$, from successive micrometer measurements. The optical density at 2·7 μ was measured after each section had been removed. The specimen was kept in the jig throughout the whole of the sectioning experiment.

THEORY

The 2·7 μ optical density of a saturated thin specimen can be expressed as

$$d_2 = E\sigma l \tag{1}$$

where E is the extinction coefficient at this wavelength per absorbing centre, σ is the solubility of centres (expressed here as number of centres per unit volume) and l is the thickness. If d_2, E and l are known, the solubility σ is calculable.

If d_1 is the 2·7 μ optical density of a thick specimen after exposure to water vapour,

$$d_1 = EN_t, \tag{2}$$

where N_t is the total number of absorbing centres which have entered and are contained in a prism of unit cross-section extending from face to face of the slab.

The solution [3] of Fick's second equation appropriate to diffusion into a semi-infinite solid gives for the thick slab

$$N_t = 4n(Dt/\pi)^{\frac{1}{2}}, \tag{3}$$

where n is the constant concentration of centres assumed to be maintained in the surface during the diffusion process, D is the diffusion coefficient, and t is time. As stated previously, for thick and thin specimens heated together under the same conditions of temperature and water vapour, it is assumed that $n = \sigma$.

Hence, from eqn. (1), (2) and (3), D for entry of absorbing centres is given by

$$D = (\pi l^2/16t)(d_1^2/d_2^2). \tag{4}$$

When a thin parallel-sided specimen initially containing a uniform concentration of centres throughout its volume is heated *in vacuo*, the number of centres n_t at any subsequent time t contained in a prism extending from face to face of the specimen is given by [4]

$$\frac{n_t}{n_0} = \frac{8}{\pi^2}\sum_{m=0}^{m=\infty}\frac{1}{(2m+1)^2}\exp\left[\frac{-D(2m+1)^2\pi^2 t}{l^2}\right], \tag{5}$$

where n_0 is the number of centres initially present in the prism and l is the specimen thickness. It is assumed that throughout the diffusion process the surface concentration remains at zero. It can be shown that, to an accuracy of approximately 0·001 %, eqn. (5) leads to the following expression for the diffusion coefficient,

$$D = 8{\cdot}17 \times 10^{-12}(l^2/t_{\frac{1}{2}})\ \mathrm{cm^2\ sec^{-1}}, \tag{6}$$

where l is measured in microns and $t_{\frac{1}{2}}$ is the time in minutes required to make $(n_t/n_0) = \frac{1}{2}$. This expression was used for the evaluation of D for removal of the absorbing centres from the glass.

The heat $(\Delta H)_s$ of solution of water into the silica glass was calculated from the equation

$$2\ln\frac{\sigma_1}{\sigma_2} = -\frac{(\Delta H)_s}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right), \tag{7}$$

where σ_1 σ_2 are the solubilities at T_1 and T_2°K and R is the gas constant in cal mole^{-1} deg.$^{-1}$ The factor 2 arises because of the parabolic relationship (see below) between the solubility and the water vapour pressure.

RESULTS

Fig. 1 shows the absorption spectrum of a thick specimen before and after heating for 5 h at 1200°C in water vapour at approximately 700 mm Hg pressure. The same figure shows the change in the 2·7 μ band as layers were ground away from the faces of the sample.

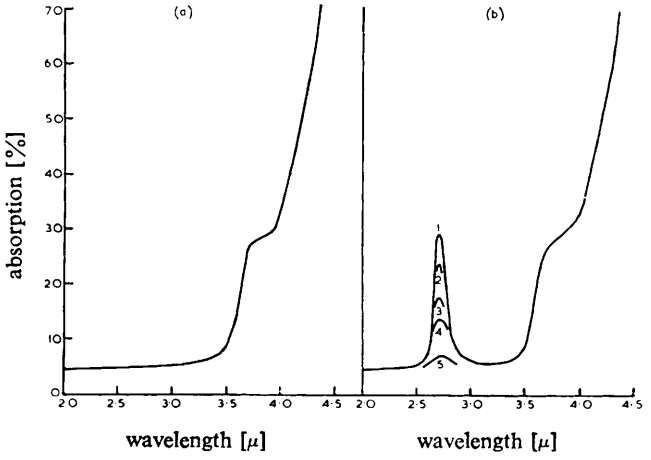

FIG. 1.—Infra-red absorption spectra of thick specimen (*a*) before treatment, and (*b*) (1) after heating at 1200°C in water vapour at approx. 700 mm Hg pressure for 5 h and (2), (3), (4) and (5) after the subsequent removal of 6 μ, 25 μ, 35 μ and 60 μ respectively, from each face.

SOLUBILITY

The solubility variation in the temperature range 600°-1200°C and under 700 mm Hg water vapour pressure is shown in fig. 2. There is some suggestion of a variable heat of solution over the temperature range studied, but, in view of the magnitude of the estimated experimental uncertainty, the results were considered in terms of a constant heat. The value estimated from the graph and eqn. (7) is -6 kcal/mole.

Solubilities at 1000°C and under water vapour pressures in the range 100-700 mm Hg are shown in fig. 3. The observed parabolic relationship between solubility and water-vapour pressure suggests that the water in the glass is dissociated.

The infra-red spectra of the solutions of triphenylsilanol in carbon disulphide showed a strong, sharp band at approximately 2·7 μ attributed [5] to the stretching vibration of the hydroxyl group in the unassociated molecule, together with a broad, weaker band extending from approximately 2·7 to 3·3 μ which is believed to be caused by the same vibration of molecules associated by hydrogen bonding. At the lowest concentrations used (0·004 and 0·009 g/ml) only the sharp band was evident and it was concluded therefore that only monomers were present. At these concentration levels E had the value $9{\cdot}23 \times 10^4/N$ cm^2 per hydroxyl group, where N is Avogadro's number.

DIFFUSION

Fig. 4 shows that the optical density at 2·7 μ of a thick specimen heated at 1160°C under a water vapour pressure of 700 mm Hg varies with the square root of the heating time, as expected for a diffusion process. D for entry of centres

into the glass (eqn. (4)) between 600° and 1200°C is shown in fig. 5 (upper line) and is given by

$$D = (1{\cdot}0 \pm 0{\cdot}2) \times 10^{-6} \exp\left(\frac{-18{,}300 \pm 500}{RT}\right) \text{cm}^2\ \text{sec}^{-1},$$

where R is the gas constant in cal. mole^{-1} deg^{-1} and T is the absolute temperature.

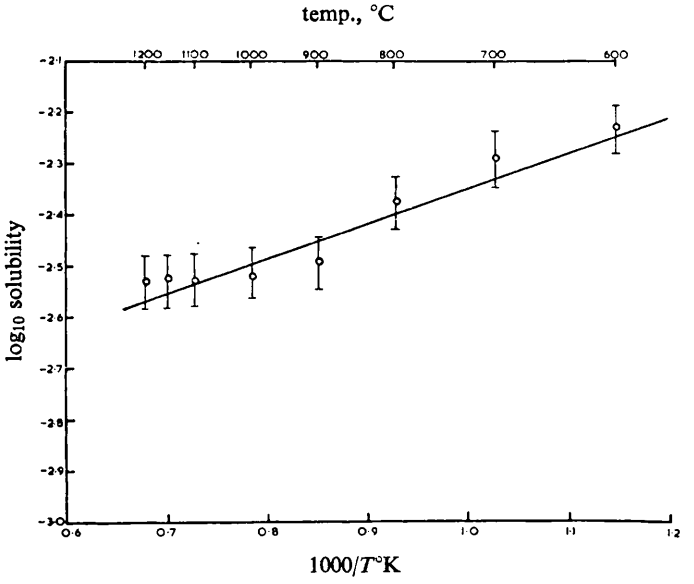

FIG. 2.—Variation of solubility (number of hydroxyl groups per SiO_2 " molecule ") with temperature (at a constant water vapour pressure of 700 mm Hg).

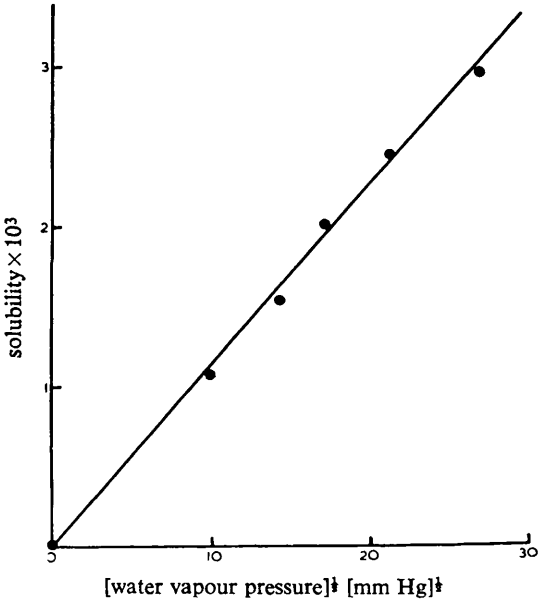

FIG. 3.—Variation of solubility (number of hydroxyl groups per SiO_2 " molecule ") with water vapour pressure (at a constant temperature of 1000°C).

Fig. 6 shows the variation in optical density with heating time when thin specimens, which had initially been saturated with centres at 1000°C and in 700 mm Hg

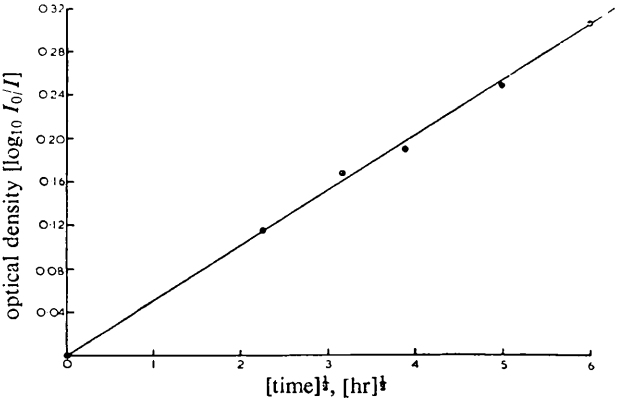

FIG. 4.—The variation with time of optical density at 2·7 μ of a thick specimen heated in water vapour at 700 mm Hg and 1160°C.

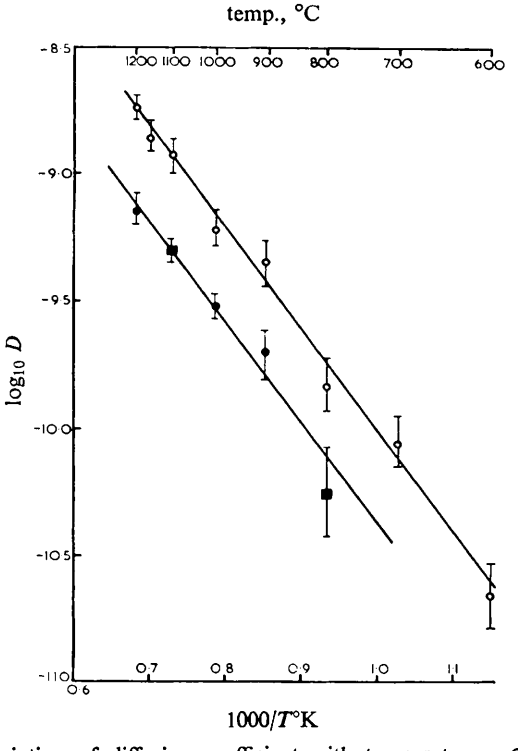

FIG. 5.—The variation of diffusion coefficient with temperature. ⊙ entry of centres into ordinary grade material, ● removal of centres from ordinary grade material, ■ removal of centres from samples manufactured from synthetic silica.

water-vapour pressure, were heated *in vacuo* (approx. 10^{-4} mm Hg) at temperatures in the range 900° to 1200°C. Values of $t_{\frac{1}{2}}$ were read off these curves and D

calculated from eqn. (6). D for removal of centres is shown in fig. 5 (lower line) and is given by

$$D = (2{\cdot}7 \pm 1{\cdot}0) \times 10^{-7} \exp\left(\frac{-17{,}300 \pm 2000}{RT}\right) \text{cm}^2 \text{ sec}^{-1}.$$

(Because of the slow rate of diffusion at 800°C, the D value at this temperature was calculated from an expression of the same form as (6) after a single heating period (1625 min) had reduced n_t/n_0 to the value 0·73.)

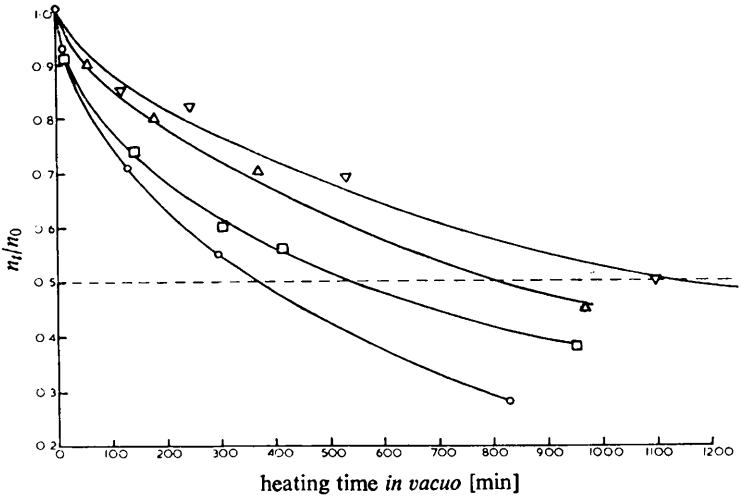

FIG. 6.—The removal of centres from thin specimens by heating *in vacuo*. ▽ 900°C (ordinary quality), △ 1000°C (ordinary quality), □ 1100°C (synthetic silica), ○ 1200°C (ordinary quality).

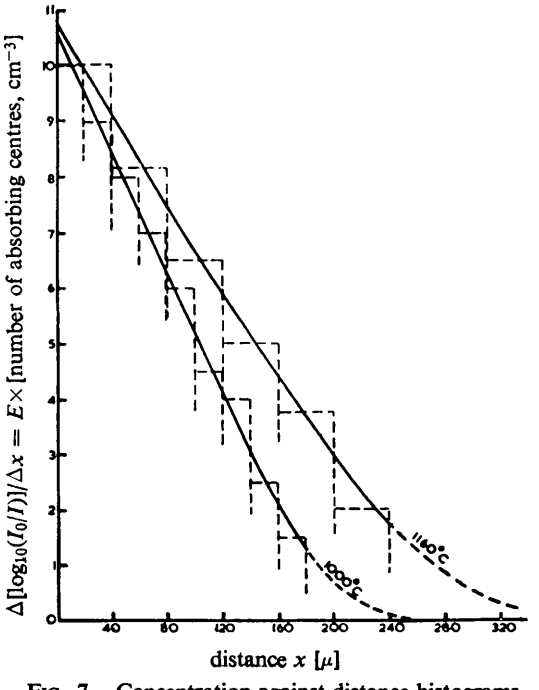

FIG. 7.—Concentration against distance histograms.

The following sectioning experiments were an attempt to determine the concentration profile after diffusion into the specimen had taken place. Two thick specimens, initially heated for 36 h in water vapour at 700 mm Hg and at temperatures of 1000° and 1160°C respectively, were sectioned. From the plots of optical density against thickness removed, histograms showing the variation of concentration with distance were derived (fig. 7). From them, it was confirmed that (i) their shape was not inconsistent with that expected for volume diffusion, (ii) the depth of penetration of the centres justified the treatment of the thick specimens as semi-infinite, and (iii) the values for the surface concentration were in close agreement with those obtained from the measurements on thin slips.

DISCUSSION

The dissociation of the water molecule can probably be represented by

$$(H_2O)_{vapour} + (\equiv Si—O—Si\equiv)_{glass} \rightleftharpoons 2(\equiv Si—OH)_{glass}.$$

The rupture of the silicon-oxygen-silicon bridge and consequent weakening of the structure would be consistent with observations [6, 7] that a glass containing water has lower viscosity than the corresponding water-free glass at the same temperature. The small negative heat of solution indicates that the process is slightly exothermic. Energy is therefore released when two ($\equiv$Si—OH) groups form following the dissociation of the water molecule into H^+ and OH^- and the rupture of the ($\equiv$Si—O—Si$\equiv$) bridge. Because of the stability of the silicates this may seem surprising but in a glass there is a continuous range of interionic bond strengths and presumably it is the rupture of the weaker bonds that is involved.

Within the limits of experimental error the activation energies for diffusion into and out of the specimens are equal. The diffusion activation energy of 18,300 cal mole^{-1} is lower than the values of 27,000 cal mole^{-1} obtained by Scholze and Merker [8] for the diffusion of water through a molten soda-lime-silica glass, and of 50,000 cal mole^{-1} obtained by Todd [9] for diffusion of water out of a similar glass below its softening temperature. The more open structure of silica glass compared with that of the alkali silicate glasses may account for this.

The diffusion coefficients for the removal of the centres are lower than those for entry at the corresponding temperatures by a factor of approximately 3·5. This would be explained if the assumption that the concentration of centres at the surface of the thin specimens remains zero throughout the removal process is invalid. It is conceivable that the necessary recombination on the surface of the hydroxyl groups diffusing out of the glass could lead to an appreciable non-zero concentration just below the surface.

The accuracy of the infra-red method did not allow exact determination of the diffusion profile. However, it is hoped to make a detailed study of its shape in tracer work with tritiated water; this is now in progress.

The solubilities derived with the extinction coefficient for triphenylsilanol are of the order expected from extrapolation of data obtained by Kurkjian and Russell [10] on the solubility of water in molten complex silicates. Jack *et al.*[11] have recently obtained similar values by direct weighing using a microbalance technique.

In the experiments on the removal of centres, the results obtained with synthetic silica glass fit in well with those obtained using glass of the ordinary grade. Since these two grades have very different impurity levels, it is concluded that the impurity atoms present do not have a marked influence on the movement of hydroxyl groups in the silica glass.

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