Dissolution of Hydrogen in Fused Silica

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THE amount of hydrogen dissolved in fused SiO_2 glass as H_2 molecules as opposed to the reacted form, which can increase the OH concentration in the glass, was investigated. Information on the amount[1-3] and form of the hydrogen in glass is of use in studies of the mechanism of radiation coloration resistance in hydrogen-impregnated glasses.

In the ideal case, when hydrogen gas is dissolved in the glass, the OH formation is proportional to the square root of the concentration of hydrogen to which the glass is exposed. The second mechanism of solution results in H_2 molecules in the interstices of the glass, the concentration of which should be proportional to the concentration of gas to which the glass is exposed.[3-5] The concentration of hydrogen in the atmosphere was approximately proportional to the pressure under the conditions of the present work.

Previous work[6,7] has indicated that nonideal conditions in the glass in the low-pressure range can affect the amount of OH formation. In the present work at high H_2 pressures, it was found that not all of the OH formation results from the ideal mechanism.

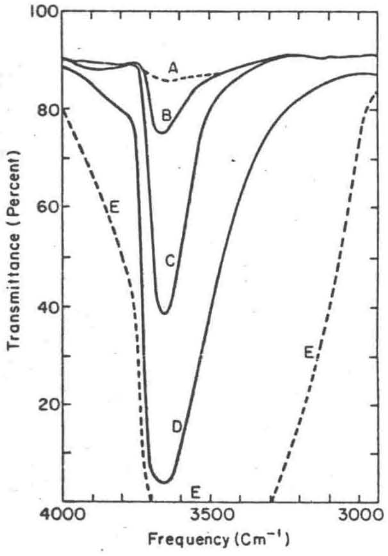

Fig. 1. Infrared spectra of SiO_2 glass after impregnation with H_2 at 2 kbars. *(A)* Before H_2 impregnation, *(B)* impregnated at 500°C, *(C)* impregnated at 600°C, *(D)* impregnated at 800°C, and *(E)* impregnated at 500°C and irradiated at a dose of 1.3×10^{19} n/cm^2 plus 1.5×10^{10} rd of γ radiation.

Figure 1 shows the ir absorption spectra of SiO_2 glass* specimens 2 mm thick after hydrogen impregnation for 15 h at 500°, 600°, and 800°C at 2 kbars. There is a substantial increase in the concentration of OH^- with temperature. However, the spectra show that, even under the most extreme conditions used, $<\approx 0.0033$ wt% or 0.1 mol% hydrogen exists in the form of OH groups in the impregnated glass. The extinction values used for calculating the concentration of hydrogen from the ir spectra are similar to the values used by other workers.[8,9] The total amount of hydrogen recorded after impregnation varied from 0.07 to 0.1 wt% ($\approx$3 mol%), as indicated by the total weight increase of the sample. This result implies that most of the gas remained as H_2 during the impregnation step and did not react to form OH^- groups.

A second phenomenon confirmed that substantial amounts of gas remained as molecular hydrogen and had not reacted with the glass during the thermal treatment. After such glasses were irradiated at a dose of 1.3×10^{19} n/cm^2 plus 1.5×10^{10} rd γ radiation, the concentration of OH^- was measured. The dashed curves in Fig. 1 illustrate the relatively large increase in OH^- absorption of a glass impregnated at 500°C and 2 kbars when it was subjected to this radiation dose.† The 2 to 3 mol% hydrogen in the unirradiated glass is thereby shown to exist largely in an unreacted form (a molecular species) after high-pressure impregnation at temperatures as high as 800°C.

A third indication that most of the gas was not chemically bound was reflected in the diffusion characteristics of H_2 in a 96% SiO_2 glass.‡ After $\approx$100 days, as much as half of the gas initially present had diffused out of specimens 1 mm thick.[3] This result is consistent with other data[10-12] concerned with hydrogen diffusion in glass. Both of the latter phenomena are indications of the great predominance of molecular H_2 over the OH^- species.

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*Containing 100 ppm Al, 10 ppm Mg, and 10 ppm Ca.

†The mechanism for radiation protection in such samples (Refs. 3–5) depends on the reaction of dissolved hydrogen with a defect produced by irradiation, resulting in formation of Si–OH and Si–H pairs (Ref. 5); hence the magnitude of the OH absorption frequency, which depends on the initial availability of H_2, increases strongly.

‡Code 7900, Corning Glass Works, Corning, N. Y.

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Figure 2 shows the transmittance of glass 2 mm thick after hydrogen treatment at 800° and 15, 1000, and 30,000 psi for 15 h. Increasing pressure results in increasing OH^- absorption, but to a much lesser degree than would be expected for chemical solubility. For such solubility in the ideal case, the concentration of reacted gas in the form of OH groups will increase proportionately with the square root of pressure. Calculation of the absorbance, which is proportional to the concentration of OH groups, reveals that a 2000-fold increase in pressure results in increase in the concentration of OH of only ≈ 5 times. In addition, the amount of gas reacting to form OH^- groups at 15 psi and 800°C is greater than the amount reacting at 500°C at pressures as high as 30,000 psi. The behavior of hydrogen furthermore is expected to approximate ideality under these conditions, with the concentration of the gas in the gaseous phase being nearly proportional to the pressure.

In sum, it appears that under ambient conditions a limited number of defects or reactive sites exists in a particular glass, and hydrogen impregnation results in OH^- formation at such sites. Higher temperatures during impregnation substantially increase the number of reactive defect sites in the glass, and at constant pressure with increasing temperature the amount of OH^- formed is larger. Increasing the pressure during impregnation at constant temperature also increases the number of defects reacting with the hydrogen and the resulting concentration of OH^-, but the number of OH^- groups formed at higher pressures is much less than would be expected on the basis of ideal chemical solubility.

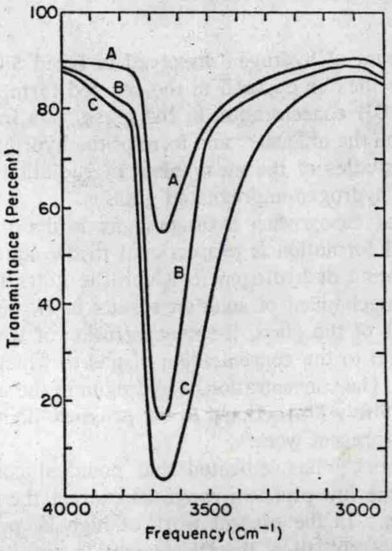

Fig. 2. Infrared spectra of SiO_2 glass after impregnation at 800°C at *(A)* 15 psi, *(B)* 1000 psi, and *(C)* 30,000 psi.