## SOLUBILITY AND SOLVATION REACTIONS OF QUARTZ

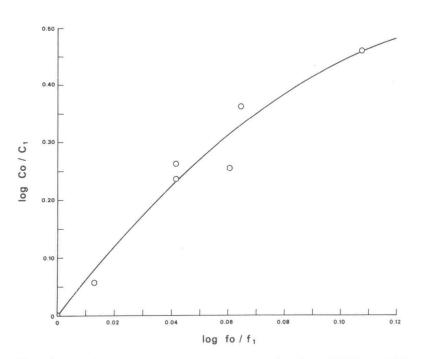


Fig. 5. Quartz solubility in water as a function of water fugacity at  $500^{\circ}$ C and 1000 bars total pressure – omitting data for which  $\log f_0/f_1$  exceeds 0.12. Subscripts "0" and "1" refer to water containing zero and finite argon concentrations respectively, so that solubility decreases upwards along the ordinate and argon concentration increases to the right along the abscissa.

Fig. 4 gives Sommerfeld's data at  $500^{\circ}$ C along with the quadratic least-squares curve found to best fit his points. Fig. 5 shows the least-squares quadratic best fitting those  $500^{\circ}$ C data points having  $\log f_0/f_1$  less than 0.12. A non-intercept model has been used as the calculated fit must pass through the origin. This has the additional advantage of preserving resolution beyond the lowest experimental Ar concentrations. Excluding the badly scattered high-argon points significantly reduces the error of the calculated value for  $n_0$ . Similar statistical treatments of the 400°C data produced results varying too widely with the order of computed fit to be considered useful. This effect is attributable to the significantly greater scatter of the lower temperature data.

The equations of the curves fitting the 500°C data are, all points (Fig. 4):

$$\log C_0 / C_1 = 4.17 \log f_0 / f_1 + 6.80 \left( \log f_0 / f_1 \right)^2 \tag{12}$$

selected points (Fig. 5):

$$\log C_0/C_1 = 6.43 \log f_0/f_1 - 19.8 \left(\log f_0/f_1\right)^2 \tag{13}$$

From the first derivative of eq. 12 and 13 at the origin, the hydration number n of the

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aqueous silica complex at  $500^{\circ}$ C is given by 4.2 (all points) ± 2.4, and 6.4 (selected points) ± 1.5. The tolerance intervals were computed from confidence intervals of the regression coefficients of eq. 12 and 13, using a level of confidence of 90%.

In order to preserve the characteristic tetrahedral coordination of silicon, only four of the surrounding oxygen atoms are directly bonded to the silicon atom. The remaining water molecules are probably associated with the complex only through weaker electrostatic attraction. Hence, a more realistic formula for the aqueous silica complex would be given by  $H_4 SiO_4 \cdot xH_2 O$ , where x = n - 2.

## Sulfur-bearing aqueous silica complexes

Quartz solubilities in subcritical Na<sub>2</sub>S aqueous solutions have been given by Dickson (1966) and Learned et al. (1967). These authors tentatively postulated the existence of a sulfide or bisulfide-bearing (i.e.,  $S^{2-}$  or HS<sup>-</sup>) silica complex as an explanation for their observed high solubilities.

It is possible to make a limited quantitative test for such complexing in a manner completely analogous to that outlined for sodium-silica complexing.

The solubility model consists of eq. 2, 3, 4 and 8, plus the following equations, and is based on the assumption that silica-sulfide complexes do not exist:

$$K_{\text{H}_2\text{S}} = \frac{\gamma(\text{H}^+) \cdot \gamma(\text{HS}^-)}{(\text{H}_2\text{S})_{\text{aq.}}}$$

$$K_{\text{HS}^-} = \frac{\gamma(\text{H}^+) \cdot \gamma_{\text{S}^{2-}}(\text{S}^{2-})}{(\text{HS}^-)}$$

$$K_{\text{H}_3\text{SiO}_4^-} = \frac{\gamma(\text{H}^+) \cdot \gamma(\text{H}_2\text{SiO}_4^{2-})}{\gamma(\text{H}_3\text{SiO}_4^-)}$$

$$K_{\text{NaHS}} = K_{\text{NaOH}} = \frac{\gamma(\text{Na}^+) \cdot \gamma(\text{HS}^-)}{(\text{NaHS}^-)}$$

 $\Sigma Na = (Na^+) + (NaHS^0) + (NaOH^0)$ 

 $\Sigma S = (NaHS^{0}) + (HS^{-}) + (H_{2}S) + (S^{2-})$ 

 $(OH^{-}) + (HS^{-}) + 2(S^{2-}) + (H_3 SiO_4^{-}) + 2(H_2 SiO_4^{2-}) = (H^{+}) + (Na^{+})$ 

 $K_{\rm H_2S}$  is the first dissociation constant of H<sub>2</sub>S, in aqueous solution,  $K_{\rm HS}$ - is the second dissociation constant of H<sub>2</sub>S,  $K_{\rm H_3SiO_4^-}$  is the second dissociation constant of H<sub>4</sub>SiO<sub>4</sub>, and all other quantities are as previously defined.

The dissociation constant for NaHS is completely unknown, but from the similarity between HS<sup>-</sup> and OH<sup>-</sup> we estimate that it should be very similar to  $K_{\text{NaOH}}$ , and for the purposes of these calculations we assume it is identical. Values for  $K_{\text{H},S}$  and  $K_{\text{HS}}$ - were