TABLE V

Predicted values of the stoichiometric coefficient "y"

Temperature (°C)	Observed quartz solubility in system SiO_2-H_2O or (H_4SiO_4) (p.p.m. SiO_2)	Observed quartz solubility in system $SiO_2-H_2O-NaOH$ (p.p.m. SiO_2)	Stoichiometric coefficient "y"
225	344	689	0.79
176	158	617	1.01
125	83	529	1.14

We thus conclude that under the equilibrium temperature–pressure–composition conditions here considered, and in both the systems SiO_2-H_2O and $SiO_2-H_2O-NaOH$, the best value for the polymerization factor y of the silica complex is close to 1.0, and the complex exists dominantly as a monomeric species.

The hydration number of the aqueous silica complex

As noted above, the hydration number "n" of the aqueous silica complex $y SiO_2 \cdot n H_2O$ (eq. 1) is currently the subject of considerable debate. A summary of the relevant literature has been given by Anderson and Burnham (1965) and Sommerfeld (1967).

Prior to the publication of Sommerfelds' (1967) data, all calculations of n were based on theoretical treatment of solubilities of quartz in pure water over wide ranges of pressure and temperature. All such treatments neglected the effect of pressure on the solute activity coefficients, and it is logically impossible to determine n in this way, as pointed out by Anderson and Burnham (1965).

A recent independent experimental technique devised by Sommerfeld (1967) utilizes quartz solubility measurements in the system SiO_2-H_2O-Ar for a variety of argon concentrations at any one temperature and pressure. The argon dilutes the water in the system, (or lowers its fugacity), thus varying the concentration of silica which is water-dependent by virtue of eq. 1. Because the equilibrium constant for reaction (1), remains unchanged if only argon concentration is varied at constant temperature and pressure, the following relationship holds:

$$\frac{\gamma_0 C_0}{(f_0)^n} = \frac{\gamma_1 C_1}{(f_1)^n} = K_{(1)} \qquad (10)$$

where subscripts "0" and "1" refer to systems containing no argon and finite argon concentrations respectively, and f_0 and f_1 refer to the fugacity of water in each of these two separate states. $K_{(1)}$ is the thermodynamic equilibrium constant of reaction (1). "γ_0" and "γ_1" are true activity coefficients of solvated silica, and C_0 and C_1 refer to total silica under both conditions. The activity of solid quartz in equilibrium with the solution at constant temperature and pressure remains constant and therefore cancels out of the expression.

Rearranging and differentiating the logarithm of both sides of (10) gives:

$$\left[\frac{d\log C_0/C_1}{d\log f_0/f_1}\right]_{T,P} = \left[\frac{d\log \gamma_1/\gamma_0}{d\log f_0/f_1}\right]_{T,P} + n + \log\frac{f_0}{f_1}\left[\frac{dn}{d\log f_0/f_1}\right]_{T,P} \tag{11}$$

Under the very dilute silica concentrations encountered at the temperatures investigated by Sommerfeld, both coefficients γ_0 and γ_1 remain approximately constant at the value unity (when activity is referred to the ideal one molal standard state at temperature and pressure). Hence, the first term in the right hand side of eq. 11 effectively vanishes over the entire small range of argon concentrations considered. The term $\log f_0/f_1$ vanishes in the limit as argon concentration approaches zero, and f_1 approaches f_0 (the fugacity of pure water). Thus, a plot of the log of measured concentration ratio C_0/C_1 versus log of water fugacities f_0/f_1 has a limiting slope "*n*" where argon concentration is zero.

The above procedure differs from that used by Sommerfeld (1967), who neglected the effect of activity coefficients and the last term of eq. 11, implicitly assuming n to be independent of argon concentration. His value for n was obtained from the averaged slope of a $\log C_0/C_1$ vs. $\log f_0/f_1$ plot considered over a wide range of argon concentrations, and the resulting hydration numbers were unrealistically large. It should be noted that the last term of eq. 11 would be expected to attain non-zero values for all positions on the plot representing finite argon concentrations.

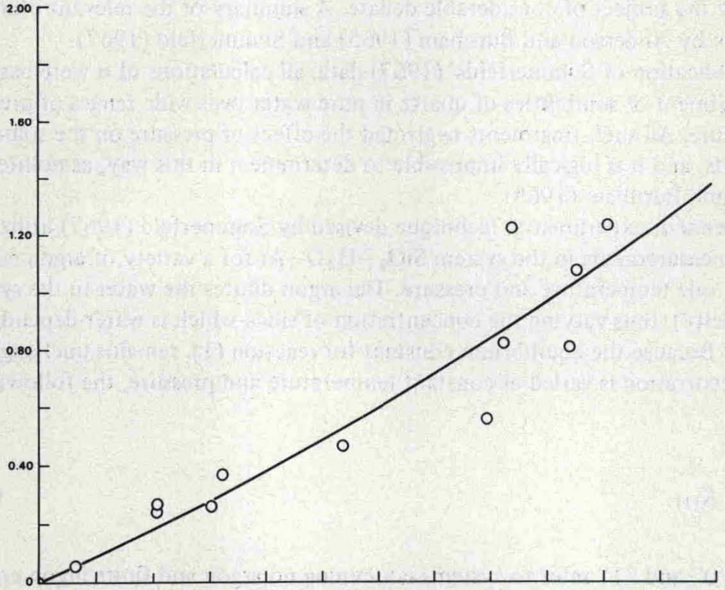

Fig. 4. Quartz solubility in water as a function of water fugacity at 500°C and 1000 bars total pressure. Subscripts "0" and "1" refer to water containing zero and finite argon concentrations respectively, so that solubility decreases upwards along the ordinate and argon concentration increases to the right along the abscissa.