

$$K_{\text{H}_4\text{SiO}_4} = \frac{\gamma(\text{H}^+) \cdot \gamma(\text{H}_3\text{SiO}_4^-)}{(\text{H}_4\text{SiO}_4)} \quad (3)$$

$$K_{\text{H}_2\text{O}} = \gamma(\text{H}^+) \cdot \gamma(\text{OH}^-) \quad (4)$$

$$\Sigma\text{Na} = (\text{Na}^+) + (\text{NaOH}) \quad (5)$$

$$\Sigma\text{Si} = y(\text{H}_4\text{SiO}_4) + y(\text{H}_3\text{SiO}_4^-) \quad (6)$$

$$(\text{Na}^+) + (\text{H}^+) = (\text{H}_3\text{SiO}_4^-) + (\text{OH}^-) \quad (7)$$

$$y(\text{H}_4\text{SiO}_4) = \text{total silica solubility in system SiO}_2\text{--H}_2\text{O at same temperature and pressure} \quad (8)$$

Parentheses denote molal concentration, and “ $\gamma$ ” is the single ion stoichiometric molal activity coefficient referred to the ideal 1 molal standard state at experimental temperature and pressure, and here assumed to be equal for all singly charged species. The parameter “ $y$ ” is the polymerization factor of eq. 1. Choosing arbitrary values of  $y$  and total sodium, and utilizing the values of  $K_{\text{H}_2\text{O}}$ ,  $K_{\text{H}_4\text{SiO}_4}$ , and  $K_{\text{NaOH}}$  and measured quartz solubilities leaves seven equations in the seven unknowns ( $\text{Na}^+$ ), ( $\text{NaOH}$ ), ( $\text{H}^+$ ), ( $\text{H}_3\text{SiO}_4^-$ ),  $\Sigma\text{Si}$ , ( $\text{H}_4\text{SiO}_4$ ), and ( $\text{OH}^-$ ). The quartz solubilities used were those obtained by us, since their precision is greater than that of the combined data represented in Fig. 1.

Eq. 2–8 were algebraically rearranged and solutions were computed using the Newtonian iterative method. In the first set of solutions, all activity coefficients were set equal to 1.0. Concentrations thus calculated were then used to compute ionic strength and an estimate of  $\gamma$  through the use of the Davies extension of the Debye–Hückel equation as given by Harned and Owen (1958). A new set of solutions was then computed with this estimate of  $\gamma$ , and iterations were continued until a sufficient level of precision was attained. Calculated values of  $\gamma$  for the 0.01 m NaOH solutions were in the range 0.95–1.0 for all temperatures.

Fig. 2 represents a set of such solutions carried out over the temperature and total sodium ranges  $10^{-3}$  to 10.0 molal and  $125^\circ$  to  $225^\circ\text{C}$ . This is contoured in terms of pH and total sodium molality. Use of this diagram plus eq. 2–8 readily reproduces the complete set of solutions for all seven unknowns over a wide range of conditions. At higher concentrations of  $\Sigma\text{Na}$  in Fig. 2 (above approximately 1 molal) various sodium silicate compounds should form according to the data of Rowe et al. (1968). Thus the upper part of Fig. 2 refers to metastable solutions.

The quartz solubility model outlined above predicts total quartz solubility in the system  $\text{SiO}_2\text{--H}_2\text{O--NaOH}$  as a function of total sodium concentration at any temperature for which all required parameters are known. No consideration of sodium–silica complexing was included in the derivation. Hence, if such complexing actually exists it must constitute yet another solvation mechanism over and above those covered by the model. If this were the case, quartz solubilities measured experimentally in the system  $\text{SiO}_2\text{--H}_2\text{O--NaOH}$  would be expected to exceed those predicted by the model.

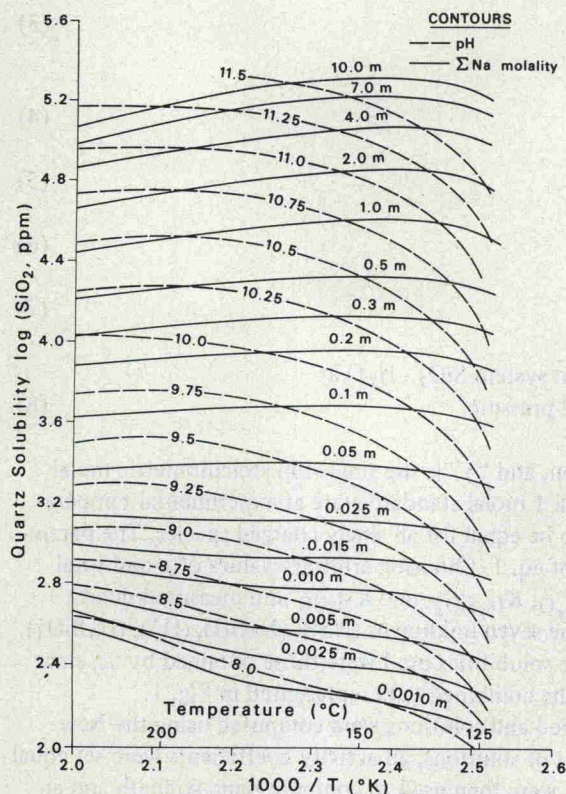
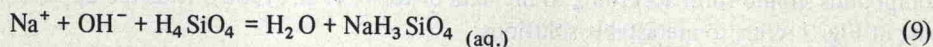


Fig. 2. Predicted quartz solubilities as a function of temperature, pH and total sodium concentration. Solubilities in solutions above about 1 m NaOH are metastable.

Fig. 3 includes the curve predicted by the quartz solubility model as a function of temperature for a total 0.01 molal analytic NaOH concentration along the subcritical, three-phase region. The value of  $\gamma$  was here set equal to 1.0 for reasons discussed in the following section. We have also included the curve representing the total analytic silica that would be expected should all of the available sodium in the system be converted to a sodium-silica complex. The position of this latter curve was estimated on the basis of the reaction:



where  $\text{H}_4\text{SiO}_4$  symbolizes the silica complex and  $\text{NaH}_3\text{SiO}_4(\text{aq.})$  the sodium-silica equivalent. In this limiting case of total conversion of analytic NaOH to  $\text{NaH}_3\text{SiO}_4(\text{aq.})$ , consumption of hydroxyl ions in the formation of water is essentially complete and pH approximates that of neutral water. Total analytic silica would then be given by the sum of the concentration of the two species  $\text{NaH}_3\text{SiO}_4(\text{aq.})$  and  $\text{H}_4\text{SiO}_4$ , the latter being independent of pH. It may then be readily shown that the region between the two curves of