

TABLE I

Quartz solubility in the system  $\text{SiO}_2\text{--H}_2\text{O}$  along the three phase subcritical curve

| Temperature<br>(°C) | Quartz<br>solubility<br>(p.p.m. $\text{SiO}_2$ ) | 90% tolerance<br>interval on<br>quartz solubi-<br>lity (p.p.m.<br>$\text{SiO}_2$ ) | Analytical<br>method (Co-<br>lorimetric<br>"C" or atomic<br>absorption "A") | Approach to<br>equilibrium<br>(from unsatu-<br>rated "u" or<br>supersaturated<br>"s" state) | Run time<br>(number of days<br>after tempera-<br>ture change) |
|---------------------|--|--|---|---|---|
| 329                 | 640.8  | ± 45 p.p.m.  | C   | u   | 6   |
| 329                 | 622.1  | ± 45   | C   | u   | 6   |
| 326                 | 631.1  | ± 45   | C   | u   | 11  |
| 326                 | 631.4  | ± 45   | C   | u   | 11  |
| 324                 | 665.1  | ± 45   | A   | u   | 36  |
| 323                 | 637.5  | ± 45   | C   | u   | 8   |
| 323                 | 624.1  | ± 45   | C   | u   | 8   |
| 323                 | 676.3  | ± 45   | A   | u   | 39  |
| 321                 | 640.9  | ± 45   | C   | u   | 7   |
| 321                 | 619.2  | ± 45   | C   | u   | 7   |
| 305                 | 605.3  | ± 40   | C   | u   | 14  |
| 305                 | 607.3  | ± 40   | C   | u   | 14  |
| 302                 | 606.9  | ± 40   | A   | u   | 18  |
| 277                 | 519.7  | ± 30   | C   | u   | 23  |
| 277                 | 520.0  | ± 30   | C   | u   | 23  |
| 276                 | 520.3  | ± 30   | C   | u   | 21  |
| 276                 | 528.8  | ± 30   | C   | u   | 21  |
| 276                 | 512.5  | ± 30   | C   | u   | 24  |
| 276                 | 518.3  | ± 30   | C   | u   | 24  |
| 275                 | 501.4  | ± 30   | A   | s   | 35  |
| 274                 | 514.7  | ± 30   | A   | s   | 33  |
| 273                 | 524.7  | ± 30   | C   | u   | 20  |
| 273                 | 536.4  | ± 30   | C   | u   | 20  |
| 273                 | 516.2  | ± 30   | C   | s   | 6   |
| 273                 | 503.4  | ± 30   | C   | s   | 6   |
| 270                 | 518.0  | ± 30   | A   | s   | 27  |
| 229                 | 406.1  | ± 25   | A   | u   | 20  |
| 181                 | 167.8  | ± 10   | A   | s   | 8   |
| 180                 | 163.0  | ± 10   | A   | u   | 14  |
| 179                 | 171.0  | ± 10   | A   | u   | 7   |
| 179                 | 173.0  | ± 10   | A   | u   | 7   |

TABLE II

Regression coefficients ( $a$ ,  $b$ ,  $c$ ) of the least-squares polynomial fit ( $y_i = a + bx_i + cx_i^2$ ) to the quartz solubility data for the three phase sub-critical system  $\text{SiO}_2\text{--H}_2\text{O}$  over the temperature range  $125^\circ$  to  $350^\circ\text{C}$ .  $y_i$  is log (p.p.m.  $\text{SiO}_2$ );  $x_i$  is  $1000/T(K)$ .

| Data                              | $a$      | $b$     | $c$      |
|-----------------------------------|----------|---------|----------|
| present data                      | -0.50121 | 4.2842  | -1.3802  |
| literature data                   | 3.4449   | 0.14579 | -0.29981 |
| present data plus literature data | 3.3105   | 0.25293 | -0.32168 |

TABLE III

Quartz solubility in the three phase subcritical region of the system  $\text{SiO}_2\text{--H}_2\text{O--NaOH}$  at 0.01 NaOH molality \*

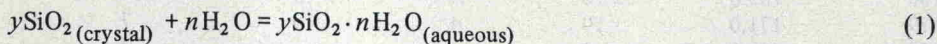
| Temperature<br>(°C) | Quartz<br>solubility<br>(p.p.m. $\text{SiO}_2$ ) | 90% tolerance<br>interval on<br>quartz solubility<br>(p.p.m. $\text{SiO}_2$ ) | Approach to equilibrium (from unsaturated "u" or supersaturated "s" state) | Run time (number of days after temperature change) |
|---------------------|--|---|--|--|
| 225                 | 689.3  | $\pm 14$  | u  | 38   |
| 226                 | 687.5  | $\pm 14$  | u  | 39   |
| 177                 | 621.8  | $\pm 13$  | s  | 15   |
| 176                 | 617.5  | $\pm 13$  | s  | 16   |
| 175                 | 630.0  | $\pm 13$  | u  | 35   |
| 125                 | 528.6  | $\pm 10$  | s  | 15   |
| 125                 | 523.2  | $\pm 10$  | s  | 19   |

\* All analyses were made using the atomic absorption method.

The values of  $K_{\text{NaOH}}$  used in the following determinations were interpolated from the experimental data of Noyes (1907) and Gimblett and Monk (1954), using a theoretical regression equation derived by Helgeson (1967). Experimental dissociation constants of water have been summarized by Barnes et al. (1966). The recent values for  $K_{\text{H}_4\text{SiO}_4}$  given by Ryzhenko (1967) span the temperature range of present interest and estimates of this parameter extrapolated through his data agree well with independent values at both higher and lower temperatures. It may be shown that the second acid dissociation constant of silicic acid is of negligible importance over the temperature and pH range of present concern. It has for this reason been omitted from the following model.

A model is proposed to explain the total saturation solubility of quartz in aqueous NaOH solutions in terms of solvated ionic and molecular species. By neglecting the possibility of sodium-silica complexing, the model predicts quartz solubility as a function of pH and total sodium concentration.

The solvation reaction of quartz with water may be written:



The values of  $y$  and  $n$  are most often taken to be 1 and 2 respectively, although considerable controversy exists about the actual values of both.

Since the following calculations are not affected by the value of  $n$ , let  $n = 2y$ , so that the complex can be represented by  $\text{H}_4\text{SiO}_4$  if monomeric and  $y(\text{H}_4\text{SiO}_4)$  if polymeric, where  $y$  is a polymerization factor.

It is proposed that the only species of importance in the system  $\text{SiO}_2\text{--H}_2\text{O--NaOH}$  are NaOH,  $\text{Na}^+$ ,  $\text{OH}^-$ ,  $\text{H}^+$ ,  $\text{H}_4\text{SiO}_4$ ,  $\text{H}_3\text{SiO}_4^-$ , and  $\text{H}_2\text{O}$ . The following series of equations represents the inter-relationships of these species:

$$K_{\text{NaOH}} = \frac{\gamma(\text{Na}^+) \cdot \gamma(\text{OH}^-)}{(\text{NaOH})} \quad (2)$$