SOLUBILITY AND SOLVATION REACTIONS OF QUARTZ

TABLE I

Quartz solubility in the system SiO₂-H₂O along the three phase subcritical curve

Temperature (°C)	Quartz solubility (p.p.m. SiO ₂)	90% tolerance interval on quartz solubi- lity (p.p.m. SiO ₂)	Analytical method (Co- lorimetric "C" or atomic absorption "A")	Approach to equilibrium (from unsatu- rated "u" or supersaturated "s" state)	Run time (number of days after tempera- ture change)
329	640.8	± 45 p.p.m.	С	и	6
329	622.1	± 45	С	u	6
326	631.1	± 45	С	u	11
326	631.4	± 45	С	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	14	39
321	640.9	± 45	C	u	7
321	619.2	± 45	C	14	7
305	605.3	± 40	C	1/	14
305	607.3	± 40	C	u	14
302	606.9	± 40	A	14	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	14	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	С	u	20
273	536.4	± 30	С	u	20
273	516.2	± 30	С	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	ü	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 SiO₂-H₂O over the temperature range 125° to 350°C. y_i is log (p.p.m. SiO₂); x_i is 1000/T(K).

Data	a	Ь	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	

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TABLE III

Quartz solubility in the three phase subcritical region of the system $SiO_2-H_2O-NaOH$ at 0.01 NaOH molality *

Temperature (°C)	Quartz solubility (p.p.m. SiO ₂)	90% tolerance interval on quartz solubility (p.p.m. SiO ₂)	Approach to equi- librium (from un- saturated "u" or supersaturated "s" state)	Run time (number of days after temperature change)
225	689.3	9.3 ± 14 u	u	
226	687.5	± 14	u	39
177	621.8	± 13	S	15
176	617.5	± 13	S	16
175	630.0	±13	u	35
125	528.6	± 10	\$	15
125	523.2	± 10	S	19

* All analyses were made using the atomic absorption method.

The values of K_{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:

$$ySiO_2(crystal) + nH_2O = ySiO_2 \cdot nH_2O_{(aqueous)}$$

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 $H_4 SiO_4$ if monomeric and $y(H_4 SiO_4)$ if polymeric, where y is a polymerization factor.

It is proposed that the only species of importance in the system $SiO_2-H_2O-NaOH$ are NaOH, Na⁺, OH⁻, H⁺, H₄ SiO₄, H₃ SiO₄, and H₂O. The following series of equations represents the inter-relationships of these species:

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

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(1)