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SOLUBILITY AND SOLVATION REACTIONS OF QUARTZ IN DILUTE HYDROTHERMAL SOLUTIONS

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ABSTRACT

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Equilibrium solubilities of quartz in both the SiO_2-H_2O and $SiO_2-H_2O-NaOH$ systems have been measured along the three-phase subcritical curve at temperatures up to $325^{\circ}C$. The solubility data show that quartz dissolves primarily as a monomeric aqueous species and that sodium-silica complexing is of no analytical importance under these conditions. A model has been devised which predicts silica solubility as a function of NaOH concentration in this three-phase, three-component system. A reinterpretation of pre-existing quartz-solubility measurements in the SiO_2-H_2O-Ar system has yielded a value of 4.2 for the hydration number of the aqueous silica complex at 1,000 bars total pressure and 500°C. A new treatment of earlier solubility measurements in the system $SiO_2-H_2O-Na_2S$ has shown that sulfide-bearing silica complexes may not be of any quantitative significance at $150^{\circ}C$ at the vapor pressure of the system.

INTRODUCTION

Geochemists have displayed an increasing interest in solubility studies pertinent to natural hydrothermal systems. These natural solutions are highly complex, and preliminary experimentation may only generally be carried out over a range of limiting, simplified systems. Necessary fundamental data such as the nature of specific constants are usually most readily obtained only through investigation of simple systems. The gradual accumulation of such thermodynamic information allows increasingly comprehensive studies of complicated natural solutions.

The systems SiO_2-H_2O and $SiO_2-H_2O-NaOH$ were selected for study partly because of the observed alkalinity and sodium content of many natural hydrothermal solutions and the ubiquity of hydrothermal silica deposits, and partly because of the considerable amount of experimental data on these two systems, which facilitate theoretical interpretations. However, the data presented herein are of interest not so much because of any similarity between the experimental solutions and natural hydrothermal solutions, but

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because they allow tests to be made for polymerization and for the presence of sodiumsilica complexing, features which, if present, would greatly affect all subsequent theoretical treatments of silicate-bearing solutions.

A re-interpretation of the solubility data of Dickson (1966) and Sommerfeld (1967) is also included, which bears on the hydration number of the aqueous silica complex and on the possibility of a sulfide-bearing silica species in aqueous solutions of Na_2S .

The main body of the present work may be considered a continuation of the research presented by Anderson and Burnham (1967), which consisted chiefly of quartz and corundum solubility measurements in supercritical aqueous chloride and hydroxide solutions. They proposed several possible quartz solvation mechanisms at that time, but lack of the relevant thermodynamic information still prevents thorough quantitative or theoretical treatments of such supercritical systems today. However, the necessary background data do exist over limited portions of the boiling curves of pure water, and $H_2O-NaOH$, H_2O-SiO_2 and H_2O-H_2S systems, thus permitting preliminary quantitative treatment in the subcritical range.

PREVIOUS WORK

The solubility of quartz in pure water along the lower three-phase region (coexisting quartz, aqueous solution and vapor), has been previously established by four independent studies: Kennedy (1950), Kitahara (1960a), Morey et al. (1962) and Siever (1962). These results are compiled in Fig. 1 along with the solubility measurements of the present study.



Fig. 1. Least squares quadratic fit to all published solubility data for the three-phase subcritical region of the quartz-water system up to 325°C.

Solubility data in supercritical water for the same system have been summarized by Anderson and Burnham (1965).

Friedman (1948), Laudise and Ballman (1961), Anderson and Burnham (1967) and Learned et al. (1967), have presented several values of quartz solubility in supercritical aqueous NaOH solutions. Sprauer and Pearce (1940), Seidell and Linke (1965), Alexander et al. (1954), Goto (1955), and Greenberg and Price (1957) give quartz solubilities in the temperature range $25^{\circ}-35^{\circ}$ C of the same system. Rowe et al. (1967) have determined the phase relations involving several sodium–silicate compounds in the system SiO₂–H₂O–Na₂O. According to their data, no sodium–silicate compounds should be stable at the NaOH concentration used by us (0.01 molal).

Dickson (1966) and Learned et al. (1967) have proposed that the observed solubility of quartz in the system $H_2O-Na_2S-SiO_2$ might be due to the coexistence of simple hydrated silica species and a new, sulfide-bearing complex. Anderson and Burnham (1967) postulated that a similar sodium-bearing silica complex might explain their observed quartz solubilities in supercritical $SiO_2-H_2O-NaOH$ at pressures of 3-4 kbars and temperatures of $500^\circ - 700^\circ$ C. Alexander et al. (1954) derived a theoretical model which accurately predicted the solubility of amorphous silica as a function of pH alone at 25° C in the same system. The fit between their experimental solubilities and the solubility model rules out the possibility of quantitatively important sodium-silica complexing under these conditions. Greenberg and Price (1957) used a similar model to calculate the first acid ionization constant of silicic acid at 25° and 35° C. Their results agree sufficiently well with later values determined electrochemically by Greenberg (1958) to justify the pH model used and to again rule out sodium-silica complexing at these lower temperatures.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

In the present work, total quartz solubility has been measured in the three-phase subcritical portion of the systems SiO_2-H_2O and $SiO_2-H_2O-NaOH$ at 0.01 molal sodium hydroxide concentration.

Reagent grade NaOH and distilled water were used. The silica was obtained from a piece of optically clear Brazilian quartz pulverized and screened to minus 100 mesh. The powder was chemically cleaned using a method outlined by Van Lier et al. (1960), which includes washing in hot 1N HCl followed by a short soaking in 10% HF and successive NaOH rinsings of increasing dilution. This treatment also removes disturbed surface layers on the grains which result from the grinding process.

The solutions were contained in the autoclave of a Barnes volumetric hydrothermal system (Barnes, 1963). This system includes a 1.1-liter stainless steel autoclave and a valve mechanism permitting sampling during operation. Temperature was measured with two chromel—alumel thermocouples inserted several inches into the bomb wall at either end. Front and rear furnace windings were separately controlled by twin Thermo-Electric solid state controllers, giving an end to end temperature gradient never exceeding $\pm 1^{\circ}$ C and an overall temperature drift always less than $\pm 2^{\circ}$ C. Thermocouples were calibrated at the boiling point of water and the melting point of lead (327°C).

Samples drawn from the bomb were analyzed immediately using either a colorimetric method outlined by Ingamells (1966), or an atomic absorption technique. The latter

analyses were made using a Perkin–Elmer atomic absorption spectrophotometer and hollow-cathode silica lamp. Optimal instrument settings for silica determination have been given by Van Loon and Parissis (1968). Standards for both techniques were prepared from pulverized quartz fused with Na₂CO₃ according to the method outlined by Kolthoff and Sandell (1952). The precision of the atomic absorption and colorimetric methods was $\pm 2.0\%$ and $\pm 2.5\%$ respectively, at a 90% level of confidence. Further details as to experimental, analytical and statistical procedures are available in Crerar (1968).

As shown in Table II, the observed solubilities were approached from either the supersaturated or undersaturated state, depending upon the temperature of the preceding sampling during any one run. The duration of a run at any one temperature varied from 6 to 39 days.

EXPERIMENTAL RESULTS

Our experimental measurements of quartz solubility are presented numerically in Table I and compared with other data in Fig. 1. Solubility measurements were made at temperatures ranging from 179° to 325°C. Three separate polynomial regression equations have been fitted to the data of fig. 1: one on the present analyses, one on pre-existing data alone, and one on the present and pre-existing determinations combined (Table II). In each case, second order fits of logarithmic solubility versus the reciprocal of absolute temperature were found to best represent the data both visually and statistically. Regression coefficients for each of the three second order, best fit curves are given in Table II. Tolerance intervals calculated according to deviation of each data set from the regression fit at a 90% level of confidence are included in Fig. 1 and Table I. Our measurements in pure water are clearly in agreement with previous determinations.

Our measurements of quartz solubility in the system $SiO_2 - H_2O - NaOH$ are given in Table III. In this case all analyses were made using the atomic absorption method. The 90% tolerance interval was calculated from the estimated precision of the analytical technique. These data points have been plotted against reciprocal temperature in Fig. 3.

INTERPRETATION

Sodium-silica aqueous complexing

It is possible to test the experimental data for the presence of sodium-silica complexing in the $SiO_2-H_2O-NaOH$ system. A theoretical prediction of total quartz solubility as a function of NaOH concentration may be made on the assumption that no sodium-silica complexing occurs. A comparison of observed quartz solubilities in NaOH solutions with the results given by this model permits an estimate of the actual importance of sodium-silica complexing. The model may be set up when the following parameters are known for every temperature and pressure under consideration:

 $K_{\text{H}_4\text{SiO}_4}$ - the first acid dissociation constant of silicic acid;

 $K_{\rm H_2O}$ – the ionization constant of water;

 K_{NaOH} – the basic dissociation constant of NaOH.

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	u	6
329	622.1	+ 45	C	11	6
326	631.1	+ 45	C	11	11
326	631.4	+ 45	C	11	11
324	665.1	+ 45	4	11	36
323	637.5	+ 45	C	11	8
323	624 1	+ 45	C	11	8
323	676.3	+ 45	A	11	39
321	640.9	+ 45	C	u u	7
321	619.2	± 45	C	u u	7
305	605.3	+ 40	C	11	14
305	607.3	± 40	C	14	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	С	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	C	Ś	6
273	503.4	± 30	С	S	6
270	518.0	± 30	A	S 1	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	С
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 $SiO_2-H_2O-NaOH$ 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	± 14	u	38
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	S	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:

$$vSiO_2$$
 (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 H₄SiO₄ if monomeric and $y(H_4SiO_4)$ 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⁺, H₄SiO₄, H₃SiO₄, and H₂O. The following series of equations represents the inter-relationships of these species:

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

(1)

(2)

$$K_{\mathrm{H}_{4}\mathrm{SiO}_{4}} = \frac{\gamma(\mathrm{H}^{+}) \cdot \gamma(\mathrm{H}_{3}\mathrm{SiO}_{4}^{-})}{(\mathrm{H}_{4}\mathrm{SiO}_{4})}$$
(3)

 $K_{\rm H_2O} = \gamma(\rm H^+) \cdot \gamma(\rm OH^-) \tag{4}$

$$\Sigma Na = (Na^{+}) + (NaOH)$$
⁽⁵⁾

$$\Sigma \operatorname{Si} = y(\operatorname{H}_{4}\operatorname{SiO}_{4}) + y(\operatorname{H}_{3}\operatorname{SiO}_{4}^{-})$$
(6)

$$(Na^+) + (H^+) = (H_3 SiO_4^-) + (OH^-)$$
 (7)

$$y(H_4 SiO_4) = \text{total silica solubility in system } SiO_2 - H_2O \text{ at}$$

same temperature and pressure (8)

Parentheses denote molal concentration, and " γ " 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_{NaOH} and measured quartz solubilities leaves seven equations in the seven unknowns (Na⁺), (NaOH), (H⁺), (H_3 SiO_4), Σ Si, (H₄ SiO₄), and (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 γ 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 γ , and iterations were continued until a sufficient level of precision was attained. Calculated values of γ 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° to 225° 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 Σ 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 $SiO_2-H_2O-NaOH$ 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 $SiO_2-H_2O-NaOH$ would be expected to exceed those predicted by the model.

Chem. Geol., 8 (1971) 107-122



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 y 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:

$$Na^{+} + OH^{-} + H_4 SiO_4 = H_2 O + NaH_3 SiO_4 (ag)$$
 (9)

where $H_4 SiO_4$ symbolizes the silica complex and $NaH_3 SiO_4(aq.)$ the sodium-silica equivalent. In this limiting case of total conversion of analytic NaOH to $NaH_3 SiO_4(aq.)$, 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 $NaH_3 SiO_4(aq.)$ and $H_4 SiO_4$, the latter being independent of pH. It may then be readily shown that the region between the two curves of



Fig. 3. Comparison of predicted and observed quartz solubilities in the system SiO₂-H₂O-NaOH.

Fig. 3 represents partial conversion of NaOH to NaH₃SiO_{4 (aq.)}. For example, a curve representing 50% conversion of NaOH would lie approximately half way between the two limiting curves illustrated.

The actual experimental measurements of silica solubility lie very close to the predicted solubility curve of Fig. 3, and it thus follows that sodium—silica complexing can be of no quantitative significance under these conditions. It should be noted that this conclusion is dependent upon the accuracy of the analytic quartz solubility measurements, on the parameters $K_{\rm H_2O}$, $K_{\rm H_4SO_4}$, $K_{\rm NaOH}$, and on the assumed value of 1.0 for y. It was further assumed that all aqueous species obeyed the Davies extension of the Debye-Hückel equation, and that the second acid dissociation constant of silicic acid had little effect on the observed solubilities. These last two assumptions, in particular, become increasingly tenuous as NaOH concentration is increased. It remains possible that some degree of sodium—silica complexing might yet exist in more concentrated solutions, or under conditions varying widely in temperature and pressure from the range considered here. Fig. 2 is intended to facilitate a similar test for sodium—silica complexing for anyone working with the same system within the temperature—composition region covered by the plot.

The degree of polymerization of solvated silica

The solvation reaction of quartz with water has been given by eq. 1. Under the temperature—pressure equilibrium conditions of present concern, the value of the polymerization factor "y" of the silica complex has generally been considered to be 1.0, (see Brintzinger and Brintzinger, 1931; Alexander et al., 1954; Kitahara, 1960b, 1960c, and Morey et al., 1962). This value of y has been adopted largely because of the very good agreement between solubilities as given by the silicomolybdate colorimetric method and those obtained by other methods, combined with the fact that the silicomolybdate method has been shown to be sensitive to the monomeric silica species alone (Alexander, 1953). Recently, Weill and Bottinga (1970) have reconsidered this problem and concluded that cristobalite and quartz solubility data are better explained if one assumes the presence of a polymerized species in an amount which varies with temperature. The concentration of polymerized species proposed by them, however, is too small to be detected by the method described below.

An independent test for the value of y is possible using the computing routines outlined in the previous section. First, eq. 2–8 may be solved using values of y differing from 1.0. As an example, Table IV contains total quartz solubilities predicted by the model for the case where y equals 2.0. The predictions are incorrect being far higher than the observed solubilities, and the discrepancy widens as y is increased. Only when y is close to 1.0 are predictions consistent with the observed data. Note that this conclusion still obtains if sodium-silica complexing should occur in the system. This latter effect would tend to raise the net observed solubility above that predicted by the model (which ignores sodium-silica complexing), and would further increase the discrepancy between observed and predicted silica solubilities for values of y differing from 1.0.

TABLE IV

Predicted quartz solubilities in the system $SiO_2-H_2O-NaOH$ at 0.01 NaOH molality for the case where "y" equals 2.0

Temperature (°C)	Observed quartz solubility in the system SiO_2-H_2O (p.p.m. SiO_2)	Observed quartz solubi- lity in the system $SiO_2-H_2O-NaOH$ (p.p.m. SiO_2)	Predicted quartz solubility in the system $SiO_2-H_2O-NaOH$ (p.p.m. SiO_2)
225	344	689	1020
176	158	617	961
125	83	529	835

Values of y are also calculated using a program similar in format to the quartz solubility model. The same eq. 2 to 8 were used, but in this case, "Total Silica" (total analytic silica as measured in the system $SiO_2-H_2O-NaOH$) was considered a given parameter, and y an unknown whose value would be determined from the solution of the equations. Solutions for y at three separate temperatures are given in Table V. Note that all values approximate 1.0. This test is obviously crude enough to allow for a small amount of polymerization as proposed by Weill and Bottinga (1970).

Temperature (°C)	Observed quartz solu- bility 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

Predicted values of the stoichiometric coefficient "y"

TABLE V

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 $ySiO_2 \cdot nH_2O$ (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:

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

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



Fig. 5. Quartz solubility in water as a function of water fugacity at 500°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° 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° 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):

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

From the first derivative of eq. 12 and 13 at the origin, the hydration number n of the Chem. Geol., 8 (1971) 107–122

aqueous silica complex at 500° 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 $Na_2 S$ 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⁻) 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:

$$\begin{split} K_{\rm H_2 S} &= \frac{\gamma({\rm H}^-) \cdot \gamma({\rm HS}^-)}{({\rm H_2 S})_{\rm aq.}} \\ K_{\rm HS^-} &= \frac{\gamma({\rm H}^+) \cdot \gamma_{\rm S^{2-}}({\rm S}^{2^-})}{({\rm HS}^-)} \\ K_{\rm H_3 SiO_4^-} &= \frac{\gamma({\rm H}^+) \cdot \gamma({\rm H_2 SiO_4^{2^-}})}{\gamma({\rm H_3 SiO_4^-})} \\ K_{\rm NaHS} &= K_{\rm NaOH} = \frac{\gamma({\rm Na}^+) \cdot \gamma({\rm HS}^-)}{({\rm NaHS}^-)} \\ \Sigma {\rm Na} = ({\rm Na}^+) + ({\rm NaHS}^0) + ({\rm NaOH}^0) \\ \Sigma {\rm S} = ({\rm NaHS}^0) + ({\rm HS}^-) + ({\rm H_2 S}) + ({\rm S}^{2^-}) \\ ({\rm OH}^-) + ({\rm HS}^-) + 2({\rm S}^{2^-}) + ({\rm H_3 SiO_4^-}) + 2({\rm H_2 SiO_4^{2^-}}) = ({\rm H}^+) + ({\rm Na}^+) \end{split}$$

 $K_{\rm H_2S}$ is the first dissociation constant of H₂S, in aqueous solution, $K_{\rm HS}$ - is the second dissociation constant of H₂S, $K_{\rm H_3SiO_4^-}$ is the second dissociation constant of H₄SiO₄, and all other quantities are as previously defined.

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

calculated from a constant $-\Delta C_p$ extrapolation of existing measurements up to 90°C as summarized by Barnes et al. (1966), and including the more recent measurements by Ellis and Milestone (1967). The $K_{H_3SiO_4^-}$ of Ryzhenko (1967) used in the computation is believed to be rather uncertain. However, at the calculated pH of 9.8, $H_2SiO_4^{2^-}$ is not the dominant species, and moderate errors in the second ionization constant do not significantly affect final results.

At 150°C and a total analytical Na₂S content of 0.113 m/kg Dickson (1966) reports a quartz solubility of 0.078 m/kg. For the same conditions the above model results in a total silica concentration of 0.061 m/kg. In view of the considerable (but unknown) uncertainties involved in the values of $K_{\rm H_2S}$, $K_{\rm HS^-}$, and $K_{\rm NaHS}$, the fairly close agreement between observed and calculated solubilities indicates that complexes containing both sulfur and silica are not necessarily of major significance under the conditions tested.

While this paper was under review, Ostapenko et al. (1969) published additional data on the solubility of quartz in NaOH and Na₂S solutions at 280°C, and also came to the conclusion that silica-sulfur complexing is not quantitatively significant.

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Chem. Geol., 8 (1971) 107-122

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