

THE SOLUBILITY OF CRISTOBALITE ALONG THE  
THREE-PHASE CURVE, GAS PLUS LIQUID PLUS  
CRISTOBALITE<sup>1</sup>

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ABSTRACT

The solubility of cristobalite in liquid water in the presence of gaseous water was determined in the temperature interval from 80° to 250° C. The measured solubility at 250° C. is 730 ppm and at 100° C. is 122 ppm, and the extrapolated solubility at 25° C. is 27 ppm. The heat of solution is 4.58 kcal/mole and the free energy change in going from cristobalite to quartz at 25° C. is -0.90 kcal/mole.

INTRODUCTION

The authors and their associates in the U. S. Geological Survey have several investigations underway concerned with the behavior of various forms of silica in water at temperatures below the critical temperature of water. As part of this program the solubility of cristobalite along the three-phase curve, gas+liquid+cristobalite, was investigated.

PROCEDURE

The cristobalite used in this investigation was manufactured from grains of a crushed quartz crystal. The quartz grains, sized 100 to 140 mesh, were heated at 1400° C. until they were converted entirely to cristobalite, determined optically and by  $x$ -rays. The optical and  $x$ -ray character of the cristobalite was unchanged at the termination of the solubility measurements.

Two and a half grams of cristobalite were placed in a silver-lined Morey bomb of internal capacity 16.5 ml. For each run an amount of distilled water was added such that at the temperature of the run, cristobalite and liquid water filled approximately 90 per cent of the internal volume of the bomb; gaseous water filled the remaining 10 per cent. The bomb was sealed and continuously rotated end to end at 50 revolutions per hour inside a thermostatically regulated electric resistance furnace. Periodically the rotation of the bomb was stopped and the temperature measured after placing thermocouples in wells in the cap and base of the bomb. The temperature of the bomb was found to remain constant to  $\pm 1^\circ$  C.

At the termination of a run the bomb was quickly quenched and the solution from inside the bomb analyzed for dissolved silica by the colorimetric molybdenum blue method. The colorimetric analytical procedure

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

measures only monomeric silica in solution, as discussed by Krauskopf (1956). To check on the possible presence of more highly polymerized silica species, portions of some solutions were evaporated to dryness, fused with sodium hydroxide, and re-dissolved in water to convert highly polymerized species to the monomeric form.<sup>1</sup> Identical monomeric silica contents were measured in the solutions before and after sodium hydroxide treatment, indicating that all the dissolved silica was present in the monomeric state. Generally, less than 10 minutes elapsed between the time that the bomb was removed from the furnace and the start of the silica analysis. It is unlikely that precipitation or polymerization of dissolved silica occurred when the bomb was quenched. Many studies have shown that colorimetrically determinable silica, present in concentration in the range encountered in this study, will undergo polymerization in slightly acid solutions only after prolonged periods of time, if at all (White and others 1956; Kitahara, 1960; Morey and others, 1961; Morey and others, in press). The water used in this study was slightly acidic, pH 5 to 6, due to dissolved CO<sub>2</sub>.

The precipitation of crystalline silica compounds from initially supersaturated solutions within the temperature and pH range of this investigation does not readily take place and would probably crystallize quartz rather than the metastable cristobalite. For these reasons solubility values were established only by leaving distilled water in contact with cristobalite for long periods of time. The duration of time necessary to attain equilibrium under the experimental conditions employed in this investigation were determined in the course of previous work on the solubility of quartz (Morey and others, in press). The experimental uncertainty is approximately  $\pm 10$  ppm.

## RESULTS

The experimental results are tabulated in Table 1 and plotted in Figs. 1 and 2. For comparison in Figure 1 are shown the concentrations of silica in solution dissolved from quartz and amorphous silica under comparable conditions, *e.g.*, along the three-phase curve, gas+liquid water +solid SiO<sub>2</sub>. In Fig. 2 the solubility data from Table 1 are plotted in terms of  $-\log C$ , versus  $10^3/T$ , where  $C$  is the concentration of dissolved SiO<sub>2</sub> in moles/kg of solvent and  $T$  is the absolute temperature. Where solubility values at nearly the same temperature are listed in Table 1, only the value representing maximum duration of run is plotted in Fig. 2.

As indicated above, tests of the analytical procedures employed in this investigation established that the silica which dissolved from cristobalite

<sup>1</sup> Such treatment will convert crystalline quartz entirely to monomeric silica.

TABLE 1. SOLUBILITY DATA FOR CRISTOBALITE

Temperature ° C.	Duration of run in days	Solubility ppm	moles/kg	-log C	1/T° K. × 10 <sup>3</sup>
84±1°	23	96	.00160	2.796	2.80
99	79	122	.00206	2.686	2.69
149	29	244	.00353	2.388	2.37
152	13	240	.00400	2.398	2.35
168	10	335	.00557	2.254	2.27
169	15	350	.00583	2.235	2.26
198	15	462	.00768	2.115	2.12
227	8	602	.0100	2.000	2.00
252	5	740	.0123	1.910	1.90
255	2	739	.0123	1.910	1.89

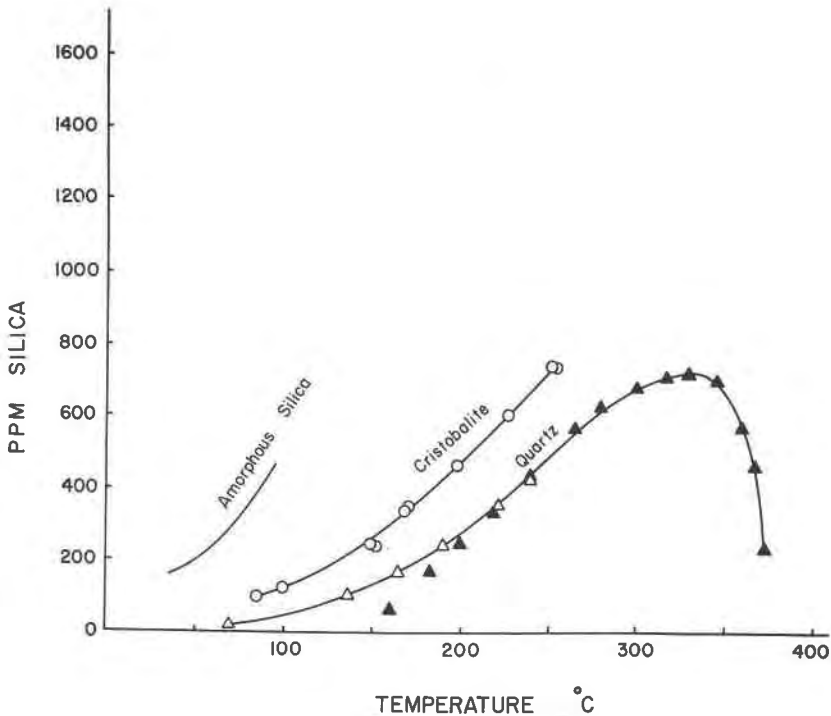


FIG. 1. The solubility of amorphous silica, cristobalite, and quartz in water along the respective three-phase curves, gas+liquid+solid  $\text{SiO}_2$ . The curve for amorphous silica is from Elmer and Nordberg (1958). The solid triangles along the quartz curve are from Kennedy (1950) and the hollow triangles are from from Morey and others (in press).

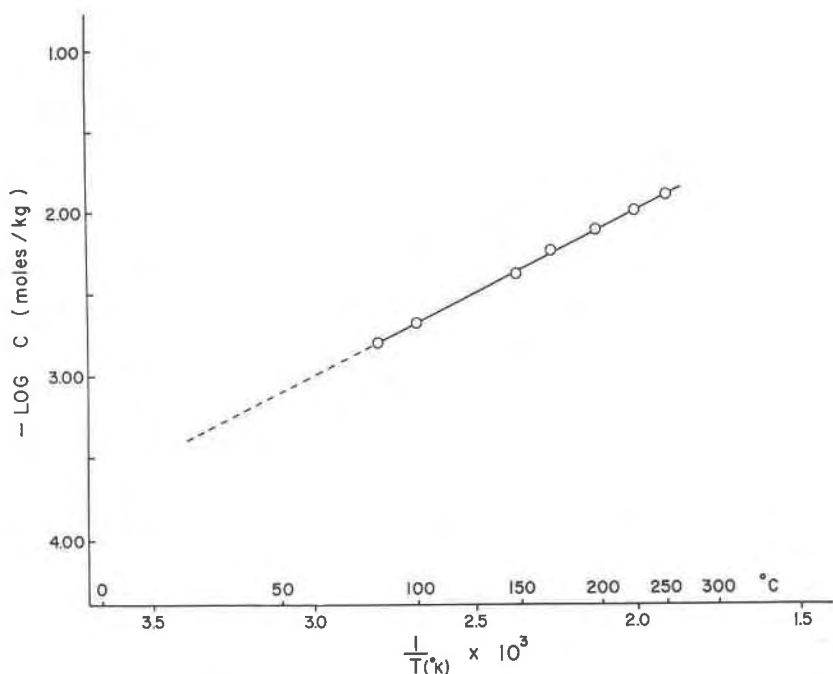
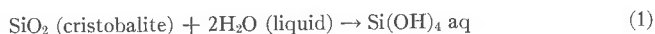


FIG. 2. Semilog plot of cristobalite solubility in water as a function of temperature.

was present in solution entirely in the form of monomeric silica. Therefore the equation for the dissolution reaction may be written



and the equilibrium constant,  $K_c$ , for the reaction is essentially equal to the activity of  $\text{Si}(\text{OH})_4 \text{ aq}$ . The solutions are very dilute and it is assumed that the activity of  $\text{Si}(\text{OH})_4 \text{ aq}$  is equal to its concentration so that

$$K_c = C_{\text{Si}(\text{OH})_4 \text{ aq}} \quad (2)$$

The variation of the equilibrium constant with temperature is given by the relationship

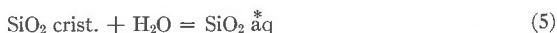
$$\frac{d \ln K_c}{dT} = \frac{\Delta H^0}{RT^2} \quad (3)$$

where  $\Delta H^0$  is the sum of the heat contents of the substances produced less the sum of the heat contents of the substances consumed when each substance is in its standard state,  $T$  is the absolute temperature, and  $R$  is the gas constant. If  $\Delta H^0$  is independent of temperature, equation (3) may be integrated and combined with equation (2) so that

$$\log C_{\text{Si}(\text{OH})_4 \text{ aq}} = -\frac{\Delta H^0}{4.576T} + \text{constant} \quad (4)$$

Figure 2 shows the experimental data plotted in the form of equation (4). The data fall along a straight line indicating that  $\Delta\bar{H}^0$  is independent of temperature in the temperature interval investigated. The slope of the curve in Fig. 2 allows an approximate calculation of the value of  $\Delta\bar{H}$ , the partial molal or differential heat of solution of cristobalite. The data plotted in Fig. 2 afford only an approximation of  $\Delta\bar{H}$  as the pressure is different for each point on the curve. The pressure differences are not great, however, and the effect on solubility would be very small. The value of  $\Delta\bar{H}$  obtained is 4.58 kcal/mole.

Extrapolation of the solubility data to 25° C. yields a value of 27 parts per million or .00045 moles/kg for the solubility of cristobalite. Using this solubility value, the standard free energy of solution  $\Delta F^0_{298^\circ\text{K}}$  of cristobalite in water may be calculated. From the equation  $\Delta F^0_{298^\circ\text{K}} = -RT \ln C_{298^\circ\text{K}}$ , the standard free energy of solution of cristobalite is computed to be 4.56 kcal/mole. The free energy change in the transformation of cristobalite to quartz may be calculated by using the data of Morey, Fournier, and Rowe (in press) for the solubility of quartz along the three phase curve, gas+liquid+quartz. In making this calculation it must be assumed that in the following reactions



the standard states of the system  $\text{SiO}_2^* \text{ aq}$  and  $\text{SiO}_2^{**} \text{ aq}$  are the same, *i.e.*, composed of the same distribution of polymerized and hydrolyzed species. The solubility of quartz at 25° C. and 1 atm pressure is 6 parts per million and  $\Delta\bar{H}$  is 6.0 kcal/mole. These numbers yield a value of 5.46 kcal/mole for the standard free energy of solution of quartz and the free energy change in going from cristobalite to quartz at 25° C. is  $-0.90 \pm .3$  kcal/mole.

R. A. Robie (written communication), has tabulated the free energies of formation from their elements of cristobalite,  $\Delta F^0 = 196.582 \pm .300$  kcal per gram formula weight and of quartz,  $\Delta F^0 = 197.151 \pm .450$  kcal/GFW. These values yield a change in free energy of  $-0.569 \pm .750$  kcal/mole in going from cristobalite to quartz as compared with  $-0.90 \pm .3$  kcal/mole obtained by the experimental methods employed in the present work.

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