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The solubility of amorphous silica in water at high temperatures and high pressures

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Abstract

The solubility of amorphous silica in water at high temperatures and high pressures was investigated, using commercial gel and vitreous silica (fused quartz) as starting materials. The experiments were carried out in an Inconel X bomb at temperatures from 180° to 382°C and pressures from 200 to 1379 bars. Periodically, small amounts of solution were withdrawn from the bottom of the bomb through a stainless steel filter into high-pressure stainless steel capillary sampling line, quenched in an ice bath, and immediately diluted with previously weighed silica-free water. The diluted samples were analyzed for colorimetrically-reactive and total silica. The silica gel gave the same colorimetric silica as the vitreous silica.

The solubility of amorphous silica at the vapor pressure of the solution, from 0° to 250° C, is given by the equation $\log C = -731/T + 4.52$, where C is the silica concentration in mg/kg and T is absolute temperature. The maximum solubility at the vapor pressure of solution is 1660 mg/kg at 340°C, and the extrapolated solubility at the critical point is 890 mg/kg. At a constant pressure of 1034 bars, the solubility of amorphous silica from 0° to 380°C is given by the equation $\log C = -810T + 4.82$. The differential heat of solution, $\Delta\bar{H}$, is 3.71 ± 0.05 kcal/mole, and the differential entropy of solution, $\Delta\bar{S}$, is 13.9 ± 0.05 cal/mole.

Introduction

Much has been published on the solubility of amorphous silica at temperatures below 100°C but relatively little of its solubility above 100°C.[1] Morey *et al.* (1964) concluded that the combined results of Kitahara (1960) and Hitchen (1935) best described the solubility from 0° to 335°C at the vapor pressure of the solution. In 1966 we (Fournier and Rowe) published a curve showing solubility values at temperatures above about 250°C significantly lower than those obtained by Hitchen. Because our 1966 results were probably in error, we decided to study the solubility of amorphous silica at high temperatures and high pressures using a technique that would allow quenching the solution to room temperature in a few seconds rather than in minutes. In this work we used pressures greater than the vapor pressure of the solution and then calculated solubilities at vapor pressure by extrapolation of the high-pressure results. The curves of Figure 1 show results obtained by various workers for the solubility of amorphous silica at the vapor pressure of the solution compared with the solubility of quartz under similar conditions.

Experimental apparatus and procedure

The experiments were carried out in a bomb made of Inconel X with an internal capacity of 89 cm^3, using experimental apparatus similar to that described and illustrated by Morey and Hesselgesser (1951). Because noble-metal liners were not used, there may have been some corrosion of the bomb and generation of hydrogen gas during the experiments. The final solutions were not analyzed to determine if any dissolved constituents were present that could have been contributed by corrosion of Inconel X or stainless steel. Because distilled water was used as the solvent, any corrosion of the bomb would be expected to be small, giving little interference. The bomb was suspended vertically in a doubly-wound

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[1] Heitmann (1965) measured the solubility of gelatinous silica over a wide range of temperatures (20° to 265°C) and pressures (0.3 to 400 kg/cm^2). However, most of his results apply to the transport of dissolved silica in superheated steam.

electric-resistance furnace. Temperatures were monitored with thermocouples placed in wells at each end of the bomb and inside the bomb in a stainless steel sheath projecting to the center of the sample chamber. The thermal gradient along the length of the bomb was less than 5°C, and the thermal gradient within the sample chamber was probably much less than that. The temperature variation with time at any given point along the bomb during a run was ±2°C.

Periodically, small amounts of solution were withdrawn for analysis through a stainless steel capillary tube and valve at the bottom of the bomb. A stainless steel filter with a mean pore opening of 20 microns was placed inside the bomb at the tip of the capillary sampling tube. Near the exit end of the capillary tube, a six-inch-long segment was immersed in an ice bath to bring the temperature of the solution below 15°C before it emerged at atmospheric pressure. During sampling, the pressure in the bomb was maintained nearly constant by means of an automatically actuated pump that transferred silica-free distilled water into the top of the sample chamber when the pressure dropped below a preselected value. An external high-pressure water reservoir with a capacity of 2 liters prevented large pressure drops and surges during sampling.

Starting material

Commercially available vitreous and gelatinous silica were used as starting materials. The vitreous silica was General Electric Company type 204 clear fused quartz rod (0.5 cm in diameter broken into 3 to 5 cm lengths). Approximately 57-gram portions were used to fill the bomb each time a renewal of the charge was required. Initially, the vitreous silica was anhydrous, but undoubtedly the surfaces quickly hydrated at the high temperature and high water pressures of the experiments. The gelatinous silica was 100–200 mesh certified high-purity material from the Fisher Chemical Company, grade 923. Approximately 35-gram portions were used in the experiments.

Sampling and analytical procedure

The bomb and charge were maintained at temperature and pressure for a time sufficient to attain chemical equilibrium, usually of the order of 2 to 5 days. Each time the bomb was sampled, the first 2 milliliters of solution were discarded in order to rinse the sampling tube and to assure that the next portions of solution to be analyzed came directly from the main chamber of the bomb. Two samples of approximately 0.5 gm were then successively collected directly into two previously weighed flasks containing a known amount of silica-free water. This procedure reduced the concentration of dissolved silica to a value below the solubility of amorphous silica in water at 25°C, and thereby prevented the polymerization of silica after the solutions were brought to room temperature at atmospheric pressure. After one or more days, a second sampling was carried out at the same temperature and pressure to verify the attainment of a steady state, presumably equilibrium. The temperature and/or pressure was then changed to a different value and the process repeated.

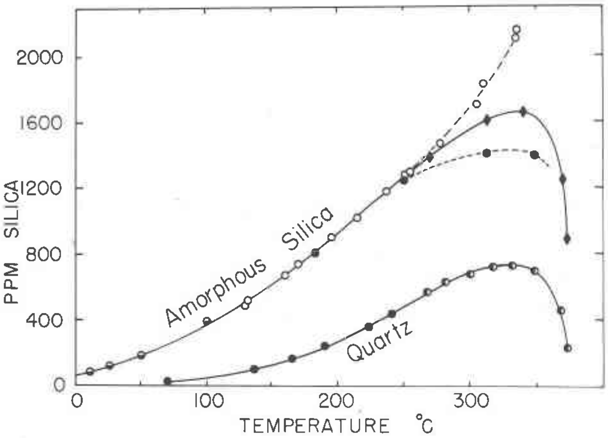

Fig. 1. Solubility in water of amorphous silica relative to quartz at the vapor pressure of the solution. Along the quartz curve, the solid circles are from Morey and others (1962), the half-filled circles from Kennedy (1950). Along the amorphous silica line, the half-filled circles are from Kitahara (1960), the hollow circles from Hitchen (1935), the solid circles from Fournier and Rowe (1966); the diamonds represent results extrapolated from higher-pressure data plotted in Fig. 4.

One portion of each of the diluted solutions was then analyzed immediately for colorimetrically-reactive silica, using a modification of the molybdenum blue method of Shapiro and Brannock (1956); a second portion was analyzed for total silica by treatment with NaOH to convert all polymerized species to colorimetrically-reactive species (Morey *et al.*, 1962). All dilutions were done by weight, and replicate analyses generally agreed within 20 mg/kg for the initial colorimetric silica and within 100 mg/kg for the total silica. The colorimetric silica values for successive samples collected within a few minutes of each other had a mean average difference of 0.94 percent, with a standard deviation of 1.39 and standard error of the mean of 0.14. In the same samples the total silica values had a mean average difference of 2.46 percent, with a standard deviation of 3.62 and standard error of the mean of 0.38.

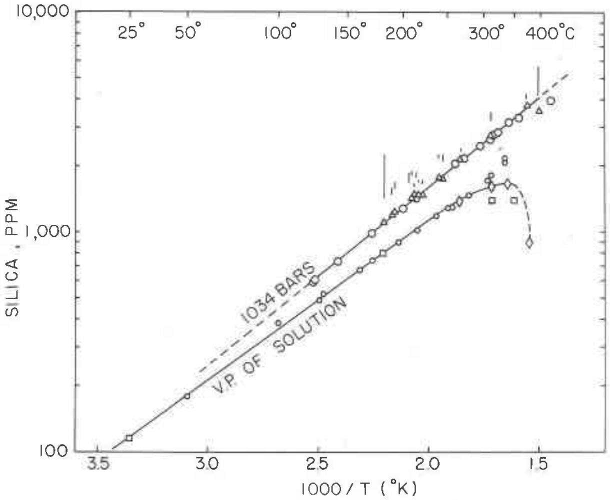

Fig. 2. The solubility of amorphous silica at 1034 bars compared with the solubility at the vapor pressure of the solution, plotted on a logarithmic scale relative to the reciprocal of absolute temperature. Along the vapor pressure line, the small circles are from Kitahara (1960) below 100°C and Hitchen (1935) above 100°C. The squares are from Fournier and Rowe (1966); the diamonds represent results extrapolated from high-pressure data plotted in Fig. 4. Along the 1034 bar line, the circles show colorimetrically-reactive silica in solution using fused quartz as the starting material, the triangles the colorimetrically-reactive silica using gelatinous silica as the starting material. The vertical lines extending above the triangles show the range in total silica values obtained from gelatinous silica starting material.

Results

The experimental results[2] are plotted in Figures 2, 3, and 4. The experimental uncertainties are about ±1 percent in silica, ±2 percent in pressure, and ±3°C in temperature. Within the analytical precision the same amounts of colorimetric and total silica were obtained using vitreous silica as the starting material. The gelatinous silica gave the same colorimetric silica as the vitreous silica, but higher and erratic amounts of total silica (Fig. 2). The erratically high total-silica values were probably produced by small amounts of very fine-grained solid particles of silica that disaggregated from the gelatinous starting material and passed through the 20-micron filter during sampling.

In Figure 2, the straight line drawn through the results for runs at 1034 bars was determined by a least-squares fit of the data. The equation of the line is

$$\log C = -810/T + 4.82, \qquad (1)$$

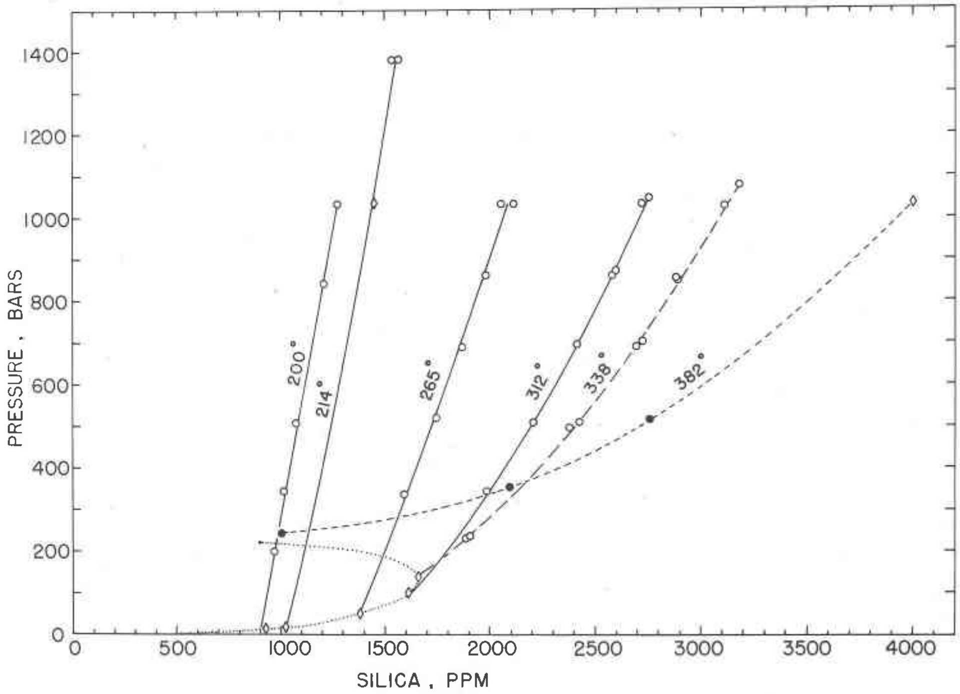

Fig. 3. The solubility of amorphous silica (colorimetrically-reactive silica in solution) at various constant temperatures and variable pressure. The circles show the distribution of the experimental results, the triangles calculated solubilities using relations shown in Figs. 2 and 4. The dotted line shows the solubility results at the vapor pressure of the solution.

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[2] To receive a table listing the experimental results, order document AM-77-051 from the Business Office, Mineralogical Society of America, Suite 1000 lower level, 1909 K Street, N.W., Washington, D. C. 20006. Please remit $1.00 in advance for the microfiche.

where C is the colorimetric silica concentration in mg/kg and T is absolute temperature. The R^2 value for the least-squares fit is 0.998. The errors in the slope and intercept of the regressed line are ±6 and ±0.01 respectively. The least-squares straight line through the data for runs at the vapor pressure of the solution from 0° to 250°C is given by the equation

$$\log C = -731/T + 4.52, \qquad (2)$$

and the R^2 value again is 0.998. The errors in the slope and intercept of the regressed line are ±21 and ±0.01 respectively.

Following the assumption of Morey *et al.* (1962), the partial molal or differential heat of solution, $\Delta\bar{H}$, of amorphous silica at a pressure of 1034 bars can be calculated from equation 1; $\Delta\bar{H}$ equals 3.71 ±0.05 kcal/mole (4.1840 cal = 1 joule). This compares to a $\Delta\bar{H}$ of 5.38 ±0.15 kcal/mole for quartz at approximately 1000 bars. The change in free energy, ΔG, obtained by dissolving amorphous silica at 1034 bars pressure is approximately given by the equation

$$\Delta G \cong -RT\log C_1 = 810R - 304, \qquad (3)$$

where C_1 is the concentration of dissolved silica in moles/kg of water and R is the universal gas constant. The partial molal entropy of solution, $\Delta\bar{S}$, can be obtained from the equation

$$S = -(\delta\Delta G/\delta T)_{P,X} = 3.04R, \qquad (4)$$

and ΔS equals 13.9 ± 0.05 cal/mole.

In Figure 3, the solubility results at constant temperature and variable pressure lie along a straight line at 200°C. At higher temperature, the results depart from a straight line, and progressively more curvature is shown. Interpolation and extrapolation of the data are difficult using this type of diagram. When the solubility values are plotted relative to the density of the pure solvent, however, as in Figure 4, the data at constant temperature fall along nearly parallel straight lines over the entire range of the temperatures measured, 200° to 382°C, at pressures between 1034 bars and the vapor pressure of the solution.

Discussion

The similar amounts of colorimetric silica found in solution using vitreous silica and gelatinous silica suggest that most amorphous silica materials will have about the same solubility irrespective of the manner of preparation. However, very fine-grained or highly-stressed material could give higher solubility values. Evidently the fused quartz rods used in this study initially had highly stressed zones running lengthwise through their centers that dissolved more rapidly than the surrounding glass; at the end of each series of experiments, each of the rods had a central cluster of 10 to 20 tiny "pin holes" of channels extending from one end to the other.

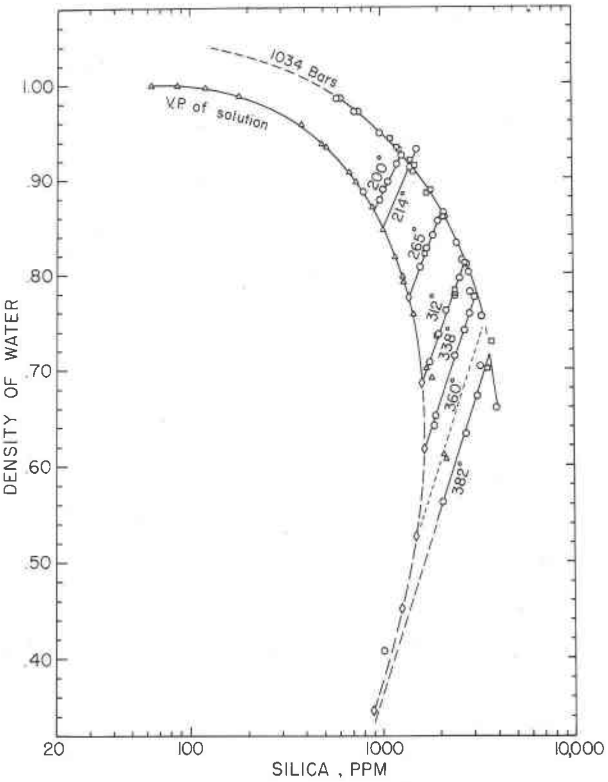

Fig. 4. The solubility in water of amorphous silica (colorimetrically-reactive silica) as a function of the density of the pure solvent. The triangles are from Kitahara (1935) and Hitchen (1960). The circles show results using fused quartz and the squares gelatinous silica as starting materials. The diamonds indicate where isothermal lines, emanating from given temperatures along the 1034 bar curve and drawn parallel to other nearby isothermal lines, attain densities equal to the vapor pressure of pure water at the given temperatures. These diamonds define the amorphous silica solubility curve at the vapor pressure of the solution above 300°C, assuming the density and vapor pressure of the dilute solutions to be about equal to pure water.

At temperatures above 300°C, the solubility values obtained by extrapolating higher-pressure results to the vapor pressure of the solution are significantly lower than Hitchen's values (1935) and higher than our 1966 results (Fournier and Rowe, 1966). It is likely that Hitchen's gravimetric determinations of dissolved silica are too high above 300°C, for cristobalite probably nucleated and grew in his solutions while amorphous material continued to supply nutrient. This behavior was observed in some of the experiments performed as part of the work reported here.

Our 1966 results are probably too low, as three to five minutes were required to cool and open the bombs used for those experiments. During that relatively slow quench, some silica could have precipitated onto the walls of the container or onto the amorphous silica starting material.

Four experiments reported by Heitmann (1965) are in the temperature and pressure range of our experiments. His apparatus was based on a continuous flow principle, and he used both gravimetric and colorimetric methods of analysis for dissolved silica. Unfortunately specific analytical procedures are not given. Presumably he determined total silica carried by the solution flowing from the autoclave. His results are similar to the values we obtained for total silica using gelatinous silica starting materials and about 10 to 15 percent higher than our colorimetric silica values.

At the vapor pressure of the solution, taking the solubility values extrapolated from higher pressure data as more reliable than previous direct measurements, the maximum solubility is 1660 mg/kg at 340°C and 890 mg/kg at the critical point. These data can be used to set the maximum limit for dissolved silica that is likely to be found in hydrothermal systems, and therefore may be useful in solving problems of scaling in the utilization of geothermal energy.

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