

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°–35°C of the same system. Rowe et al. (1967) have determined the phase relations involving several sodium–silicate compounds in the system $\text{SiO}_2\text{--H}_2\text{O--Na}_2\text{O}$. 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 $\text{H}_2\text{O--Na}_2\text{S--SiO}_2$ 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 $\text{SiO}_2\text{--H}_2\text{O--NaOH}$ at pressures of 3–4 kbars and temperatures of 500°–700°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 $\text{SiO}_2\text{--H}_2\text{O}$ and $\text{SiO}_2\text{--H}_2\text{O--NaOH}$ 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 1*N* 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 $\pm 1^\circ\text{C}$ and an overall temperature drift always less than $\pm 2^\circ\text{C}$. 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 Na_2CO_3 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 super-saturated 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 $\text{SiO}_2\text{—H}_2\text{O—NaOH}$ 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 $\text{SiO}_2\text{—H}_2\text{O—NaOH}$ 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;
- $K_{\text{H}_2\text{O}}$ — the ionization constant of water;
- K_{NaOH} — the basic dissociation constant of NaOH.