

## Pressure-Volume-Temperature Behavior in the System $H_2O-NaOH-SiO_2$ and Its Relationship to the Hydrothermal Growth of Quartz

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*We have measured the pressure-volume-temperature relations in the high-pressure solutions used to grow electronic quartz and used this data to establish safe operating conditions for commercial production. High-temperature aqueous solution (hydrothermal) quartz growth, because of the importance of its product to electronics, must be ranked as one of the more important crystal-growth processes. We report here a convenient laboratory method for hydrothermal p-V-T measurements and give pressure data in 1.0-mol NaOH and in 1.0-mol NaOH saturated with quartz as a function of temperature up to 450°C and 30,000 psi. These results are compared with pressures measured on production-sized equipment. The results are used to establish the temperature at which the gas phase disappears under various conditions. The steels used for construction of high-pressure production autoclave equipment are brittle below a specific temperature, which increases slowly with service. Our p-V-T data can be used to assure that high pressures are avoided at temperatures where the autoclave is brittle. Finally, the depressions of pressure are used to glean information about the nature of the solute species present during growth, and can ultimately be of use in quartz rate and perfection studies.*

### I. INTRODUCTION

Commercial hydrothermal growth of single-crystal  $\alpha$ -quartz has been practiced for more than twenty years. It is arguably second only to Si

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in its importance to electronics. The hydrothermal *mineralizer* or solvent used is either NaOH or Na<sub>2</sub>CO<sub>3</sub> and, particularly in the case of the more generally used NaOH, both the physical chemistry and crystal-growth aspects have been quite extensively studied, including phase relations,<sup>1</sup> solubility,<sup>2</sup> growth kinetics,<sup>3</sup> distribution of impurities (especially OH),<sup>4</sup> perfection,<sup>5</sup> and electrical properties<sup>6</sup> of grown quartz. However, the pressure-volume-temperature (p-V-T) relations for neither Na<sub>2</sub>CO<sub>3</sub> nor NaOH for mineralizer solutions saturated with quartz have been determined. Data on p-V-T for aqueous solutions of NaOH<sup>7-9</sup> and Na<sub>2</sub>CO<sub>3</sub><sup>7</sup> are available, but their relationship to the silica-saturated solution used in growth is tenuous. For our purposes the system H<sub>2</sub>O—NaOH—SiO<sub>2</sub> is of particular interest since it is most used and probably most studied. We have directed our studies to it and have adopted it for production.<sup>10</sup> Indeed, except for recent p-V-T measurements in the system H<sub>2</sub>O—H<sub>3</sub>PO<sub>4</sub>—AlPO<sub>4</sub>,<sup>11</sup> under conditions of AlPO<sub>4</sub> saturation like those used for AlPO<sub>4</sub> growth, no p-V-T measurements of mineralizers saturated with the solutes used in hydrothermal crystal growth have been made. In the paper of Kolb et al.,<sup>11</sup> we described a technique and equipment for rather rapid p-V-T measurements that can be easily applied to other saturated hydrothermal systems, and reviewed the literature summarizing p-V-T measurements in hydrothermal mineralizers. As a result of this work and our research and factory experience with quartz, it is our belief that p-V-T measurements in the system H<sub>2</sub>O—NaOH—SiO<sub>2</sub> would be particularly useful for the following reasons:

(i) It has been shown<sup>12</sup> that the brittle-ductile transition temperature of low-carbon steels of the sort used in hydrothermal autoclaves gradually increases when such steels are aged in the temperature range of quartz growth. For safety reasons it is important to be sure no autoclave is exposed to substantial pressure while in the brittle regime. To assure this, accurate p-V-T data for the hydrothermal solution are essential. The need for such data becomes particularly important when autoclaves have been in service for periods of years.

(ii) Pressures are regularly measured, monitored, and used for control in commercial growth. In such growth a temperature differential,  $\Delta T$ , between dissolving-nutrient zone and seed-growth zone, is necessary to produce supersaturation. It would be especially useful to have p-V-T data for both isothermal *and*  $\Delta T$  conditions for comparison with production data. Pressure changes during growth could possibly be used to monitor internal  $\Delta T$  changes during growth.

(iii) Pressure depression in comparison with H<sub>2</sub>O and H<sub>2</sub>O—NaOH may be useful in gleaning information concerning the species present during hydrothermal growth.

(iv) Pressure data may provide insights into kinetics, distribution

of impurities, and perfection, which could further improve the speed, economics, and perfection of commercial growth.

For the foregoing reasons we decided to study and here report p-V-T measurements in the system  $\text{H}_2\text{O}-\text{NaOH}-\text{SiO}_2$  under isothermal conditions and with temperature differentials over the range of conditions relevant to quartz growth. For comparison purposes we also studied the system  $\text{H}_2\text{O}-\text{NaOH}$ .

## II. EXPERIMENTS

This section describes procedures used in laboratory measurements. Measurements in production vessels are described later. The apparatus and procedures used are similar to those reported in our study of  $\text{H}_2\text{O}-\text{H}_3\text{PO}_4-\text{AlPO}_4$ ,<sup>11</sup> except that Pt-lined Morey vessels were not required when quartz was present. This is due to the fact that low-carbon steel autoclaves are relatively inert in the system  $\text{H}_2\text{O}-\text{NaOH}-\text{SiO}_2$  because of the formation of insoluble sodium-iron silicates that protectively coat the vessel.<sup>5</sup> Thus a 1-1/4-in ID x 12-inch IL autoclave with a modified Bridgman closure made by Autoclave Engineers (Erie, PA) fabricated from Timken 17-22-AS steel was used. A series of runs at fills of 65, 75, 80, 83, 86, and 89 percent were made as were calibration runs using pure water at fills of 70, 80.1, and 80.9 percent. Pressure was measured with 0- through 5000-psi (350-bar), 0- through 20,000-psi (1380-bar), and 0- through 40,000-psi (2760-bar) Bourdon gauges (Heise Co., Newtown, Conn.), precalibrated on a dead-weight tester. Pressures above the coexistence curve were measured with gauges with a resolution of  $\pm 20$  psi ( $\sim 1$  bar), while those along the coexistence curve (where liquid and vapor are in equilibrium) were obtained using the 0- through 5000-psi gauge whose resolution is  $\pm 5$  psi ( $\sim 0.3$  bar). The pressure gauges were connected to the cover of the autoclave by 0.017-inch ID stainless capillary tubing brazed to a 1/4-inch diameter high-pressure cone seal.

Separate measurements in the system  $\text{H}_2\text{O}-\text{NaOH}$  were made using a Pt-lined Morey autoclave and pressure take-off of the sort described in our aluminum phosphate p-V-T work.<sup>11</sup> Autoclave volume for both autoclaves was measured by filling with  $\text{H}_2\text{O}$  as previously described.<sup>11</sup> The volumes of the steel plunger and steel coupling were calculated from dimensions. The Bourdon-gauge tube volumes were determined by forcing  $\text{H}_2\text{O}$  through the tube with a calibrated syringe that was fitted to the inlet and measuring the water collected at the exit (gauge-bleed port). The volume of  $\text{H}_2\text{O}$  in the tube is arrived at as a difference that is taken only when bubble-free water is collected at the exit. The volumes of the steel and Pt-lined pressure take-offs and the stainless steel capillary were determined as described previously.<sup>11</sup> Table I lists typical volumes.

Table I—Typical volumes

Bridgman Autoclave	250.0 cc	Morey Pt-Lined Autoclave	30.0 cc
Steel Take-off	1.00 cc	Pt-lined Take-off	0.15 cc
Steel Capillary	0.30 cc	Steel Capillary	0.30 cc
Gauge 40,000 psi	18.0 cc		
20,000 psi	5.0 cc		
5,000 psi	13.0 cc		

The placement of heaters and thermocouples for the Pt-lined autoclave was as described previously,<sup>11</sup> while for the Bridgman autoclave heating was provided by a hot plate on the bottom and band heaters appropriately spaced so as to obtain minimum  $\Delta T$  or, if desired, a particular  $\Delta T$ . An improved temperature-control system using an Electronix III controller with silicon-controlled rectifiers (Leeds and Northrup, N. Wales, PA) was employed in the present work. Temperatures are estimated to be controlled within  $\pm 0.5^\circ\text{C}$ .

To assure saturation and protect the steel autoclave walls from attack, quartz plates 1- x 2- x 0.04-inches were mounted in the Bridgman autoclave, along with 75 gm of small-particle quartz nutrient. Standard NaOH solutions of  $1.000 \pm 0.003$  mol concentration were purchased from Fisher Scientific.

### III. RESULTS AND DISCUSSION

#### 3.1 Calibration

As a check of our procedures we elected to investigate how well our system reproduced the p-V-T data of Kennedy<sup>13</sup> for pure water. Three runs were made at fills of 70, 80.1, and 80.9 of the autoclave. The p-T behavior at 80.1- and 80.9-percent fill was measured in the unlined Bridgman vessel up to pressures of  $\sim 25,000$  psi ( $\sim 1725$  bar) to simulate our measurements in  $\text{H}_2\text{O}-\text{NaOH}-\text{SiO}_2$ . The p-T behavior at 70-percent fill was measured in the Pt-lined Morey vessel with a Pt lead through to the stainless steel capillary coupling so as to simulate our measurements in  $\text{H}_2\text{O}-\text{NaOH}$ . Of necessity we were limited to the pressure capability of Morey autoclaves ( $\sim 10,000$  psi  $\sim 700$  bar) for all work in lined vessels.

Table II gives representative pressures obtained in these runs and the equivalent percent fill for  $\text{H}_2\text{O}$  from Kennedy's data.<sup>13</sup> Furthermore, in Table II the experimental percent fills are corrected for: (i) temperature expansion of the vessel, (ii) pressure dilatation of the vessel, and (iii) compression of the water in the lines and gauge. The temperature expansion of the vessel was obtained using eq. (1) of Kolb and Laudise.<sup>11</sup> The Morey and Bridgman vessels were made of Timken 17-22-AS steel so that the coefficient of expansion in Fig. 5 of Kolb and Laudise<sup>11</sup> was used. The pressure dilatation of the vessels was calculated using eq. (2) of Kolb and Laudise<sup>11</sup> and the values  $Y$  and  $\nu$

Table II—Representative pressures and percent fills for H<sub>2</sub>O

Experimental Percent Fill	80.9	80.9	80.9	80.9	80.1	80.1	80.1	80.1	70
Measured Temperature (°C)	250	300	350	400	300	350	400	400	400
Measured Pressure (bar)	46.9	676	1307	2060	572	1172	1765	1765	903
Experimental Percent Fill Corrected for Temperature Expansion and for Initial Fill on a Volume Basis (a)	80.0	79.8	79.6	79.4	79.0	78.8	78.7	78.7	68.6
Experimental Percent Fill Corrected for (a) + Pressure Dilatation (b)	79.9	79.7	79.5	79.2	78.9	78.7	78.5	78.5	68.6
Experimental Percent Fill Corrected for (a) + (b) + Compressibility of H <sub>2</sub> O in Lines, Leads and Pressure Gauge (c)	79.9	79.5	79.1	78.7	79.7	78.4	78.0	78.0	68.0
Kennedy <sup>13</sup> Percent Fill for Measured <i>p</i> - <i>T</i>	79.7	79.8	79.3	79.8	78.5	78.2	77.7	77.7	67.6

for Timken 17-22-AS suggested.<sup>11</sup> The correction owing to the compressibility of H<sub>2</sub>O in the tubing connecting the high-pressure gauges and to water in the Bourdon tubes of the gauges was made using the specific volumes of water as a function of  $p$  and  $T$ , as tabulated in Landolt-Börnstein.<sup>14</sup>

In addition, it should be pointed out that Kennedy's  $p$ - $V$ - $T$  data<sup>13</sup> are given in terms of specific volume,  $\bar{V}$ , cm<sup>3</sup>/g. Our experimental percent fill (as reported in the first row of Table II) is based on the quantity: volume H<sub>2</sub>O/free volume of autoclave. The corrected fills shown in the fourth, fifth, and sixth rows of Table II are multiplied by the density of water at room temperature so that the fill in these rows is reported as gm H<sub>2</sub>O/free volume of autoclave and can be directly compared with Kennedy's data (last row of Table II). As can be seen, the agreement between our corrected data and Kennedy's data is excellent, suggesting that our procedures are reasonable. For the convenience of those wishing to apply corrections at other conditions, Table III summarizes some useful data.

### 3.2 $p$ - $V$ - $T$ behavior of H<sub>2</sub>O-NaOH-SiO<sub>2</sub>

Figures 1 and 2 show the  $p$ - $T$  behavior of 1.0-mol NaOH saturated with SiO<sub>2</sub> at fills of 65, 75, 80, 83, 86, and 89 percent. The concentration of 1.0-mol NaOH was chosen as comparable to conditions used in commercial growth. Figure 1 shows the low-pressure region, while Fig. 2 covers higher pressures. The line  $A$ - $B$  is the coexistence curve. The fills shown on these figures are based on the initial cold volumes of solution and autoclave and no correction for temperature or pressure dilatation of the vessel is made to them. This is consistent with the definition of fill that is conventional in crystal growth. Such corrections could be made if desired using the data of Table III and the procedures outlined in the previous section and in Kolb and Laudise.<sup>11</sup>

Equilibrium was assured by holding at temperature until pressure stabilized, usually after a few hours. Pressures were not recorded until they were invariant for 12 or more hours. Pressures were observed to reproduce regardless of whether the equilibration temperature was approached from above or below. As a further check to ensure the 12-hour equilibration time was sufficient, a 1.0-mol NaOH run at 89-percent fill was equilibrated with quartz for one week at 214°C and then the temperature was abruptly raised to 303°C. The dependence of pressure on time in this experiment is shown in Fig. 3. As we can see, pressure equilibrium is again established after 250 min. It should be noted that the pressure (23,350 psi, 1610 bar) for 89-percent fill at 303°C for 250 min in Fig. 3 is the same as the pressure at 303°C in Fig. 2. Thus, 12-hour equilibrium times are more than sufficient.

The points in Figs. 1 and 2 at 65-percent fill were obtained in a

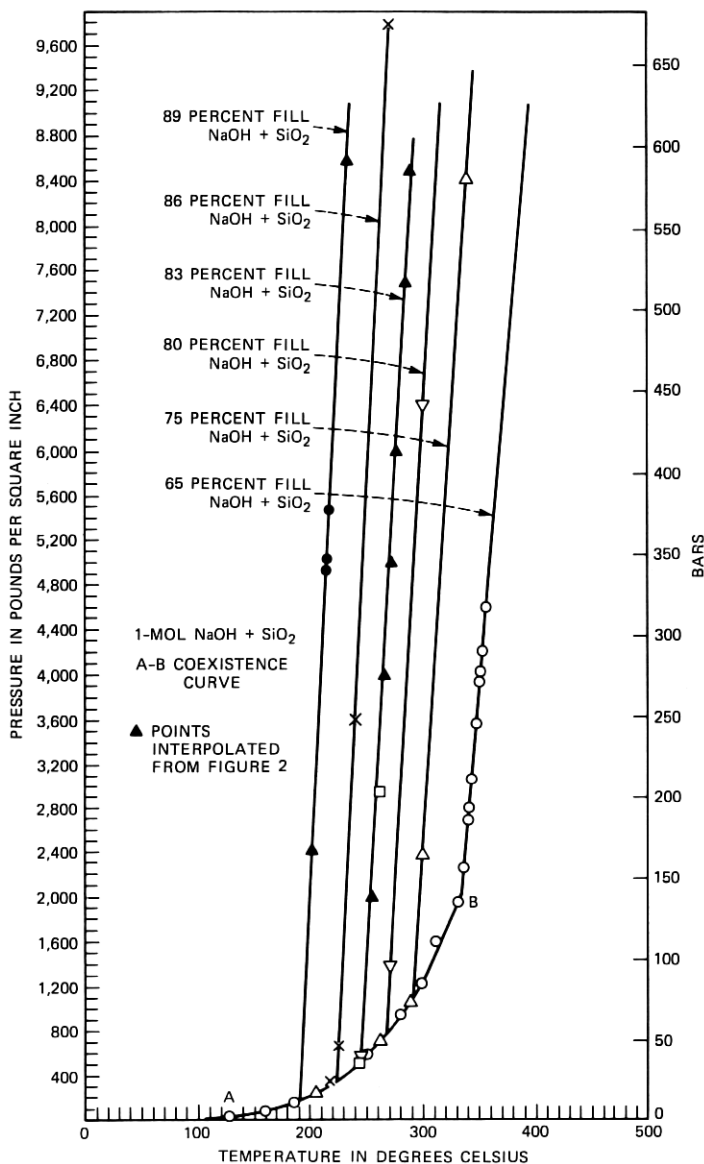


Fig. 1— $p$ - $T$  behavior of 1.0-mol NaOH saturated with quartz in a low-pressure region at several percent fills.

Morey autoclave using a 5000-psi gauge with a resolution of  $\pm 5$  psi. These data are used to define the curve *A-B* where liquid and vapor saturated with quartz coexist. As we can see, at a particular fill once the autoclave has filled with liquid, the pressure departs from the coexistence curve and is linear with temperature; the slope of the  $p$ - $T$

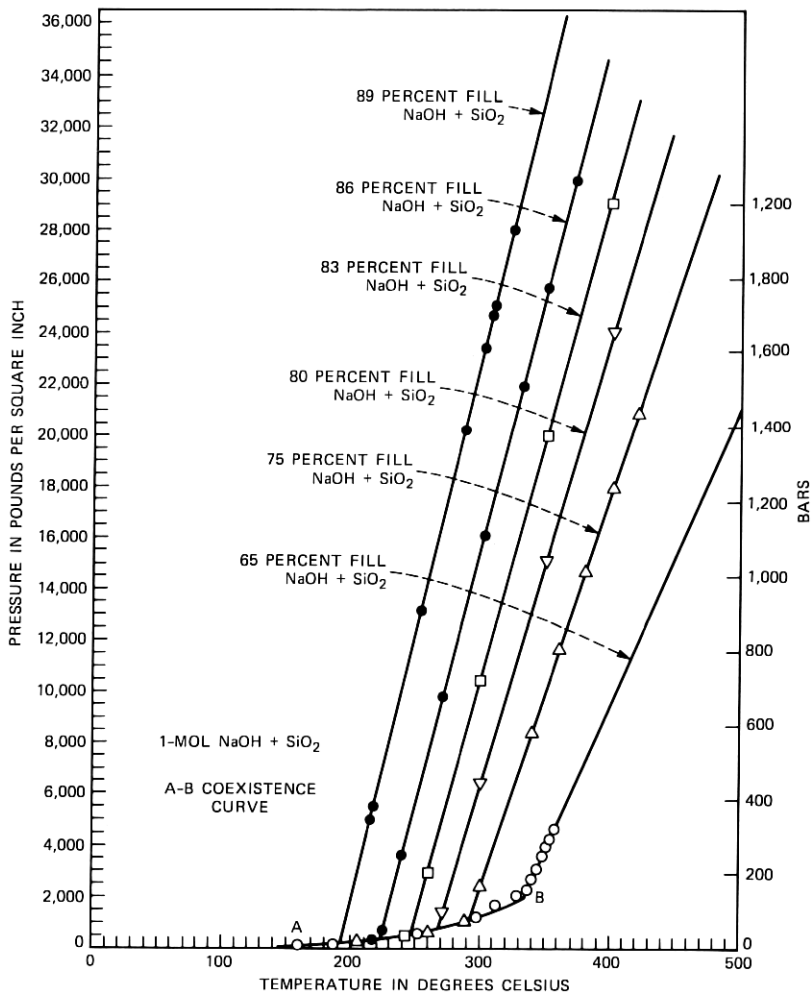


Fig. 2— $p$ - $T$  behavior of 1.0-mol NaOH saturated with quartz in a high-pressure region at several percent fills.

curves at constant-percent fill,  $(\partial p/\partial T)_{\%f}$  is constant, and greater at higher-percent fills. Indeed, the data of Fig. 1 may be used to show the temperature at which the system departs from the coexistence curve as shown in Fig. 4.

The data of Figs. 1 and 2 may be displayed as in Fig. 5 to show the dependence of pressure on fill at constant temperatures. Similar to results on  $H_2O^{13}$  and  $H_2O-H_3PO_4-AlPO_4$ ,<sup>11</sup> the slope of these curves is not a constant.

### 3.3 $p$ - $V$ - $T$ behavior of $H_2O$ -NaOH

The Pt-lined Morey vessel was used to determine pressures in NaOH solutions. Figure 6 shows typical results, which are compared to



Table III—Data for temperature and pressure expansion of autoclaves

Temperature (°C)	Expansion Coefficient Timken 17-22-A (in/in°F)	$V/V_0^*$	Young's Modulus Timken 17-22-A* (psi)
250	$6.92 \times 10^{-6}$	1.0086	$2.84 \times 10^7$
300	$7.13 \times 10^{-6}$	1.0108	$2.78 \times 10^7$
350	$7.31 \times 10^{-6}$	1.0131	$2.74 \times 10^7$
400	$7.44 \times 10^{-6}$	1.0153	$2.68 \times 10^7$
450	$7.53 \times 10^{-6}$	1.0175	

\*  $V$  = Volume at temperature,  $V_0$  = volume at 25°C,  $\nu$  (Poisson's ratio) = 0.3, independent of temperature over this range.

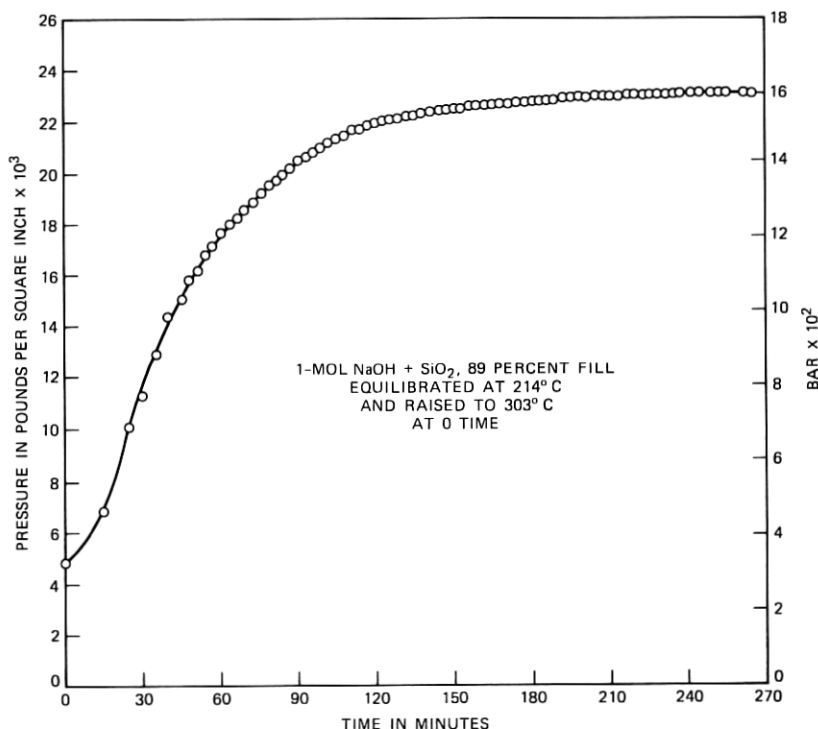


Fig. 3—Dependence of pressure on time when temperature of equilibrated vessel is increased from 214°C to 310°C (89-percent fill 1.0-mol NaOH initially saturated with quartz).

pressures of similar solutions saturated with quartz and with pure water. Some data from Samoilovich<sup>15</sup> and Kijama<sup>16</sup> are also plotted. However, the data of Kanahara, Yamasaki, and Matsuoka<sup>9</sup> for NaOH-H<sub>2</sub>O are not plotted. Their pressures for 1-mol NaOH are much lower than ours or those of Refs. 15 and 16. Liebertz<sup>7</sup> reports pressures for 4-mol NaOH, which are much higher than those of Kanahara et al.<sup>9</sup> but

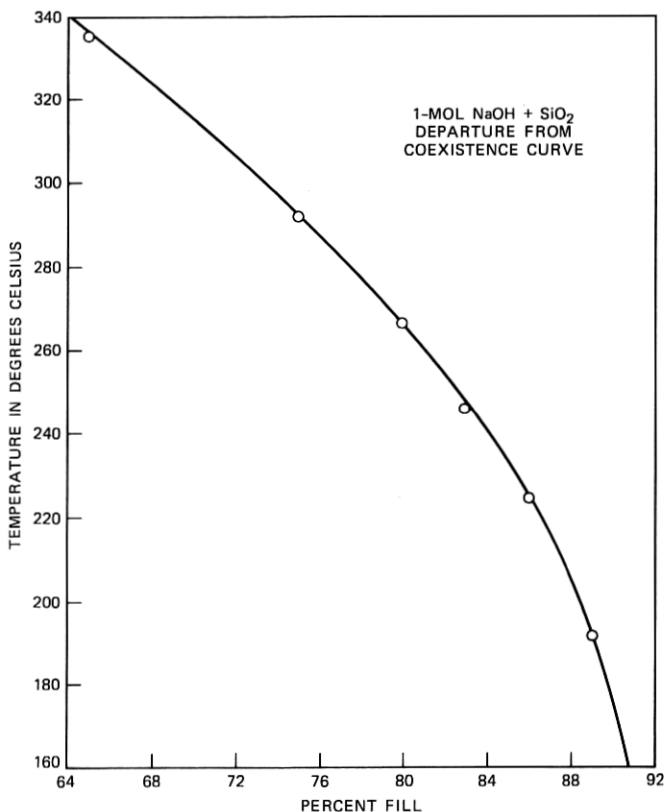
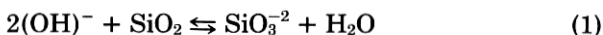


Fig. 4—Temperature at which autoclave fills for 1.0-mol NaOH saturated with quartz as a function of initial fill.

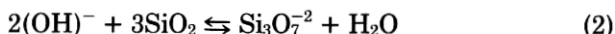
consistent with those of Refs. 15 and 16 at that concentration, suggesting a systematic error in (9).

As we can see in Fig. 6 our NaOH data are consistent with Refs. 15 and 16 obtained at slightly different NaOH concentrations. NaOH depresses the pressure along the coexistence curve and beyond, and  $(\partial p/\partial T)_{\%f}$  is a constant in NaOH solutions above the coexistence curve.

When quartz is added to 1-mol NaOH, as shown in Fig. 6, the pressure is increased about 600 psi (40 bar) at 83-percent fill and more than 2000 psi (140 bar) at 65-percent fill. In previous work<sup>2</sup> we suggested silicate formation such as



for dissolving in  $(\text{CO}_3)^{-2}$ , and



for dissolving in  $(\text{OH})^-$ . In eq. (1) the  $(\text{OH})^-$  is produced by  $(\text{CO}_3)^{-2}$

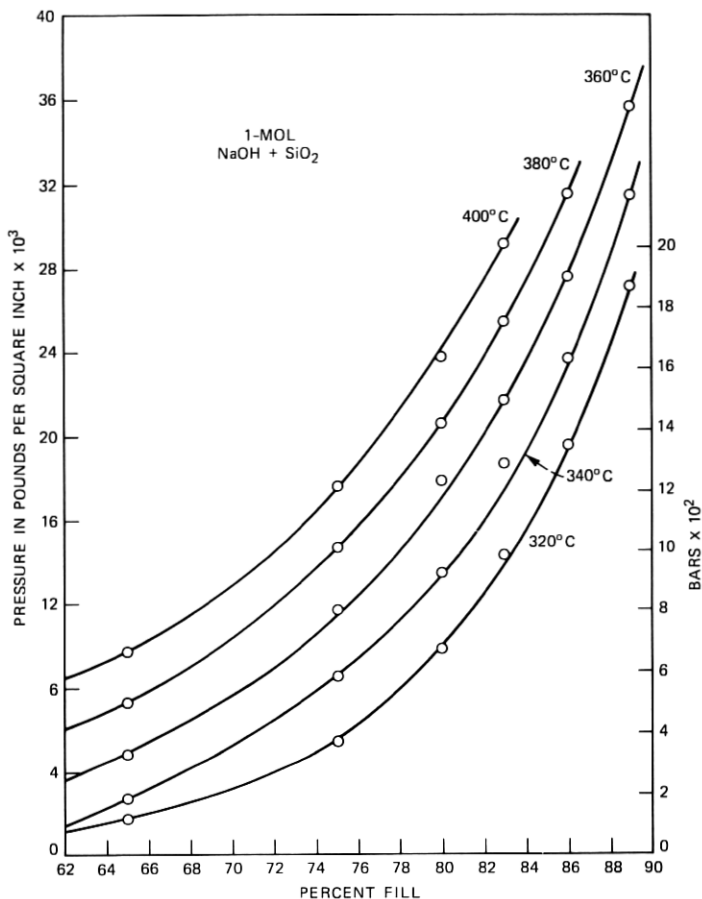


Fig. 5—*p*-percent-fill behavior of 1.0-mol NaOH saturated with quartz at several temperatures.

hydrolysis. Regardless of the details of such reactions it is likely that more than one  $(OH)^-$  is consumed for each silicate ion formed. Consequently, the number of negative ions is decreased. If we make the reasonable assumption that the number and/or strength of the bonds of water molecules held in the first coordination shell by  $2(OH)^-$  is greater than by a single  $(SiO_3)^{-2}$ ,  $(Si_3O_7)^{-2}$  or similar silicate then, as we observe in Fig. 6, the pressure will increase when  $SiO_2$  dissolves in  $(OH)^-$ . The effect might be larger at lower fills because the  $H_2O$  shell about an  $(OH)^-$  is compressed more relative to bulk  $H_2O$  when the  $H_2O$  density is less.

#### IV. RELATIONSHIP TO AUTOCLAVE EMBRITTLEMENT

Figure 7 shows the brittle-ductile transition temperature of some autoclave steels as a function of exposure time at quartz production

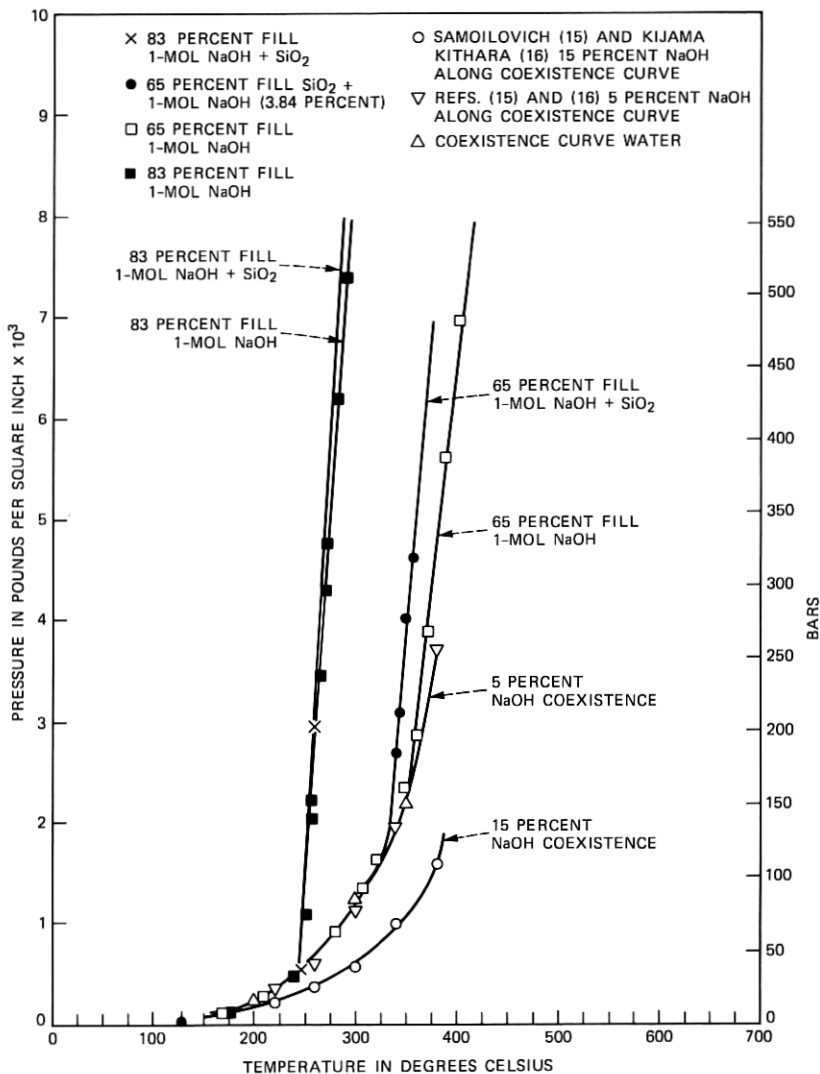


Fig. 6—p-T behavior of 1.0-mol NaOH compared to pure water and 1.0-mol NaOH saturated with quartz.

conditions (350°C crystallization temperature, 400°C nutrient temperature with the usual ~18-hr warm-up and ~24-hr cool-down and typical run time of ~30 days). Further identification of the steels is given in Ref. 12. The data of Fig. 7 were obtained by Charpy impact measurements.<sup>12</sup>

The autoclave operating conditions, primarily fill, should be chosen such that high pressure is not developed until the temperature is above the brittle range. On a practical basis, this requires that conditions be

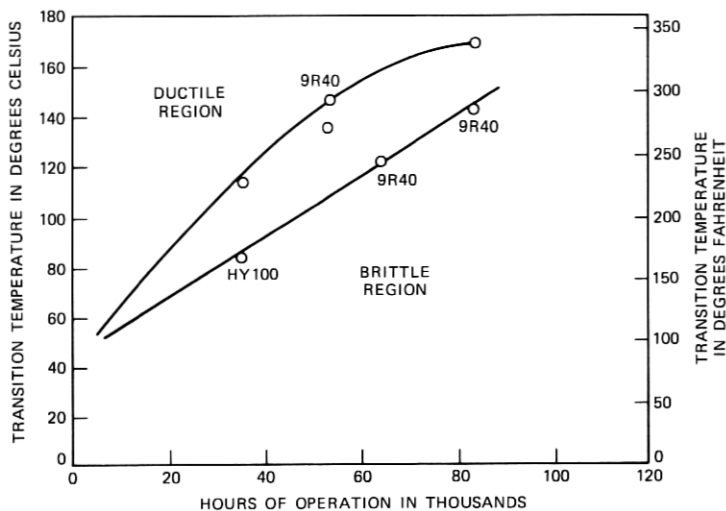


Fig. 7—Brittle-ductile transition of autoclave steels as a function of time at 350 to 400°C.

chosen using data in Figs. 4 and 7 so that pressures do not depart from the coexistence curve until the autoclave temperature is in the ductile region. For example, from Fig. 7, an autoclave with 80,000 hours of exposure (about 10 years at a typical 90-percent duty cycle) will be brittle for temperatures below 140 to 175°C. From Fig. 4, this suggests that fill should be limited to 90 percent. Thus, p-V-T data are very useful in establishing safe operating conditions and should be obtained for other mineralizers and conditions used in commercial hydrothermal processes.

## V. EFFECT OF TEMPERATURE DIFFERENTIALS

For practical crystal growth saturation occurs in a hotter, lower region of the autoclave containing relatively finely divided quartz nutrient, and growth takes place in an upper, supersaturated, cooler region containing seeds. To obtain information about the effect of temperature differentials on measured pressures a series of experiments in non-isothermal vessels were conducted. All experiments were done in 1.0-mol NaOH saturated with quartz at various fills. Figure 8 summarizes these results. We designate temperatures as follows:

$T_1$  = upper, cooler temperature region of autoclave

$T_2$  = midpoint temperature of autoclave

$T_3$  = lower, hotter temperature region of autoclave

$$\Delta T_1 = T_3 - T_1 \quad (T_2 \sim \text{constant})$$

$$\Delta T_2 = T_2 - T_1 \quad (T_3 \sim \text{constant}).$$

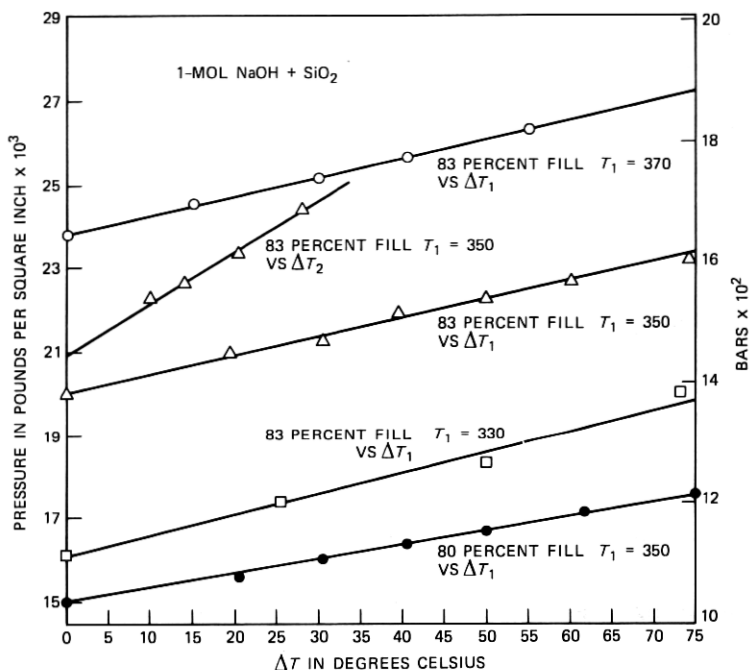


Fig. 8—p-T behavior of 1.0-mol NaOH saturated with quartz as a function of temperature as defined:

$$\Delta T_1 = T_{\text{Upper cooler region}} - T_{\text{Lower hotter region}} \quad \text{and}$$

$$\Delta T_2 = T_{\text{Mid}} - T_{\text{Upper cooler region}}$$

As we can see, pressure is approximately linear with  $\Delta T_1$  and  $\Delta T_2$ . Figure 8 can be used to estimate the correction necessary for converting isothermal data to  $\Delta T$  data. It is interesting to point out that neither the hotter, lower region, upper, cooler region, nor average temperature determines pressure, but a fair fit can be obtained using an average weighted in favor of the upper, cooler temperature.

For example, consider Table IV, made from the data of Fig. 2 and Fig. 8, for 83-percent fill, 1-mol NaOH saturated with  $\text{SiO}_2$ . Row (a) is the upper, cooler temperature region of the autoclave ( $T_1$ ); Row (b) the measured pressure; Row (c) the temperature difference,  $\Delta T_1$ ; Row (d) the temperature,  $T_4$ , which gives the same pressure in an isothermal autoclave; Row (e)  $\Delta T_3 = T_4 - T_1$ ; and Row (f)  $\Delta T_3/\Delta T_1$ . If the average temperature determined the pressure in a non-isothermal autoclave, then  $\Delta T_3/\Delta T_1 = 0.5$ . As we can see from Row (f), the average is weighted toward the upper, cooler temperature region and the weighting factor is reasonably constant.

The pressure is of course uniquely determined by a knowledge of local density and temperature anywhere in the vessel. For example, in

Table IV—Effect of temperature differentials

(a) Upper Cooler Temperature Region of Autoclave ( $T_1$ ) ( $^{\circ}\text{C}$ )	350	350	350	350	350
(b) Pressure $P$ (psi)	23,250	23,000	22,000	21,000	20,000
(c) $\Delta T_1$ ( $^{\circ}\text{C}$ )	75	67.5	45.0	22.5	0
(d) $T_4$ to Give $P$ in Isothermal Autoclaves ( $^{\circ}\text{C}$ )	368	367	361	356	350
(e) $\Delta T_3$ ( $^{\circ}\text{C}$ )	18	17	11	6	0
(f) $\Delta T_3/\Delta T_1$	0.240	0.252	0.244	0.267	

a vessel whose average percent fill is 83 percent, if the  $\Delta T$  is  $50^{\circ}\text{C}$  with a top temperature of  $350^{\circ}\text{C}$ , the observed pressure is 22,180 psi (1530 bar). Using isothermal data for percent fill and taking density as percent fill/100 (Fig. 5), this suggests a local density of 0.85 g/cc for the region at  $350^{\circ}$  and 0.79 g/cc for the region at  $400^{\circ}$ . These densities are clearly subject to some errors since they are based on initial percent fills (Fig. 5) and do not include contributions attributable to dissolved solutes. Procedures of this sort might be used to calculate density gradients and hence be used to calculate the driving force for convective circulation in the system.

## VI. COMPARISON OF LABORATORY AND FACTORY MEASUREMENTS

Measurements of p-T were made on a production crystal-growth vessel filled with nutrient, 5-percent baffle, and seeds, using the heater placement and power inputs normal for commercial growth. The volume of the vessel was determined by filling with water to the corrosion mark indicating where the seal ring had rested in the previous run. Volume corrections were made for the leads in the cover. Capillary lead tubing and Bourdon pressure gauge were filled with water using procedures similar to those of the laboratory. The vessel was filled to a nominal fill of 83 percent with 1-mol NaOH and warmed from room temperature to operating conditions:  $350^{\circ}\text{C}$  (crystallization temperature),  $400^{\circ}\text{C}$  (nutrient region),  $\Delta T$   $50^{\circ}\text{C}$  in a period of 18 hours. During the warm-up temperatures and pressures were recorded and are shown in Fig. 9.

The results are compared with isothermal laboratory data for 83- and 86-percent fills. Careful examination of the ring-seating region at the conclusion of the run and calculations of the volume from the autoclave dimensions lead us to conclude that the true percent fill in the vessel was  $84 \pm 0.5$  percent. On this assumption we can see that the pressures obtained are in reasonable agreement with isothermal laboratory data.

## VII. CONCLUSIONS

A reasonably rapid and convenient method for the measurement of the pressures of saturated hydrothermal solutions of the sort used in

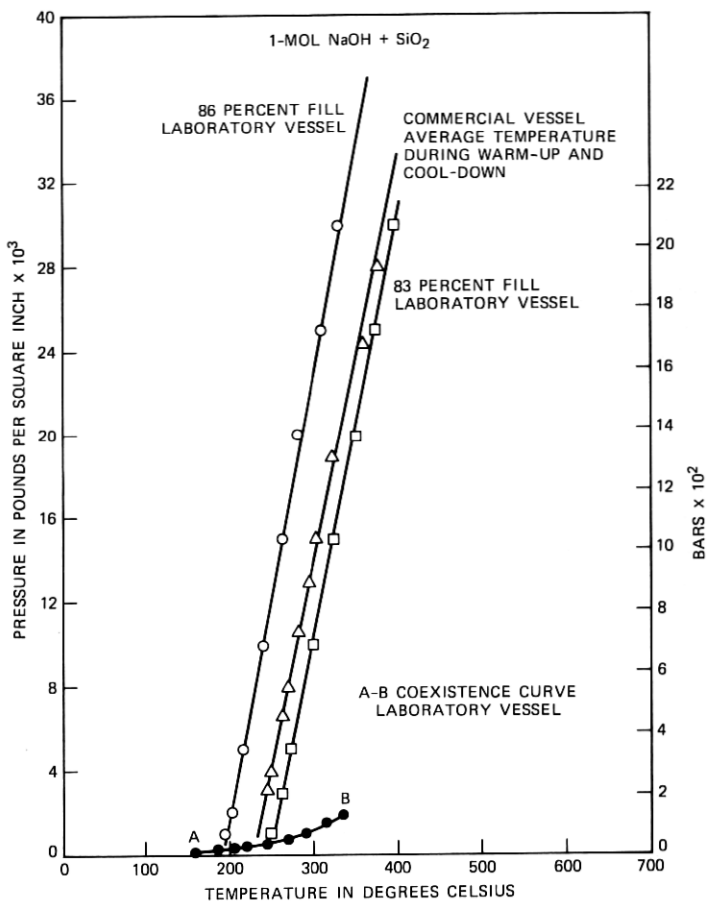


Fig. 9—Pressure-temperature of 1.0-mol NaOH plus quartz in commercial autoclaves during warm-up and cool-down.

crystal growth has been developed and applied to the determination of p-V-T relations in 1.0-mol NaOH and 1.0-mol NaOH saturated with quartz at degrees of fill from 65 to 89 percent, pressures up to ~30,000 psi (2070 bar), and temperatures up to ~450°C. The accuracy of our experimental procedures was tested in measurements on pure water where published pressure data were reproduced. Temperature and pressure dilatation effects are estimated.

For both 1-mol NaOH and NaOH saturated with quartz,  $(\partial p / \partial T)_{\%f}$  is constant above the coexistence curve. Along the coexistence curve and above, the pressure of 1-mol NaOH is less than the pressure of water but the pressure of 1-mol NaOH saturated with quartz is greater than the pressure of 1-mol NaOH. The increase of pressure when quartz dissolves in 1-mol NaOH is explained on the basis of a decrease



in the number of ions in solution when  $(\text{OH})^-$  reacts with  $\text{SiO}_2$  to form silicates.

After about 10 years of service the brittle-ductile transition temperature of autoclave steel increases to  $\sim 170^\circ\text{C}$  so that substantial pressures should be avoided below that temperature. The p-V-T data are used to show the relationship between initial fill and temperature at which the pressure departs from the coexistence curve and  $(\partial p/\partial T)_{\%f}$  becomes large. These data may be used as a guide for the choice of safe operating conditions.

Pressure measurements were made on autoclaves with temperature differentials and the data were related to pressure measurements on isothermal vessels. A weighted average temperature (weighted in favor of the upper, cooler region) for the temperature differential reproduced the isothermal measurements. On the assumption that local density and temperature determine pressure, p-V-T data can be used to estimate density differences associated with typical temperature differences ( $\Delta T$ ). A  $\Delta T$  of  $50^\circ$  at  $350^\circ\text{C}$  growth temperature for 83-percent fill 1-mol NaOH saturated with quartz produces a density differential of  $\sim 0.06$  g/cc.

Finally, pressure measurements were made on large-scale factory autoclaves under conditions of commercial growth and these measurements are compared to laboratory results.

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