

HYDROXYL ION CATALYSIS OF THE CRYSTALLIZATION
OF AMORPHOUS SILICA AT 330° C. AND SOME
OBSERVATIONS ON THE HYDROLYSIS
OF ALBITE SOLUTIONS

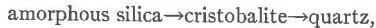
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ABSTRACT

The rate of crystallization of amorphous silica to quartz at 330° C. in liquid water is proportional to the square of the hydroxyl ion concentration. Saturated solutions of albite have only slight catalytic effect on the reaction indicating a low hydroxyl ion concentration. This low concentration is a reflection of the depression of the solubility of albite in the presence of amorphous silica. In albite solutions the concentration of aluminosilicate ions must be small and the framework hydrolysed, most of the silica being in the same form as in solutions of pure modifications of SiO₂.

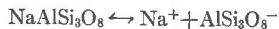
INTRODUCTION

In a previous study Campbell and Fyfe (1960) followed the rate of crystallization of amorphous silica in alkaline solutions at 245° C. The path of crystallization was always:



and the time required to form quartz, a linear function of $1/(\text{OH}^-)$. It was suggested that this catalysis could be used as a pH indicator under hydrothermal conditions. The present results are concerned with an attempt to use this reaction to obtain information on the reaction of albite with water at 330° C.

The solution of a framework silicate such as albite, may be considered to follow the pattern:



followed by



In such a reaction it would be of considerable interest to know if appreciable concentrations of aluminosilicate ions exist, and what hydrolysis species are present. Some indication of the pH of the resultant solutions would be of interest.

To obtain such information with albite a series of measurements have been made. First, for a given batch of amorphous silica the hydroxyl ion dependence of the time required to form quartz is established. The same reaction is then studied in solutions saturated with albite. Second, the solubility of albite in water must be measured and the depression of this solubility by amorphous silica. If this depression is appreciable it follows

TABLE 1

NaOH, Moles/Litre	Length of Run, Hours	Products
0.100	$\frac{3}{4}$	C, Q
0.100	1	Q, C=K
0.100	$1\frac{1}{2}$	Q, C=K
0.100	$1\frac{3}{4}$	Q, C=K
0.100	2	Q, C
0.100	3	Q=100%
0.100	4, 5, 10, 36	Q=100%
0.0500	5	C, K, Q
0.0500	6	C=Q
0.0500	7	C=Q
0.0500	8	Q, C
0.0500	9, 10	Q=100%
0.025	4	C (weak)
0.025	8	C, Q
0.025	12	C, Q
0.025	16	C, Q
0.025	20	C, Q
0.025	24	Q, C
0.025	28, 32, 36	Q=100%
0.0125	8	C (weak)
0.0125	16	C
0.0125	40	C, Q
0.0125	48-80	C, Q
0.0125	90	C=Q
0.0125	120, 124	Q=100%
0.00625	120	C, Q
0.00625	278	C, Q

that a common species must be present. In all cases activity effects will be small as solutions are quite dilute. A summary of the results of these various steps follows.

HYDROXYL ION CATALYSIS OF SILICA CRYSTALLIZATION

Experimental details were essentially similar to those of Campbell and Fyfe (1960). Ignited silicic acid was crystallized in the presence of sodium hydroxide at five concentrations. The results obtained are summarized in Table 1 below. The major differences between these results at 330° C. and those found previously at 245° C. are (1), the rate of quartz formation is a linear function of $1/(\text{OH}^-)^2$ not $1/(\text{OH}^-)$ and (2), silica-K (keatite) appeared in runs using strong sodium hydroxide.

An attempt has been made to analyse these results in terms of the species present in the solutions. This requires knowledge of the first and second dissociation constants of silicic acid at the temperature of the ex-

periments. To obtain approximate data the values of Greenberg and Price (1957) and Roller and Ervin (1940) obtained at 25° C. were extrapolated using a relation found by Pitzer (1937). It is important to note that the concentration of singly charged silicate ions is proportional to (OH^-) whereas that of doubly charged silicate ions is proportional to $(\text{OH}^-)^2$. It is thus possible, given the time for complete formation of quartz at one concentration, to estimate times at other concentrations assuming various species to be rate controlling. The results of this analysis are shown in Table 2. It is clear that the best fit to the data is obtained if the rate is considered to be proportional to $1/(\text{OH}^-)^2$. A similar analysis for the time to obtain well formed cristobalite indicates a rate proportional to $1/(\text{OH}^-)$ but in this case the time cannot be fixed with any precision due to the rather gradual changes involved. The dependence on $(\text{OH}^-)^2$ found, could equally well mean that the actual mechanism depends on H_2SiO_4^- , or $\text{OH}^- \times \text{H}_3\text{SiO}_4^-$ or $(\text{H}_3\text{SiO}_4^-)^2$. As discussed previously (Campbell and Fyfe, 1960) the large effect of pressure on the rate in pure water is suggestive that a silicate ion may play an important part.

THE SOLUBILITY OF ALBITE IN WATER AT 330° C.

Morey and Chen (1955) have made some determinations of the solubility of albite by their flow method and have shown that albite does not necessarily dissolve congruently. Under conditions close to those used in this study, the ratio of $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$ found was 1.05:1:6.71 indicating a fairly close approach to stoichiometric solution. The present results were obtained by the static method of measuring weight loss of single

TABLE 2

Predicted Times (Experimental reference and species assumed to be rate controlling)	NaOH Concentration				
	10^{-1}	5×10^{-2}	2.5×10^{-2}	1.25×10^{-2}	6.25×10^{-3}
2 hours (OH ⁻)	2	4	8	16	32
2 hours (OH ⁻) ²	2	8	32	128	510
8.5 hours (OH ⁻)	4.3	8.5	17	34	68
8.5 hours (OH ⁻) ²	2.1	8.5	34	136	544
27 hours (OH ⁻)	6.8	13.5	27	54	108
27 hours (OH ⁻) ²	1.7	6.8	27	108	430
115 hours (OH ⁻)	14	29	58	115	230
115 hours (OH ⁻) ²	3.6	7.3	29	115	460
Observed times for quartz formation:	2	8.5	27	115	>278

TABLE 3

Time (hours)	Weight Loss, Wt. %
16	0.0277
21	0.0245
21	0.0269
29	0.0295
46	0.0269
58	0.0267

crystals of albite in a fixed quantity of water. The albite was from Amelia County, Virginia. The results of 27 determinations were consistent and indicated a solubility of 0.027 weight per cent. Results of six experiments using large albite fragments are given in Table 3. This solubility, if stoichiometric, corresponds to a 10^{-3} molar solution. The present results are similar to those of Morey and Chen (1955), who found a solubility of 0.0318 wt. % at 350° C. and 5000 psi.

THE SOLUBILITY OF QUARTZ IN WATER AT 330° C.

As the depression of the solubility of albite by quartz solutions was to be measured, further measurements of the solubility of quartz at 330° C. were made by determining weight loss of large quartz plates. Times for solution varied from 1 hour to 23 days and the value selected was 0.069 wt. % or 1.15×10^{-2} molar in moderate agreement with Kennedy's (1950) value of 0.074 wt. % (Morey (1957) also gives rather lower values than Kennedy in this range). Results are recorded in Table 4.

DEPRESSION OF ALBITE SOLUBILITY BY QUARTZ AND AMORPHOUS SILICA

Several measurements were made of the solubility of albite in solutions which were saturated with amorphous silica and quartz. The technique

TABLE 4

Time (hours)	Weight Loss, Wt. %
1	0.0363
2	0.0497
4	0.0601
8	0.0619
12	0.0693
17	0.0683
24	0.0677
61	0.0683
23 (days)	0.0682

involved was simple. The albite crystals were suspended from the top of a vertical bomb containing crushed quartz or amorphous silica and water in the bottom. The albite was thus held in the vapor phase during saturation of the solution with silica. After sufficient time for saturation, the vessel was inverted so that the solution came in contact with the albite. When amorphous silica was used, slight difficulties were encountered because some of the fine silica adhered to the albite. The results showed clearly, however, that the solubility of albite in these solutions was almost completely suppressed and could not be more than a few % of that in pure water. With solutions saturated with quartz, the solubility was much reduced but still measurable, and a value around 0.005 wt.% was found which is much less than the value of 0.027 wt.% in pure water. The results show beyond doubt that when albite dissolves much of the silica must be in the same form as present in solutions of silica polymorphs.

THE EFFECT OF ALBITE ON SILICA CRYSTALLIZATION

If the solubility of albite was not depressed by silica, and if the hydrolysis of the aluminosilicate framework was considerable, albite solutions would have an alkalinity near that of 10^{-3} molar sodium hydroxide. Such solutions should form quartz from amorphous silica much more rapidly than quartz forms in pure aqueous solutions. In view of the solubility depression found, such an alkalinity is not to be expected. Studies were made over a ten month period of the crystallization of amorphous silica in the presence of coarsely ground albite. Over the period 1-5 months only amorphous silica was present in the products but after ten months cristobalite was well developed. These observations confirm the slight alkalinity of albite solutions. Although only very broad limits can be placed from these data, it seems unlikely that the hydroxyl ion concentration of these solutions could exceed 10^{-5} molar.

DISCUSSION OF RESULTS

The most significant conclusions from the above experiments are concerned with the species formed on solution of albite. First, the framework must be largely ruptured to simple species with the form of silica being the same as present in solutions of silica polymorphs. We shall assume this to be $\text{Si}(\text{OH})_4$. Second, the level of alumina in such solutions, near 10^{-3} molar, requires that extensive formation of aluminate ions must occur. Morey and Chen (Morey, 1957) have shown that corundum has a very low solubility in pure water, a result confirmed by D. Weill working in this laboratory. The flow experiments of Morey and Chen (1955) also show that most of the alumina formed from albite solutions must be in solution.

All these observations can be explained if it is assumed that albite solution occurs mainly as expressed by the reaction below:



(Note, the aluminate ion is probably hydrated as suggested by Sidgwick (1950) who indicates that both $\text{Al}(\text{OH})_4^-$ and $\text{Al}(\text{OH})_6^{3-}$ are possible.) The above reaction applies only to the P-T conditions studied here. We may thus write an equilibrium constant:

$$K \simeq (\text{Na}^+)(\text{AlO}_2^-)(\text{Si}(\text{OH})_4)^3 \simeq 27 \times 10^{-15}$$

at 330° C. in liquid water. This must only be an approximation due to some degree of nonstoichiometric solution. Using the above equilibrium constant and the solubility of quartz in water, the solubility of albite in quartz-saturated solutions would be estimated to be about 1.6×10^{-4} molar in reasonable agreement with the observed value of approximately 2×10^{-4} . From the solubility data for amorphous silica of Hitchen (1934) we would anticipate an albite solubility of about 2×10^{-5} which explains the negligible solubility observed in the presence of amorphous silica.

Clearly the equilibrium as written above is oversimplified for considerable hydrolysis of aluminate ions must occur and some silicate ions must be present but the above relation explains the present data reasonably. Any equilibrium involving extensive formation of polymerized AlSi anions would not explain the silica depressions.

It follows from the above treatment that under these conditions, aluminic acid must be stronger than silicic and that the hydrolysis of the aluminate ion must be small. Such a conclusion may not be unreasonable. There is a trend as noted by Fyfe, Turner and Verhoogen (1958) that as acids become weaker, their temperature of maximum dissociation in water tends to occur at higher temperatures. Data given by Latimer (1952) suggest that silicic acid is slightly stronger than aluminic acid at 25° C. This relation could well be reversed at 330° C. Both acids would be stronger at 330° C. with aluminic stronger than silicic. At the present time studies are in progress to test this proposal by measuring the solubility of corundum in dilute solutions of sodium hydroxide at elevated temperatures.

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