[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND GEOLOGY, ANTIOCH COLLEGE[1]]

The Mechanism of the Hydrothermal Transformation of Silica Glass to Quartz under Isothermal Conditions

BY J. F. CORWIN, A. H. HERZOG, G. E. OWEN, R. G. YALMAN AND A. C. SWINNERTON[2]

RECEIVED DECEMBER 29, 1952

The hydrothermal conversion of silica glass to α-quartz occurs in alkaline solutions when alkali metal ions are present. In neutral solution, acid solution and solutions containing ammonium ions the conversion results in α-cristobalite and similar mineral structures. From *p*H measurement, variation of solution contents, and X-ray analysis a mechanism which accounts for the difference in the resulting crystalline structures is proposed.

The conditions for hydrothermal conversion of silica glass to quartz and its transfer to a seed plate of α-quartz by alkali halide solutions[3,4] and a mechanism for the conversion in sodium fluoride solution[5] have been reported from work done at Antioch College supported by contract with the Signal Corps Engineering Laboratories. In the course of this work, major effects on the transfer of quartz to a suspended seed plate were found on variation of the *p*H and of the salt content of the solutions even though the crystallization of the glass seemed to proceed as usual. X-Ray examination of the devitrified material showed that the glass has been transformed to α-quartz and α-cristobalite in varying amounts depending upon the nature of the solution. A series of experiments was designed in which the solutions were varied in order to determine the limiting factors of the transformation. The results of these experiments combined with references to previously reported results[3–5] present an explanation of the mechanism of transformation of silica glass to crystalline silica.

Experimental

The apparatus and control equipment have been described in a previous publication.[4] The reaction vessels were 250-ml., stainless steel autoclaves. Constant conditions were used in all experimental runs, *i.e.*, isothermal at 400°, 340 atmospheres pressure, 50% liquid filling, 48 hr., either clear or satin-surface fused silica as a source, and an α-quartz seed plate suspended from the lid of the autoclave. Where *p*H measurements were made the autoclave was cleaned and brought to neutrality before the run was made. The only changes were in the concentration and content of the solutions. For X-ray examination the crystalline material was freed from the solution by decantation, washed several times with water and dried in an oven at 120°. The *p*H measurements were done with a Beckman *p*H meter.

Experimental Results

Table I contains the results when water alone, dilute hydrochloric acid, alkali hydroxides, several concentrations of alkali halides and combinations of alkali halides with their corresponding hydroxides are used.

Table II contains data obtained when ammonium ions are present in addition to halide or hydroxide ions.

Discussion

The results in Table I show that when the solution is neutral or acid, the small amount of crystallization that takes place results in α-cristobalite and when solutions of NaCl and KCl are used the result is primarily α-cristobalite. However, when sufficient alkalinity is present either in the form of added alkali hydroxide or by reaction of the silica glass with fluoride ions[5] the results show α-quartz to be the major constituent.

Experiments with O^{18} enriched water[5] show that bridge oxygens between the silica are at a minimum and that the probable ions in solution that account for crystallization result from salts of orthosilicic acid. Since the problem of making *p*H measurements or in fact any instrumental measurements in the autoclaves under conditions necessary for crystallization of the glass has not been solved due to the high pressures and solubility of all insulating materials in water, any explanation of the *p*H data recorded in the tables must be made by extrapolating literature information obtained at 25° to the conditions of the experiments. Such an extrapolation helps to explain the mechanism of quartz and cristobalite formation.

Selecting the second ionization constant determined by Mukherjee and Chatterjee[6] as a basis for calculation, the following ratio of ions of orthosilicic acid controlled by the OH^- concentration is the result.

$$H_3SiO_4^- = H^+ + H_2SiO_4^{--},\ K_2 = 5 \times 10^{-10} \quad 25° \qquad (1)$$

The hydrolysis of the $H_2SiO_4^{--}$ ion in water solution should follow equation (2)

$$H_2SiO_4^{--} + H_2O = OH^- + H_3SiO_4^- \qquad (2)$$

Setting up equation (2) in the usual form for calculation of degree of hydrolysis and solving for the concentration ratio of the two silicate ions and substituting the usual values for K_w and the above value for K_2, equation (3) is obtained.

$$\frac{(H_3SiO_4^-)}{(H_2SiO_4^{--})} = \frac{K_w}{(OH^-)K_2} = \frac{10^{-14}}{(OH)\ 5 \times 10^{-10}} \qquad (3)$$

When a high hydroxide ion concentration (*p*H 12) is substituted into equation (3) the ratio $H_3SiO_4^-/H_2SiO_4^{--}$ is $^1/_{500}$. As the alkalinity decreases (*p*H 10) the ratio becomes $^1/_5$. The ratio $^1/_{500}$ is accompanied by complete transformation to α-quartz and the ratio $^1/_5$ results in a mixture of the two forms but still favors quartz formation. Further reduction in *p*H to neutrality produces

---

(1) The results and interpretations presented here are derived from work supported on contract between Antioch College and the U. S. Army Signal Corps through its Signal Corps Engineering Laboratories at Fort Monmouth, New Jersey.

(2) Deceased.

(3) J. F. Corwin and A. C. Swinnerton, THIS JOURNAL, **73**, 3598 (1951).

(4) A. C. Swinnerton, G. E. Owen and J. F. Corwin, *Discussions Faraday Soc.*, **5**, 172 (1949).

(5) J. F. Corwin, R. G. Yalman, G. E. Owen and A. C. Swinnerton, THIS JOURNAL, **75**, 1581 (1953).

(6) J. N. Mukherjee and B. Chatterjee, *Nature*, **155**, 85 (1945).

TABLE I

α-C = α-Cristobalite; α-Q = α-Quartz.

Solutions	No. runs	$p\mathrm{H}_{i25°}$	$p\mathrm{H}_f$	Growth seed, mg.	Devitrification source, %	X-Ray data
H_2O alone	5	7.3	6.7	None	Slight	α-C only identified
HCl to *p*H 5	4	5.0	6.5	None	Slight	α-C only identified
N/2 NaCl	2	6.3	6.4	25	95	α-C primarily
N/10 NaCl	1	6.3	6.1	62	100	α-C primarily
N/40 KCl	2	6.5	7.0	94	19	α-C
N/40 NaF	5	6.4	6.7–9.6	400	100	α-Q only identified
N/40 NaCl NaOH to *p*H 10	3	10	5.4	235	90	α-Q small amount α-C
N/40 NaF NaOH to *p*H 10	2	10	5.2	331	100	3/4 α-Q 1/4 α-C
N/40 NaOH	2	12.4	10.5	−70	100	α-Q only
N/40 KOH	2	12.5	10.5	66	100	α-Q only

TABLE II

α-C = α-Cristobalite; α-Q = α-Quartz.

Solutions	No. runs	$p\mathrm{H}_{i25°}$	$p\mathrm{H}_f$	Growth seed, mg.	Devitrification source, %	X-Ray data
N/40 NH_4Cl	1	6.6	6.0	15	2.2	3 strongest lines α-C
N/40 NH_4OH	1	12.1	11.2	22	50.0	α-C
N/40 NH_4HF_2	1	2.5	5.5	9	1.5	"Precious Opal," Queretara, Mexico. α-C
N/40 NH_4HF_2 NH_4OH to *p*H 7	1	7.0	6.5	0	4.5	Close to α-C
N/40 NaCl NH_4OH to *p*H 10	1	10.0	8.0	0	1.0	"High" β-C

only cristobalite formation. Franke[7] has reported that when the concentration of hydroxide ion falls below 0.004 *N* α-cristobalite crystals become evident.

If the commonly accepted theory for the formation of silicate structures[8–10] is assumed, then the tetrahedral silicate structures would go together with the elimination of water to form either quartz or cristobalite. The repulsion of the charges on the ionic, silicate tetrahedra would cause the twisting spiral formation of α-quartz while the less-ionic forms or molecular orthosilicic acid would contribute to the formation of α-cristobalite.

When the chlorides alone are used and only α-cristobalite is formed from solution a small amount of increase in weight of the seed is noticed. This increase has the appearance of α-quartz and its presence could be explained by a small amount of ionic material that probably exists because of the salt content of the solution.

The data, Table II, when ammonium ions are present seems to indicate a condition like that of pure water or neutral salt solutions. The resulting crystalline material was difficult to identify by X-ray methods,[11] but all showed some form of cristobalite and no evidence of quartz formation. The indication is that under the experimental conditions, the ammonium compounds decompose with liberation of ammonia and no ionic silicate structures are present for quartz formation.

YELLOW SPRINGS, OHIO

---

[7] I. Franke, *Bull. soc. franc. mineral. cristallograph*, **74**, 207 (1951).

[8] R. E. Gibbs, *Proc. Roy. Soc. (London)*, **A109**, 405 (1926).

[9] R. E. Gibbs, *ibid.*, **A110**, 443 (1926).

[10] R. E. Gibbs, *ibid.*, **A113**, 351 (1927).

[11] C. S. Hurlbut, Jr., Department of Mineralogy, Harvard University, identified these structures.