[Contribution from the Departments of Chemistry and Geology, Antioch College[1]]

The Growth of Quartz in Alkali Halide Solutions

By James F. Corwin and A. C. Swinnerton

The shortage of oscillator grade quartz and the demand for it in the communications area prompted the investigation of the possibility of its growth artificially. The conditions necessary for the growth of α-quartz in alkali halide solutions at high temperatures and pressures using fused quartz as a source material and α-quartz as seed have been described. The process is isothermal and depends on the greater solubility of the fused silica for saturation of the solution. X-Ray analysis of materials and physical measurements made at room temperature have been extrapolated to the conditions of growth and a possible mechanism for the reaction is discussed.

The hydrothermal conversion of silica glass to crystalline quartz has been performed by a number of investigators since Spezia[2] reported success by heating a mixture of sodium metasilicate, sodium chloride and scrap quartz crystals in a high-pressure vessel to 300°. This same method with substitution of potassium acid fluoride for sodium chloride and transparent quartz glass for quartz crystals as a source material has been developed to a high degree of perfection by Wooster and Wooster.[3] R. Nacken,[4] in Germany, developed a process for growing quartz in sodium carbonate and alkali halide solutions.

In 1946 the U. S. Army Signal Corps established two projects[5] concerned with the growth of quartz for use in oscillator units. One of these projects established at Antioch College has reinvestigated and extended Nacken's work. The primary objectives of this project have been the determination of optimum conditions for quartz growth and development of a theory to account for the transfer of silica under isothermal conditions.

Experimental

The apparatus and control equipment have been described in a previous publication.[6] Because of the difficulty of making any sort of instrumental measurements at 300–450° and 204 to 476 atmospheres pressure except temperature and pressure, a series of experimental growth reactions were conducted under controlled conditions and the degree of success or failure in adding good quartz growth to the seed plate was used as a measure of the process. The contents of the autoclave, after the selected growth runs, were analyzed by X-ray methods. Each reported result is an average of at least two complete runs.

The volume of the autoclave (250 ml.) was the same for each experiment and the upper limits of temperature and pressure were those imposed by the design of the equipment (450° and 476 atmospheres). The seed plates in every case were natural quartz, either AT-cut oscillator blanks or plates cut parallel to the minor rhombohedral face 12.7 × 15.2 × 0.76 mm. in size and weighing close to 0.400 g. Since the growth process under isothermal conditions has a tendency to run down in 48 hours, almost all of the runs were made for this length of time. A large number of preliminary experiments[6] have indicated that the optimum *p*H for starting a growth reaction is 10 and all solutions used were adjusted to that value by the addition of sodium hydroxide solution. By comparative runs the positive ion of the hydroxide showed little influence because of its very low concentration.

Experimental Results

The best source material for promoting growth of quartz is transparent silica glass as is shown in Table I.

Table I

Average % increase in weight of seed plate: *N*/40 NaCl, *p*H 10, 48 hr., 400°, 50% charge, 340 atm.

Source material	Growth, %
Natural quartz (chunks)	−5.5
Natural quartz (finely divided)	−7.5
Cristobalite (standard super-cel)	1.0
Cristobalite (natural)	5.0
Chalcedony	9.3
Fused silica (finely divided)	16.7
Fused silica (satin surface tubing)	134.0
Fused silica (transparent chunks)	143.0

The results of using different halides and alkali metal ions on the growth reaction are shown in Table II.

Table II

Average % increase in weight of seed plate: *N*/40 halide concentration, *p*H 10, 48 hr. 400°, 50% charge, 340 atm., 19 g. source material.

Satin surface fused silica		Transparent fused silica	
Halide solution	Growth, %	Halide solution	Growth, %
NaBr	103	KF	199
NaCl	134	NaF	185
NaF	138	LiF	175

An extensive series of growth runs was made early in the investigation using sodium chloride and satin-surface vitriosil to determine the optimum conditions of concentration of halide, charge and pressure.[6]

These runs and spot check experiments with all of the halides indicated that the optimum concentration was *N*/40 and the charge 50%. Group experiments in smaller autoclaves with transparent vitriosil gave the same indication.

A series of runs was made by adjusting the temperature and charge in such a way that the pressure was kept constant; Table III.

Table III

Average % increase in weight of seed plate: *N*/40 NaF, *p*H 10, 40 hr., transparent fused silica

Pressure, atmospheres	Charge in % filling 30	40	50	60	70	80
476			245			
408		24.5	218			
340		−9	185	118^a	35^a	25
272			117	50^a		
204	−20	−17	60^a	55^a		5^a

^{a} Unsound growth, encrusted quartz that flaked off. Only the solid, good growth was measured.

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[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] Spezia, *Atti Accad. Torino*, **41**, 132 (1906).

[3] Wooster and Wooster, *Nature*, **157**, 297 (1946).

[4] R. Nacken, Report on Research Contract for Synthesis of Oscillator Crystals, U. S. Army Signal Corps, Interrogations (1946).

[5] Brush Development Co., Cleveland, Ohio; Antioch College, Yellow Springs, Ohio.

[6] Swinnerton, Owen and Corwin, *Discussions Faraday Soc.*, **5**, 172 (1949).

Since the volume of the autoclave was constant in every experiment the effect of concentration of the dissolved halide was studied by keeping the ratio of number of ions present constant, the pressure constant and varying the degree of filling and the temperatures. The results of this series are in Table IV.

TABLE IV

NaF, *p*H 10, 48 hr., 340 atm., transparent fused quartz source

Normality	Charge % filling	Average % increase in weight of seed plate	T., °C.
N/24	30	−1.1	422
N/32	40	1.2	411
N/40	50	185.0	400
N/48	60	66.5[a]	383
N/56	70	46.8[a]	360

[a] Unsound growth. See Table III.

The measurement of *p*H during the course of the reaction is eliminated by the conditions of temperature and pressure. Nearly all of the common insulating materials used in electrical measurements either decompose or are soluble.[7] As a consequence *p*H measurements were made before starting a run and after completion. All attempts to start with a *p*H above 10 or to maintain that *p*H with buffers during an isothermal[8] growth reaction have resulted in disintegration of both the source and seed material. In every run in which growth of the seed occurs there is a reduction in the *p*H of the solution during the run. All attempts to maintain growth below *p*H 6 have failed. With some halides growth terminates at even higher *p*H values. Table V shows the range of the terminal values for the different halide solutions tried.

TABLE V

N/40 halide, starting *p*H 10, 400°, 48 hr., 340 atm., different source materials indicated, charge 50% filling

Halide used	Source material	Terminal *p*H range	Average growth, %
NaCl	Quartz crystal	5–7	None
NaCl	Cristobalite Super-Cel	7–8	1.0
NaCl	Cristobalite natural	6–7	5.0
NaCl	Chalcedony	6–7	9.3
NaBr	Satin-surface fused quartz	6–8	103.0
KBr	Satin-surface fused quartz	8–9	58.0
KCl	Satin-surface fused quartz	7–9	66.0
LiCl	Transparent fused quartz	7–8.5	25.0
NaF	Transparent fused quartz	7–9	185.0
KF	Transparent fused quartz	7.5–9	199.0
LiF	Transparent fused quartz	7–9	175.0

In all experiments except those containing fluoride ions, the growth terminated in 48 hours and further extension of time or replenishment of the solution resulted in no further growth. Table VI shows the effect of extending time in fluoride runs.

TABLE VI

N/40 NaF, starting *p*H 10, 415–416°, 408 atm., transparent fused quartz source, charge 50% filling

Time of run, hr.	*p*H at end of run	Growth weight % added to seed
48	8.5	218
48	9.0	263
96	8.5	251
144	6.5	244

The condition of the interior of the autoclave, the source material and the solutions were strikingly similar in all runs where growth occurred and compared very well with descriptions of isothermal growth made by Van Praagh,[9] Nacken[4] and Wooster.[3] Devitrified or disintegrated source material was found in the bottom along with some unused source material. The sides above the solution line and the top of the autoclave were covered with crystalline deposit. The solution was usually opalescent with suspended material that finally settled out on long standing, but even after two weeks the solutions still showed evidence of a colloidal suspension. The chemical analysis of the solutions and solid material left in the autoclave was complicated by the presence of this suspended material and impurities from the autoclave. Consequently no consistent quantitative results could be obtained. Qualitative spectrographic, X-ray and microscopic examinations were used to evaluate the results of the growth reaction. The data collected by these methods are found in Table VII.

TABLE VII

N/40 halide, starting *p*H 10, 400°, 48 hr., 340 atm., charge 50% filling; solution in autoclave filtered and evaporated to dryness at 110°; solids in autoclave washed and dried at 110°

Source material	Halide used	Sample used	Method of examination	Results
Crystalline quartz	NaCl	Soln.	X-Ray[10]	NaCl
		Solid	X-Ray	Quartz
Cristobalite	NaCl	Soln.	X-Ray	NaCl
		Solid	X-Ray	Cristobalite
Hyflo Super-Cel 100% Cristobalite	NaCl	Soln.	X-Ray	NaCl
		Solid	X-Ray	Quartz and Cristobalite
Fused quartz Satin-surface	NaCl	Soln.	X-Ray	NaCl
		Solids	X-Ray	Quartz
Fused quartz Clear	NaCl	Soln.	X-Ray	NaCl
		Solids	X-Ray	Quartz
Fused quartz Clear	NaF	Soln.	X-Ray	NaF
		Solids	X-Ray	Quartz
Fused quartz Satin-surface	NaCl	Soln.	Spectrographic	In addition to ions placed in autoclave: Cu, Ag, Mo and Fe

When the solutions from the autoclave were just evaporated to dryness there was always X-ray evidence of amorphous material present with the NaCl. When the material was completely washed free of NaCl and dehydrated by ignition below the

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(7) Conductivity measurements at super-critical conditions have been made under this project and reported in another journal[4] but the process has not yet developed to the stage that growth reactions can be followed.

(8) Growth in solutions containing high concentrations of Na_2CO_3 (2 *N*) have been successful at the Bell Telephone Laboratories and the Brush Development Co., but in all cases a thermal gradient of 10 to 20° in the autoclave has been maintained.

(9) Van Praagh, *Discussions Faraday Soc.*, No. **5**, 338–341 (1949); Van Praagh, *Research* (*London*), **1**, 458–464 (1948).

(10) The authors wish to acknowledge the valuable assistance of the Central Research Laboratory of the Monsanto Chemical Co., Dayton, Ohio, for the use of their X-ray and spectrographic equipment and to I. B. Johns and A. H. Herzog for preparation and evaluation of the analyses.

transition point of quartz to cristobalite the amorphous material remained but when ignited to above the transition point X-ray examination showed the presence of cristobalite and amorphous material. Removal of the siliceous material by treatment with hydrofluoric acid left only an unweighable residue but upon treating the crucible with a drop of water the solution gave a positive flame test for sodium.

Discussion

The results in Table I show that for growth of quartz under conditions where there is no temperature gradient in the autoclave, the source material must be chosen so that a solubility gradient is established and the growth is greater when the solubility difference is greater between source and seed. The growth difference between natural quartz, cristobalite and quartz glass is in the same order as their increasing energy contents[11] and increasing temperatures of transition and in turn solubilities. In fact the mechanism of solubility of forms of silica other than quartz in water and alkaline solutions involves the transformation of all or a portion of the source material from its original form into α-quartz. The data in Table I and the X-ray examinations in Table VII substantiate this statement. The same conclusion was reached by others[9,4] in a different manner. The difference in growth between types of fused silica and the state of subdivision of the source material is not only an indication of a difference in solubility, but also a difference in the rate of transformation of the material into α-quartz. The exposure of greater surface to the devitrification effects of the solutions converts the vitreous material to quartz and destroys the solubility gradient so fast that it does not have time to deposit much on the seed.

In order to produce 0.6 g. of good crystalline growth on a seed plate, it is necessary to use approximately 20 g. of fused quartz source material. During the growth the entire amount of source material is devitrified and transformed to α-quartz which is distributed over the inside surface of the autoclave and also formed into an envelope which completely surrounds and takes the form of the original fused silica piece. Similar observations have been made by Wyart,[12] Wooster[3] and Van Praagh.[9]

The perfect nature of the growth of the seed plate when the conditions are optimum and the slowness of the growth seem to indicate that the transfer is made in small units of material. This observation, coupled with the fact that the glassy structure is modified to α-quartz, suggests that single SiO_2 molecules are removed from the glassy mass by the action of the solution, and, in turn, the α-quartz is built up by precipitation of these single molecules on the surface of the seed.

Table V shows that the growth of quartz is closely connected to the *p*H of the solution. When the *p*H of the solution is lowered to neutrality and lower, no growth and little devitrification of the source is evident. Other workers[3,4,9] have reported the same experience.

Considerable information has been collected by Morey[13] and Friedman[14] concerning the ternary systems H_2O–K_2O–SiO_2 and H_2O–Na_2O–SiO_2 at high temperatures. Although most of their experiments involve concentrations much higher than those used in the Antioch Quartz Research, some general conclusions were reached that prove helpful in developing a mechanism to account for quartz growth. These conclusions are as follows: In the system of Na_2O–SiO_2–H_2O, $Na_2SiO_3 \cdot H_2O$ and $Na_2Si_2O_5 \cdot H_2O$ are present, and as the amount of SiO_2 increases, the phase content changes from Na_2SiO_3 to $Na_2Si_2O_5$ at temperatures near 400°. When the Na_2O content is small, quartz and liquid are present. When the $K_2O \cdot SiO_2$ ratio is high and the water content less than 50% at a temperature of 600°, $K_2Si_2O_5 \cdot H_2O$ is present. With a smaller amount of K_2O and a larger amount of water, $K_2SiO_3 \cdot H_2O$ exists when the temperature is held near 400°. Following these trends, the authors suggest that at the low concentration of SiO_2 actually in solution, the transfer ion is either an orthosilicate or a hydrated metasilicate. More complex silicates are possible but the clear crystalline growth on the seed plate favors an ion that furnishes SiO_2 in small increments.

Orthosilicic acid and its salts have been shown to exist in solutions at room temperature.[15,16] The first two ionization constants for orthosilicic acid have been measured by Mukherjee and Chatterjee[17] and Oka, Kawagahi and Kadoya[18] with very good agreement. The postulation of the salts of orthosilicic or metasilicic acids would necessitate a higher *p*H than is present in these solutions, but since it has been shown[19] that the *p*H of the sodium salts of these acids has a negative temperature coefficient, the *p*H during growth will be much lower than those measured at room temperature. In fact, if an extrapolation of the results measured up to 60° is made to 400° the *p*H is on the acid side. On the other hand, the ion product constant for water calculated at 400° is 10^{-10}. If the assumption is made that these changes with temperature result in a balancing effect and that the ratios between the ions present remain constant, then the presence of the monosilicate ions would not be eliminated by the *p*H of the solution.

The actual deposition of SiO_2 on the seed should be the reverse of the solution of the quartz glass and, in that case, the process should be regenerative and the *p*H remain constant. The fact that the *p*H decreases and the presence of alkali halides enhances the growth reaction suggests that these two conditions are interdependent. By examination of Table II it is evident that the fluoride and potassium ions promote growth. J. W. Gruner[20] in a review of silicate structures, called attention to the fact that the OH ion will substitute for the

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[11] F. Singer, *Z. Elektrochem.*, **32**, 385 (1926).

[12] J. Wyart, *Discussions Faraday Soc.*, **5**, 323 (1949).

[13] G. W. Morey, *Proc. Am. Soc. Test. Mat.*, **42**, 980 (1942).

[14] Irving Friedman, THIS JOURNAL, **72**, 4570 (1950).

[15] Willstätter, Kraut and Lobinger, *Ber.*, **61**, 2280 (1928).

[16] Ray, Ganguly and Lal, *Trans. Faraday Soc.*, **38**, 104 (1942).

[17] Mukherjee and Chatterjee, *Nature*, **155**, 85 (1945).

[18] Oka, Kawagahi and Kadoya, *J. Chem. Soc. Japan*, **64**, 718 (1943).

[19] Kuentzel, Hensley and Bacon, *Ind. Eng. Chem.*, **35**, 1286 (1943).

[20] J. W. Gruner, *American Mineralogist*, **33**, 679 (1948).

oxygen atom in many silicate structures while the positive ions like sodium and lithium will substitute for the hydrogen in the OH ion addition. Since all of the experiments result in the formation of a large amount of disintegrated and devitrified material, the inclusion of single OH ions in these structures would account for the decrease in *p*H, especially if a positive ion reacts with the included OH ion to displace the hydrogen. Such a proton displacement would reduce the *p*H. The positive test for sodium on volatilization of the devitrified material after being washed free of sodium ions gives support to this explanation.

The better fit of the lithium ion in silicate structures as shown by Newkirk and Tooley[21] through permeability measurements of alkali–silica glasses to metallic ions would account for the more rapid decrease in *p*H and smaller growth when lithium halide is used.

The ability of the halide ion to promote growth can be explained by referring to Table II which shows that the fluoride ion aids growth more than the other halides. The fluoride ion maintains a more constant *p*H by its ability to form the complex SiF_6^{--}. The replacement of OH or oxygen by fluoride ions in the silica or orthosilicate structures would replenish the solution. The presence of SiF_6^{--} when growth reactions involve fluoride ions has been shown.[3] Although not as well, the bromide and chloride ions could react in the same manner but not exist in the residues at room temperature and pressure.[22] Fluoride ion, Table VI, has the ability to extend the growth time by maintaining a growth *p*H longer while the other negative ions have not succeeded in doing the same thing.

Tables III, IV and V emphasize the fact that good growth depends upon optimum conditions of equilibrium between the rate of solution of the source and rate of deposition on the seed. With a constant surface area of seed, the relation between *p*H, halide concentration and number of water molecules is at *p*H 10, *N*/40 halide and 50% charge. A change in temperature under these conditions simply speeds up or slows down the reaction. Speeding up the reaction by increasing the density of the solution or amount of halide results in furnishing growth ions or molecules to the seed so fast that good crystalline growth is not possible.

[21] Newkirk and Tooley, *J. Am. Ceram. Soc.*, **32**, 272 (1949).

[22] L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Aqueous Solubility of Silver Molybdate and the Ternary Systems Ag_2MoO_4–$AgNO_3$–H_2O and Ag_2MoO_4–Na_2MoO_4–H_2O at 25°

BY JOHN E. RICCI AND WILLIAM F. LINKE

The 25° isotherms of the systems Ag_2MoO_4–$AgNO_3$–H_2O and Ag_2MoO_4–Na_2MoO_4–H_2O show that silver molybdate forms neither double compounds nor solid solutions with the salts from which it is usually prepared by precipitation. The aqueous solubility of silver molybdate is reported for the range 10 to 70°.

Silver molybdate is usually prepared by the interaction of solutions of silver nitrate and sodium molybdate, and it seems important to know whether or not the phase relations of the salts involved would lead one to expect any equilibrium contamination of the precipitate. In the analogous problem of the preparation of silver bromate from aqueous silver nitrate and aqueous sodium bromate, for example, the precipitate of silver bromate forms, with excess of sodium bromate, a solid solution (besides a double salt) with such relations that the precipitate is always contaminated with the sodium salt.[1] Although double salts of silver nitrate with other silver salts are rare,[2] it was decided to investigate the 25° isotherms of both the simple systems involved, Ag_2MoO_4–$AgNO_3$–H_2O and Ag_2MoO_4–Na_2MoO_4–H_2O, for information helpful in the preparation of pure Ag_2MoO_4. In both cases the salt pairs were found to form neither double salts nor solid solution, so that the precipitation method for the preparation of silver molybdate may be expected to give a pure product, except for mechanical contamination. At the same time, the solubility of silver molybdate over a range of temperature was also determined, to extend the available information on this salt.

Reagent grade silver nitrate was used; its purity was checked with various qualitative tests, and its consumption of KCNS was found to remain unchanged both after drying at 110° and after fusion. Sodium molybdate was used as the anhydrous salt obtained by heating the C.P. dihydrate at ~250° as discussed elsewhere.[3]

Silver molybdate was made by the simultaneous dropwise addition, with vigorous stirring, of solutions of silver nitrate and sodium molybdate to a large volume of hot water. The product so prepared, apparently amorphous, is white in color, with sometimes a very pale pink tint from photochemical or thermal decomposition. It was washed repeatedly with water by decantation until no significant flame test for sodium was obtained from either the precipitate or the wash water. The salt was air-dried and then stored in a vacuum desiccator over calcium chloride. The dry material was dissolved in nitric acid and analyzed for silver by titration with standard KCNS solution, and showed a purity of 99.9%. Heating in a drying

[1] J. E. Ricci and J. J. Aleshnick, THIS JOURNAL, **66**, 980 (1944).

[2] For those with AgI, AgBr, AgCN and AgCNS, see K. Hellwig, *Z. anorg. Chem.*, **25**, 157 (1900).

[3] J. E. Ricci and W. F. Linke, THIS JOURNAL, **69**, 1080 (1947).