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THE POLYMERIZATION OF SILICIC ACID OBTAINED BY THE HYDROTHERMAL TREATMENT OF QUARTZ AND THE SOLUBILITY OF AMORPHOUS SILICA

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The polymerization of silicic acid in the solution obtained by treating quartz with water at temperature 400°C and under a specific volume of water 1.6 ml/g was investigated from the changes in the concentration of molecular silica, the results were compared with those already reported, in which the silicic acid prepared from sodium silicate solution was used. The rate of the polymerization of silicic acid showed the maximum at about pH 7.5, and became lower on both sides of this pH. The polymerization reaction seemed to be the second order on the acid side and the third order on the alkaline side with respect to the concentration of molecular silica. The effect of temperature was observed at temperatures from 0 to 100°C, and it was ascertained that the rate of the polymerization increased with temperature. The activation energy was estimated to be 9.8 kcal/mol in the original solution (pH 6.0).

The solubility curve of amorphous silica was obtained by determining the concentrations of monomeric silica in the equilibrium state of polymerization, and the results were compared with those already obtained by the author and his co-worker and others. The heat of solution of amorphous silica was estimated to be 3.2 kcal/mol.

Introduction

The author\(^1\) has studied the solubility equilibrium of silica at high temperatures and pressures. It is of both geochemical and physicochemical interest to know how this equilibrium system changes when it is quenched. The author found that the silicic acid obtained by the hydrothermal treatment of quartz polymerized and reached the equilibrium state when it was left at room temperature.

The study of the polymerization of silicic acid has been carried out by many workers\(^2\) to \(^{12}\).

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1) S. Kitahara, This Journal, 30, 122 (1960)
6) S. A. Greenberg and D. Sinclair, ibid., 59, 435 (1955)
9) R. Richardson and J. A. Wadden, Research, 7, 542 (1942)
The silicic acids used by these workers were almost prepared from sodium silicate solution. The present investigation appears to have the following advantages over these studies: the present silicic acid is not influenced by other ions during the preparation, in addition to the fact that the present transformation of silica resemble the behaviors of silica in the mineral kingdom.

The effects of pH and temperature on the rate of polymerization were studied by measuring the changes in the concentration of molecular silica. The order of the polymerization reaction was determined, and the activation energy was obtained from the relation between the rate of polymerization and temperature. The solubility curve of amorphous silica was obtained from the concentration of monomeric silica in the equilibrium state, and the heat of solution was estimated.

The Polymerization of Silicic Acid

The apparatus and the samples used were the same as in the previous paper. The quartz blocks were treated with pure water in the autoclave at temperature 400°C and under specific volume 2 ml/g for the time required. Then the autoclave was quickly quenched in to cold water and immediately the solution was removed, divided into some parts and stored in polyethylene bottles. The measurements of the concentration of molecular silica were made by a colorimetric method periodically. By this method only molecular silica can be determined in the presence of silica of other forms.

The adjustment of pH was carried out by adding hydrogen chloride or sodium hydroxide solution to the original solution. Temperature was controlled by putting the bottles in the constant temperature baths.

Figs. 1 and 2 represent the effects of pH on the changes in the concentration of molecular silica in the solution on the acid side and the alkaline side respectively. As the changes appeared to depend somewhat on the hydrothermal treatment, it was desirable to use the same original solution in all the measurements. However this procedure was technically difficult. Therefore the original solutions obtained by the respective treatment were used respectively. The curves of the same mark in Figs. 1 and 2 represent the values of measurements obtained from the same original solution. It is seen in Fig. 1 that the change in concentration decreases at lower pH and the change can not be observed at about pH 4.0 for a few days.

It has been ascertained by many workers that molecular silica was stabilized at lower pH. It is seen in Fig. 2 that the change in concentration is most rapid at about pH 7.5 and becomes slower on the both sides of this pH.

The polymerization of molecular silica may be a complex reaction, but simplifying the behavior of silica, as K. Goto has reported, the following equation is assumed to be applicable to the polymerization:

13) S. Kitahara, This Journal, 30, 109 (1960)
The Polymerization of Silicic Acid obtained by the Hydrothermal Treatment of Quartz

where \( C \) is the concentration of molecular silica (\( C_e \) at equilibrium), \( k \) is the rate constant and \( n \) is the order of the reaction. It may be concluded that the polymerization follows the second-order reaction rate on the acid side, and the third-order reaction on the alkaline side by obtaining the value of \( n \) according to Equation (1) using the curves of the changes in concentration of molecular silica represented in Figs. 1 and 2. G. B. Alexander\(^2\) reported that the polymerization might follow the second-order reaction over pH 4.36, and K. Goto\(^3\) studied that the third-order reaction was assumed to be applicable to the polymerization in the alkaline solutions. The present conclusions agree with these informations.

The relations between the rate constant \( k \) and pH were investigated. As might be expected from the curves in Figs. 1 and 2, \( k \) had the maximum at about pH 7.5 and decreased with increasing pH over this value and with decreasing pH below it. K. Goto\(^3\) reported that the polymerization occurred more rapidly at higher pH. On the other hand, A. P. Brady et al.\(^7\) calculated from light scattering measurements that the optimum pH for polymerization was about pH 8, while S. A. Greenberg et al.\(^6\) on the basis of similar experiments, reported a maximum rate of polymerization
at pH 8.6. R. Richardson et al.\textsuperscript{9} found that in the pH range 4\textemdash{}8, polymerization was most rapid between pH 8\textemdash{}9. Iwasaki et al.\textsuperscript{5} stated that the polymerization was most rapid at neutral point. The present results are reasonable in comparison with those reports except Goto's. But at the beginning of polymerization, it is slightly indicated by the curves for the pH range 7\textemdash{}9 in Fig. 2 that the polymerization will occur more rapidly at higher pH, as K. Goto\textsuperscript{9} has reported.

Fig. 3 represents the effect of temperature on the changes in the concentration of the molecular silica in the original solution (pH 6.0). The rate of polymerization increased with temperature. The rate constants at each temperature were obtained on the basis of Equation (1). In Fig. 4, \(-\log k\) was plotted against \(1/T\), and the straight line was obtained. From the slope of this line, the activation energy was estimated to be 9.8 kcal/mol for the polymerization in the original solution (pH 6.0). C. B. Hurd et al.\textsuperscript{3} reported an activation energy of 9\textemdash{}11 kcal/mol in the acid solution. The present value agrees with this value.
The Polymerization of Silicic Acid obtained by the Hydrothermal Treatment of Quartz

Fig. 3 Effect of temperature on the changes in the concentration of the molecular silica

Fig. 4 Relation between \(-\log k\) and \(1/T\)

Solubility of Amorphous Silica

The concentration of molecular silica in the solution decreased with time to a constant value.
In this state the solubility-equilibrium between molecular silica and amorphous silica must be actually established, therefore by measuring this constant values at each temperature the solubility curve of amorphous silica may be obtained. The result is shown in Fig. 5 together with the values already reported by others\textsuperscript{15,16}. The present values are generally lower than others. The solubility values of amorphous silica are variable\textsuperscript{17}, and it is difficult to obtain exactly the same value by the different procedures. For instance, G. B. Alexander et al.\textsuperscript{15} reported that when amorphous silica powder was suspended in water the concentration of monomeric silica increased to a value of 0.014% SiO\textsubscript{2}. On the other hand, in a solution of polysilicic acid supersaturated with monosilicic acid which was permitted to be polymerized for six months, the concentration of monomer decreased until it was about the same value, i.e. 0.012% SiO\textsubscript{2}. The latter value is smaller than the former. As the present procedure is the same as the latter one, it is probable that the present solubility values are lower than the others. The present values are the lowest among the values which have been determined by the author et al.\textsuperscript{17} They appear to be the lower limit of the various solubility values reported till now.

The reasonable chemical equilibrium between amorphous silica and saturated aqueous solution may be represented by the following equation:

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\text{SiO}_2 \text{ (amorphous silica) } + m\text{H}_2\text{O (liquid) } \rightleftharpoons \text{Si(OH)}_4 \text{ aq.}
\]

\textsuperscript{17} S. Kitahara et al., unpublished
The equilibrium constant for this reaction $K_e$ is equal to the activity of the monosilicic acid. Because the concentration of silicic acid in saturated solution is small, it is possible to equate activity with concentration. In Fig. 6, $-\log[\text{Si(OH)}_4]$ was plotted against $1/T$, and the heat of solution $\Delta H$ was estimated to be 3.2 kcal according to the van't Hoff equation. This value was reasonable in comparison with the values 3.4 and 2.65 kcal/mol obtained by K. Goto\(^{18}\) and S. A. Greenberg\(^{19}\) respectively.

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\(^{19}\) S. A. Greenberg, J. Phys. Chem., 61, 196 (1957)