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THE SOLUBILITY EQUILIBRIUM AND THE RATE OF SOLUTION OF QUARTZ IN WATER AT HIGH TEMPERATURES AND HIGH PRESSURES

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The reasonable chemical equilibrium for solution of quartz in water under supercritical conditions seems to be represented by the following equation:

$$SiO_2\,(\text{quartz}) + 2H_2O\,(\text{gas}) \rightleftharpoons Si(OH)_4\,(\text{gas}).$$

The constants K_f and K_c for this equilibrium were calculated using the data already published by the author. From a comparison of K_c as a function of temperature, the heat of solution ΔE was estimated to be 7.80 kcal/mol.

The changes in the amount of dissolved quartz were measured by the quenching method at temperatures 400, 440 and 480°C and under specific volumes of solvents, 3.0, 2.0 and 1.6 ml/g. The following rate equation was found to be applied to the solution of quartz under supercritical conditions: $-dC/dt = kS(Ce - C)/Ce$, where k is the rate constant, C, the concentration of monosilicic acid (Ce at equilibrium) and S, the constant for the surface of quartz. The rate of solution was accelerated by sodium chloride added to water.

PART I Solubility Equilibrium

Introduction

It has not yet been determined what sort of equilibrium is reached for the solution of silica in water. C. S. Hitchen[1] reported that an equilibrium among molecular dispersion, colloidal dispersion and the solid phase, would be the only type to be expected for solubility. It can be represented by the following equation:

solid phase $\rightleftharpoons$ molecular dispersion $\rightleftharpoons$ colloidal dispersion.

A. F. Frederickson and J. E. Cox, Jr.[2] reported from the results of the observation of electron micrographs of withdrawal products from the bomb where the equilibrium existing could be represented by the following equation:

parent crystal $\rightleftharpoons$ solid fragments + silicate ions $\rightleftharpoons$ solid fragments and, or, colloidal dispersion.

On the other hand, G. W. Morey and J. M. Hesselgesser[3] reported that the silica content of the condensed steam was determined by a colorimetric method which was supposed to differentiate molecular silica from colloidal one, the agreement between gravimetric and colorimetric results

1) C. S. Hitchen, *Econ. Geol.*, 40, 361 (1945)
2) A. F. Frederickson and J. E. Cox, Jr., *Am. Mineral*, 39, 886 (1954)
3) G. W. Morey and J. M. Hesselgesser, *Econ. Geol.*, 46, 821 (1951)

was good, and so the silica appeared not to be colloidal but molecular. E. L. Brady[4] attempted to determine the chemical nature of the volatile species in steam by calculating the equilibrium constants for the following equation:

$$SiO_2(\text{solid quartz}) + 2H_2O(\text{gas}) \rightleftharpoons Si(OH)_4(\text{gas}), \quad (1)$$

$$2SiO_2(\text{solid quartz}) + 3H_2O(\text{gas}) \rightleftharpoons Si_2O(OH)_6(\text{gas}). \quad (2)$$

From the results he concluded that $Si(OH)_4$ was the volatile species at steam pressure above a few hundred atm, while at lower pressures a higher molecule, perhaps the dimer $Si_2O(OH)_6$, existed in the vapor phase.

The reasonable chemical equilibrium for solution of quartz in water seems to be represented by Equation (1). The equilibrium constants K_f and K_c for this equation were calculated using the data already published by the author[5]. From a comparison of K_c as a function of temperature, the heat of solution was estimated.

Species of Silica in Steam

The author *et al.*[6] have investigated the state of silica in the solutions obtained by the hydrothermal reaction of quartz. This investigation involves the following informations.

The forms of the silica in the solution obtained by the hydrothermal reactions of quartz, were determined by the following colorimetric methods.

1) The molybdate reagent was added to the solution which was not pretreated.
2) The solution was boiled with sodium carbonate before the reagent was added.
3) The solution was evaporated, the residue was fused with sodium carbonate and the reagent was added.

These methods[7] are supposed to define the difference among molecular, colloidal and crystal silica. The values measured according to these three methods were essentially 3)>2)>1) as might be expected, but the differences between these values were small. These differences seem to be due to the fact that monosilicic acid changed into colloidal or crystal form while the autoclave was quenched. On the other hand, in the solution of amorphous silica in water, the fact that the soluble silica is present as monomeric molecule in the solution has been found by H. and W. Brintzinger[8], G. B. Alexander *et al.*[9,10] and others[11]. From these facts the species of silica in steam under supercritical conditions appear to be the monosilicic acid.

4) E. L. Brady, *J. Phys. Chem.*, **57**, 706 (1953)
5) S. Kitahara, *This Journal*, **30**, 109 (1960)
6) S. Kitahara and H. Oshima, *unpublished*
7) Chem. Soc. Japan, *Lectures on Experimental Chemistry*, **15**, No. 2, 396 (1958)
8) H. and W. Brintzinger, *Z. anorg. allgem. Chem.*, **196**, 44 (1931)
9) G. B. Alexander, *J. Am. Chem. Soc.*, **75**, 2887 (1953)
10) G. B. Alexander, W. M. Heston and R. K. Iler, *J. Phys. Chem.*, **58**, 453 (1954)
11) For the excellent discussion see R. K. Iler, *The Colloid Chemistry of Silica and the Silicates*, Cornell Univ. Press, Ithaca, N. Y. (1955)

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Calculations of Equilibrium Constant and Considerations

Based on the considerations of species of silica in steam, the reasonable chemical equation for the solubility equilibrium of quartz may be represented by Equation (1) as reported by Brady.[4] The equilibrium constant as a function of fugacity, K_f is defined by

$$K_f = f_{Si(OH)_4} / f_{SiO_2} \cdot f^2_{H_2O}, \qquad (3)$$

where f represents the fugacities of all species involved in Equation (1). The fugacities of all species must be known in order to calculate K_f. These values were obtained from the following method using the solubility values already published by the author[5].

The fugacity of steam was obtained from H. Hiraoka's[12] data and W. T. Holser's[13]. The fugacity of SiO_2 (quartz) as a function of pressure was calculated from the following equation,

$$\ln(f_B/f_A) = \int_{P_B}^{P_A} (V/RT)dP, \qquad (4)$$

where f_B/f_A is the ratio of the fugacities in the two states, A and B in which the pressures are P_A and P_B, and V is the molal volume. From these calculations the molal volume of quartz was assumed constant at 22.65 ml/mol. The fugacity of $Si(OH)_4$ could not be obtained from the available data. Therefore it was assumed that the partial pressure is equal to the product of mole ratio and total pressure, and that the fugacity is equal to the partial pressure multiplied by the fugacity coefficient for steam at the same temperature and total pressure.

Table 1 represents the working data. Weight per cent of SiO_2 in steam is the solubility values of quartz already reported by the author[5], and P is the value obtained from the P–V–T relations

Table 1 Working data for the calculation of equilibrium constant

Sp. vol. ml/g	P_{H_2O} atm	f_{H_2O} atm	SiO_2 in steam wt. %	$P_{Si(OH)_4}$ atm	f_{SiO_2} (quartz)
			380°C		
4	234	150	0.018	0.0127	1.10
3.5	234	150	0.023	0.0162	1.10
3.0	240	152	0.030	0.0216	1.11
2.7	246	153	0.036	0.0266	1.11
2.4	254	154	0.044	0.0336	1.12
2.2	263	156	0.053	0.0419	1.12
2.0	276	158	0.067	0.0555	1.12
1.8	337	162	0.087	0.0879	1.15
1.6	484	176	0.112	0.163	1.21
1.5	646	192	0.125	0.242	1.25

12) H. Hiraoka, *This Journal*, 26, 52 (1956)
13) W. T. Holser, *J. Phys. Chem.*, 58, 316 (1954)

(Table 1 *continued*)

Sp. vol. ml/g	P_{H_2O} atm	f_{H_2O} atm	SiO_2 in steam wt. %	$P_{Si(OH)_4}$ atm	f_{SiO_2} (quartz)
			400°C		
4	277	174	0.022	0.0183	1.13
3.5	283	175	0.028	0.0238	1.13
3.0	297	178	0.036	0.0321	1.13
2.7	309	181	0.043	0.0399	1.14
2.4	329	184	0.052	0.0514	1.15
2.2	352	188	0.064	0.0678	1.16
2.0	379	191	0.080	0.0912	1.17
1.8	460	200	0.103	0.142	1.22
1.6	645	223	0.131	0.254	1.31
1.5	819	238	0.147	0.362	1.40
			420°C		
4	319	201	0.027	0.0259	1.15
3.5	335	205	0.034	0.0343	1.15
3.0	358	210	0.044	0.0475	1.16
2.7	373	214	0.052	0.0582	1.16
2.4	403	219	0.063	0.0762	1.18
2.2	436	225	0.076	0.0996	1.20
2.0	479	231	0.094	0.135	1.22
1.8	577	244	0.120	0.208	1.27
1.6	780	273	0.158	0.370	1.37
			440°C		
4	363	228	0.033	0.0363	1.15
3.5	385	234	0.041	0.0476	1.16
3.0	417	241	0.053	0.0668	1.18
2.7	441	247	0.062	0.0825	1.19
2.4	479	255	0.075	0.109	1.21
2.2	522	263	0.090	0.142	1.22
2.0	585	274	0.110	0.195	1.26
1.8	699	292	0.140	0.295	1.31
			460°C		
4	403	255	0.040	0.0484	1.16
3.5	431	263	0.049	0.0632	1.17
3.0	469	270	0.063	0.0888	1.19
2.7	503	279	0.075	0.113	1.20
2.4	560	292	0.092	0.155	1.22
2.2	610	300	0.108	0.198	1.25
2.0	689	316	0.132	0.273	1.28
1.8	820	340	0.165	0.406	1.34

(Table 1 *continued*)

Sp. vol. ml/g	P_{H_2O} atm	f_{H_2O} atm	SiO_2 in steam wt. %	$P_{Si(OH)_4}$ atm	f_{SiO_2} (quartz)
			480°C		
4	445	285	0.047	0.0630	1.18
3.5	479	295	0.059	0.0856	1.19
3.0	527	307	0.075	0.119	1.21
2.7	570	319	0.090	0.155	1.23
2.4	634	335	0.111	0.213	1.26
2.2	698	349	0.130	0.274	1.29
2.0	794	369	0.158	0.379	1.33
			500°C		
4	487	321	0.055	0.0803	1.18
3.5	529	335	0.070	0.111	1.20
3.0	587	352	0.090	0.158	1.22
2.7	638	367	0.106	0.203	1.25
2.4	714	371	0.130	0.278	1.28
2.2	788	407	0.155	0.367	1.31
2.0	900	419	0.187	0.533	1.37

of steam by the author *et al.*[14] and G. C. Kennedy[15]. Table 2 represents the values of K_f. From the table it may be seen that K_f is not constant over the range measured.

The solubility of quartz seems to rather depend simply on the concentration of water molecules than on the pressure of steam as reported by G. C. Kennedy[16]. So the equilibrium constant. K_c as a function of concentration was calculated according to the equation,

$$K_c = [(C_{Si(OH)_4}/V)/(C_{H_2O}/V)^2] \cdot K_T$$
$$K_c = (C_{Si(OH)_4}/C_{H_2O}{}^2) \cdot V \cdot K_T, \qquad (5)$$

Table 2 $K_f \times 10^6$

°C / ml/g	380	400	420	440	460	480	500
4.0	0.330	0.337	0.352	0.381	0.406	0.421	0.436
3.5	0.420	0.426	0.435	0.456	0.476	0.508	0.561
3.0	0.533	0.538	0.546	0.562	0.594	0.607	0.624
2.7	0.637	0.626	0.629	0.637	0.672	0.692	0.696
2.4	0.765	0.738	0.730	0.737	0.776	0.797	0.784
2.2	0.910	0.879	0.846	0.848	0.866	0.870	0.874
2.0	1.13	1.08	0.998	0.965	0.980	0.974	1.03
1.8	1.40	1.26	1.16	1.10	1.09		
1.6	1.58	1.35	1.28				
1.5	1.56	1.35					

14) R. Kiyama, H. Kinoshita and S. Kitahara, *This Journal*, 25, 21 (1955)
15) G. C. Kennedy, *Am. J. Sci.*, 248, 540 (1950)
16) G. C. Kennedy, *Econ. Geol.*, 45, 629 (1950)

where $C_{Si(OH)_4}$ and C_{H_2O} represent mole number of $Si(OH)_4$ and H_2O respectively, V is the volume of the reaction vessel, and $K_T=\gamma_{H_2O}/f_{SiO_2}$, γ_{H_2O} being the fugacity coefficient of water, and f_{SiO_2}, the fugacity of quartz. K_T depends on the pressure; it approaches unity at low pressures, and becomes small at high pressures. Table 3 represents the results of the calculation of K_c. K_c shows better constancy than K_f in the specific volume range investigated. In Fig. 1 the negative

Table 3 $K_c \times 10^6$

°C / ml/g	380	400	420	440	460	480	500
4.0	2.27	2.69	3.40	4.13	4.78	5.42	6.66
3.5	2.54	2.95	3.64	4.22	4.90	5.78	6.98
3.0	2.76	3.14	3.84	4.52	5.06	5.83	7.20
2.7	2.95	3.26	3.98	4.52	5.13	6.00	7.15
2.4	3.10	3.33	4.05	4.60	5.15	6.10	7.20
2.2	3.33	3.55	4.18	4.75	5.12	6.00	7.30
2.0	3.69	3.78	4.31	4.75	5.17	6.00	6.93
1.8	3.58	3.58	4.19	4.68	5.03		
1.6	2.90	2.89	3.74				
1.5	2.40	2.47					

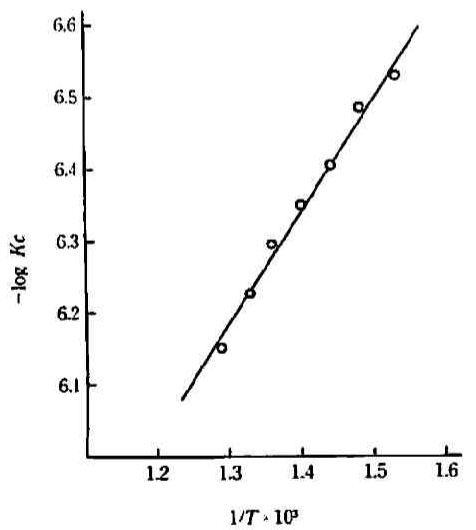

Fig. 1 Relation between $-\log K_c$ and $1/T$

logarithm of the mean value of K_c at specific volume from 4 to 2 ml/g is plotted as a function of the reciprocal of the absolute temperature. According to the van't Hoff equation ΔE value was found to be 7.80 kcal/mol from the slope. S. A. Greenberg[17] evaluated the heat of solution in water at temperatures from 160 to 300°C, and reported it to be 7.34 kcal/mol.

As mentioned above, the heats of solution above and below the critical temperature are in

17) S. A. Greenberg, *J. Phys. Chem.*, 61, 196 (1957)

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agreement with each other. This suggests the same mechanism of solution of silica in water irrespective of state.

PART II The Rate of Solution

G. C. Kennedy[6] reported that the factors such as the temperature, the surface area of the quartz plate, the type of finish, *i. e.* smoothness or roughness of grind, and the orientation of the plate in the quartz crystal effect on the rate of solution of quartz, and that at 360°C the time required for equilibrium is ranged from 4 to 16 hours, and above 500°C equilibrium probably attained in less than 1 hour. L. H. Adams[18] studied that the solution reaction is rapid and in less than 10 minutes the solution is three-quarters saturated. But the rate of solution has not yet been quantitatively mesured. In the present investigation the changes in the amount of dissolved quartz were observed by the quenching method under the conditions that temperatures were 400, 440 and 480°C and specific volumes 3.0, 2.0 and 1.6 ml/g. The rate equation was found to be applied to the solution of quartz under supercritical conditions. The effect of sodium chloride on the rate of solution was also observed.

Experimentals

Apparatus and samples The apparatus and the samples used were the same as the ones used in the previous paper[5]. All the quartz blocks used had the same surface area and the orientation of their faces was constant, as reported in the previous investigation[5]. The surface of the quartz block was not etched by any reagent, and the quartz blocks with faces subjected to the attack of water were used repeatedly without pretreatment.

Procedures The method of determining the amount of the dissolved quartz was the same as the one used in the previous investigation. The five autoclaves were heated in the same electric furnace at the same time. The measurements were carried out by removing and quenching the five autoclaves with time.

Results and Considerations

The results of the measurements are shown in Figs. 2 and 3. Fig. 2 represents the changes in the amount of quartz dissolved in water under conditions that the specific volumes of water are 3.0, 2.0 and 1.6 ml/g at the temperature 440°C, and 3.0 ml/g at the temperatures 400, 440 and 480°C respectively. The equilibrium was attained about 4 hours for each run. Fig. 3 represents the effects of sodium chloride on the changes in the weight loss of quartz. The

18) L. H. Adams, *Carnegie Inst. of Washington, Year Books*, 48, 40 (1949)

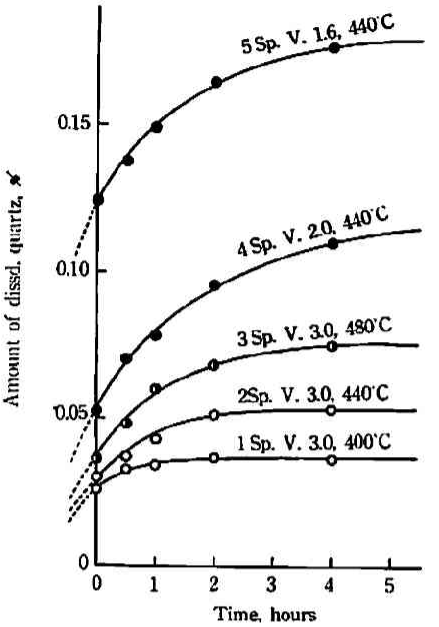

Fig. 2 Changes in the amount of quartz dissolved in water

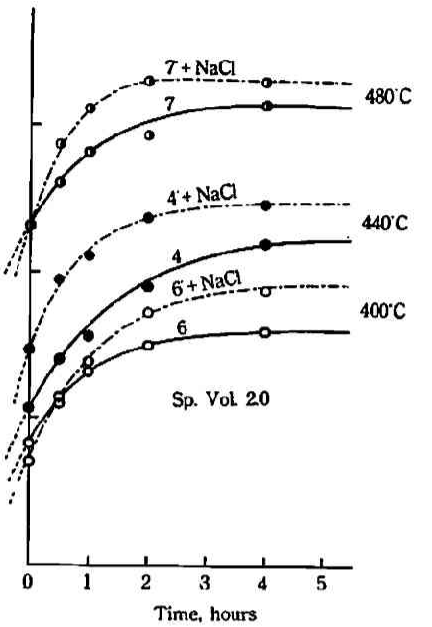

Fig. 3 Effect of sodium chloride on the changes in weight loss of quartz

presence of NaCl increases the rate of solution of quartz as well as the solubility of it. The equilibrium was attained about 3 hours in the aqueous solution of 1% sodium chloride concentration.

The following equation was found to be applied to the solution of quartz under supercritical conditions:

$$-dC/dt = k \cdot S(Ce - C), \qquad (6)$$

where k is the rate constant, C is the concentration of monosilicic acid (Ce at equilibrium) and S is the constant for the surface of quartz. If it is assumed that $C=0$, at $t=0$, then the integral of Equation (6) is

$$\log[(Ce-C)/Ce] = k'St, \qquad (7)$$

where $k'=-k$.

Equation (7) is in the same form as that obtained by assuming that a diffusion step is rate determining[19]. Log[$(Ce-C)/Ce$] was plotted against the time and the straight lines were given as in Figs. 4 and 5. The relative values of rate constant k were obtained from the slopes of these lines. These results are shown in Table 4. It appears that the rate of solution in pure water decreases with increasing Ce. On the other hand, the presence of sodium chloride increases the rate of solution, and the effect of it appears to become greater with temperature at constant specific volume. These results seem to show that the mechanism of solution can not be explained

19) J. Crank, *The Mathematics of Diffusion*, Oxford, (1956)

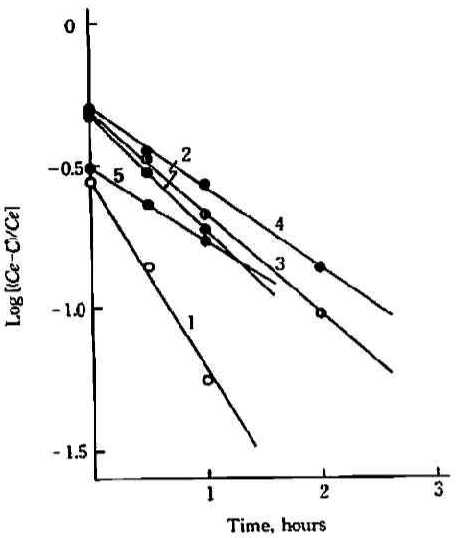

Fig. 4 Relations between $\log[(Ce-C)/Ce]$ and time in water

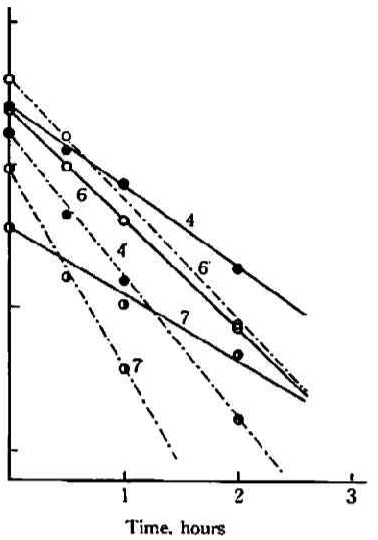

Fig. 5 Effect of sodium chloride on relations between $\log[(Ce-C)/Ce]$ and time in water

Table 4 Relative value of rate constant

Solvent	Temp. °C	Sp. vol. ml/g	Ce %	Relative value of rate constant
Pure water	400	3	0.046	6.8
〃	440	〃	0.053	4.0
〃	480	〃	0.075	3.6
〃	440	2	0.110	2.8
〃	〃	1.6	0.130	2.6
〃	400	2	0.080	3.8
〃	480	〃	0.158	2.8
1% NaCl solution	400	〃	0.098	4.2
〃	440	〃	0.123	5.0
〃	480	〃	0.165	7.0

by the simple diffusion process only. More study should be required to obtain the plausible explanation for the mechanism.

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