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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 $\Delta E$ 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:

$$\text{solid phase} \rightleftharpoons \text{molecular dispersion} \rightleftharpoons \text{colloidal dispersion}.$$

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:

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

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

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[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.

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[4] E. L. Brady, *J. Phys. Chem.*, **57**, 706 (1953)

[5] S. Kitahara, *This Journal*, **30**, 109 (1960)

[6] S. Kitahara and H. Ôshima, *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)

## 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 |

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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 $K_f \times 10^6$

| ml/g \ °C | 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 | | | | | |

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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)

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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 $K_T = \gamma_{H_2O}/f_{SiO_2}$, $\gamma_{H_2O}$ 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 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 $\Delta E$ 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.

Table 3 $K_c \times 10^6$

| ml/g \ °C | 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 | | | | | |

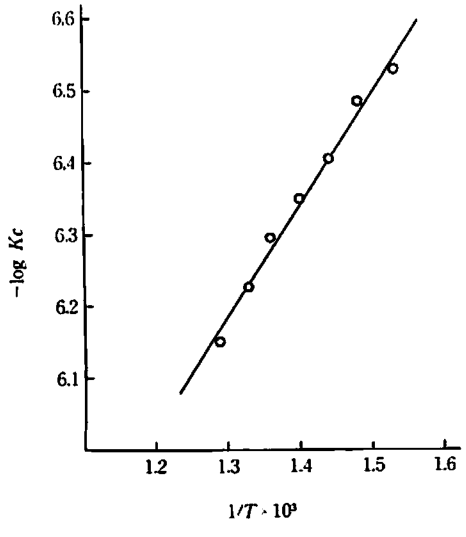

Fig. 1 Relation between $-\log K_c$ and $1/T$

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

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

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

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

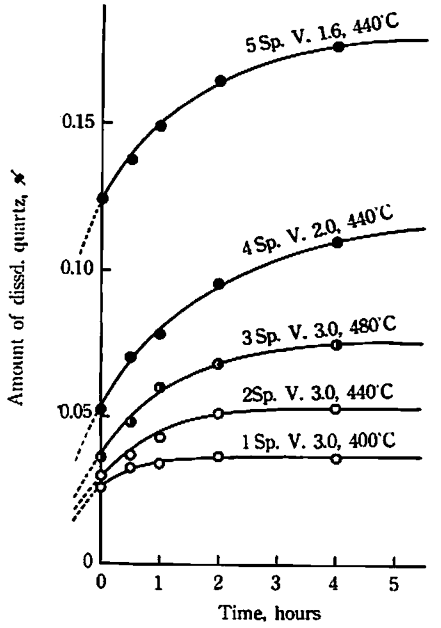

Fig. 2 Changes in the amount of quartz dissolved in water

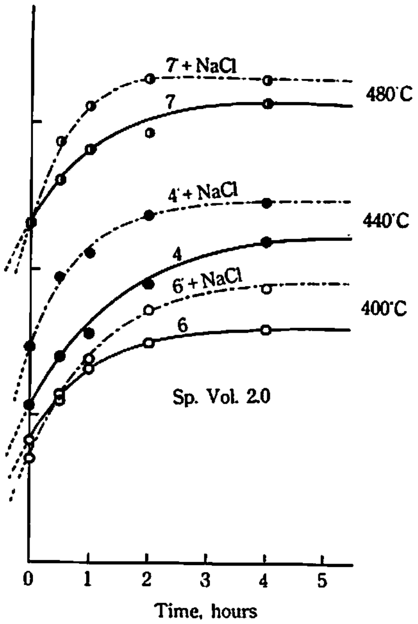

Fig. 3 Effect of sodium chloride on the changes in weight loss of quartz

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 $C=O$, 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]. $\mathrm{Log}[(Ce-C)/Ce]$ 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

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

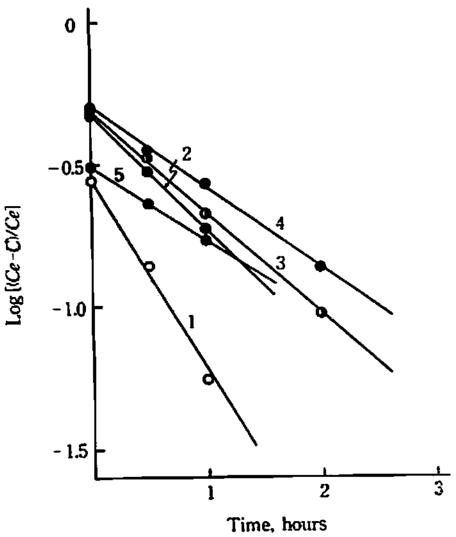

Fig. 4 Relations between log[$(Ce-C)/Ce$] and time in water

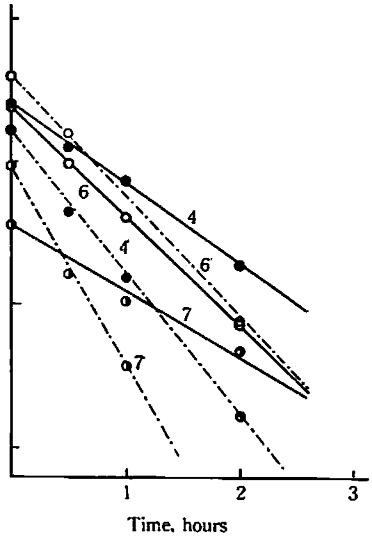

Fig. 5 Effect of sodium chloride on relations between log[$(Ce-C)/Ce$] and time in water

Table 4 Relative value of rate constant

| Solvent | Temp. °C | Sp. vol. ml/g | $Ce$ % | Relative value of rate constant |
|---|---|---|---|---|
| Pure water | 400 | 5 | 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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