THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 30, NO. 2, DEC. 1960

THE SOLUBILITY OF QUARTZ IN WATER AT HIGH TEMPERATURES AND HIGH PRESSURES

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(*Received October 31, 1960*)

The solubility of quartz in water was measured at the temperature range up to 500°C and at the pressure range up to 900 atm by observing the loss in the weight of quartz blocks in contact with water. The measurements were made along the three-phase boundary, quartz-gas-liquid, and in the two-phase field, quartz-gas, under supercritical conditions. The present values are generally lower than those already published, and the maximum value for the discrepancy is about 10 per cent. The solubility is proportional to the fugacity under supercritical conditions except the portion under higher pressures at temperatures below 420°C, provided that the temperature is kept constant.

Introduction

The solubility of quartz in water at high temperatures and high pressures is important from the geochemical standpoint, and the determination of it was made by G. C. Kennedy¹⁾, G. W. Morey *et al.*²⁾ and others³⁾. The author has a plan to determine the solubility of quartz in the aqueous sodium chloride solution. As the preceding work of it, the present investigation was made. Comparing the results of the present investigation with the data already published, some discrepancy was found between the two data.

Experimentals

Samples *Quartz block* The natural transparent quartz crystal produced in Brazil was cut in about 5×10×15 mm blocks parallel to the basal plane and the prism face, and vertical to both the basal plane and the prism face. Early in the measurement the blocks were frosted and then etched with a mixture of hydrogen fluoride and ammonium fluoride before each run, but no change was found in the solubility values, whether this treatment was taken or not. Therefore in the subsequent measurement the quartz blocks were only washed and dried.

Water Distilled water was employed.

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1) G. C. Kennedy, *Econ. Geol.*, **45**, 629 (1950)
2) G. W. Morey and J. M. Hesselgesser, *ibid.*, **46**, 821 (1951)
3) C. J. van Nieuwenburg and P. M. van Zon, *Rec. trav. chim. Pays-Bas*, **54**, 129 (1935)
L. H. Adams, *Carnegie Inst. of Washington, Year Books*, **48**, 40 (1949)
N. I. Khitarov, *Geokhimiya*, **1**, 62 (1956)

Apparatus The apparatus used was the same as the one in the investigation on the *P–V–T* relations of aqueous sodium hydroxide solutions4). But the solubility measurement was made without the pressure gauge, because the *P–V–T* relations of water were already measured by the author and co-workers5) and others6).

Procedures Measurement was made by the constant volume method. A given quantity of water was put into the autoclave and the two quartz blocks are weighed and suspended in it by the loops of silver wire. The autoclave was then sealed and heated for the time sufficient to attain to equilibrium. The autoclave was quickly quenched into cold water: the quartz blocks removed, washed, dried and reweighed. Once the equilibrium between the quartz and the solution was established, the loss in the weight of the quartz blocks, in addition to the amount of water in the autoclave, gave the solubility value at the temperature and pressure.

After a run the amount of silica in the solution in the autoclave was also determined by gravimetry. The solubilities determined by this method were sometimes a few per cent lower than those determined by the weight change of the quartz block. It seems that such lower values will be attributed to the silica which adheres tightly to the wall of the autoclave when it is quenched.

Results and Considerations

The solubility in the three-phase field The results of the measurements are given in Table 1 together with the data published by G. C. Kennedy1). The present solubility values are plotted with Kennedy's values in Fig. 1. The time required for equilibrium is determined by the results of Kennedy's investigation. It is confirmed that this time is sufficient for equili-

Table 1 The solubility in the three-phase field

Temperature °C	Pressure atm	Time hr	Solubility weight %	
			This work	G. C. Kennedy
140	4	120	0	
160	6	120	0.008	0.007
200	15	120	0.026	0.027
240	33	120	0.045	0.043
280	63	96	0.058	0.063
300	87	96	0.062	0.068
320	113	48	0.065	0.071
340	145	48	0.065	0.071
360	184	24	0.053	0.056
370	208	24	0.025	0.023

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4) R. Kiyama and S. Kitahara, *This Journal*, **27**, 48 (1957)
5) R. Kiyama, H. Kinoshita and S. Kitahara, *ibid.*, **25**, 21 (1955)
6) G. C. Kennedy, *Am. J. Sci.*, **248**, 540 (1950)

brium to be established. The error of the solubility values is probably 1%, and it is almost attributed to the error in observing the weight change of the quartz blocks.

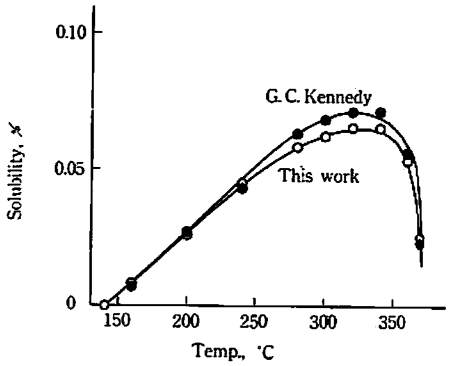

Fig. 1 Solubility curves in the three-phase field

At 140°C the solubility of quartz is so small that it cannot be measured by the present methods. The solubility rises at a constant rate until the temperature of approximate 330°C, and at temperatures above this, the solubility falls off sharply until the critical temperature. The present values are about 10% smaller than Kennedy's values at temperatures from 240 to 360°C.

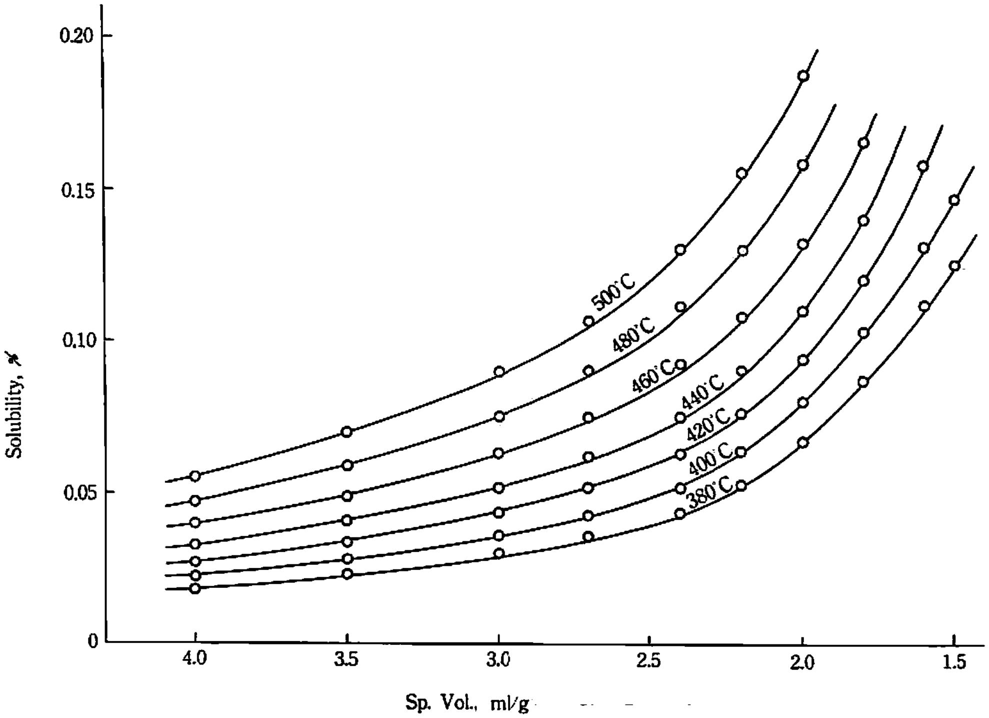

Fig. 2 Isothermal solubility curves under the supercritical conditions

Table 2 The solubility under the supercritical conditions

weight %

Temp., °C / Sp. vol. ml/g	380	400	420	440	460	480	500
4.0	0.018	0.022	0.027	0.033	0.040	0.047	0.055
3.5	0.023	0.028	0.034	0.041	0.049	0.059	0.070
3.0	0.030	0.036	0.044	0.053	0.063	0.075	0.090
2.7	0.036	0.043	0.052	0.062	0.075	0.090	0.106
2.4	0.044	0.052	0.063	0.075	0.092	0.111	0.130
2.2	0.053	0.064	0.076	0.090	0.108	0.130	0.155
2.0	0.067	0.080	0.094	0.110	0.132	0.158	0.185
1.8	0.087	0.103	0.120	0.140	0.165		
1.6	0.112	0.131	0.157				
1.5	0.125	0.147					

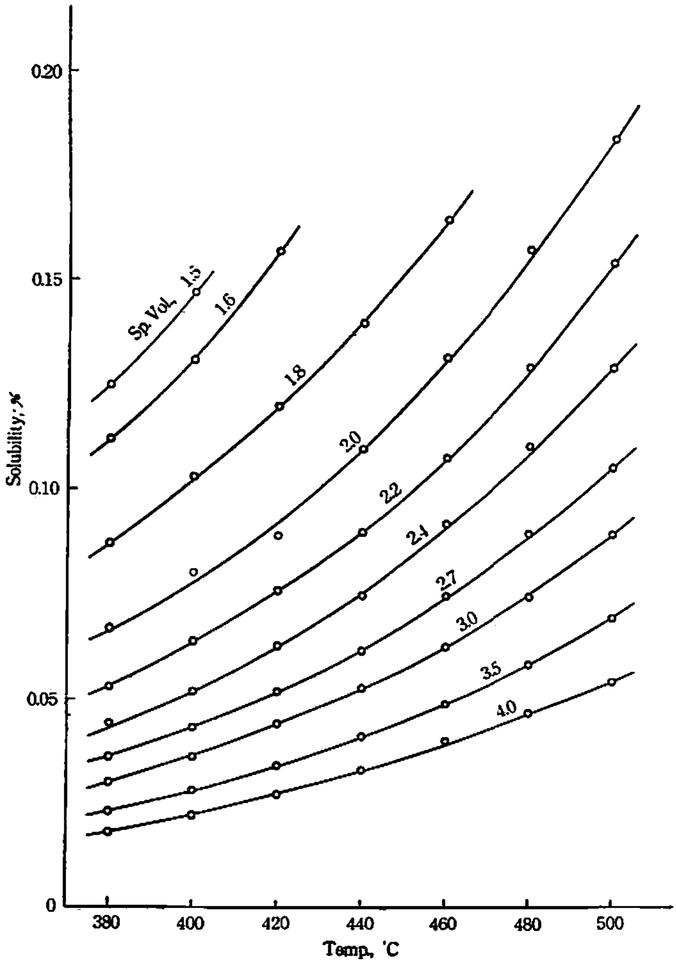

Fig. 3 Isovolumetric solubility curves under the supercritical conditions

The solubility under the supercritical conditions The results of the measurements are given in Table 2. The time of reaction is from 18 to 24 hours. Fig. 2 shows the isothermal solubility curves. Fig. 3 shows the isovolumetric solubility curves. The solubility increases with the density of water and temperature. The comparison between the results of the present investigation and the data published by G. C. Kennedy[1] and G. W. Morey *et al.*[2] at 400 and 500°C, is given in Fig. 4. The present solubility values are plotted in the middle of those by G. C. Kennedy and G. W. Morey at 400°C, and are about 10% smaller than the higher one of their values at 500°C. The solubility values in the three-phase field are also smaller than Kennedy's. This discrepancy will result from the difference of the material of the quartz crystal.

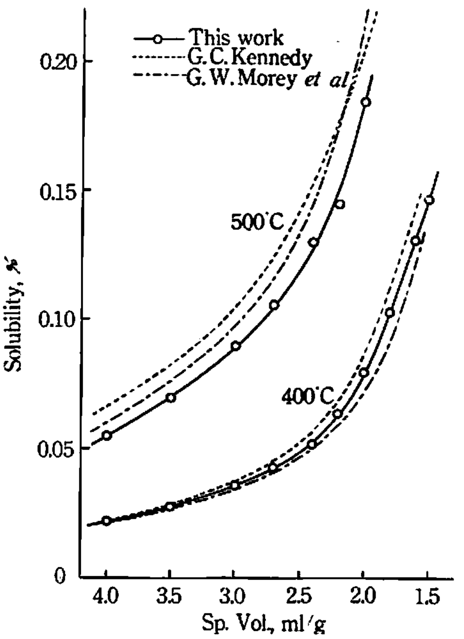

Fig. 4 Comparisons between this work and others at 400 and 500°C

The *P–V–T* relations at temperatures up to 460°C are obtained from the data published by the author *et al.*[5] and above 460°C from the data published by G. C. Kennedy[6]. The fugacities at temperatures up to 460°C and above 460°C are obtained from Hiraoka's[7] data and W. T. Holser's[8] respectively. Fig. 5 shows the solubility-fugacity relations at each temperature. The solubility-fugacity curves are almost linear except the portion under higher pressures at temperatures below 420°C, provided that the temperature is kept constant.

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7) H. Hiraoka, *This Journal*, 26, 52 (1956)

8) W. T. Holser, *J. Phys. Chem.*, 58, 316 (1954)

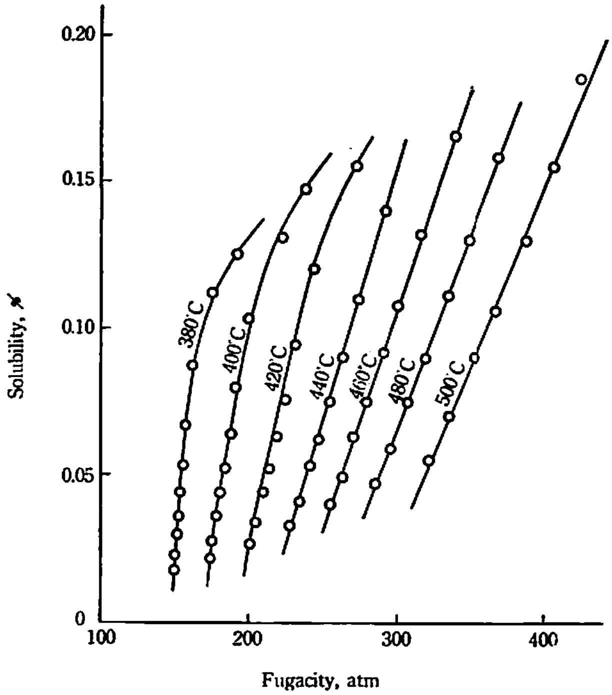

Fig. 5 Relations between solubility and fugacity

The author has great pleasure in expressing his sincere thanks to the late Prof. Ryo Kiyama under whose direction this work started. and to Prof. Wasaburo Jono for his valuable guidance and encouragement throughout this work. The author wishes to thank Dr. Hiroshi Teranishi for his discussion and assistance.

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