

## THE SOLUBILITY OF QUARTZ

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The surface structure of finely ground quartz particles, ranging in size from 1 to 50  $\mu$ , was studied by dissolution measurements in NaOH solutions. The results indicate the presence of a disturbed surface layer. The thickness of this layer is estimated to be approximately 300  $\text{\AA}$ , a result agreeing with values reported by other workers. After removal of this disturbance, the solubilities of quartz in  $\text{H}_2\text{O}$ ,  $10^{-2} N$  NaCl solutions and  $10^{-2} M$  borax solutions were measured at temperatures ranging from 60 to 100°. The solubility of quartz in  $\text{H}_2\text{O}$  at these temperatures is shown to be in good agreement with the solubilities above 180° as measured by Kennedy.<sup>3</sup> The solubility of quartz in  $\text{H}_2\text{O}$  follows the empirical equation,  $\log c = 0.151 - 1162/T$  ( $c$  expressed in moles of  $\text{SiO}_2$  per kg.) from 25 up to 473°. The extrapolated solubility at 25° is  $1.8 \times 10^{-4}$  mole/kg. The standard heat, the standard entropy and the standard free energy of the dissolution reaction were calculated. The rate constant of the dissolution reaction at 25° is of the order of  $10^{-18}$  g. of  $\text{SiO}_2$  per  $\text{cm}^2$  surface per second. The rate of dissolution is not controlled by diffusion. The reaction is strongly accelerated by the presence of NaCl in concentrations below  $10^{-1} N$ , without any measurable effect on the position of the equilibrium. If  $10^{-1} N$  NaCl is used, the solubility increases in addition to the increase in reaction velocity.

## Introduction

Only a few measurements of the solubility of quartz at room temperature are reported in the literature. Gardner<sup>4</sup> mentions a value of  $1 \times 10^{-4}$  mole/kg. without specification of method and particle size. Lenher<sup>5</sup> gives a value of  $5 \times 10^{-3}$  mole/kg. for particles of 4  $\mu$  in diameter. Paterson and Wheatly<sup>6</sup> found a constant concentration of  $1.8 \times 10^{-4}$  mole/kg. for an HF-treated quartz sample (0.5–2  $\mu$  in diameter) after successive leachings with Ringer's solution<sup>7</sup> at 37°. They expected this value to be close to the solubility of quartz. Kennedy<sup>3</sup> concluded from his measurements in the hydrothermal temperature range that quartz is essentially insoluble at room temperature. Stöber<sup>8</sup> and Baumann<sup>9</sup> consider the dissolution of quartz in water at room temperature as an irreversible process. In the opinion of these authors, the only species participating in the equilibrium is silica gel. For this hypothesis to be true, quartz would have to be less stable thermodynamically than silica gel. No experimental evidence is found in the literature supporting this hypothesis.

Several authors in the field of silicosis research have worked with fine quartz dust. Gibb<sup>10</sup> and co-workers presented evidence for the existence of a layer of highly disordered structure on the surface of finely ground quartz particles. Their estimate of the thickness of this layer is about 300  $\text{\AA}$ . The presence of a disturbance of considerable depth on the ground quartz particles was also concluded by others.<sup>11–13</sup>

## Experimental

**Materials.**—Large colorless crystals of Brazilian quartz were crushed. Material finer than 3 mm. in diameter was screened out and discarded. Further reduction was carried out in a roll crusher. The fraction containing particles between 3 and 0.5 mm. was collected and kept for fine grinding. This fraction was cleaned repeatedly in hot 1  $N$  HCl solution and washed free from HCl with distilled water. The final grinding was carried out between two fused silica discs of optical quality. The ground quartz was sized by sedimentation in distilled water. The sized material was dried at 110°.

For the preliminary studies at room temperature three size ranges of quartz were used; 1–5, 5–25 and 25–50  $\mu$  with respective specific surfaces of 21,500, 3400 and 1150  $\text{cm}^2/\text{gram}$ . The studies at elevated temperatures were made with narrower size ranges; 3–5, 5–10 and 10–15  $\mu$  with respective surfaces of 10,000, 5000 and 3200  $\text{cm}^2/\text{gram}$ . The surface area measurements<sup>14</sup> were obtained by the B.E.T. method with krypton gas as adsorbate. The determinations were made at  $-195^\circ$  and a value of 19.5  $\text{\AA}^2$  was used for the cross-sectional area of the krypton molecule.

In the initial phase of this work the quartz was used without any further treatment. In later stages of this investigation some additional treatments were necessary. These additional treatments will be referred to as Methods I and II. Method I consisted of washing the quartz with an HF solution. The strength of the solution (9–15% HF by weight) and the amount of quartz (up to 10 g. per 50 ml. of HF solution) were chosen such that approximately 25% of the quartz was dissolved within 5 minutes. The HF was removed by successive washings with NaOH solutions of decreasing strength (0.1, 0.01 and 0.001  $N$ ). The NaOH was removed by repeated washings with conductivity water and then the quartz was dried in a vacuum desiccator over  $\text{P}_2\text{O}_5$ . Method II included the HF treatment of Method I followed by agitation of the quartz in 0.1  $N$  NaOH at 90° for 20 to 30 days until a constant  $\text{SiO}_2$  concentration independent of particle size and amount of quartz was reached. The NaOH was removed by washing the quartz with conductivity water. The specific surface of the quartz decreased as a result of this further treatment, values of 7500, 3600 and 2300  $\text{cm}^2/\text{g}$ . were obtained for the 3–5, 5–10 and 10–15  $\mu$  size ranges, respectively.

All chemicals used were of reagent grade and with the exception of NaCl were not further purified. The NaCl used in the dissolution rate experiments was further purified by precipitating it from a near-saturated solution in conductivity water by the addition of absolute alcohol. Double

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(3) G. C. Kennedy, *Econ. Geol.*, **45**, 629 (1950).(4) L. U. Gardner, *Mining Technology*, **2**, A.I.M.E. Techn. Publ. 929.(5) V. Lenher, *J. Am. Chem. Soc.*, **43**, 391 (1921).

(6) M. S. Paterson and K. H. Wheatly, Safety in Mines Research Establishment, Research Report Number 124 (Dec. 1955).

(7) Ringer's solution is made up of a solution of chlorides of potassium, sodium, calcium and magnesium in concentrations comparable to those in blood. Paterson and Wheatly added dimethylglyoxaline to keep the pH at 7.4.

(8) W. Stöber, *Kolloid-Z.*, **147**, 131 (1956).

(9) H. Baumann, "Beiträge zur Silikose-Forschung," Heft 37 (Bochem 1955).

(10) J. Gibb, P. D. Ritchie and J. W. Sharpe, *J. Appl. Chem. (London)*, **3**, 182 (1953).(11) A. F. Boyer, *Bull. soc. franc. mineral. et crist.*, **77**, 116 (1954).(12) R. L. Gordon and G. W. Harris, *Nature*, **175**, 1135 (1955).

(13) A. J. Beal and A. L. Godbert, Safety in Mines Research Establishment, Research Report Number 115 (1955).

(14) R. Tregan, *Compt. rend.*, **241**, 219 (1955).(15) O. S. Heavens, *Acta Cryst.*, **6**, 571 (1953).(16) G. S. Khodakow and E. R. Plutskis, *Dokl. Akad. Nauk. S.S.S.R.* **123**, 725 (1958).(17) M. Cignitti and A. Uva, *Ricerca Sci.*, **28**, 1915 (1958).(18) J. A. Waddams, *Research (London)*, **11**, 370 (1958).

(19) These measurements were made by Mr. S. Mitchell of the Metallurgy Department at MIT.

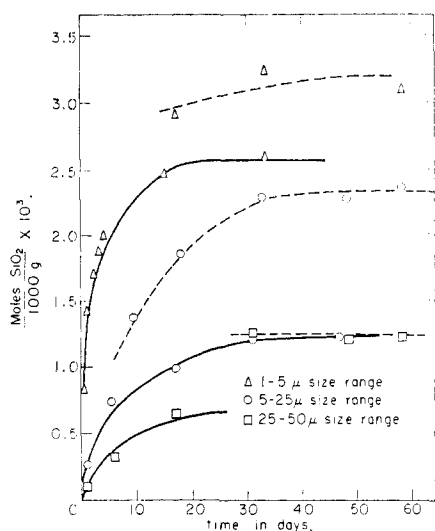


Fig. 1.—Dissolution rate of quartz in  $10^{-3}$  N NaOH at  $25^{\circ}$ .

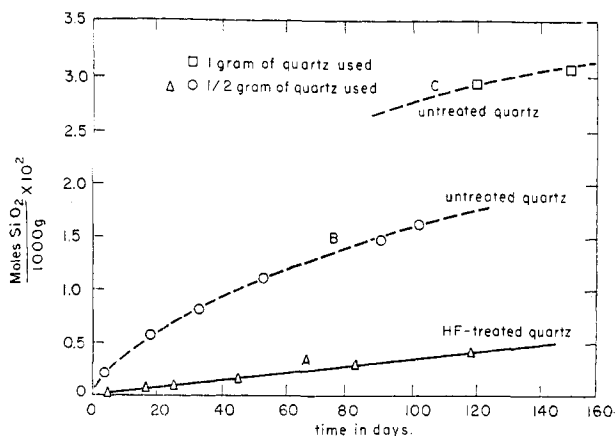


Fig. 2.—Dissolution rate of  $1-5 \mu$  quartz particles in  $10^{-1}$  N NaOH at  $25^{\circ}$ .

distilled water of a specific conductance lower than  $5 \times 10^{-7}$  ohm $^{-1}$ cm. $^{-1}$  was used throughout the work.

Polyethylene bottles of 35-ml. capacity were used for the measurements at room temperature. At higher temperatures a stainless steel tube, 80 mm. long, 25 mm. in diameter and 3.75 mm. thick was used. These cylinders were fitted with Pt tubes of 0.125 mm. thickness. A vapor-tight seal on these containers was obtained as follows: the Pt-liner had a flange resting on the wall of the stainless steel container, a thin Pt-Ruthenium ring (diameter 0.125 mm.; 5% Ru) was soldered onto this flange with pure gold, then the top of the container was covered with a thin disc of pure gold (thickness 0.0075 cm.) and a Teflon disc was placed on top of the gold disc. Thus upon tightening the stainless steel screw cap the ring pressed the gold into the Teflon and a perfect seal was obtained. The reaction vessels were attached to stainless steel racks which were placed on the bottom of the constant temperature water or oil-baths. The assemblage was rotated at a constant speed of 30 r.p.m.

**The pH-measuring Cell.**—The cell consisted of a 1-liter Pyrex beaker filled with saturated (at  $25^{\circ}$ ) KCl solution, containing the calomel reference electrode. A small wide-mouthed polyethylene bottle (Ziegler-type) was suspended in the KCl solution. This bottle served as compartment for two platinized Pt electrodes. Thus the solution of which the pH had to be measured did not come in contact with glass. The two solutions were in electrical contact through a small hole (0.015 cm.) in the bottom of the polyethylene bottle. To ensure a flow of KCl into the solution to be measured, the level of the KCl solution was always kept approximately 0.5 cm. higher than the level of the solution inside the hydrogen electrode compartment. The hydrogen

was purified by bubbling it through two wash bottles filled with alkaline pyrogallol, one wash bottle containing chromous chloride dissolved in 1.5 N HCl in contact with Zn-amalgam, one wash bottle containing 37% KOH solution and finally through two wash bottles filled with conductivity water. From here the  $H_2$  was led into the measuring cell via a copper spiral 3 meters in length, immersed in the constant temperature bath.

The cell was calibrated by using a  $10^{-2}$ M borax solution for which the pH was determined by Bates<sup>20</sup> from 0 to  $95^{\circ}$ .

**Experimental Techniques.**—The procedure used in making solubility measurements was straight-forward. The amounts of quartz used in the experiments were varied but approximately 30 g. of solvent was used in most experiments except in those tests with large amounts of quartz when the quantity of solution was slightly reduced. It should be mentioned that at elevated temperatures more than one sample was taken from the same Pt-lined steel container for analysis. Some time before a sample was to be taken, the container was removed from the agitator and placed on the bottom of the constant temperature bath to allow the quartz to settle at the measuring temperature. Then the container was removed from the bath, a sample (0.5–1.5 g.) was taken and the container was returned to the bath.

**Analytical Method.**—The amount of silica in solution was determined colorimetrically by the molybdenum blue method. For the formation of the yellow silica-molybdate complex the recommendations of Strickland<sup>21</sup> were followed. The yellow complex was reduced by an acidic-metol-sulfite solution. This method of reduction was developed by Mullin and Riley.<sup>22</sup> The advantage of this method over other reduction methods is the stability of both the reducing solution as well as the reduced blue complex. The extinction of the blue solution does not change over a period of up to 5 days. The extinction was measured in a Beckman D. U. spectrophotometer using a one cm. cell at 810 m $\mu$  and a slit width of 0.03 mm. Conductivity water to which the same reagents were added, was used as a blank. The calibration was carried out with solutions containing accurately known amounts of  $Na_2SiO_3 \cdot 9H_2O$ . Duplicate  $SiO_2$ -determinations did not differ by more than 0.2%.

## Results

**Nature of the Quartz Surface.**—Figure 1 shows the results of a series of experiments at room temperature in  $10^{-3}$ N NaOH solutions. The dotted curves in Fig. 1 indicate experiments in which twice as much quartz was used as in the experiments represented by the solid curves. For both the 5–25 and 25–50  $\mu$  size ranges the concentration of  $SiO_2$  in solution after about 20 days is proportional to the amount of quartz in suspension. This is not the case in the experiments with quartz of the 1–5  $\mu$  size range. The solid curve for the 1–5  $\mu$  size range shows a final concentration of  $2.5 \times 10^{-3}$  mole/kg., the dotted curve for the same size range approaches a concentration of approximately  $3.3 \times 10^{-3}$  mole/kg. This is perhaps not surprising because the solubility of amorphous silica at the final pH in these experiments (9.4–9.5) is also approximately  $3.3 \times 10^{-3}$  mole/kg.<sup>23</sup>

The picture suggested by Fig. 1 agrees with the presence of a superficial amorphous layer on the quartz particles. Estimates of the layer thickness in the literature vary from 300–1000 Å. To check on these estimates, a few experiments were carried out in a 0.12 N NaOH solution because the more alkaline solution would dissolve cracked structures

(20) R. G. Bates, "Electrometric pH Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 74.

(21) J. D. Strickland, *J. Am. Chem. Soc.*, **74**, 862 (1952).

(22) J. B. Mullin and J. P. Riley, *Anal. Chim. Acta*, **12**, 162 (1955).

(23) G. B. Alexander, W. H. Heston and R. K. Iler, *This Journal*, **58**, 453 (1954).

and small fragments in addition to any amorphous silica. The results of some of these experiments are shown in Fig. 2. It is clear that the "layer effect" is considerably stronger than would be concluded from the experiments at lower pH (Fig. 1). The thickness of the disturbed layer as estimated from the experiments at high pH is approximately 300 Å. To check whether any amorphous silica was present in suspension a series of experiments were run in which the silica concentration was determined both gravimetrically and colorimetrically. The results are given in Table I.

TABLE I

COMPARISON OF THE RESULTS OF GRAVIMETRIC AND COLORIMETRIC ANALYSIS

Agitation time, days	Amt. of quartz, g.	Concn. SiO <sub>2</sub> , mole/kg. × 10 <sup>2</sup>		Final pH
		Colorimetric	Gravimetric	
3	0.5464	1.8	..	12.40
10	.5737	3.1	3.1	12.46
17	.7023	4.7	4.9	12.20
31	.5293	4.8	5.3	12.20
52	.4088	4.8	5.1	12.34
74	.3854	4.8	5.3	12.30

This table shows no significant differences in concentration between the results of both methods, indicating the absence of amorphous silica in the suspensions.

After the results reported above had been obtained it was clear that a "clean" quartz surface was necessary for solubility measurements. This was accomplished by washing the quartz with HF solution according to treatment Method I. The result of this treatment is shown in Fig. 2. The low rate of dissolution (about  $7 \times 10^{-15}$  mole SiO<sub>2</sub>/cm.<sup>2</sup> sec.) and the fact that there is a straight-line variation between concentration and time suggest the dissolution of one species only. Quartz treated in this way was also used for the experiments at elevated temperatures.

Figure 3 shows the results of a series of experiments at 90° in 10<sup>-3</sup> N NaOH solution. The amount of quartz was varied from 1 to 4 g. The final pH in the horizontal part of the curve was  $8.95 \pm 0.05$  (at 90°), whereas the pH was 0.1 to 0.2 unit lower along the hump in the curve. The occurrence of the hump is probably the result of damage done to the particle surfaces by the HF treatment. Small fragments broken off from the quartz particles will have a higher solubility and thus tend to supersaturate the solution with respect to the larger particles. To prevent the occurrence of supersaturation in subsequent experiments, the quartz was given an additional treatment according to Method II.

**Solubility Studies at Elevated Temperatures.**—Measurements in water and 10<sup>-2</sup> N NaCl solutions were carried out at 5 different temperatures. The results at 100, 90, 80 and 70° are shown in Figs. 4 to 7 and those at 60° in Table II. Shaded symbols in these figures indicate experiments in 10<sup>-2</sup> N NaCl, open symbols indicate experiments in H<sub>2</sub>O and crosses indicate experiments in 10<sup>-4</sup> N NaOH solutions. These figures illustrate the approach to equilibrium from above and below.

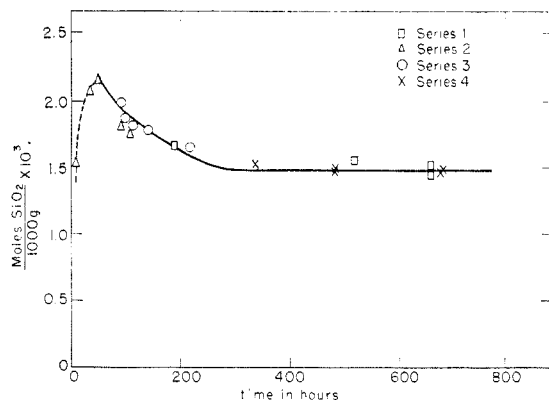


Fig. 3.—Solubility of quartz in 10<sup>-3</sup> N NaOH at 90°; size ranges 2-5 μ and 5-10 μ.

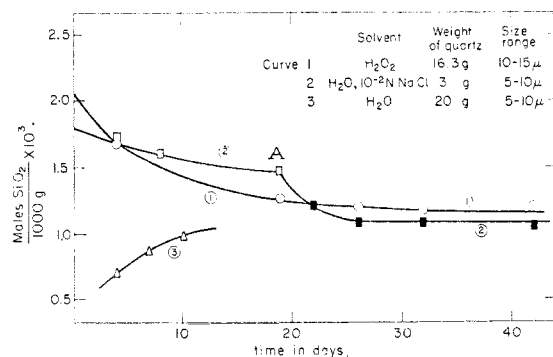


Fig. 4.—Solubility of quartz in H<sub>2</sub>O and 10<sup>-2</sup> N NaCl at 100°.

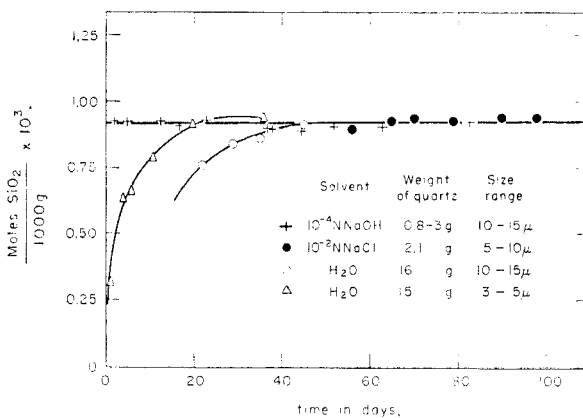


Fig. 5.—Solubility of quartz in H<sub>2</sub>O, 10<sup>-2</sup> N NaCl and 10<sup>-4</sup> N NaOH solutions at 90°.

At 100°, samples were taken after quenching the containers in ice-water. The high starting concentrations (Fig. 4 and Table II) were obtained by heating container and contents in a drying oven at 135° for 24 hours prior to the start of an experiment. Curve 2 in Fig. 4 is the result of an experiment in water, to which at point A (after a sample had been taken) a small amount of 10<sup>-1</sup> N NaCl solution was added to yield an NaCl concentration of approximately 10<sup>-2</sup> N. The second part of curve 2 shows a strong acceleration of the recrystallization of quartz by NaCl. The total surface area of quartz used to determine curve 1 was roughly four times that of the quartz used in establishing curve 2.

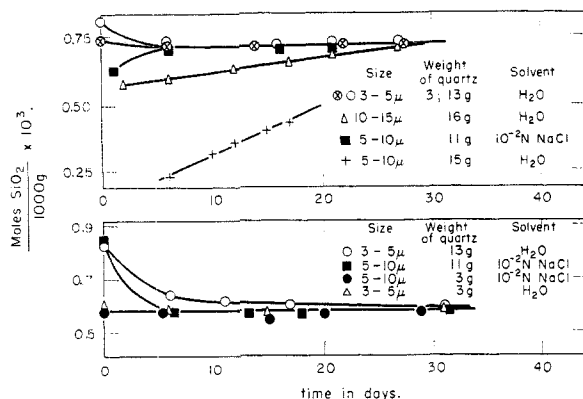


Fig. 6.—(Top) rate of dissolution of quartz at 80°.

Fig. 7.—(Bottom) rate of dissolution of quartz at 70°.

TABLE II

DATA OBTAINED AT 60° IN 10<sup>-2</sup> N NaCl SOLUTION

Amt. of quartz, g.	Amt. of solvent, g.	Size range of quartz, μ	Reaction time, days	Concn. SiO <sub>2</sub> (moles/kg. × 10 <sup>4</sup> )	
				Final	Initial
10.4	30	10-15	1	5.2	19.4
			3	4.7	
			7	5.2	
			12	4.9	
			16	5.1	
			19	5.1	
11	25	5-10	3	4.5	5.8
			6	4.7	(equilibrium)
			9	4.8	concn. at 70°)
			14	4.6	
			21	4.5	

From Fig. 7, it becomes evident, that 70° represents the practical lower limit for the solubility measurements in pure water. In the experiment indicated by open circles, a total surface of 90,000 cm.<sup>2</sup> was used per 32 g. of water. Even with this large surface area it took one month to reach equilibrium from a starting concentration only  $2.4 \times 10^{-4}$  mole/kg. higher than the equilibrium concentration.

No attempt was made to measure the solubility in H<sub>2</sub>O below 70°. As previous experiments had shown an accelerating effect of NaCl, two experiments in 10<sup>-2</sup> N NaCl solution were run at 60°. The results of these experiments are given in Table II. Of interest is the decrease of concentration by  $1.4 \times 10^{-3}$  mole/kg. within one day in the first experiment. Both experiments indicate that it should be possible to obtain results at 50° or even lower, when 10<sup>-2</sup> N NaCl is used as a solvent.

Because of the difficulties in measuring pH at elevated temperatures, the solubility of quartz was also determined in alkaline solutions of known pH. A 10<sup>-2</sup> M borax solution was chosen because its pH is known over the desired temperature range.<sup>20</sup> Table III summarizes the results of the measurements in these solutions.

The observed solubilities of quartz in neutral and alkaline solutions at different temperatures are summarized in Table IV.

**Rate Studies.**—The dissolution rates of quartz in pure water and in the presence of 10<sup>-1</sup>, 10<sup>-2</sup> and 10<sup>-3</sup> N NaCl solutions were studied at 90,

80 and 70°. The quartz was pretreated in the same way as described before except that after the treatment with 10<sup>-1</sup> N NaOH, the washed quartz was again agitated in conductivity water at 90° for 14 days and then filtered and washed with fresh conductivity water and dried over P<sub>2</sub>O<sub>5</sub> *in vacuo*. The results of the experiments are given in Figs. 8, 9 and 10. The dotted curves indicate experiments in which 0.96 g. of quartz was used. All other tests were made with 3 g. of quartz. A strong accelerating effect of NaCl is evident. The influence of 10<sup>-1</sup> N NaCl is very remarkable. With reference to the upper curve in Figs. 9 and 10 the quartz is seen to keep on dissolving, even though the concentration in solution is higher than the equilibrium concentration found in previous experiments in 10<sup>-2</sup> N NaCl solution and in H<sub>2</sub>O as indicated by the arrows. A similar behavior in 10<sup>-1</sup> N NaCl solution at 90° (upper curve, Fig. 8) is not evident. Perhaps this may be related to the fact that the starting silica concentration in the 10<sup>-1</sup> N NaCl experiment at 90° was zero whereas in the 10<sup>-1</sup> N NaCl experiment at 70° (Fig. 10) the initial SiO<sub>2</sub> concentration in solution was  $4.9 \times 10^{-4}$  mole/kg. The reason for the difference in results, when using 10<sup>-1</sup> N NaCl solution as compared to 10<sup>-2</sup> N NaCl solution as solvent is not clear. It may indicate a higher solubility of quartz in NaCl solutions. Sadek<sup>24</sup> reports the formation of a complex between SiO<sub>2</sub> (in solution) and HCl in a ratio of 1:1. He reports, however, a decrease in the formation of this complex with decreasing SiO<sub>2</sub> concentration. His lowest SiO<sub>2</sub> concentration was  $1.5 \times 10^{-1}$  mole/kg. whereas the highest SiO<sub>2</sub> concentration in our NaCl experiments was about  $1.2 \times 10^{-3}$  mole/kg. On the other hand, Wyart and Sabatier<sup>25</sup> report the same solubility for quartz in H<sub>2</sub>O and in 10<sup>-1</sup> N NaCl at 500° and 500 atmospheres of pressure. Piryutko<sup>26</sup> found that high salt concentrations, especially chloride and nitrates lower the solubility of silicic acid. Greenberg and Price<sup>27</sup> report that NaCl and Na<sub>2</sub>SO<sub>4</sub> in concentrations below 1 N do not change the solubility of colloidal silica. In 1 N solutions of these salts they found a slight decrease in solubility. More measurements are needed to explain this effect.

### Discussion

The presence of a disturbance of considerable thickness on the surface of finely ground quartz has been verified in this investigation (see Figs. 1 and 2). If this layer were amorphous silica, enough material would be present to saturate the solution with respect to amorphous silica at the lower pH (Fig. 1). The dissolution rate of amorphous silica at room temperature is sufficiently high, even in pure water, to cause saturation within the time of the experiments.<sup>23</sup> Thus the disturbance certainly consists of a material closer to quartz in structure. A combination of cracks, dislocations and protruding edges seems to disturb

(24) H. Sadek, *J. Indian Chem. Soc.*, **29**, 507 (1952).(25) J. Wyart and G. Sabatier, *Compt. rend.*, **240**, 2157 (1955).(26) M. M. Piryutko, *Izvest. Akad. Nauk, S.S.S.R. Otdel. Khim. Nauk*, 379 (1959).(27) S. A. Greenberg and E. Price, *THIS JOURNAL*, **61**, 1539 (1957).

TABLE III  
EXPERIMENTS IN 10<sup>-2</sup> M BORAX SOLUTION

Temp., °C.	Amt. of quartz, g.	Amt. of solvent, g.	Size range of quartz, μ	Reaction time, days	Concn. of SiO <sub>2</sub> , moles/kg.		pH
					Final	Initial	
60	10	30	5-10	24	6.9 × 10 <sup>-4</sup>	0	8.96
70	7.5	30	10-15	35	1.0 × 10 <sup>-3</sup>	1.1 × 10 <sup>-3</sup>	8.92
80	7.5	34	10-15	27	1.2 × 10 <sup>-3</sup>	0	8.88
90	7.5	34	10-15	29	1.5 × 10 <sup>-3</sup>	0	8.85
100	3	35	3-5	23	1.6 × 10 <sup>-3</sup>	0	8.83 <sup>a</sup>

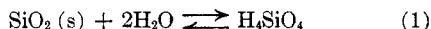
<sup>a</sup> This value is not given by Bates<sup>20</sup> but was obtained by extrapolation from his data.

TABLE IV  
SOLUBILITIES OF QUARTZ IN WATER AND 10<sup>-2</sup> M BORAX SOLUTIONS

Temp., °C.	Solubility, moles/kg.		pH <sup>20</sup> of borax soln.	pK
	Water	Borax soln.		
60	4.42 × 10 <sup>-4</sup>	6.87 × 10 <sup>-4</sup>	8.96	9.3
70	5.79 × 10 <sup>-4</sup>	1.01 × 10 <sup>-3</sup>	8.92	9.1
80	7.15 × 10 <sup>-4</sup>	1.18 × 10 <sup>-3</sup>	8.88	9.1
90	9.06 × 10 <sup>-4</sup>	1.48 × 10 <sup>-3</sup>	8.85	9.1
100	10.89 × 10 <sup>-4</sup>	1.64 × 10 <sup>-3</sup>	8.83	9.1

the original quartz structure in such a way that abnormal solubilities<sup>10,13,14,16</sup> are obtained and that the results of X-ray diffraction,<sup>12,28</sup> differential thermal analysis<sup>11</sup> and infrared absorption<sup>17</sup> deviate from the results on a pure quartz specimen. After removal of the disturbed layer it was shown that a true measure of the solubility of quartz could be obtained.

**Solubility of Quartz in H<sub>2</sub>O and 10<sup>-2</sup> N NaCl Solution.**—The dissolution of quartz in H<sub>2</sub>O may be represented by the reaction



In writing this reaction the assumption is made that H<sub>4</sub>SiO<sub>4</sub> is the chemical species in solution. Evidence for this can be found in the work of Weitz,<sup>29</sup> Alexander<sup>23</sup> and Wood.<sup>30</sup> The equilibrium constant (*K*) for reaction 1 may be written

$$K = c_{\text{H}_4\text{SiO}_4} \quad (2)$$

and the variation of *K* with temperature will be given by the well-known relation

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\theta}{RT^2} \quad (3)$$

where Δ*H*<sup>θ</sup> is the differential standard heat of the dissolution reaction 1. On combining equations 2 and 3 and integrating we obtain

$$\log c_{\text{H}_4\text{SiO}_4} = -\frac{\Delta H^\theta}{4.576T} + \text{constant} \quad (4)$$

This relation was plotted for the five different temperatures used in this investigation. By extrapolation of the straight line obtained to 25°, a solubility of quartz in water of 1.8 × 10<sup>-4</sup> mole/kg. was found. The temperature variation of the solubility of crystalline quartz as based on our measurements assumes the form

$$\log c_{\text{H}_4\text{SiO}_4} = 0.151 - 1162/T \quad (5)$$

With the help of equation 5 the standard heat (Δ*H*<sup>θ</sup>), standard free energy (Δ*G*<sup>θ</sup>) and standard

(28) G. Sabatier, *Compt. rend.*, **237**, 77 (1953).  
 (29) E. Weitz, H. Franck and M. Schuchard, *Chem. Z.*, **74**, 256 (1950).  
 (30) J. A. Wood, *Am. J. Sci.*, **256**, 40 (1958).

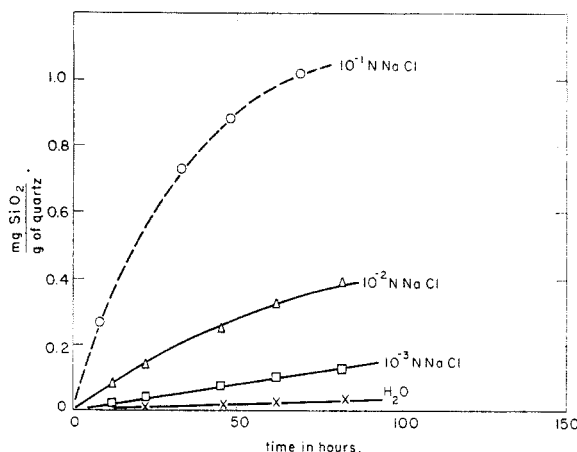


Fig. 8.—Dissolution rate of quartz in H<sub>2</sub>O and NaCl solutions at 90°.

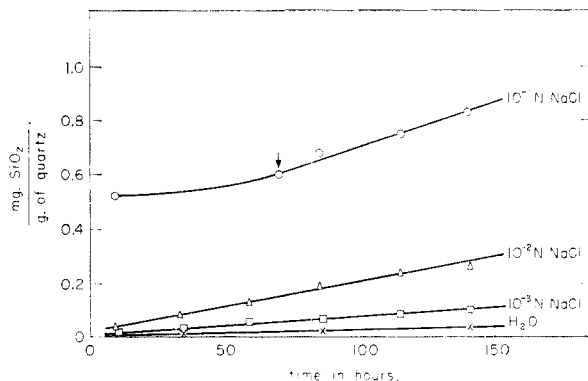


Fig. 9.—Dissolution rate of quartz in H<sub>2</sub>O and NaCl solutions at 80°.

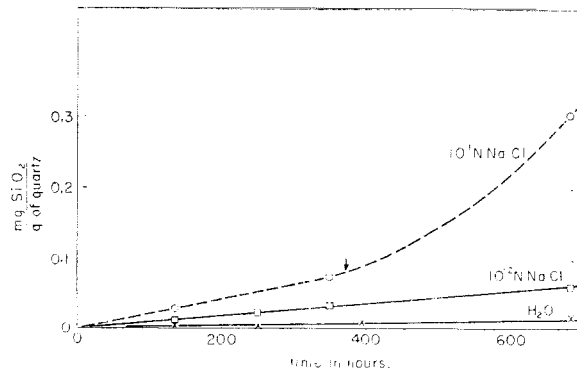


Fig. 10.—Dissolution rate of quartz in H<sub>2</sub>O and NaCl solutions at 70°.

entropy (Δ*S*<sup>θ</sup>) of dissolution may be calculated. The following values for these thermodynamic quantities are found at 25°. <sup>31</sup>

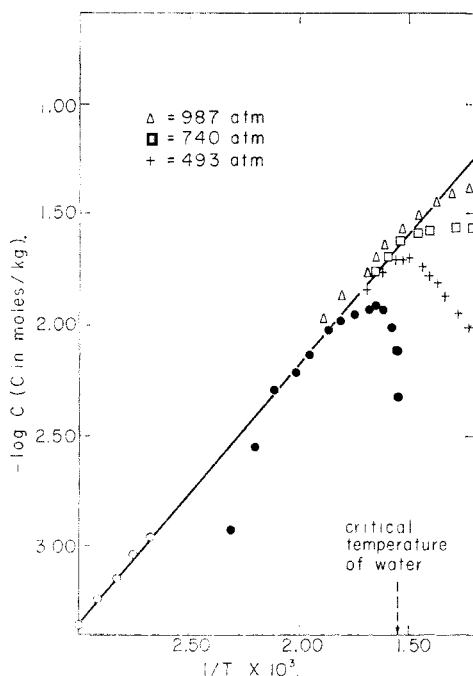


Fig. 11.—Comparison of solubility data of quartz as obtained by Kennedy<sup>3</sup> with data obtained in this investigation.

$$\Delta H^\theta = 5.32 \text{ kcal./mole}; \Delta G^\theta (25^\circ) = 5.11 \text{ kcal./mole}; \\ \Delta S^\theta (25^\circ) = 0.7 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \approx 0$$

The standard heat of dissolution was also calculated by Greenberg<sup>32</sup> who used Kennedy's<sup>3</sup> data, which he extrapolated to 200°. Greenberg reports a value of 7.34 kcal./mole for  $\Delta H^\theta$ . Unfortunately, it is not clear from Greenberg's paper, what part of Kennedy's data he has used. Two factors are important in this respect, Kennedy's measurements at the lowest temperatures are according to himself the least reliable and secondly the assumption of a constant  $\Delta H^\theta$  is unjustified at temperatures around the critical temperature of water. Both factors are evident from Fig. 11 where the results of Kennedy's<sup>3</sup> work are compared with the results of the authors. The line in Fig. 11 is described by equation 5. The solid points indicate Kennedy's measurements in the three-phase region, *i.e.*, quartz in H<sub>2</sub>O with a vapor pressure present. The open circles represent our data at lower temperatures and the other symbols indicate several series of experiments (Kennedy) at constant high pressures. The decrease in solubility along the constant pressure curves may be due to the decreasing density along these curves. This has been discussed by Kennedy<sup>3</sup> and by Iler.<sup>33</sup> It is clear, however, that the agreement between Kennedy's data above 200° and our data is excellent as long as the density of the solutions does not change too much. The two lower values of Kennedy at 160 and 182° could be explained by assuming that insufficient time was allowed for equilibrium to be reached. This becomes more obvious when it is realized that in Kennedy's measurements only 12 cm.<sup>2</sup> of quartz surface

(31)  $\Delta H^\theta$  is assumed to be independent of temperature.

(32) S. A. Greenberg, *THIS JOURNAL*, **61**, 196 (1957).

(33) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell University Press, Ithaca, N. Y., 1955.

were exposed to probably 150 cc. of water. Not all of Kennedy's data are included in Fig. 11, as this would cause too much crowding, but the data not shown do not deviate any more from the straight line than the data that are shown.

**The Solubility of Quartz in Alkaline Solutions.**—The following assumptions will be made with regard to the dissolution of quartz in alkaline solutions: (a) The concentration of the species H<sub>4</sub>SiO<sub>4</sub> is independent of pH; (b) H<sub>3</sub>SiO<sub>4</sub><sup>-</sup> is the only ionic species present in solution.

In alkaline solution the equilibrium constant for the dissolution of quartz may then be written

$$K = \frac{[H^+][H_3SiO_4^-]}{[H_4SiO_4]} \quad (6)$$

or because of assumption (a)

$$K' = [H^+][H_3SiO_4^-] \quad (6a)$$

Alexander and co-workers<sup>23</sup> have shown that this relation is reasonable at room temperature and a value of 10<sup>-9.8</sup> for  $K$  at room temperature is given by Roller and Ervin.<sup>34</sup>

In Table IV the calculated  $pK$  values based on measurements in the borax solutions are shown. The  $pK$  values were calculated with the aid of the two assumptions previously mentioned and compare reasonably well with the value of 9.8 reported by Roller and Ervin.<sup>34</sup>

Some further results of solubility measurements in unbuffered alkaline solutions at 90° are given in Table V. This table also includes calculated quantities needed to obtain an estimate of the  $pK$ .

TABLE V  
SOLUBILITIES IN ALKALINE SOLUTIONS AT 90°

Solubility, moles SiO <sub>2</sub> /kg.	[OH <sup>-</sup> ], moles/kg.		[H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup> ], moles/kg.	$pK$
	Initial	Final		
$9.2 \times 10^{-4}$	10 <sup>-4</sup>	$1.3 \times 10^{-5}$	$3.1 \times 10^{-5}$	9.1
$1.5 \times 10^{-3}$	10 <sup>-3</sup>	$2.5 \times 10^{-4}$	$6.2 \times 10^{-4}$	9.1
$6.7 \times 10^{-3}$	10 <sup>-2</sup>	$4.2 \times 10^{-3}$	$5.8 \times 10^{-3}$	9.3
$6.7 \times 10^{-2}$	10 <sup>-1</sup>	$3.4 \times 10^{-2}$	$6.6 \times 10^{-2}$	9.2

The first three columns in this table give the experimental data with the exception of the last two values in the third column. The final pH was not measured in these two tests, but was calculated by assuming that the final OH<sup>-</sup> concentration equals the difference in concentration between the starting OH<sup>-</sup> concentration and the amount required for the formation of H<sub>3</sub>SiO<sub>4</sub><sup>-</sup>. The H<sub>3</sub>SiO<sub>4</sub><sup>-</sup> concentration was calculated with the aid of equation 6a. It may be shown that if ions of the type H<sub>2</sub>SiO<sub>4</sub><sup>=</sup> or H<sub>3</sub>Si<sub>2</sub>O<sub>7</sub><sup>=</sup> were present, the final pH would be so low that the experimentally observed SiO<sub>2</sub> concentrations would be much too high. Furthermore the presence of polymeric ions at concentrations of SiO<sub>2</sub> far below the saturation concentration of amorphous silica is very unlikely. The  $pK$  values shown in Table V agree well with those calculated in borax solutions (Table IV) and one may conclude that the assumptions on which these calculations are based are thus validated.

In Table VI, the solubility of quartz in H<sub>2</sub>O and 10<sup>-4</sup> *N* NaOH as determined in this investiga-

(34) P. S. Roller and G. E. Ervin, *J. Am. Chem. Soc.*, **62**, 461 (1940).

tion is compared with data on the solubility of amorphous silica from the literature.

TABLE VI

COMPARISON OF THE SOLUBILITY OF QUARTZ AND AMORPHOUS SILICA

T, °C.	Solubility (moles/kg.)			
	H <sub>2</sub> O		NaOH 10 <sup>-4</sup> N	
	Quartz	Amorphous silica	Quartz	Amorphous silica
90	9.0 × 10 <sup>-4</sup>	7.5 × 10 <sup>-3</sup> <sup>35</sup>	9.2 × 10 <sup>-4</sup>	1.3 × 10 <sup>-2</sup> <sup>35</sup>
25	1.8 × 10 <sup>-4</sup>	2 × 10 <sup>-3</sup> <sup>35</sup>	~1.8 × 10 <sup>-4</sup>	~6.7 × 10 <sup>-3</sup> <sup>35</sup>

**Reaction Velocity in Water.**—Very little is known about the rate of dissolution of quartz in aqueous solutions. Recently Laudise<sup>36</sup> discussed the kinetics of crystallization of quartz under hydrothermal alkaline conditions.

Removal of the disturbed layer at the quartz surface before any kinetic measurements can be made has been shown to be essential in the present investigation. O'Connor and Greenberg<sup>37</sup> and Brown, Paap and Ritchie<sup>38</sup> also came to the same conclusion.

In the present investigation it was observed that the rate of dissolution of quartz in water at a fixed temperature is constant (see for example Figs. 8 to 10). From this observation a rate constant ( $k_1$ ) may be evaluated as

$$\frac{dc}{dt} = \text{constant} = k_1 \frac{S}{V} \quad (7)$$

where  $c$  is the concentration of soluble silica at time  $t$ ,  $V$  is the volume of solution and  $S$  the total quartz surface. The dependence of the rate of dissolution on the total surface area is a reasonable assumption although this relationship could not be well established because of limited experimental data. In Table VII the calculated rate constants for the dissolution of quartz in pure water at several temperatures are shown. These values were obtained from measurements in which extreme care was taken to remove any disturbance from the surface of the quartz. The values marked by an asterisk are considered to be the most accurate and reliable as they were obtained from experiments specifically designed to give kinetic information.

TABLE VII

RATE CONSTANTS FOR THE DISSOLUTION OF QUARTZ IN WATER AT 70, 80 AND 90°

T, °C.	Total surface area, cm. <sup>2</sup>	$k_1$ , g. SiO <sub>2</sub> cm. <sup>-2</sup> sec. <sup>-1</sup>	Reaction time, hr.	Boundary layer thickness ( $\delta$ ), cm.
90	10,000	3.3 × 10 <sup>-14</sup>	813	
90	10,000	5 × 10 <sup>-14</sup>	1000	
90	43,000	1.2 × 10 <sup>-14</sup>	500	
90	10,000	3.6 × 10 <sup>-14</sup> *	83	30,000
80	10,000	1.8 × 10 <sup>-14</sup> *	140	38,000
70	10,000	3.6 × 10 <sup>-15</sup> *	680	130,000

In view of the proposed dissolution reaction (equation 1) for quartz in water, the above kinetic

(35) Go Okamoto, T. Okura and K. Goto, *Geochim. et Cosmochim. Acta*, **12**, 123 (1957).

(36) R. A. Laudise, *J. Am. Chem. Soc.*, **81**, 562 (1959).

(37) T. L. O'Connor and S. A. Greenberg, *THIS JOURNAL*, **62**, 1195 (1958).

(38) J. Brown, W. J. Paap and P. D. Ritchie, *J. Appl. Chem. (London)*, **9**, 153 (1959).

relation 7 suggests that the dissolution rate is controlled by the chemical reaction. To rule out the possibility that the kinetics may be diffusion-controlled, the following analysis will be helpful. If the dissolution rate were controlled by diffusion of soluble silica from the quartz surface through a boundary layer of effective thickness  $\delta$  then it follows that

$$V \frac{dc}{dt} = DS \frac{(c_s - c)}{\delta} \quad (8)$$

where  $D$  is the diffusivity of the soluble species (H<sub>4</sub>SiO<sub>4</sub>) and  $c_s$  the saturation concentration. A value for  $\delta$ , the effective diffusion boundary layer thickness, may be determined from equation 8 if the diffusivity of H<sub>4</sub>SiO<sub>4</sub> in water is known. According to Jander and Jahr<sup>39</sup> the diffusivity at room temperature is  $6.15 \times 10^{-6}$  cm.<sup>2</sup>/sec.<sup>40</sup> The calculated values for  $\delta$  are also shown in Table VII and are unreasonably large to be in agreement with a diffusion controlled kinetic process. It may be concluded that the rate of dissolution of quartz in pure water at temperatures below 100° is controlled by the dissolution reaction 1 for which the rate constants are given in Table VII.

A value of about 10<sup>-13</sup> g. of SiO<sub>2</sub> cm.<sup>-2</sup> sec.<sup>-1</sup> is found for the rate constant at 25° by a rough extrapolation from  $k_1$  values at higher temperatures. This should be compared with a dissolution rate of  $4 \times 10^{-13}$  g. of SiO<sub>2</sub> cm.<sup>-2</sup> sec.<sup>-1</sup> in a 0.1 N NaOH solution at 25°.

The presence of NaOH or NaCl results in a considerable increase in the reaction velocity but the absolute rate is still very small.

The rate constant for the crystallization of quartz from solutions supersaturated with H<sub>4</sub>SiO<sub>4</sub> may be estimated from the available data. According to equations 1 and 7 the rate of crystallization of quartz may be written

$$-\frac{V}{S} \frac{dc}{dt} = k_2 [\text{H}_4\text{SiO}_4] \quad (9)$$

The rate constant  $k_2$  at 90° may be obtained from the solubility of quartz in pure water ( $9 \times 10^{-4}$  moles/kg.) and the rate constant for the dissolution reaction ( $3.6 \times 10^{-14}$  g. cm.<sup>-2</sup> sec.<sup>-1</sup>)

$$k_2 = \frac{k_1}{K} = 6.67 \times 10^{-10} \text{ g. (soln.) cm.}^{-2} \text{ sec.}^{-1}$$

Assuming the density of quartz to be 2.65 g./cc. it is seen from equation 9 that a thousandfold supersaturation; that is, a concentration of 0.9 mole/kg. would give only a linear rate of crystallization of  $1.4 \times 10^{-11}$  cm./sec. or 4.3  $\mu$  per year. Even the accelerating effects of alkaline pH and NaCl very probably will not be sufficient to grow quartz crystals normally at these temperatures.

### Conclusions

1. Quartz has a well-defined solubility at temperatures below 100°.

2. The solubility of quartz in NaCl solutions below a concentration of 10<sup>-1</sup> N NaCl is the same as the solubility in H<sub>2</sub>O.

(39) G. Jander and K. F. Jahr, *Kolloid-Beihfte*, **41**, 48 (1934).

(40) The relation  $D_{T_1}/D_{T_2} = T_2/T_1\eta$ , where  $\eta$  is the viscosity of the solution, was used to obtain the diffusivity at temperatures above 25°.

3. Quartz has a definite solubility in alkaline solutions of  $\text{OH}^-$  concentrations up to at least  $10^{-1} N$ .

4. The solubilities of quartz in  $\text{H}_2\text{O}$  and  $\text{NaOH}$  solutions are approximately ten times lower than the corresponding solubilities of amorphous silica at the same temperature.

5. The rate of dissolution of quartz in  $\text{H}_2\text{O}$  is extremely slow at temperatures below  $100^\circ$ . The dissolution rate is not controlled by diffusion.  $\text{NaCl}$  in solution has a strong accelerating effect

on the dissolution reaction as well as on the crystallization reaction.

6. The surface of finely ground quartz particles is disturbed in such a way as to cause abnormally high dissolution rates of the quartz in water and alkaline solutions.

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## MASS SPECTRA OF DEUTERATED DIBORANES<sup>1</sup>

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The mass spectrum of completely deuterated diborane and approximate spectra of the five partially deuterated diboranes have been determined by an extrapolation technique based on a series of spectra of diborane of varying protium/deuterium ratios. For the partially deuterated compounds it was possible to obtain the spectra of formula groups only; the spectra of compounds labelled at specific positions were not resolvable. From the ion intensities of peaks for which there were no overlapping contributions, it was observed that the relative fragmentation of H *versus* D is substantially lower than is reported for deuterated hydrocarbons.

Mass spectra have been published,<sup>3,4</sup> for isotopically normal diborane and for slightly protiated deuterodiboranes, but not for completely deuterated diborane nor any of the partially deuterated species. Determination of these latter spectra is rendered particularly difficult by two factors, *viz.*, the existence of an equilibrium between the diborane molecule and the borane species ( $\text{B}_2\text{H}_6 \rightleftharpoons 2\text{BH}_3$ ),<sup>5</sup> and the negligibly small parent ion intensity of diborane at the usual ionizing voltages. Because of the diborane-borane equilibrium, a sample that is subjected to deuteration undergoes transition to a mixture of all the various species,  $\text{B}_2\text{H}_6$ ,  $\text{B}_2\text{H}_5\text{D}$ ,  $\text{B}_2\text{H}_4\text{D}_2$ , . . . . .  $\text{B}_2\text{D}_6$ , both bridge and terminally substituted, in equilibrium with one another through their respective borane radicals. The half-life of the protium-deuterium exchange in diborane is of the order of minutes at room temperature,<sup>5</sup> so it is impossible to isolate a particular deuterated species and analyze it separately in the mass spectrometer. The concentrations of the various formula groups in an equilibrium mixture can be calculated from the expression

$$[\text{B}_2\text{H}_z\text{D}_{6-z}] = W[\text{H}]^z[\text{D}]^{6-z} \quad (1)$$

where  $W$  is the statistical weight, numerically given by the binomial coefficients for six entities. A discussion of this relationship as well as a graph showing the changes in distribution with changing

deuterium concentration has been published previously.<sup>6</sup>

The second complication, that of the negligibly small parent ion intensity, renders conventional stripping techniques useless even if any or all of the spectra might be known, since none of the species have unique peaks available for stripping. For example, a sample composed of  $\text{B}_2\text{D}_6$  and  $\text{B}_2\text{D}_5\text{H}$  (plus small amounts of less deuterated species) would have a mass spectral cut-off at  $m/e$  32, corresponding to  $\text{B}_2^{11}\text{D}_5^+$ , but since this ion comes from both  $\text{B}_2\text{D}_6$  and  $\text{B}_2\text{D}_5\text{H}$  there is no way to determine relative contributions. Since the spectra also overlap on all other peaks, it would not be possible to strip known spectra from a composite spectra unless one could determine concentrations independently. The technique of determining relative concentrations by lowering the ionizing potential in the instrument to the point where only the parent ions are observed cannot be employed because the appearance potentials of several of the lower mass ions of diborane are essentially equal to that of the parent ion.<sup>4,7</sup> Consequently, one cannot produce the parent ions without simultaneously producing lower mass ions. Since the ion currents due to the parent ions are not equivalent if lower mass ions are produced (because of differences in zero point energies of the fragment ions),<sup>8</sup> the relative amounts of the parent compounds cannot be determined from the parent ion intensities.

To circumvent the difficulty we utilized a dilution technique to obtain the spectra and to measure the concentrations of all species. The general method involved mass spectral analysis of a series of samples

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