FLUOSILICIC ACID. II

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It has generally been considered as an accepted fact that fluosilicic acid may occur undecomposed in the vapor state as well as in solution. This assumption received apparent verification in the results of experiments by E. Baur and A. Glaessner [Ber., 36, page 4215 (1903)]. These experimenters conclude, however, that at a temperature over 100° more than two-thirds of the fluosilicic acid present will be decomposed.

Examining their results it is seen that the mean molecular weight of the gas obtained from BaSiF_6 and H_2SO_4 at 23° was 82.7 while that at 31.5° was 81.9. If the H_2SiF_6 had come over undecomposed a vapor density of 144.31, on the basis of $\text{O}_2 = 32$, would have been obtained. According to the results of Thorpe and Hamby¹ the density of hydrogen fluoride on the same basis was 51.59 at 26.4° , 49.8 at 27.8° , 45.9 at 29.2° , 40.06 at 32° , and 20.75 at 88.1° . These values when extrapolated will show a vapor density of 59 at 23° , which is the temperature at which Baur and Glaessner (loc. cit.) obtained a vapor density of 82.3 for the gas mixture from fluosilicic acid at a pressure of 764 mm. When the vapor density of hydrogen fluoride is 60 its molecular composition must be H_3F_3 .

At the temperatures in question it is more than likely that hydrogen fluoride is present both as H_2F_2 and H_3F_3 with a preponderance of H_3F_3 since this is the stabler form at 23° . When the decomposition of fluosilicic acid takes place in two ways simultaneously as shown in reactions (1) and (2),

31.1% going according to (1) and 68.9% according to (2) the vapor density of the mixture or mean molecular weight

¹ Jour. Chem. Soc., 55, 163 (1899).

will be 82.1, which is very close to the values of Baur and Glaessner. On this basis no molecules of H_2SiF_6 are present. In the

previous paper it is seen that upon distilling fluosilicic acid a distillate was obtained yielding a concentration of 49.61% of this acid, and therefore it might be contended that the acid exists in the vapor phase.

Four series of experiments have been undertaken, bearing upon the state of this acid. Three of these depend upon the coexistence of water vapor and SiF_4 in the vapor phase without precipitating silica. It became necessary, therefore, to determine with great care if the following reaction, suggested by Hudleston and Bassett,¹ could take place in the vapor state.

An apparatus as shown in Figure 1 was assembled, the right hand side of which served for the generation of silicon-tetrafluoride and the left hand side for water vapor. A mixture of fluorspar, precipitated silica, and six to seven parts of conc. H_2SO_4 were introduced into flask A, which was con-

Fig. 1

¹ Jour. Chem. Soc., 119, 412 (1921).

nected with B by means of a glass tube ending below mercury in the bottom of this tube. This arrangement was to permit a better control of the flow of gas. B was in turn connected with a Peligot tube C containing glass wool, to remove any traces of HF that might get over. Bulb D was especially constructed of glass so as to permit the two vapors to enter it simultaneously, and then pass out through an opening at the top. D had a capacity of about 150 cc. SiF_4 was admitted through Tube 3, and water vapor through Tube 4. The two gases were then aspirated out through G, containing water.

E was a 100 cc round bottom flask fitted with a two hole rubber stopper holding a glass bubbler. Through the other hole in the stopper passed a glass tube connecting with flask F, which contained glass wool, to intercept any particles of liquid water which might be carried over from E. About 50 cc of water was put in E, and air aspirated through the same into D, by means of a filter pump connected with G. This flask had a capacity of two liters and was half full of water. In the bottom of G was a small beaker containing mercury, into which the glass tube connected with D dipped. H was another two liter flask half full of water, connected with C by means of a T tube and a glass tube bent at right angle, as shown in the cut. This flask was also provided with a small beaker of mercury like G, and served to absorb the excess of silicon tetrafluoride.

With this apparatus experiments were run at three different temperatures, but a different tube at D was used for each temperature, in order that the slightest deposit of silica in the same might be detected. Tube D was supported in a beaker of water, the water extending to within an inch of the top. Flasks E and F were also immersed in water contained in beakers.

For the first experiment the water in the beaker surrounding bulb D was held at 35° , while that surrounding E and F remained at room temperature. Air was aspirated through these flasks in a slow but constant stream. The generation of SiF_4 was started in flask A, with the screw clamp on the tube

connecting with H open, while that on the tube connecting with 3 closed. As soon as the air had been driven out of C, the latter clamp was opened gradually, while the former was screwed up little by little, until a slow stream of SiF_4 was admitted into D, where it met the moist air from E. The two gases were allowed to pass in together for about twenty minutes, after which D was taken out and examined. A very light deposit of silica was observed on the glass near the confluence of the two gases, but toward the top of the tube there was no deposit visible. The second and third experiments were performed exactly like the first, except that a new tube was used at D in each case, and the bath containing this tube was held at 80° in the second experiment, and $95\text{--}96^\circ$ in the third, while flasks E and F were kept at 40° for the second, and 45° for the third experiment. At the end of these experiments a scarcely visible trace of deposited silica was found in D from the second experiment, while in the third D remained perfectly clean, without a trace of deposited silica. In all these experiments that portion of D which was above the bath liquid condensed water and held a very heavy deposit of silica. A fourth experiment was performed, admitting live steam together with SiF_4 into a tube of different construction corresponding to D, which was kept at a temperature of $120\text{--}125^\circ$ in a bath of paraffin. At the end of twenty minutes no trace of deposited silica could be observed in the tube except where a few drops of water fell into it from the connecting tube.

These experiments establish the fact that reaction (1) does not take place in the gaseous phase between 95° and 125° , and in all probability does not take place at higher temperatures. The experiments also show that silicon tetrafluoride and water vapor do not react with each other between 30° and 80° C, except to a very insignificant degree.

The first method arranged for throwing light upon the state of H_2SiF_6 consisted of a gas flow meter constructed of glass, having a capacity of about 100 cc per minute under a pressure of 10 cm of water. This flow meter was accurately calibrated, and a curve drawn for the same. The flow of air in cc per

minute could thus be read directly from the curve for any given pressure maintained during the experiments.

Three 100 cc flasks were clamped in a water bath, immersed to the neck in water. Two of the flasks contained 50 cc each of the H_2SiF_6 solution to be examined, and the third flask 50 cc of water. Two hole rubber stoppers were fitted into these, each holding two glass tubes, one ending just below the stopper, and the other drawn to a narrow opening and ending below the surface of the liquid. A fourth flask containing water for absorption was clamped outside of the bath and connected with the second flask containing the acid solution. The flasks were all connected with one another by means of glass tubing and very short rubber connections, in such a manner that the measured air first bubbled through the water and then through the acid solutions. This was done in order to minimize concentration of the acid solutions due to evaporation of water into the stream of air. The results of the nine experiments performed with this apparatus are summarized in the following table.

TABLE I

Concentration of H_2SiF_6 %	Temp. °C	Pressure in mm of H_2O	Time in minutes	No. of cc passed	Gm H_2SiF_6 found in absorption H_2O
9.75	50	155	180	24,300	0.00126
9.75	70	155	180	24,300	0.00202
9.75	88	160	174	24,306	0.01210
15.00	50	165.5	155	22,382	0.00076
15.00	70	168	166	24,528	0.00760
15.00	88	170	164	24,420	0.02922
23.98	50	185	151	24,235	0.00479
23.23	70	166	168	24,276	0.01335
21.75	88	176	159	24,327	0.08692

These results show in a striking manner, that a rising temperature accelerates the decomposition of H_2SiF_6 much more rapidly than the increase in concentration up to 24%. If negative results had been obtained in these experiments they would have been fairly conclusive in establishing that, up to the

temperature and concentration employed the acid does not exist in the vapor phase.

For the second method the apparatus shown in the foregoing paper was employed. For Experiment 1, a strong solution of H_2SiF_6 was put into A. Then a large porcelain boat, nearly filled with recently boiled concentrated sulfuric acid, was placed in C, the receiver B connected up and packed in an ice-salt mixture, and the apparatus evacuated to 8 mm. At the end of 24 hrs. the receiver was taken out and examined. There was no trace of a liquid of any sort in it. A duplicate experiment was run with fresh H_2SO_4 , yielding the same result.

Experiments 3, 4, and 5 were carried out in the same manner as the first two, except that anhydrous copper sulfate, calcium chloride, and phosphorus pentoxide were used respectively as desiccating agents, and held in two porcelain boats instead of one. Negative results were obtained in every case except when calcium chloride was used. Here a fine dew like deposit had formed on the sides of the flask. After the silicon tetrafluoride vapors had been removed from the receiver, this liquid deposit was washed out with water and titrated, showing that a small amount of H_2SiF_6 was present.

The third method is a modification of the second in that it provides for the removal of silicon tetrafluoride, one of the gaseous products of decomposition of the acid, which would accumulate and interfere with the passage of the fluosilicic acid vapors if they were present. The apparatus as arranged for the experiment is depicted in Figure 2.

Flask A had a capacity of 300 cc and was connected with flask B by a glass tube ending just below the rubber stopper. This tube was bent at two right angles, and the other end inserted in B, ending just above the surface of the liquid in B. This flask was similarly connected with C, the latter being connected with a long narrow side neck glass tube D, which was surrounded with ice in the tall four inch glass cylinder, as shown in the cut. A small glass tube was drawn out to a fine point, but not sealed, and inserted in D so that the apparatus could

be exhausted by means of it through the filter flask E. Another glass tube was drawn out to a fine point and fitted into A, so that the pin point opening was below the surface of the liquid. A rubber tube with screw cock being fitted on its upper end, so as to permit air to be drawn through in a very fine stream.

The three flasks were mounted in an air bath G, and about 100 cc of the 60% solution of fluosilicic acid, obtained as explained in the foregoing paper, were introduced into A, and connected up with B, C, and D in the manner just described. For the preliminary experiments, B and C were empty. The

Fig. 2

system was exhausted through E, by means of a water filter pump, and the temperature of the air bath raised to about 90° , when the acid solution in A began to boil briskly. The temperature was dropped to 83° , and a slow ebullition continued for twenty minutes, while an exceedingly fine stream of air was admitted to A through the glass tube. The experiment was then stopped, all SiF_4 removed from D, and the condensed liquid in this tube washed out and titrated, showing that 0.039833 g H_2SiF_6 had been formed, which would have amounted to 0.119499 g if the experiment had been continued for one hour.

For the second experiment the apparatus remained exactly as in the first, but in flask B were introduced 100 cc of recently boiled concentrated sulfuric acid. This time the acid in A was kept at 85° , and therefore boiled a little more strongly than before, and the boiling continued for exactly one hour. After blowing out the SiF_4 from D its liquid contents were titrated, showing the presence of 0.008840 g H_2SiF_6 . Experiment 3 was identical with the preceding with the exception that 100 cc H_2SO_4 were kept in each of the flasks B and C. The temperature of the air bath was 85° , and the boiling continued for one hour. This time the contents of D yielded 0.002201 g H_2SiF_6 . These results are to each other as 54:4:1, which would indicate, that with perfect desiccation of the stream of vapor, no H_2SiF_6 would be found in the receiver D. The results of this method as well as those of the second point strongly toward the assumption that fluosilicic acid is non-volatile.

The apparatus for the fourth method was that used for the concentration of the acid, shown in the foregoing paper. 27.6 g pure dry sodium fluosilicate were introduced into A and in this powder was put a short specimen tube of conc. H_2SO_4 , placed in an upright position. The receiver B, was packed in ice and salt, and surrounded with mohair packing. After exhausting the apparatus it was tilted so that the sulfuric acid ran into the salt. A slow effervescence began immediately and continued for several hours. Bulb A was kept at room temperature, and the pressure inside the apparatus was watched by means of an attached manometer. At the end of twenty-four hours the apparatus was demounted and examined. In the receiver B was not a drop of liquid of any kind, not even a sign of a deposited mist. Water was then added to B, whereupon a voluminous precipitate resulted, suggesting that SiF_4 had been present. H_2SiF_6 was identified in the filtrate.

The following observation should receive mention here since it throws light upon the chemical properties of this acid. Bulb A, Figure 1 in the foregoing paper, was employed as

the distillation flask and B as the receiver. After continued use A became etched but B remained clear, except for a cloudiness near the bottom. The etching in A was most pronounced at the surface line of the liquid, but was etched to a considerable extent all over the surface covered by the liquid. The etching faded about an inch above the water line and the glass remaining clear throughout the entire length of the tubes C and D. Undoubtedly the phenomenon can be explained as follows:

the H_2F_2 dissolved in the water and attacked the glass, yielding more SiF_4 and water as shown below:

The SiF_4 and water vapor passed through the tubes uncombined until H_2O condensed in the receiver B and immediately reacted with SiF_4 to form H_2SiF_6 and H_4SiO_4 according to the reaction:

No free HF was present in the connecting tubes or receiver, and therefore remained unetched, but when the concentration of H_2SiF_6 in B mounted up there would be some decomposition of the acid, especially at such times when the cooling mixture was used up and the temperature rose.

Conclusion

The results of four different types of experiments have been recorded. In the first case air was passed through dilute solutions of fluosilicic acid at different temperatures and the resulting products passed through water for absorption. In the second and third cases strong solutions of H_2SiF_6 were distilled, first at room temperature and then by boiling, with various desiccating agents introduced in the stream of vapor. In every experiment where the water was removed from the vapor mixture no trace of H_2SiF_6 was obtained in the receivers. In the fourth case an attempt was made to liberate H_2SiF_6 from sodium fluosilicate by means of conc. H_2SO_4 and con-

dense the acid in a receiver cooled in a freezing mixture of ice and salt. No liquid condensed, however, because H_2SO_4 removed the water from the gas mixture, leaving the apparatus filled with silicon tetrafluoride.

The observation of the etching of the glass flasks is shown to be in perfect harmony with the theory that undecomposed H_2SiF_6 does not pass into the vapor state. Lastly, it has been pointed out that the vapor density measurements, made by Baur and Glaessner (*loc. cit.*) upon the gas resulting when barium fluosilicate is treated with concentrated sulfuric acid, indicate the complete decomposition of H_2SiF_6 into the products H_2F_2 , H_3F_3 , and SiF_4 .

Summarizing all the foregoing we are entitled to conclude, with a reasonable degree of certainty, that fluosilicic acid is a nonvolatile acid, like H_2CO_3 and H_2SO_3 , and cannot exist under ordinary conditions in the vapor state.

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