ART. XIV.—*The Thermochemistry of Silicon; Heat of Combination of Silica with Water; by W. G. MIXTER.*

[Contributions from the Sheffield Chemical Laboratory of Yale University.]

THIS article contains experimental work by the writer and a review of the thermochemistry of silicon, which has been regarded as very uncertain. Some of it is undoubtedly good and some of the fundamental values from which others are derived are far from accurate. The writer's results are given first as they are used in discussing the work of others.

There is nothing in the literature bearing on the heat effect of $\text{SiO}_2 + \text{Aq}$ except the heat of formation of $\text{SiO}_2 \cdot \text{Aq}$, 179.6 Cal. and of SiO_2 , 191 Cal. These indicate that it is endothermic. The problem of finding the heat of union of silica with water is complicated since they do not combine directly and because molecules of silica are complex at temperatures required to dehydrate silicic acid. It is impossible to determine with an approximation to accuracy the quantity of heat required to separate a small quantity of water firmly held, but it appears practicable with silicic acid containing much water. Two methods have been tried, one by fusion with sodium peroxide with unsatisfactory results and the other by solution in hydrofluoric acid.

In order to learn whether or not silicic acid prepared at room temperature differs from that made at 100° , two preparations were made as follows: A solution of sodium silicate was added gradually to hydrochloric acid and the silicic acid which separated after a time was washed with water at room temperature. It was dried in the air, then by a current of dry air under diminished pressure passing through the powder, and in vacuo over oil of vitrol until the water content was reduced to 6.9 per cent.* Another preparation was made by adding a solution of sodium silicate to an excess of hydrochloric acid and evaporating on a steam bath. The dry residue was moistened with acid and the silicic acid was washed with hot water. It was then left some time in a steam drying oven and then over oil of vitriol. It contained 8.0 per cent of water. The results on p. 126 show that the silica of silicic acid prepared at 100° is in the same molecular condition as that made at room temperature. Hence other lots of silicic acid were made by the second method, as it is somewhat simpler. The water content was found by the common method, heating finally over a large blast lamp to constant weight. The determinations of

* Since gelatinous silicic acid dries to hard tough lumps it should be pulverized from time to time during the drying process in order to obtain a uniform product.

water were made either before and after the calorimetric tests of a preparation or with a portion weighed at the time of a test, since silicic acid with small water content gains weight rapidly in the air while that having much water may have lost some combined water in a closed vessel if the room is hot. For example, preparation A (Table II) contained 0.3 per cent of combined water and 0.2 per cent absorbed during the necessary exposure to the air. The term "silicic acid" is applied to all preparations having combined water.

The following are the results obtained with fusions of mixtures of silica or silicic acid, sodium peroxide and lampblack:

TABLE I.

Amorphous silica which was heated to a constant weight over a blast lamp: 1218, 1217, 1226: mean 1220 cal.

Silicic acid having

6.9 per cent of H ₂ O	1316, 1307, 1301:	mean 1308 cal.
8.0 " "	1302, 1341	" 1322 "
12.5 " "	1386, 1390	" 1388 "
21.5 " "	1230, 1402, 1310, 1204	" 1236 "

The reason for the wide variation in the last results is this. The silicic acid in the dry air of the mixture gives off water which reacts with the sodium peroxide. A thermometer placed in the last mixture before closing the bomb showed a slight rise in temperature. The silicic acids with 6.9 and 8.0 per cent of water have vapor pressures too low to affect the determinations. Any of the results may be low owing to a little silica left unchanged in a fusion which can not be determined since it would dissolve in the water solution of the fusion.

From the results with the silicic acids containing 6.9 and 8.0 per cent of water we have the equations

$$\begin{aligned} 0.931x + 0.069y &= 1308 \\ 0.92x + 0.08y &= 1322 \end{aligned}$$

in which $x = 1250$ and $y = 2100$ cal., in which x equals the heat effect for 1 gm. SiO₂ and y is the heat effect for 1 gm. of water. The value for y is 200 cal. higher than the heat of the reaction of solid water, ice, with sodium oxide. These derived values are only approximations. They indicate, however, that little energy is required to separate water from silica. For the heat of polymerization of silica we have $1250 - 1220 \times 60.4 = 1800$ cal. or about 2.0 Cal. This small value accords with the fact that silica does not glow when heated.

The apparatus in which silicic acid was dissolved in hydrofluoric acid is shown in fig. 1. It is an old sterling silver bomb with a new silver-plated brass top and fixtures. The disc *b* is held in place by the rod *d*. The cup *c*, shown better

FIGS. 1 AND 2.

in fig. 2, is made of thin sheet silver. The small hole in the bottom allows air to escape so that *c* may sink in the acid. The hole is covered by a disc of silver. The silicic acid for an experiment is placed in *c* which is closed by a cover not shown in the figure. The weight is taken and *c* is at once placed in *a*. The cover is removed and *a* is closed by *b* and the joint is made

tight with beeswax. The hydrofluoric acid is weighed in the open bomb and then the top is put on. After the preliminary observations of temperature in the calorimeter the disc *b* is pushed down, thus allowing the silicic acid and cup *c* to fall into the acid. The mixture is stirred by moving *d* and *b* up and down.

Hydrofluoric acid having a density of 1.079 and containing approximately 22 per cent of HF was used in the work. The specific heat of it was found by cooling about 200 g. in a platinum bottle in snow for hours, in one case over night, and then placing it in the calorimeter used for the work. Two determinations gave 0.80 and 0.81. The method is not a good one, but the result is sufficiently accurate for the work as shown by 0.994 found for the specific heat of water. The heat capacity of the hydrofluoric acid solution was so small compared to the total heat capacity, that an extremely accurate value is unnecessary. The calorimetric experiments were made under fairly uniform conditions and hence the results are comparable. One source of a small error was the undetermined specific heat of the solution of hydrofluosilicic acid.

The line *e* of Table II shows the heat effect of 1 g. of SiO_2 if the water is combined with the silica without heat effect. These *e* values indicate that little energy is required to separate the water. The heat effect of 1 g. of SiO_2 derived algebraically from the *d* values of B and C is 594 cal.; from E and F, 588; E and G, 587; F and G, 588 cal. Now the heat of combination of water in B is calculated thus:

$592 - (594 \times 0.99) = 4$ cal. That is 4 cal. are required to separate 0.01 g. of water from 0.99 g. of silica and for 1 gram molecule, 7200 cal. Likewise we find that 7000 cal. are required to separate 18 g. of water in preparation C. These results are within the experimental errors, but they indicate that energy is required to separate the small quantity of water retained by silica at a red heat. The values found algebraically for the heat of solution of the silica in E, F and G in hydrofluoric acid are the same as the *e* values. This indicates that water is combined without heat effect in silicic acid containing 7.5 to 21.4 per cent. It should be understood that the silicic acid giving this result was made at 100° and may have contained capillary water. Such water would not affect the result essentially.

Silicon dioxide in its union with water with small or no heat effect resembles the anhydrides of weak metallic acids. The oxides given below are more or less polymerized, hence the difference between the heat of formation of an acid or hydroxide and that of a corresponding oxide is not in all cases the heat effect of the combination of water.

The heat of solution of 1 g. of silica in hydrofluoric acid found in experiments E, F and G, Table II, is 588 cal. or 35.5 Cal. for 1 gram molecule. (Si = 28.4.) Guntz* obtained 33.6 Cal. (Si = 28.) Thomsen† found in the reaction of hydrofluoric acid on a solution of silicic acid that the heat effect rises regularly until eight molecules of acid are added and ceases with the tenth. With 6HF it is 32.3 cal. In the writer's experiments 12 to 17 HF were used to 1SiO₂. It may be stated that anhydrous silica dissolves too slowly in hydrofluoric acid for a calorimetric test.

The heat of formation of silicic acid is most important, as other values may be obtained from it. Berthelot‡ derived from the heat of the reaction of SiCl₄ with water

The only uncertain value used is that for the heat of formation of SiCl₄. Troost and Hautefeuille§ burned impure amorphous silicon in chlorine and gave as the result 157.6. B corrected for an error in the water equivalent given by T. and H. for the mercury calorimeter used, and for Si (amor.) → Si (crys.) and states that

The heat effect of SiCl₄(liq.) + Aq is, according to Berthelot, 69.0 cal.: to Thomsen, 69.3 Cal.

The heat of oxidation of silicon has been determined by two methods with fairly concordant results. The writer|| burned crystalline silicon, 99.95 per cent pure, carbon and silicon carbide in sodium peroxide, and the last two in oxygen, and from the results derived

von Wartenburg¶ burned amorphous silicon, containing 2.5 per cent of SiO₂, in oxygen and from nine experiments obtained a mean of 194.9 Cal. ± 4.1 Cal. He also found by dissolving

* Ann. Chim. Phys. (6), iii, 60.

† Ber. deutsch. Gesellsch., iii, 575.

‡ Thermochemie, II, 123 and 151.

§ Ann. Chim. Phys. (5), ix, 77.

|| This Journal, xxiv, 120, 1907.

¶ Nernst Festschrift, 459; Chem. Zentralblatt, 1912, II, 1095.

the two forms of silicon in a mixture of hydrofluoric and nitric or chromic acids in a calorimeter that $\text{Si (amor.)} \rightarrow \text{Si (crist.)} = \text{less than } \pm 2 \text{ Cal.}$ The writer* burned a mixture of crystalline silicon and carbon in oxygen in a bomb. As the results varied widely they were disregarded at the time. Seven experiments in all were made with an average of 187.2 Cal. But the average of five, leaving out the two lowest results, is 191.8 Cal. for 28.4 g. of crystalline silicon. When the products of a combustion were treated with hydrofluoric acid to dissolve the silica a little gas came off, presumably hydrogen, indicating the presence of SiO or a soluble form of silicon. In either case this would make the result a little high for $\text{Si} + 2\text{O}$. It is impossible to say which is the most accurate of the values found, but it seems best to use 191 cal. in deriving other values from results obtained by the writer.

It has been shown that $x\text{SiO}_2$ (unpolymerized) = $(\text{SiO}_2)_x$ (polymerized) + about 2 Cal. Then $191 - 2 = 189$ Cal. for the heat of formation of silicon dioxide as it exists in silicic acid. And it has also been shown that silica combines with water with very small or no heat effect. Hence the conclusion that 189 Cal. is the best value at present for the heat of formation of silicic acid from crystalline silicon, oxygen and water.

If we accept the above value for the heat of formation of silicic acid, 35.5 for $\text{SiO}_2 + 6\text{HF, Aq}$, Berthelot and Moissan's for $\text{H} + \text{F} + \text{Aq} = 50.3$, then $\text{SiO}_2, \text{Aq} + 6\text{HFAq} = 35.5 = 2\text{H} + \text{Si} + 6\text{F} + \text{Aq} + 2(2\text{H} + \text{O}) = (\text{Si} + 2\text{O} + \text{Aq})$
 $\quad \quad \quad x \quad \quad \quad 139 \quad \quad \quad 189$
 $- 6(\text{H} + \text{F Aq})$
 $\quad \quad \quad 301.8$

in which $x = 387.1$ Cal. the heat of formation of hydrofluosilic acid in water from crystalline silicon. From the heat effects of a number of reactions, using Berthelot's value 179.6 for silicic acid, Guntz† derived in a different way 374.3 ($\text{Si} = 28^\circ$ and 380 Cal. ($\text{Si} = 28.4$). Berthelot‡ gives 374.4 Cal. and gives with the reactions measured and used in the calculation Truchot's for $\text{SiF}_4 + 2\text{HF} = 34$ Cal. But Truchot's number given in the Physikalisch Chemische Tabellen for hydrofluosilic acid is 375.1 Cal. Guntz's value given in the Tabellen for $\text{Si (crys.)} + 4\text{F} = 239.8$ Cal. the same as Berthelot gives. This is obviously

$$\text{SiF}_4 = (2\text{H} + \text{Si} + 6\text{F} + \text{Aq})$$

$$\quad \quad \quad 374.4 \quad - 2(\text{H} + \text{F} + \text{Aq}) - (\text{SiF}_4 + 2\text{HF, Aq}) = 239.8$$

$$\quad \quad \quad \quad \quad \quad 100.6 \quad \quad \quad 34$$

* Loc. cit.

† Loc. cit.

‡ Thermochemie II, 152.

TABLE II.

	A		B		C		D	
	SiO ₂ 99.5	H ₂ O 0.5	SiO ₂ 99.0	H ₂ O 1.0	SiO ₂ 98.2	H ₂ O 1.8	SiO ₂ 98.2	H ₂ O 1.8
Substance (<i>a</i>)	3.406	3.540	2.677	2.691	3.003	2.890	3.261	3.457
Hydrofluoric acid, 22% HF	69	68	60	62	70	76	62	65
Water equiv. of system (<i>b</i>)	1357	1366	1366	1325	1315	1330	1345	1349
Temperature interval (<i>c</i>)	1.465	1.502	1.168	1.200	1.358	1.273	1.427	1.516
Observed heat effect, $b \times c$	1988	2051	1585	1590	1786	1697	1919	2044
Heat effect of 1 g. of <i>a</i>	584	581	592	591	595	586	588	591
Average (<i>d</i>)	580	580	592	592	590	590	590	590
$d \div \% \text{ of SiO}_2 \text{ (e)}$	583	583	598	598	601	601	601	601

	E		F		G		H		I		J	
	SiO ₂ 92.5	H ₂ O 7.5	SiO ₂ 87.5	H ₂ O 12.5	SiO ₂ 78.6	H ₂ O 21.4	D ads.	H ₂ O 25.4	D ads.	H ₂ O 19.0	D 83.4	ads. H ₂ O 16.6
	3.644	3.635	3.139	2.771	3.860	3.871	3.914	3.914	2.315	2.315	3.680	3.803 g
	69	71	57	65	50	74	64	64	50	50	65	72
	1502	1367	1300	1336	1330	1367	1341	1341	1329	1329	1327	1343
	1.497	1.446	1.240	1.223	1.345	1.306	1.259	1.259	0.804	0.804	1.303	1.352°
	1980	1977	1612	1634	1788	1785	1688	1688	1.069	1.069	1727	1807 cal
	543	544	513	516	463	461	431	431	462	462	470	478
	544		515		462		431		462		474	
	588		589		588		d	578	570		568	

A, Silicic acid heated 3 hours at about 1000°; B, Silicic acid heated about one hour at 800-900°; C, Silicic acid heated one day at about 500°; D, Silicic acid heated 6 days at about 400°; E, F, G, Dried at 100° and in desiccator; H and I, Weighed amounts of preparation D exposed in the silver cup of the calorimeter to air saturated with water vapor at room temperature; J, A thin layer of D was exposed as described, then thoroughly mixed. This treatment was repeated several times and then the substance kept in a tube closed with a rubber stopper. The adsorbed water was derived from the total loss on ignition, D containing 1.8% of water.

Evidently the values for hydrofluosilicic acid and silicon tetrachloride are subject to the uncertainty in the value for silicon tetrachloride from which the value for silicic acid is derived and also to the unestablished heat effect of $\text{Si}(\text{crys.}) \longrightarrow \text{Si}(\text{amor.})$. Nevertheless the writer's results indicate that the thermochemistry of silicon, excepting the tetrachloride and silicic acid, is fairly well established.

Table II, under II, I and J, contain experiments with silica holding 1.8 per cent of combined water and considerable adsorbed water. The results indicate that more energy is required to separate adsorbed water and convert it into the liquid state than to melt ice. This is what would be expected. The molecular condition of adsorbed water has not been found. Such water is known to have a lower freezing point than ordinary water and Foote & Saxon* have shown that it is different from combined water.