

ART. XII.—*The Heat of Combustion of Silicon and Silicon Carbide*; by W. G. MIXTER.

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

THE direct determination of the heat of combination of silicon with oxygen presents many difficulties. The reaction occurs only at high temperatures; the product is not volatile and hence encloses silicon and prevents complete oxidation. Troost and Hautfennille* from the thermal effect of the reaction of silicon tetrachloride with water obtained 227000° for the formation of silicon dioxide from crystalline silicon. Berthelot's† result by the same method was 179600° for the formation of gelatinous silicic acid from crystalline silicon. Ostwald‡ states, "die Bildungswärme sämtlicher Siliciumverbindungen ist noch sehr unsicher."

Preliminary tests made by burning a mixture of silicon and carbon in the bomb showed that more than half of the former could be burned. The method would give good results if the solid products contained only silica, silicon insoluble in hydrofluoric acid and silicon carbide. The last was always present; hence its heat of formation was determined, as described later, in order to have the data needed for the work on silicon.

The writer is indebted to the Carborundum Company, Niagara Falls, for an abundant supply of carborundum powder and silicon for the investigation. Crystallized silicon was prepared as follows: One part of silicon was dissolved in four parts of molten aluminum and the mixture allowed to cool slowly: the metal was dissolved out with hydrochloric acid, and the silicon, which was in small crystals, was digested with hot hydrofluoric acid. The product at this stage contained 2.8 per cent of aluminum. Treatment with molten potassium pyrosulphate reduced the aluminum content one-half. Next the crystals were pulverized in an agate mortar and the finer portions separated by levigation for one minute in water. Finally the powder was digested with a mixture of hot sulphuric and hydrofluoric acids, washed and then heated to drive off the acid not washed out. Thus prepared, the silicon contained a little aluminum, a trace of carbon and 99.95 per cent of silicon. The last was determined by dissolving the powder in a hot concentrated solution of pure sodium hydroxide and making the usual separation of silica. The carborundum was purified by means of molten pyrosulphate and, after washing, it was floated in water and only the finer portion retained. It was next treated with nitrohydrofluoric acid to remove silicon and silica, 40

* C. R., lxx, 252.

† *Thermochimie* ii, 125, *Ann. de Chimie et Phys.* [5], xv, 213.‡ *Grundriss der allgemeinen Chemie*, dritte Auflage, 268.

grams losing only 0.5 gram. It was finally digested with only hydrofluoric acid, but there was no further loss in weight. The purity of the product was found as follows: 0.5254 gram was fused in a platinum crucible with 5 grams of potassium nitrate and 10 of sodium carbonate, and the silica was separated with the usual precautions. Silicon found 69.9, calculated 70.3 per cent for SiC; Si=28.4.

Combustions with Sodium Peroxide.

The bomb used in all of the work was one described in the paper on carbon.* It was lined with silver cups 1^{mm} in thickness. Owing to the danger of melting the lower cup the combustible mixture was usually placed in a thick silver dish resting near but not in contact with the bottom of the bomb. This dish was usually melted by the combustion. Silver, as is well known, is oxidized by molten sodium peroxide, but the amount of oxide formed is small and the error caused is slight. A nickel dish was tried, but this was attacked much more than the silver one. After a combustion with sodium peroxide the fused mass resulting was dissolved in a large quantity of water and the insoluble unburned substance was collected, purified and its weight deducted from the amount of material used for the experiment. In case of silicon some may have dissolved in the dilute alkaline solution, but this was not likely, as silicon is taken up slowly by concentrated alkali. In order that the iron used for ignition should burn well the bomb was filled with oxygen at atmospheric pressure. The carbon used was the acetylene modification described by the writer.†

Experiment 1.

Carbon	1.0530	grams.
“ not burned	—0.0143	“
“ burned	1.0387	“
Iron for ignition	0.072	“
Sodium peroxide	19	“
Water	2954	“
“ equivalent of calorimeter	311	“
“ “ “ sodium peroxide and carbon	4	“
“ “ “ system	3269	“
Minutes.	Temperature.	Temperature interval.
0	18.452	22.012—18.458 + 0.009 = 3.563°
1	18.454	
2	18.458	Heat observed 3269 × 3.563 = 11648°
3	22.012	“ of oxidation of iron —115°
9	22.012	
10	22.009	11533°
11	22.006	
12	22.003	For 1 gram of carbon 11103°

* This Journal, xix, 435.

† Loc. cit.

Experiment 2.

Carbon	1.2214	grams.
“ not burned	—0.0107	“
“ burned	1.2107	“
Iron for ignition	0.060	“
Sodium peroxide	21	“
Water equivalent of system	3244	“

Minutes.	Temperature.	Temperature interval.
0	18.241	$22.405 - 18.245 + 0.032 = 4.192^\circ$
1	18.243	
2	18.245	
15	22.405	Heat observed $3244 \times 4.192 = 13599^\circ$
16	22.404	“ of oxidation of iron -96°
17	22.399	13503°
18	22.397	
19	22.394	
20	22.391	For 1 gram of carbon 11149°
21	22.388	The motor stopped for a time after the ignition, hence the interval before the maximum temperature was observed was longer than usual.

Experiment 3.

Silicon	1.2320	grams.
“ not burned	—0.0003	“
“ burned	1.2317	“
Iron for ignition	0.058	“
Sodium peroxide	12.5	“
Water equivalent of system	3380.6	“

Minutes.	Temperature.	Temperature interval.
0	18.176	$21.242 - 18.184 + 0.009 = 3.067^\circ$
1	18.180	
2	18.184	
8	21.242	Heat observed, $3380.6 \times 3.067 = 10368^\circ$
9	21.240	“ of oxidation of iron -93°
10	21.238	10275°
11	21.236	
12	21.234	For 9 grams of silicon 8342°
13	21.233	

Experiment 4.

Silicon	1.4934 grams.	
“ not burned	0.0031	“
“ burned	1.4903	
Iron for ignition	0.050	
Sodium peroxide	15	“
Water equivalent of system	3454	“
Minutes.	Temperature.	Temperature interval.
0	18.425	22.060—18.431 + 0.008 = 3.637°
1	18.428	
2	18.431	Heat observed, 3544 × 3.637
8	22.060	“ of oxidation of iron
9	22.059	
10	22.058	12562°
11	22.056	12482°
12	22.054	For 1 gram of silicon
13	22.052	8379°

Experiment 5.

Silicon carbide	1.105 grams.	
“ “ not burned	0.075	“
“ “ burned	1.030	“
Iron for ignition	0.072	“
Sodium peroxide	11	“
Water equivalent of system	3565.6	“
Minutes.	Temperature.	Temperature interval.
0	18.442	21.120—18.450 + 0.007 = 2.677°
1	18.446	
2	18.450	Heat observed, 3565.6 × 2.677
8	21.120	“ of oxidation of iron
9	21.120	
10	21.118	9545°
11	21.117	—115°
12	21.116	9430°
13	21.115	For 1 gram of silicon carbide
		9156°

Experiment 6.

Silicon carbide	1.3987 grams.	
“ “ not burned	0.0073	“
“ “ burned	1.3914	“
Iron for ignition	0.0534	“
Sodium peroxide	15	“
Water equivalent of system	3432.8	“

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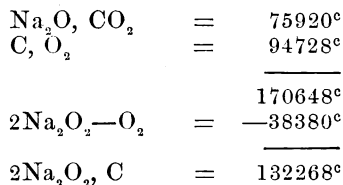
Minutes.	Temperature.	Temperature interval.
0	18·126	21·836—18·132 + 0·013 = 3·717°
1	18·128	
2	18·132	Heat observed $3432·8 \times 3·717 = 12760^\circ$
8	21·836	“ of oxidation of iron —85°
9	21·832	
10	21·829	12675°
11	21·827	
12	21·825	For 1 gram of silicon carbide 9110°
13	21·923	

The results of the combustions with sodium peroxide are as follows for 1 gram of each substance :

	Acetylene carbon	Crystalline silicon	Silicon carbide
	11103°	8342°	9156°
	11149°	8379°	9110°
Mean	11126°	8360°	9133°
For 12 grams of acetylene carbon			133512°
“ 28·4 “ “ crystalline silicon			237424°
			370936°
For 40·4 grams of silicon carbide			368973°
Difference			1963°

The above results indicate that the formation of silicon carbide is accompanied with but little thermal change. The heat of combustion of the diamond according to Favre and Silbermann is 93240°, 1488° less than that of acetylene carbon in oxygen; assuming, if the diamond had been burned with sodium peroxide, that the result would have been 1488° less, we have 515° for the heat of formation of silicon carbide from the diamond and crystalline silicon.

Using Thomsen's* data for the union of sodium oxide and carbon dioxide, deForcrand's† for the heat of formation of sodium peroxide from the oxide, and the heat of combustion of acetylene carbon, the thermal effect of carbon and sodium peroxide may be calculated thus :



* Thermochemische Untersuchungen iii, 233.

† C. R. cxxvii, 514.

The agreement of the calculated with the experimental result indicates, in the reaction between carbon and an excess of sodium peroxide, that sodium metacarbonate is formed and not the orthocarbonate. The latter is not known, but if it may result by the union of the metacarbonate and sodium oxide the thermal effect would be about the same as that of the oxidation of sodium oxide.

Combustions in Oxygen.

The combustions were made as follows: A mixture of acetylene carbon and silicon carbide or silicon was placed in a shallow silver foil dish supported near the middle of the bomb. The object was to expose a large surface of the mixture when burning to oxygen. Naphthalene and anthracene were tried but did not answer as well as finally divided carbon. That the temperature was sufficient to volatilize silicon was shown by the deposition of silica on the sides of the bomb in the form of a white powder. It settled very slowly in water and passed through filter paper. Under the microscope it was found to be spheroidal and non-crystalline. The silica from burning silicon carbide was all in a finely divided form, while in that from silicon globules 2 or 3^{mm} in diameter were found. The residue left by the combustion was treated with nitric acid to dissolve silver present and, after thorough washing, was repeatedly digested with hydrofluoric acid until its weight when dry was constant. Finally the residue was treated with nitrohydrofluoric acid, the loss being silicon and the powder remaining silicon carbide. The thick platinum electrodes, placed 4 or 5^{cm} above the combustible mixture in the bomb, were more or less melted by the combustions. In one instance a globule of platinum silicide formed which was found to contain 7 per cent of silicon. In no instance was silicon found in the platinum melted by the burning of silicon carbide.

Experiment 7.

Silicon carbide	0.9820 grams.
“ “ in residue	0.1700 “
Silicon “ “	0.0068 “
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Silicon carbide burned	0.8052 “
Iron for ignition	0.0466 “
Oxygen	11 “
Water and water equivalent of system	3433 “

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Minutes.	Temperature.	Temperature interval.	
0	18·013	$21·520 - 18·014 + 0·015 = 3·521^{\circ}$	
1	18·014		
2	18·014	Heat observed, $3433 \times 3·521$	= 12088°
7	21·520		
8	21·517	" of oxidation of iron,	—75°
9	21·513	" " " " carbon	—6331°
10	21·509		
11	21·505	" " " " silicon carbide	5682°

For 1 gram of silicon carbide 7057°

Experiment 8.

Silicon carbide	1·5029 grams.
" " in residue	0·3720 "
Silicon " "	0·0470 "
Carbon	0·6301 "
For 1 gram of silicon carbide 6659°	

Experiment 9.

Silicon carbide	0·744 grams.
" " in residue	0·158 "
Silicon " "	0·000 "
Silicon carbide burned	0·586 "
Carbon	0·931 "
Iron for ignition	0·049 "
Oxygen	11. "
Water and water equivalent of system	3448·6 "

Minutes.	Temperature.	Temperature interval.	
0	18·485	$21·818 - 18·488 + 0·007 = 3·337^{\circ}$	
1	18·488		
6	21·818	Heat observed, $3448·6 + 3·337$	= 11508°
7	21·816	" of oxidation of iron	—78°
8	21·814	" " " " carbon	—7349°
9	21·813		
10	21·811	" " " " silicon carbide	4081°
For 1 gram of silicon carbide 6963°			

Experiment 10.

Silicon carbide	1·1125 grams.
" " in residue	0·0436 "
Silicon " "	0·0422 "
Carbon	0·944 "
For 1 gram of silicon carbide 6882°	

Experiment 11.

Silicon carbide	1.0130	grams.
" " in residue	0.0984	"
Silicon " "	0.0089	"
Silicon carbide burned	0.9057	"
Carbon	1.1220	"
Iron for ignition.	0.0530	"
Oxygen	11.	"
Water and water equivalent of system.	3387.5	"

Minutes.	Temperature.	Temperature interval.	
0	18.308	22.573 — 18.314 + 0.012 = 4.271°	
1	18.311		
2	18.314	Heat observed	15322°
7	22.573	" of oxidation of iron	— 85°
8	22.571	" " " " carbon	— 8857°
9	22.567		
10	22.563	" " " " silicon carbide	6380°
11	22.561		

For 1 gram of silicon carbide 7044°

If the weight of carbide equivalent to the free silicon left by a combustion be deducted from the amount of carbide taken for an experiment, and the carbon equivalent to the free silicon be added to that taken, the results calculated on this basis will be essentially the same as those given. The following table shows the proportions of silicon carbide and free silicon remaining after the combustions:

		Silicon carbide.	Silicon.
Experiment 7	7057°	18 per cent.	0.7 per cent.
" 8	6659	25 " "	3 " "
" 9	6963	20 " "	0 " "
" 10	6882	33 " "	3.8 " "
" 11	7044	10 " "	0.8 " "

It was found in the work on silicon that where the products of combustion contain much free silicon there is a variable error. For this reason the figures of experiments 8 and 10 should not be included in the final result. The mean of the other three experiments is 7009 calories for the heat of combustion of 1 gram of silicon carbide in oxygen at 20°. For 40.4 grams it is 28216.4 calories at constant volume and 283750 calories at constant pressure.

The combustions of silicon in oxygen yielded poor results, and for this reason the details of the calorimetric work are omitted in the following statement of the results:

<i>Experiments</i>	<i>12</i>	<i>13</i>	<i>14</i>	<i>15</i>	<i>16</i>	<i>17</i>	<i>18</i>
Silicon taken	1.011	0.5331	1.4904	0.9058	1.0468	1.1932	1.2031
“ in residue	0.056	0.0300	0.3537	0.1150	0.1504	0.2159	0.2040
“ of SiC “	0.080	0.0990	0.0798	0.0224	0.0388	0.0758	0.0490
Silicon burned	0.875	0.4041	1.0569	0.7684	0.8576	0.9015	0.9500
Carbon taken	1.0033	1.2320	0.6300	0.8690	0.9511	1.0862	1.0493
Result for 1 gram of silicon...	6608°	7060°	6668°	6972°	6096°	6460°	6287°

It was observed that the products of some of the combustions of silicon gave off a gas when digested with cold dilute hydrofluoric acid. This gas was presumably hydrogen or a hydrocarbon resulting from the interaction of a soluble modification of silicon or a silicon compound and the acid. This is the most probable explanation of the wide variation in the results. The substance noted as silicon carbide in the foregoing table was the residue insoluble in nitrohydrofluoric acid. It was repeatedly found to yield carbon dioxide when fused with lead chromate and in one portion 68.7 per cent of silicon was obtained: calculated, 70.3 per cent for SiC. The carbide from the combustions was in the form of a light grey amorphous powder.

The heat of oxidation of silicon may be calculated as follows:

SiC, 2O ₂	=	283750°
Si, C	=	1963°
		<hr/>
		285713
C, O ₂	=	94728°
		<hr/>
Si, O ₂	=	190985°

Berthelot's* result is 180593° for the formation of gelatinous silicic acid from 28.4 grams of silicon.

Lithium orthosilicate is known and it is probable that sodium orthosilicate results when silicon burns in an excess of sodium peroxide. On this assumption the thermal effect of the combination of one molecule of silicon dioxide with two molecules of sodium oxide may be calculated thus:

2Na ₂ O, Si	=	237000
2Na ₂ O ₂ - O ₂	=	38000°
		<hr/>
		275000
Si, O ₂	=	-191000
		<hr/>
2Na ₂ O, SiO ₂	=	84000°

Experiments were made to determine the heat of combination as follows: Silicon dioxide in the form of a bulky impalpable powder, obtained by igniting silicic acid resulting from the decomposition of silicon fluoride in water, was used. A mixture of sodium peroxide, carbon sufficient to form an excess of sodium oxide, and silicon dioxide was ignited in the bomb. The temperature of the reaction was sufficient to melt silver. Less than 50° of oxygen were evolved. No free silica was found

* Loc. cit.

after dissolving the fused mass in a large volume of cold water. The mean of two results which agreed closely was 71000° for one molecule of silicon dioxide. The difference of 13000° between the calculated and observed result is due either to an error of 5 per cent in the heat of oxidation of silicon or to the formation of a mixture of silicates in the experiments with silica. In the latter instance the conditions are less favorable to the formation of only the orthosilicate. Hence we may consider that 84000° deduced from the reaction of silicon with sodium peroxide is the better result.

Summary of results.

$\text{SiC}, 2\text{O}_2$	=	283800°
Si crystalline, C amorphous	=	2000
Si " " , O_2	=	191000°
$2\text{Na}_2\text{O}, \text{SiO}_2$ amorphous	=	84000°

The figures given for the heat effect of the union of silicon and carbon are too small to indicate more than this, namely, that the formation of silicon carbide from its elements is accompanied with very small evolution or absorption of heat.