The Heat of Formation and the Specific Heat of Silicon Nitride.

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I. **Introduction.** The specific heat of silicon nitride has not yet been determined. Nor has the heat of formation of silicon nitride been measured directly in a calorimeter. The values so far reported in the literature are as follows: C. Matignon(1) obtained the value 159,300 cal. and W. B. Hincke and L. R. Brantley(2) reported the value 176,300 cal. at 1700°K. The object of the present paper is to determine the specific heat and from it the most probable value of the heat of formation of silicon nitride.

II. **Specimen.** (1) *Preparation of specimen.* For the preparation of silicon nitride, the following two methods were adopted: (a) In the first place, silicon amide was prepared by the action of ammonia on silicon tetrachloride:

$$SiCl_4 + 8\,NH_3 = Si(NH_2)_4 + 4\,NH_4Cl\ ,$$

(1) C. Matignon, *Bull. soc. chim.*, [4], **13** (1913), 791.
(2) W. B. Hincke and L. R. Brantley, *J. Am. Chem. Soc.*, **52** (1930), 48.

and then it was washed with liquid ammonia to remove ammonium chloride. Silicon amide thus purified was heated in nitrogen to 1200°C. and silicon nitride was obtained as follows[3]:

$$Si(NH_2)_4 \xrightarrow{0°C.} HNSi(NH_2)_2 \xrightarrow{100°C.} NSiNH_2 \xrightarrow{900°C.} HN(SiN)_2 \xrightarrow{1200°C.} Si_3N_4 .$$

Unfortunately, the product obtained in this way did not contain sufficient nitrogen.

(b) In the second place, purified nitrogen was passed over silicon (Kahlbaum) heated at 1300–1400°C. for ten hours (the method of L. Weiss and T. Engelhardt[4]). The silicon nitride thus obtained appeared greyish white and contained Si_2N_3, SiN, SiO_2, and some unchanged silicon. With the object of separating this unchanged silicon, SiN, and Si_2N_3, the nitrides were heated with 20% potassium hydroxide solution for seven hours. By this treatment, SiN was decomposed into silicon and nitrogen, and the silicon thus formed and the unchanged silicon are taken away as silicate. Next, the nitrides thus treated were put in a platinum dish containing 10 c.c. water mixed with 5 c.c. concentrated hydrofluoric acid and 5 c.c. concentrated nitric acid and left there for four days in order to take away Si_2N_3. The nitrides thus purified which contain Si_3N_4 and SiO_2 were washed with water and dried with alcohol and ether.

(2) *Analyses of specimen.* The nitrogen content of the above mentioned specimen was estimated by the method used by A. Dumas. The material to be analysed was intimately mixed with PbO and $PbCrO_4$ of equal quantity. The result thus obtained was 35.07% N. The silicon content was estimated by fusing the specimen with equal mixture of Na_2CO_3 and K_2CO_3. After dissolution in hydrochloric acid, the silica was filtered off and ignited. The result thus obtained was 58.44% Si. From the results shown above, the specimen may be considered to consist of 87.74% Si_3N_4 and 12.26% SiO_2.

III. **The Specific Heat of Silicon Nitride.** The mean specific heat of silicon nitride was measured by means of the ice calorimeter adopted by P. Oberhoffer[5]. The details of the measurement were already described in the measurement of the specific heat of aluminium nitride[6].

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(3) F. Lengfeld, *Am. Chem. J.*, **21** (1899), 531; Em. Vigoroux and C. Hugot, *Compt. rend.*, **136** (1903), 1670; M. Blix and W. Wirbelauer, *Ber.*, **36** (1903), 4220; A. Stock and F. Zeidler, *Ber.*, **56** (1923), 986.

(4) L. Weiss and T. Engelhardt, *Z. anorg. allgem. Chem.*, **65** (1909), 38.

(5) P. Oberhoffer, "Dissertation Aachen," (1907).

(6) S. Satoh, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **29** (1936), 19.

The measurement was carried out over the following three temperature intervals: 0–99.5, 0–316.4, and 0–585°C. The specimen was compressed and put into an aluminium cylinder of 8 mm. diameter and 2–3 mm. height. Over the above temperature intervals, the specific heat of pure aluminium was measured in order to see the correctness of the measurement.

(a) Measurement over the interval 0–99.5°C. Pure aluminium: 0.2193, 0.2171, 0.2175, mean: 0.2179. Specimen: 0.1761, 0.1766, 0.1753, mean: 0.1760.

The value of the mean specific heat of aluminium is in good agreement with that (0.2196) obtained by E. H. Griffiths and E. Griffiths[7]. The mean specific heat of the specimen is 0.1760 and this contains 87.74% Si_3N_4 and 12.26% SiO_2. When the correction was made on the assumption that the mean specific heat of SiO_2 in the specimen is 0.1862[8], the specific heat of pure Si_3N_4 became 0.1746.

(b) Measurement over the interval 0–316.4°C. Pure aluminium: 0.2308, 0.2321, mean: 0.2315. Specimen: 0.1972, 0.1956, mean: 0.1964.

The corresponding value of the mean specific heat of pure aluminium is not found in the literature but it is almost equal to that of the mean specific heat 0.2342 obtained by interpolating the values 0.2336 for 0–300°C. and 0.2374 for 0–400°C. which were determined by F. Wüst[9]. The mean specific heat of the specimen is 0.1964 and the author made the correction, assuming the mean specific heat of SiO_2 to be 0.2183[8], and obtained the mean specific heat of pure Si_3N_4: 0.1933.

(c) Measurement over the interval 0–585°C. Pure aluminium: 0.2440, 0.2434, 0.2448, mean: 0.2441. Specimen: 0.2188, 0.2190, 0.2195, mean: 0.2191.

The mean specific heat of pure aluminium is in accord with the value 0.2445 obtained by interpolating the values 0.2413 for 0–500°C. and 0.2452 for 0–600°C. which were shown by F. Wüst[9]. The mean value of the specimen is 0.2191, and making the correction on the supposition that the mean specific heat of SiO_2 is 0.2517[8], the mean specific heat of pure Si_3N_4 was found to be 0.2145.

The mean specific heat of pure silicon nitride (C_m) can be expressed by the following equation:

$$C_m = 0.1656 + 9.245 \times 10^{-5} t - 1.5 \times 10^{-8} t^2 .$$

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(7) E. H. Griffiths and E. Griffiths, *Phil. Trans.*, A, **214** (1914), 319.

(8) "International Critical Tables," Vol. 5, 105.

(9) F. Wüst, A. Meuthen, and R. Durrer, *Forschungsarb. Gebiete Ingenieurw.*, **204** (1918), 42.

If C is the true specific heat and is expressed by the following equation:

$$C = C_0 + \alpha t + \beta t^2 ,$$

by integration, we have

$$\int_0^t C dt = \int_0^t [C_0 + \alpha t + \beta t^2] dt = C_0 t + \frac{1}{2}\alpha t^2 + \frac{1}{3}\beta t^3 = C_m t .$$

Hence
$$C = \frac{d(C_m t)}{dt} .$$

Consequently, the true specific heat of pure silicon nitride can be expressed in the following equation:

$$C = 0.1656 + 1.847 \times 10^{-4} t - 4.5 \times 10^{-8} t^2 .$$

IV. **The Specific Heat of Silicon.** The specific heat of silicon was measured by A. Magnus[10]. By introducing $\beta\nu = 712$ into Debye's equation, C_v values can be obtained and C_p values computed from the equation

$$C_p - C_v = 1.42 \times 10^{-5} C_p^2 T$$

give a satisfactory result over a wide temperature range. But in order to simplify the calculation, the variation of the molecular heat of silicon with absolute temperature can be expressed in the following equation:

$$C_p = 3.724 + 4.816 \times 10^{-3} T - 2.186 \times 10^{-6} T^2 .$$

V. **The Heat of Formation of Silicon Nitride.** (1) *From the experimental formula.* From the equilibrium data of the reaction $Si_3N_4 = 3Si + 2N_2$ at high temperatures, the heat of formation of silicon nitride was calculated in the following way: The dissociation pressure of the above reaction at 1600°K. and 1800°K. was measured by W. B. Hincke and L. R. Brantley[2]:

$$\log P_{N_2} = -\frac{19250}{T} + 8.54 .$$

And the free energy equation is expressed as follows:

$$\Delta F^\circ = 176{,}300 - 78.35\, T.$$

Consequently, the heat of reaction at 1700°K. is 176,300 cal.

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(10) A. Magnus, *Ann. Physik*, **70** (1923), 303.

As shown in Chapter III, the molecular heat of silicon nitride at 25°C. is 23.85 which can be obtained from the equation:

$$C_p = 0.1656+1.847\times10^{-4}t-4.5\times10^{-7}t^2 .$$

As shown in Chapter IV, the atomic heat of silicon is expressed in the following equation:

$$C_p = 3.724+4.816\times10^{-3}T-2.186\times10^{-6}T^2 .$$

According to G. N. Lewis and M. Randall(11), the molecular heat of nitrogen is:

$$C_p = 6.5+0.001\,T .$$

Thus in the reactant we have Si_3N_4: 23.85, and in the resultant, we have

$$3\,Si\ :\ 11.17+1.445\times10^{-2}T-6.558\times10^{-6}T^2 ,$$

$$2\,N_2\ :\ 13.00+2\times10^{-3}T ,$$

$$\therefore\quad Si_3N_4 :\ 24.17+1.645\times10^{-2}T-6.558\times10^{-6}T^2 .$$

Consequently in the whole system, the terms referring to the specific heats are

$$0.322+1.645\times10^{-2}T-6.558\times10^{-6}T^2 .$$

Next, by combining the molecular heat terms with ΔH, the equation of the heat of reaction can be expressed as follows:

$$\Delta H = \Delta H_0+0.322\,T+8.225\times10^{-3}T^2-2.186\times10^{-6}T^3 .$$

The free energy equation of the reaction is, therefore,

$$\Delta F^\circ = \Delta H_0-0.322T\ln T-8.225\times10^{-3}T^2+1.093\times10^{-6}T^3+IT .$$

From the equation $\Delta F^\circ = 176{,}300 - 78.35T$ obtained by W. B. Hincke and L. R. Brantley(2) we find that $\Delta F^\circ = 50{,}940$ at 1600°K. and $\Delta F^\circ = 35{,}270$ at 1800°K.

Introducing these values into the free energy equation, the values ΔH_0 and I can be obtained as shown below:

$$\Delta H_0 = 162{,}204 , \qquad I = -56.84 .$$

Hence, $\Delta H = 162{,}204+0.322\,T+8.225\times10^{-3}T^2-2.186\times10^{-6}T^3 ,$

$$\Delta F^\circ = 162{,}204-0.322T\ln T-8.225\times10^{-3}T^2+1.093\times10^{-6}T^3-56.84T .$$

(11) G. N. Lewis and M. Randall, "Thermodynamics," 80, (1923).

Consequently the heat of reaction at 25°C. is $\Delta H_{298} = 163{,}024$.
As shown in the above computation, the result obtained is as follows:

$$3Si + 2N_2 = Si_3N_4 + 163{,}024.$$

(2) *From the Nernst's heat theorem.* By the use of the Nernst's heat theorem, the author calculated the heat of formation of silicon nitride as follows: In the reaction $Si_3N_4 = 3Si + 2N_2$, the change of molecular number of the gaseous system is $\Sigma n = 2$.

If Q is the heat of reaction at any temperature and Q_0 is that at absolute zero, Q may be expressed in the following equation by the Nernst's heat theorem:

$$Q = Q_0 + \sum n \cdot 3.5T + aT^2 .$$

Differentiating with respect to T, we obtain

$$\frac{dQ}{dT} = \sum mC_p = 2 \times 3.5 + 2aT .$$

The molecular heat of each substance at 25°C. follows: Si_3N_4: $C_p = 23.85$; Si: $C_p = 4.965$; N_2: $C_p = 6.798$.
Accordingly,

$$a = \frac{3 \times 4.965 + 2 \times 6.798 - 23.85 - 7}{2 \times 298} = -0.003958 .$$

The chemical constant of N_2 is 2.6. So that $\Sigma nI = 2 \times 2.6 = 5.2$, and

$$\log K = -\frac{Q_0}{4.576T} + 3.5 \log T - \frac{0.003958}{4.576} T + 5.2 .$$

According to W. B. Hincke and L. R. Brantley[(2)]

$$\log P_{N_2} = -\frac{19250}{T} + 8.54 .$$

$$\log P_{N_2} = -3.49 \text{ at } 1600^\circ\text{K}.$$

Hence, $\log K = \log P^2_{N_2} = -\frac{Q_0}{4.576T} + 3.5 \log T - \frac{0.003958}{4.576} T + 5.2$,

$$-3.49 \times 2 = -\frac{Q_0}{4.576 \times 1600} + 3.5 \log 1600 - \frac{0.003958}{4.576} \times 1600 + 5.2 .$$

$$\therefore \quad Q_0 = 161{,}250 , \quad Q = Q_0 + 2 \times 3.5T + aT = 162{,}984 \text{ (at } 25^\circ\text{C.)}.$$

This result is tantamount to that obtained by the experimental formula.

(3) C. Matignon(1) measured the equilibrium data of the reaction

$$3SiO_2 + 6C + 2N_2 = Si_3N_4 + 6CO$$

at 1700°K. and by the use of Nernst's approximate formula calculated the heat of formation of silicon nitride at room temperature to be 159,300 cal.

VI. **Discussion of the Result.** As shown above, the most probable value of the heat of formation of silicon nitride is

$$3Si + 2N_2 = Si_3N_4 + 163,000.$$

Comparison of the heat of formation of silicon nitride reported in the literature until now is as follows: 176,300 (W. B. Hincke(2)); 163,000 (S. Satoh); 159,300 (C. Matignon(1)).

The heats of formation of the nitrides of the elements: Na, Mg, Al, Si, P, S, and Cl which belong to the second series of the periodic table per one gram atom of nitrogen in the solid or liquid state are indicated in the following table in the order of their atomic numbers.

Atomic number	Nitrides	Heat of formation per one gram of nitrogen (kcal.)
11	(NaN_3)	− 1.7
12	Mg_3N_2	+57.6
13	AlN	+74.7
14	Si_3N_4	+40.7
15	P_3N_5	+16.3
16	SN	−31.9
17	NCl_3	−54.7

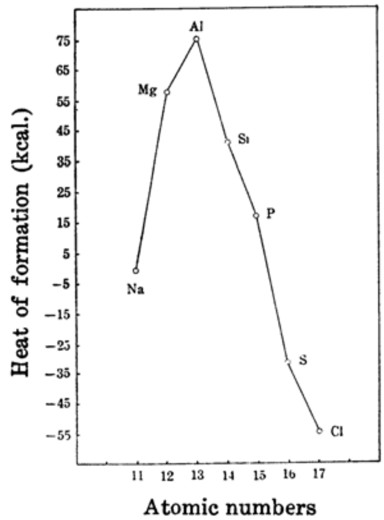

Fig. 1. Relationship between the heat of formation of nitrides of the elements belonging to the second series of the periodic table and their atomic numbers.

The heat of formation of sodium nitride is not yet known but the heat of formation of sodium azide is − 1.7 kcal. per one gram of nitrogen(12).

(12) E. Briner and P. Winkler, *J. chim. phys.*, **20** (1922), 203.

The heat of formation of magnesium nitride is 57.6 kcal.[13] and that of aluminium nitride is 74.7 kcal. as shown in the previous paper[6].

The heat of formation of silicon nitride is 40.7 kcal. as calculated above and that of phosphorus nitride is 16.3 kcal.[14]

The heat of formation of sulphur nitride is -31.9 kcal.[15] and that of nitrogen chloride is -54.7 kcal.[16]

In Fig. 1, the relation between the heats of formation of nitrides per one gram atom of nitrogen and their atomic numbers is shown graphically; the curve shows the maximum for aluminium. This bears a striking resemblance to the appearance of the maximum for beryllium in the curve showing the relationship between the heats of formation of nitrides of the elements belonging to the first series of the periodic table and their atomic numbers, which was reported in my last paper[17].

Summary.

As the specific heat of silicon nitride has not yet been determined, the mean specific heat of silicon nitride was measured by the ice calorimeter over three temperature intervals: 0–99.5, 0–316.4, and 0–585°C., and the equation of the true specific heat was obtained which holds good over the above temperature ranges:

$$C = 0.1656 + 1.847 \times 10^{-4}t - 4.5 \times 10^{-8}t^2 .$$

By using this value, the heat of formation of silicon nitride was computed from the dissociation pressure of silicon nitride at high temperatures. The result obtained is as follows:

$$3Si + 2N_2 = Si_3N_4 + 163,000.$$

The relationship between the heats of formation of nitrides of the elements belonging to the second series of the periodic table and their atomic numbers is discussed.

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(13) B. Neumann, C. Kröger, and H. Kunz, *Z. anorg. allgem. Chem.*, **207** (1932), 139.
(14) A. Stock and F. Wrede, *Ber.*, **40** (1907), 2923.
(15) M. Berthelot and Vieille, *Ann. chim. phys.*, [5], **27** (1882), 204.
(16) W. A. Noyes and W. F. Tuley, *J. Am. Chem. Soc.*, **47** (1925), 1336.
(17) S. Satoh, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **29** (1936), 53.