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HEAT OF FORMATION OF SILICON CARBIDE AND PRODUCTS OF ITS EVAPORATION

by

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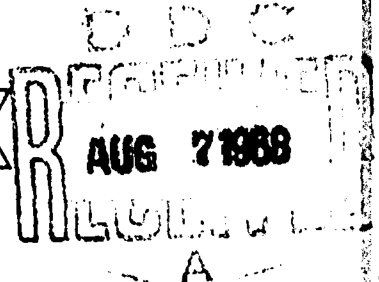

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HEAT OF FORMATION OF SILICON CARBIDE AND PRODUCTS OF ITS EVAPORATION

By: N. I. Voronin, N. L. Makarov and B. F. Yudin

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ABSTRACT: The study was undertaken in order to determine the heats of formation of SiC and products of its vaporization from vapor pressure data. Langmuir's method was used to determine the total vapor pressure over SiC and partial pressures of Si, Si_2C and SiC_2 at temperatures of 2113, 2193 and 2273°K. This method involves the use of the following formula for the equilibrium pressure of the substance during its vaporization from an open surface:

$$P = \frac{m}{St}\sqrt{\frac{2\pi RT}{M}}$$

The results of the calculations are shown in Table 1. The data are compared with those reported in the literature. Orig. art. has: 4 tables and 4 formulas. English translation: 7 pages.

Table 1. Heats of Formation of Silicon Carbide and Products of Its Vaporization

Temperature of experiment (°K)	$\Delta H^\circ_{f298.15}$ (kcal/mole)			
	SiC_{solid}	Si_{gas}	Si_2C_{gas}	SiC_{2gas}
2113	−22.75	[illegible]	148.78	152.30
2193	−26.98	[illegible]	148.14	152.86
2273	−28.22	[illegible]	151.90	151.57
Adopted value	−27.8	[illegible]	[illegible]	[illegible]

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

HEAT OF FORMATION OF SILICON CARBIDE AND PRODUCTS OF ITS EVAPORATION

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(All-Union Institute of Refractor Materials)

Silicon carbide, thanks to its specific properties, finds ever wider application in the national economy. The high thermal conductivity, thermal stability, strength, and chemical inertness, permit using this material for the manufacture of heating elements, corrosion stable refractories abrasives, and other special materials.

In period of exploitation of silicon carbide articles there often take place various chemical processes, the degree of completeness and direction of which can be estimates by thermodynamic calculation methods. But literature data on heats of formation of silicon carbide and products of its evaporation differ from each other considerably, which undoubtedly lowers the authenticity of thermodynamic analysis.

This work was undertaken for the purpose of determining heats of formation of silicon carbide and products of its evaporation according to vapor pressure data. For the determination of total vapor pressure we used the Langmuir method. According to this method, the equilibrium pressure of the substance during its evaporation from open surface is expressed by the formula

$$P=\frac{m}{St}\sqrt{\frac{2\pi RT}{M}}, \quad (1)$$

where m – change in weight (Γ); S – surface of evaporation (cm^2); M – molecular weight of vapor; R – gas constant; T – temperature (°K); t – hold time (s).

In the experiments there was used silicon carbide of the

composition (%): SiC — 98.4, Si — 0.46, MgO — 0.10, CdO — 0.07, (Fe_2O_3 + TiO_2) — 0.60, Al_2O_3, SiO_2 — 0.46. Size of grain was 50 μ.

The experiments were carried out in graphite crucibles with a diameter of 20 mm. For the value of evaporation area S we took the area of the surface section of the crucible.

The crucibles with samples of silicon carbide (∼5g) were heated to a definite temperature in a [TBB-4] [TVV-4] electrovacuum furnace and then held at the rated temperature for a known time interval (from 5 to 60 min), and after cooling they were weighted. Heating to rated temperature occurred during 20-25 minutes by one and the same regime. The vacuum in the furnace in the heating process was maintained not lower than 10^{-3} mm Hg; during holding it was 10^{-4} mm Hg. The vacuum was controlled by a [ВИТ-1] [VIT-4] instrument. The temperature during the experiment was measured by an [ОППИР-09] [OPPIR-09] optical pyrometer (accuracy ±10° over the internal surface of the crucible, simulating an absolute black body.

As basic material for the crucibles we selected graphite, as the most inert material in vacuum. In spite of greater practicality in operation, molybdenum crucibles could not be used because during their testing was established that at a temperature higher than 1600°C gaseous silicon reacts with the material of the crucible, forming a fusible compound (presumably of eutectic composition).

We have noticed, however, that the weight of the graphite crucible changes somewhat from experiment to experiment. In view of this along with control experiments there were established corrections for the change in weight of the crucible during the time of holding. Furthermore, a correction was introduced for the change in the crucible with the sample during preliminary heating. Experiments with a previously fired sample showed that during the time of heating to the rated temperature all volatile admixtures are practically completely removed. Thus, the change in weight obtained, with consideration of both corrections can be entirely referred to silicon carbide evaporation. In Table 1 are given the results of our measurements.

According to De-Maria and Inghram [1], in the process of silicon carbide evaporation the following compounds can be formed. Si (gas), $SiC_{2\,\text{газ}}$, $Si_2C_{\text{газ}}$, and in a very insignificant degree — $SiC_{\text{газ}}$. In view of this, silicon carbide evaporation can be presented by the following processes:

1) $SiC_{\text{тв}} = Si_{\text{газ}} + C_{\text{тв}}, \quad Kp_1 = P_{Si};$

2) $SiC_{\text{тв}} = {}^1/_2 Si_2C_{\text{газ}} + {}^1/_2 C_{\text{тв}}, \quad Kp_2 = P^{1/2}_{Si_2C};$

3) $SiC_{\text{тв}} = {}^1/_2 SiC_{2\,\text{газ}} + {}^1/_2 Si_{\text{газ}}, \quad Kp_3 = P^{1/2}_{SiC_2} \cdot P^{1/2}_{Si};$

4) $SiC_{\text{тв}} = SiC_{\text{газ}}, \quad Kp_4 = P_{SiC}.$

We will determine the composition of vapor at equilibrium evaporation of silicon carbide, on the basis of above reaction equations by formula

$$\Delta Z_T = \Delta I_T - T\Delta S, \tag{2}$$

where ΔZ_T – change in isobaric-isothermal potential in the course of ΔI_T – thermal reaction effect; ΔS_T – change in entropy in the course of reaction. We will find the values of Kp_1, Kp_2, Kp_3, using the relationship

$$\ln Kp = -\frac{\Delta Z_T}{RT}. \tag{3}$$

Since reactions (1) and (3) occur jointly, then

$$Kp_3 = P_{SiC_2}^{1/2} \cdot Kp_1^{1/2}$$

and

$$P_{SiC_2} = \left(\frac{Kp_3}{Kp_1^{1/2}}\right)^2.$$

Values of partial pressures of Si, Si_2C, and SiC are found directly from equilibrium constants.

According to the Dalton's law the total vapor pressure in the system is:

$$P_{общ} = P_{Si} + P_{SiC_2} + P_{Si_2C} + P_{SiC} \text{ и}$$

$$N_{SiC_2} = \frac{P_{SiC_2}}{P_{общ}}, \quad N_{Si_2C} = \frac{P_{Si_2C}}{P_{общ}}, \quad N_{Si} = \frac{P_{Si}}{P_{общ}}, \quad N_{SiC} = \frac{P_{SiC}}{P_{общ}}.$$

Using these relationships, we will determine the average molecular weight of vapors over SiC_{TB}:

$$M_{ср} = \sum_i N_i \cdot M_i.$$

The most reliable data about the composition of vapors above silicon carbide were obtained by De-Maria and Inghram [1]. These data were then used in reference book [2] for the calculation of thermodynamic functions of silicon carbide evaporation products.

Having adopted as basic the values of functions given in reference book [2], we calculated the values Kp_1, Kp_2, Kp_3, Kp_4, accordingly to N_i and M_{cp} for all investigated temperatures. Results of calculation are given in Table 2.

Table 1. Change in Weight of Sample In Dependence Upon Holding and Temperature

Temperature (°K)	Loss in weight (g).				
	300 s	600 s	900 s	1800 s	3600 s
2113	—	—	0.016 0.015	0.028	0.055
2193	0.008	0.017 0.014	0.025	0.038	0.092 0.090
2273	—	0.40 0.034	— —	0.125 0.102	0.212 0.205

Table 2. Composition and Molecular Weight of Vapor During Equilibrium Evaporation of Silicon Carbide

Temperature (°K)	N_{Si}	N_{SiC_2}	N_{Si_2C}	N_{SiC}	$M = \sum_i N_i M_i$
2113	0.896	0.058	0.046	~0	31.53
2193	0.864	0.075	0.061	~0	32.10
2273	0.829	0.093	0.078	~0	33.69

We determined partial pressures of evaporation components by the relationship

$$P_i = N_i \cdot P, \tag{4}$$

where P — vapor pressure above SiC, as measured by us. Table 3 presents values P and P_i, calculated by us by formulas (1) and (4).

Using relationships (2) and (3), we determine values of ΔI_T — of the thermal effect of processes (1)-(3) at temperature T. Since

$$\Delta I_T = \Delta H_{298} + \Delta(H_T - H_0) - \Delta(H_{298} - H_0),$$

where ΔH_{298} — thermal effect of the process at 298.15°K, and $(H_T - H_0)$ — increment in the enthalpy of the component, by using data of Table 3 and literature data [2] we will determine the thermal effects of processes (1)-(3) at 298.15°K.

Knowing the heat of evaporation of silicon [2], by the value ΔH°_{298} of process (1) we determined the heat of formation SiC_{TB} from elements in their standard states at 298.15°K. Analogously, using the value $\Delta H^\circ f_{298.15}(SiC_{TB})$ derived by us, we determined heats of formation of Si_2C_{ra3}, SiC_{2ra3} and SiC_{ra3}. Results of calculations are given in Table 4.

Table 3. Total Vapor Pressure and Partial Pressures of Components of Evaporation of Silicon Carbide

Temperature °K	$p_{общ}$ (atm)	p_{Si} (atm)	p_{SiC_2} (atm)	p_{Si_2C} (atm)
2113	$9.905 \cdot 10^{-7}$	$8.88 \cdot 10^{-7}$	$5.75 \cdot 10^{-8}$	$4.56 \cdot 10^{-8}$
2193	$1.56 \cdot 10^{-6}$	$1.35 \cdot 10^{-6}$	$1.17 \cdot 10^{-7}$	$9.51 \cdot 10^{-8}$
2273	$3.71 \cdot 10^{-6}$	$3.08 \cdot 10^{-6}$	$3.45 \cdot 10^{-7}$	$2.89 \cdot 10^{-7}$

Table 4. Values of Heats of Formation of Silicon Carbide and Products of its Evaporation

Temperature of experiment (°K)	$\Delta H^\circ f_{298.15}$ (kcal/mole)			
	SiC_{TB}	SiC_{ra3} *	2	Si_2C_{ra3}
2113	−23.75	—	143.76	118.90
2193	−26.98	—	149.14	122.02
2273	−28.22	—	151.90	123.17
Value taken by us **	−27.6	163.2	150.5	122.6

[1]Value of heat of formation of SiC_{ra3} was calculated according to the value of the heat of evaporation of SiC [2] with the use of the value of heat of formation of SiC_{TB} taken by us.

[2]The accepted values of heats of formation represent an average of measurement results at 2193 and 2273°K, since at 2113°K the vapor pressure becomes a quantity of the same order as the pressure of the medium. In these conditions the Langmuir method may lead to considerable deviations from the true value.

The error of our values $\Delta H^\circ f_{298.15}$ calculated by the quadratic formula constitutes

for $SiC(TB) \pm 5$ kcal/mole,
for $SiC_2(ra3) \pm 7.5$ »»,
for $Si_2C(ra3) \pm 7.5$ »»,
for $SiC(ra3) \pm 7.0$ »».

It should be mentioned that the basic error is determined by inaccuracy of the value of heat of sublimation of Si (± 5 kcal/mole) [1].

Ruff and Konschak [3] have also investigated the process of evaporation of silicon carbide in the temperature range 2600-2990°K by the method of boiling points. Their calculations were carried out in the assumption that evaporation products are Si and SiC, hence there was calculated the quantity of $SiC_{крист}$ evaporated in form of $SiC_{газ}$ and with decomposition into $C_{графит}$ and, $Si_{газ}$.

Later De-Maria and Inghram [1] investigated the composition of silicon carbide vapors and showed that besides silicon in gaseous state, the basic evaporation products are Si, Si_2C, and SiC_2, and the partial pressure of SiC constitutes less than 0.001 of the sum of pressures of Si, Si_2C, and SiC_2. The results of this investigation were used by us. Considering the actual composition of vapor, we recalculated the data in [3] by our method and obtained the heat of formation $SiC_{(ТВ)}$ equal to -12.7 kcal/mole. But it should be mentioned that the scattering of individual values in [3] constitutes in absolute value more than 10 kcal.

Mixter [4] measured heats of combustion of graphite, silicon and silicon carbide in sodium peroxide and by these data calculated the heat of formation $\Delta H°f_{298.15}(SiC_{ТВ})$ or -3 kcal/mole. The presence of side reactions and inaccurate analysis of combustion products lower the value of this work.

Ruff and Griger [5] conducted a repeated measurement by the same method and, having eliminated certain errors allowed in the Mixter work, they found the value -27 kcal/mole.

Wartenberg and Schuette [6] determined the heat of combustion of silicon carbide and carbon in flourine and by the obtained data they determined the heat of formation of silicon carbide as -31 ± 6 kcal/mole. This value cannot be considered fully reliable, since the heats of combustion of silicon and carbon in fluorine found by Wartenberg and Schuette are considerably different from the most exact contemporary data.

Brunner [7] calculated the value of the heat of formation of SiC on the basis of measurement of equilibrium constants of reactions

$$SiO_{2\,крист.\,кварц} + 3C_{графит} = SiC_{крист} + 2CO_{газ}.$$

The heat of formation of silicon carbide corresponds to values of equilibrium constants of this process:

$$\Delta H°f_{298.15}(SiC_{тв}) = -7 \pm 8 \text{ kcal/mole}$$

Humphrey, Todd, Coughlin and King [8] determined the heat of combustion of cubic and hexagonal modifications of silicon carbide.

Considering that during the combustion of SiC cristobalite will be formed (as in the case of silicon combustion), we will obtain a value of $\Delta H^\circ f_{298.15}$ (SiC_{TB}) = -11.8 kcal/mole.[1]

From this short survey is evident that the heat of formation of silicon carbide given in various sources varies within limits of from -3 to -31 kcal/mole. The value obtained by us is in conformity, within limits of measurement errors, with the data of Ruff and Griger [5] and Wartenberg and Schuette [6].

Conclusions

1. The total vapor pressure above silicon carbide and partial pressure of Si, Si_2Cu, SiC_2 at temperatures 2113, 2193 and 2273°K were determined by the Langmuir method.

2. Standard heats of formation of SiC_{TB}, SiC_{ra3}, SiC_{2ra3} and Si_2C_{ra3} at 25°C were determined.

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11 February 1964

[1]There is no original copy of report [8] in the Soviet Union.