M-1985(N)

J. Chem. Thermodynamics **1986,** 18, 801–802

Note

The standard molar enthalpy of formation of SiF_4(g) at 298.15 K by fluorine bomb calorimetry[a]

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(Received 3 February 1986)

Recent work at this laboratory on the determination of the enthalpy of formation of silicalite, a polymorph of SiO_2, lead us to reexamine the previous measurements(1) of $\Delta_f H_m^\circ(SiF_4, g)$ conducted at this laboratory in 1963. This quantity is used in deriving $\Delta_f H_m^\circ(SiO_2)$. Although we had no reason to suspect that the value previously derived was significantly in error, we decided to redetermine $\Delta_f H_m^\circ(SiF_4, g)$ because: the differences obtained in the energies of combustion of the powdered and granular samples in the 1963 study suggests the possibility of incorrect impurity corrections or biased analyses; there was uncertainty about how the correction for the energy of expansion ΔU(blank) of fluorine from the tank into the bomb was calculated;(2) and very pure silicon is currently available and we now have over twenty additional years' experience in conducting fluorine bomb-calorimetric measurements.

The sample of Si, batch S.70157, was obtained from Johnson Matthey Chemicals Ltd. in the form of broken ingot. Analyses showed the sample contained mass fractions ($\times 10^6$) of O, 25; C, 6; N, 1; Fe, 2; and Cr, 1. The Si, even in lump form, was spontaneously combustible in fluorine necessitating the use of a two-chambered reaction vessel. All procedures in which the bomb was opened or the sample was exposed were conducted in a helium-atmosphere glovebox. The calorimetric sample was contained in a 55 g nickel crucible and the tank was charged to 791 kPa with F_2. All reactions were complete with no discernible attack to the nickel crucible. The results of seven combustions of silicon in fluorine according to the reaction:

$$\mathrm{Si(cr)} + 2\mathrm{F_2(g)} = \mathrm{SiF_4(g)}, \qquad (1)$$

are given in table 1. Symbols in the table have the usual significance,(3) and ε(calor), the energy equivalent of the calorimetric system, was determined by five combustions of NBS standard benzoic acid in oxygen to be $(14074.4 \pm 1.3)\ \mathrm{J \cdot K^{-1}}$.

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[a] Work supported by the U.S. Department of Energy, Division of Engineering, Mathematics and Geosciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.

TABLE 1. Energy of combustion in fluorine of silicon ($p^\circ = 101325$ Pa)

Expt no.	1	2	3	5	6	7	9
$m(\mathrm{Si})/\mathrm{g}$	0.12544	0.25483	0.24975	0.24960	0.25537	0.25416	0.12642
$\Delta\theta_e/\mathrm{K}$	0.51151	1.03870	1.01774	1.01708	1.04025	1.03583	0.51527
$\varepsilon(\mathrm{calor})(-\Delta\theta_c)/\mathrm{J}$	−7199.2	−14619.1	−14324.1	−14314.8	−14640.9	−14578.7	−7252.1
$\Delta U(\mathrm{contents})/\mathrm{J}$ [a]	−13.5	−27.6	−27.0	−27.0	−27.6	−27.5	−13.6
$\Delta U(\mathrm{gas})/\mathrm{J}$ [b]	0.5	1.0	1.0	1.0	1.0	1.0	0.5
$\Delta U(\mathrm{blank})/\mathrm{J}$	4.7	4.7	4.7	4.7	4.7	4.7	4.7
$\{\Delta_c U^\circ_m/M(\mathrm{sample})\}/(\mathrm{J \cdot g^{-1}})$	−57457.7	−57454.0	−57439.0	−57436.3	−57417.9	−57446.1	−57431.6

$\{\Delta_c U^\circ_m/M(\mathrm{sample})\} = -(57440.4 \pm 5.2)\ \mathrm{J \cdot g^{-1}}$ [c]

Impurity correction $= -(2.1 \pm 0.5)\ \mathrm{J \cdot g^{-1}}$ [c]

$\{\Delta_c U^\circ_m/M(\mathrm{Si})\} = -(57442.5 \pm 16.4)\ \mathrm{J \cdot g^{-1}}$ [d]

[a] Auxiliary data used: $c_p^\circ/(\mathrm{J \cdot K^{-1} \cdot g^{-1}})$, 0.712 (Si), and 0.444 (Ni); and $C^\circ_{V,m}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$, 22.99 ($F_2$) and 65.33 ($SiF_4$) were taken from reference 4.

[b] The volumes of the empty bomb and tank were 0.3059 and 0.2361 $\mathrm{dm^3}$, respectively.

[c] Uncertainty is the standard deviation of the mean.

[d] Uncertainty is the uncertainty interval.

The ΔU(blank) correction, (4.7 ± 0.6) J, calculated as previously described,(2) is the average of five blank experiments in which fluorine was expanded into an empty bomb. The impurity correction is due solely to the oxygen impurity, assumed to be present as SiO_2. From the mean specific energy of combustion $-(57442.5 \pm 16.4)\ \mathrm{J \cdot g^{-1}}$ and the molar mass of Si, $28.0855\ \mathrm{g \cdot mol^{-1}}$, we derive for reaction (1) at $T = 298.15$ K: $\Delta_c U^\circ_m(\mathrm{Si, cr}) = \Delta_f U^\circ_m(\mathrm{SiF_4, g}) = -(1613.30 \pm 0.46)\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_c H^\circ_m(\mathrm{Si, cr}) = \Delta_f H^\circ_m(\mathrm{SiF_4, g}) = -(1615.78 \pm 0.46)\ \mathrm{kJ \cdot mol^{-1}}$. We believe this latter result to be more reliable than that previously reported from this laboratory, $-(1614.94 \pm 0.79)\ \mathrm{kJ \cdot mol^{-1}}$,(1) for the reasons previously stated. The two results, however, are clearly in agreement within their combined uncertainties.

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