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Technical Note

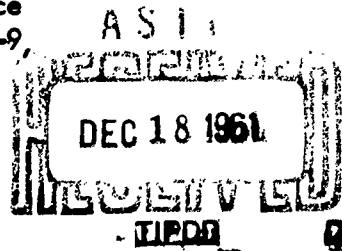
THE HEAT OF FORMATION OF SILICA

by

W. D. Good

November 1961

Propulsion Research Division, Air Force Office  
of Scientific Research, Contract No. CSO 59-9,  
ARPA Order No. 24-59, Task 3



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Communication to the Editor

THE HEAT OF FORMATION OF SILICA<sup>1</sup>

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(1) Presented at the International Calorimetry Conference, Ottawa, Canada, August 14-18, 1961.

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Sir:

The free energy of formation of silica is a subject of current interest. Chipman<sup>2</sup>

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(2) J. Chipman, J. Am. Chem. Soc., 83, 1762 (1961).

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has discussed evidence that the free energy of formation of silica (in any of its various forms) is about 5 kcal. mole<sup>-1</sup> more negative than the presently accepted value.

Recent work in this laboratory has shown that the thermochemical discrepancies noted by Chipman are due to error in the reported heat of formation data.<sup>3</sup> The earlier heat

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(3) J. P. Coughlin, U. S. Bur. Mines Bull. 542 (1954); G. L. Humphrey and E. G. King, J. Am. Chem. Soc., 74, 2041 (1952).

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of formation value was based on measurements of the heat of combustion of silicon in an oxygen bomb. The value reported here was obtained by a different thermochemical process, which avoided uncertainties inherent in the earlier method.<sup>3</sup>

In the present experiments, the heat of formation of aqueous fluosilicic acid was determined in a rotating-bomb calorimeter. Mixtures of silicon and vinylidene fluoride polymer were burned in oxygen in the presence of aqueous HF, the product

of combustion being fluosilicic acid in excess HF solution. Experimental procedures were similar to those already described.<sup>4</sup> A sample of high purity silicon (99.96% Si,

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(4) W. D. Good, D. R. Douslin, D. W. Scott, Ann George, J. L. Lacina, J. P. Dawson and Guy Waddington, *J. Phys. Chem.*, 63, 1133 (1959); W. D. Good, D. W. Scott and Guy Waddington, *ibid.*, 60, 1080 (1956).

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0.04% SiO<sub>2</sub>; 50 to 75 micron particle size) was obtained through the courtesy of Dr. J. E. Kunzler, Bell Telephone Laboratories, Murray Hill, N. J. The combustion samples were prepared by mixing the silicon and powdered vinylidene fluoride polymer inside sealed polyester bags, which were then rolled and pelleted. The samples burned completely, and all of the silicon was converted to aqueous fluosilicic acid.

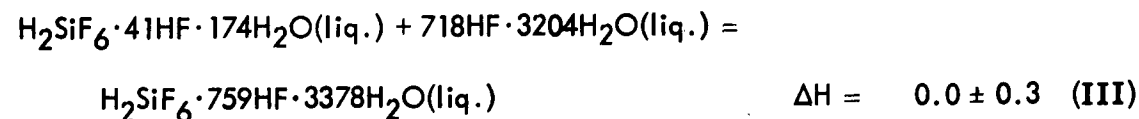
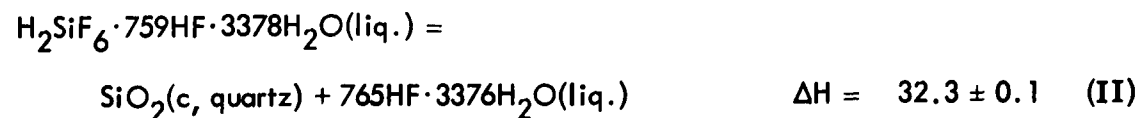
The result obtained for the heat of formation of fluosilicic acid and those for the heat of solution of silica in aqueous HF reported by King<sup>5</sup> permit calculation of

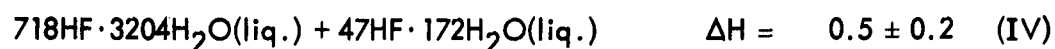
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(5) E. G. King, *J. Am. Chem. Soc.*, 73, 656 (1951).

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the heat of formation of silica. The thermochemical equations are:





The heats of reaction are expressed in kilocalories at 25°C. Equation I gives the result of the measurements of this laboratory. Equation II gives the result of the heat of solution measurements of King<sup>5</sup>, extrapolated to 25°C. and corrected for the change in the atomic weight of silicon from 28.06 to 28.09. Equation III represents a dilution reaction studied in this laboratory by a somewhat crude method already described.<sup>6</sup> The heat of eq. III was found to be very small and probably thermally

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(6) W. D. Good, D. W. Scott, J. L. Lacina and J. P. McCullough, J. Phys. Chem., 63, 1139 (1959).

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insignificant, but this result should be verified by more sensitive dilution calorimetry. The heat of dilution for eq. IV was computed from values in Circular 500.<sup>7</sup> Addition

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(7) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," N.B.S. Circular 500, (1952).

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of eq. I, II, III and IV results in eq. V, the equation for the formation of quartz from the elements and the heat of formation.

The previously accepted value for the heat of formation of quartz<sup>3</sup> is  $-209.9 \pm 1.0$  kcal., about 7 kcal. mole<sup>-1</sup> less negative than the present value. Thus, the free energy of formation of silica at 25°C. is about 7 kcal. mole<sup>-1</sup> more negative than

the earlier value<sup>3</sup>, in agreement with Chipman's conclusion.<sup>2</sup>

Full details of this investigation will be given in a paper in preparation. The results presented here are confirmed by those in the following letter, which were determined by an entirely different thermochemical method.

Contribution No. 112 from the  
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