# Notes

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Evidence for the Stability of Complex Silicon-Fluorine Species at High Temperatures[1]

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Silicon subfluorides of the composition $(SiF)_x$ or $(SiF_2)_x$ were isolated as solid high polymeric substances by Schmeisser.[2] More recent preparations of difluorosilylene, SiF_2, and polymers containing as many as ten or more repeating units of SiF_2 were reported by Pease.[3] The experimental data of Pease were used by Margrave, et al.,[4] to determine a heat of formation for $SiF_2(g)$ assuming the reaction

$$Si(c) + SiF_4(g) \rightleftharpoons 2SiF_2(g) \qquad (1)$$
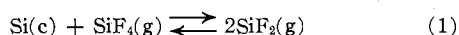
at various pressures and temperatures. A third law calculation indicated the heat of formation of $SiF_2(g)$ to be in the range -148 ± 4 kcal. mole^{-1} as compared with an earlier, estimated value of -118 ± 10 kcal. mole^{-1} from the JANAF Thermochemical Tables.[5] More recently, an experimental value, -139 ± 2 kcal. mole^{-1}, has been reported based on a mass spectrometric study of the reaction $CaF_2(s) + Si(s)$ at high temperatures.[6] The discrepancy between the -139 and -148 kcal. mole^{-1} heats of formation appears to be real and is indirect evidence that stable species Si_xF_y, where $x > 1$, exist. In the $CaF_2 + Si$ studies, however, the temperatures were too high and the pressures too low to allow detection of any polymers.

In the present work, the vapor–solid equilibrium between $Si(c)$ and $SiF_4(g)$ was studied by the transpiration technique over the temperature range 878–1000°K. to establish quantitatively the extent to which the polymerization reaction occurred and, especially, to see if there was any evidence for the reaction

$$2SiF_2(g) = Si_2F_4(g) \qquad (2)$$
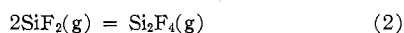
which would involve a Si to Si double bond.

Experimental

The transpiration studies were conducted in a Globar furnace

(1) Abstracted in part from the Ph.D. thesis of A. S. Kana'an, University of Wisconsin, 1963.

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(3) D. C. Pease, U. S. Patent 2,840,588 (June 24, 1954), assigned to E. I. du Pont de Nemours and Company.

(4) J. L. Margrave, A. S. Kana'an, and D. C. Pease, J. Phys. Chem., 66, 1200 (1962).

(5) D. R. Stull, Ed., JANAF Thermochemical Tables, Vol. 2, December 31, 1960, USAF Contract No. AF33(616)-6149, Advanced Research Projects Agency, Washington, D. C.

(6) (a) J. W. Green, G. D. Blue, T. C. Ehlert, and J. L. Margrave, Proceedings, ASTM Mass Spectrometry Conference, San Francisco, Calif., May 19–24, 1963; (b) T. C. Ehlert, Ph.D. Thesis, University of Wisconsin, 1963.

of the type described by Soulen and Margrave,[7] fitted with a nickel-lined Mullite tube or, in one case, a platinum-lined Mullite tube. End fittings with standard tapered joints were used to keep the system as gas tight as possible. Gas flow and pressure were monitored by a calibrated flow meter and mercury manometers, respectively.

A platinum boat was used to contain the crystalline silicon of high purity, the same as that used for the heat of formation of SiF_4 by Wise, et al.,[8] and Matheson silicon tetrafluoride (99.5%) was used without purification, except for passing through a $Mg(ClO_4)_2$ column. The impurity ($\sim 0.5\%$) was SO_2 and this was shown to be unreactive under the experimental conditions in a control experiment.

The furnace temperature was measured with a calibrated Pt–Pt 10% Rh thermocouple junction located in the center of the hot zone. The maximum temperature fluctuations were of the order of $\pm 3°$ at the low temperatures and $\pm 5°$ at the high temperatures.

In a typical experiment the furnace temperature was raised to a desired setting and the platinum boat containing a weighed amount of silicon was placed in the cold zone of the reaction tube. The system was assembled, pumped down to a few mm. pressure, and then filled with argon. The flow of SiF_4 was then initiated, adjusted to the desired rate, and continued for at least 30 min. before pulling the sample boat into the hot zone. This step was necessary to ensure that the reaction atmosphere was really SiF_4 at barometric pressure. When a steady flow of SiF_4, at the desired rate, was achieved the sample boat was pulled into the hot zone in a direction opposite to the normal flow direction by sliding a platinum wire, attached at one end of the tube through a U-shaped tube, full of Octoil. At the end of each 4-hr. transpiration period the boat was drawn from the hot zone and the SiF_4 flow was stopped immediately. A rapid stream of dry argon was started and continued for about 1 hr. before the reaction tube was opened to the atmosphere, at which time the boat was taken out, placed in a desiccator under vacuum for about 30 min., and weighed again.

Results

Numerous experiments at four temperatures (878, 916, 948, and 1003°K.) were performed at different rates of flow of SiF_4 in order to determine the proper rate at which equilibrium was established.[9] Flow rates in the range 5–9 cc./min. at STP were found to fall within the equilibrium regions for the above temperatures. Table I summarizes the equilibrium results.

In addition, transpiration studies were carried out at 1003°K. and flow rates in the range 4–12 cc./min. with a gas mixture which was 88.2% argon and 11.8% SiF_4. No weight losses were detected in these latter experiments over periods of 4–12 hr., even though pure SiF_4 at 1 atm. produced appreciable weight losses (6–12 mg./l.) in 4-hr. periods.

A possible alternative explanation for the observed extensive transpiration weight loss at relatively low temperatures would include side reactions in the system, e.g., fluorination of the reaction boat or the forma-

(7) J. R. Soulen and J. L. Margrave, Rev. Sci. Instr., 31, 68 (1960).

(8) S. S. Wise, W. N. Hubbard, and J. L. Margrave, J. Phys. Chem., 66, 381 (1962); 67, 815 (1963).

(9) U. Merten and W. E. Bell, General Atomic Report G.A. 2144 (Rev.), Sept., 1961.

TABLE I

EXPERIMENTAL TRANSPIRATION DATA

Temp., °K.	Flow rate, cc./min. (STP)	Weight loss/ unit vol., mg./cc. × 10³
878	6.5	6.18
	7.5	6.11
	8.4	6.35
916	6.23	6.96
	7.16	7.10
	7.77	6.84
948	7.16	11.59
	7.77	10.72
	8.52	11.25
1003	4.69	8.79
	5.37	8.76
	6.05	8.61
	6.54	8.73

tion of volatile products in a side reaction, like silicon oxyfluorides. Careful checks showed no appreciable weight losses of the reaction vessel. Ehlert[6] also studied the mass spectra of species produced in the reaction of CaF_2 with Si + SiO_2 and found silicon oxyfluorides to be of minor importance (<1%).

Conclusions

In the light of the synthesis of SiF_2 and $(SiF_2)_x$,[2,3] various gaseous polymers were considered in attempted calculations of equilibrium constants from the experimental results and available thermodynamic data. The general equilibrium constant at a given temperature for forming $(SiF_2)_x(g)$ is

$$K_x^T = \frac{P_{(SiF_2)_x}}{(P_{SiF_4})^{x/2}}$$

For forming gaseous perfluorosilanes (Si_xF_{2x+2}), the general equilibrium constant is

$$K_x^T = \frac{P_{Si_xF_{2x+2}}}{(P_{SiF_4})^{(x+1)/2}}$$

By varying the SiF_4 partial pressure one can learn something about the true formulas of the gaseous molecule. In particular, from the fact that the weight losses go from being easily measurable at ~1 atm. SiF_4 to being undetectable at 90 mm SiF_4 pressure, one concludes that the SiF_4 dependence is definitely not one-half or first power, which eliminates the polymers $(SiF_2)_{x=1-2}$. Further, if SiF_2 monomer is assumed, the weight losses for the 720–740 mm. SiF_4 experiments lead to an apparent heat of formation of −163 kcal. mole^{-1}, which is far too stable. If $(SiF_2)_2(g)$ were assumed to be the major species, one would require a SiF_2 dimerization energy not too different from that for CF_2 and there is no other evidence for this. Thus, the work reported here suggests the gaseous species is either $(SiF_2)_x$, where $x \geq 3$, or Si_xF_{2x+2}, where $x \geq 2$.

Qualitative molecular orbital arguments, of the type recently presented by Peters,[10] would support the existence of a stable SiF_2- polymer, possibly cyclotetraperfluorosilylene. Mass spectrometric and gas

(10) D. Peters, *J. Chem. Phys.*, **38**, 561 (1963).

chromatographic studies of low-temperature pyrolysis products from solid SiF_2 polymers[11] indicate that $Si_2F_6(g)$ and other perfluorosilanes can be formed. If the major product of this reaction is assumed to be $Si_2F_6(g)$, one finds the heat of formation of $Si_2F_6(g)$ to be −565 ± 10 kcal./mole. This corresponds to a Si–Si bond energy of 45 ± 10 kcal./mole, while the recent study of Gunn and Green[12] on Si_2H_6 indicated about 63 kcal./mole for the Si–Si interaction. The weaker bond in the perfluoro compound is consistent with other experimental data on similar systems, *e.g.*, C_2H_4 and C_2F_4, C_2H_6 and C_2F_6, etc.[13]

(11) T. C. Ehlert, P. L. Timms, and J. L. Margrave, unpublished work Rice University, Houston, Texas.

(12) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).

(13) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Academic Press, New York, N. Y., 1958.

Metal Nitrosyls. IV. On the Red and Black Isomers of Cobalt Nitrosopentaammines[1]

BY ROBERT D. FELTHAM

The earliest example of the isomerism of a compound containing a single NO group is that of the red and the black cobalt compounds $[Co(NH_3)_5NO]X_2$. The earlier literature has been summarized elsewhere.[2–4]

In general, previous workers considered one isomer to be a monomer and the other to be a dimer, the dimer usually being referred to as a hyponitrite, but disagreement has existed over whether the red or the black isomer is the dimer. The problem then is to determine which isomer is, in fact, the dimer (or monomer). Since the red isomer is the more stable of the two, it was chosen for investigation.

Experimental

The red compound $[Co(NH_3)_5NO][NO_3]_2\cdot0.5H_2O$ was prepared according to the method of Werner and Karrer.[5] A solution of 30.5 g. of $Co(NO_3)_2\cdot6H_2O$ in 50 ml. of distilled water was cooled in an ice bath and 150 ml. of concentrated ammonium hydroxide was slowly added. The solution was filtered and nitric oxide was then passed into the solution for 3–4 hr. The brick-red product was filtered and washed with ethanol, then with ether, and finally dried under vacuum. *Anal.*[6] Calcd. for $[Co(NH_3)_5NO][NO_3]_2\cdot0.5H_2O$: H, 5.25; Co, 19.2; NH_3, 27.8; N, 36.5. Found: H, 5.63; Co, 19.3; NH_3, 28.0; N, 36.3.

(1) This research was sponsored by The International Nickel Company, Inc.

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(3) E. P. Bertin, S. Mizushima, T. J. Lance, and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 382 (1959).

(4) R. W. Asmussen, O. Bostrup, and J. P. Jensen, *Acta Chem.*, **12**, 24 (1958).

(5) A. Werner and P. Karrer, *Helv. Chim. Acta*, **1**, 63 (1918).

(6) The elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.