Heat of Reaction of Hydrogen and Nitrogen Trifluoride

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The heat of reaction of hydrogen and high purity nitrogen trifluoride to form nitrogen and HF(1 in 123 H_2O) has been measured as −199.49 ± 0.22 kcal. per mole. This result when combined with published values for the heat of reaction of boron and nitrogen trifluoride agrees with other recent fluorine thermochemistry in indicating need for revision in the heat of formation of hydrogen fluoride.

PREVIOUS work (*1*, *8*) on the heat of reaction of hydrogen and nitrogen trifluoride involved relatively large uncertainties owing to lack of high purity samples or optimum calorimetric apparatus. An accurate value for this reaction aids in fixing the heat of formation of nitrogen trifluoride or aqueous hydrogen fluoride.

EXPERIMENTAL

Technical nitrogen trifluoride was purified by low temperature distillation. Analysis of the purified material by infrared spectroscopy indicated 0.02 mole % CF_4. Mass spectrometric analysis was obscured by background problems but indicated a maximum of 0.05 mole % N_2O and 0.07 mole % SiF_4. No evidence of any other impurities was found. Recently, samples prepared in a similar fashion have been shown by vapor phase chromatography to contain less than 0.01 mole % combined N_2O and SiF_4. The sample was therefore taken as 99.98 mole % NF_3. Matheson prepurified grade hydrogen (99.95% minimum) showed no impurities by mass spectrometry.

A rotating bomb calorimeter similar to that described by Hubbard, Katz, and Waddington (*3*) was employed. The 349-ml. platinum lined bomb was fitted with an annular tank as described by Nuttall, Wise, and Hubbard (*6*) except that the tank and valve were small enough that the assembly could still be rotated. The procedure was to connect the bomb to a vacuum system and evacuate to about 10^{-3} mm. The bomb was then charged with purified NF_3 to about 400 mm. from a weighed stainless steel cylinder. The exact pressure and the ambient temperature were observed. The bomb valve was closed and the material in the lines recondensed in the cylinder with liquid nitrogen. Residual pressure in the system (about 100 ml. volume) was always less than 0.5 mm. The loss in weight of the cylinder gave the sample weight. The bomb was then connected to a source of hydrogen and charged to a total pressure of 1800 mm. The annular tank was charged with 50 ml. of pure water and pressured to 45 p.s.i.g. with nitrogen. The charge was fired by electrically fusing a short length of platinum wire. Immediately after firing, the valve was opened from outside the calorimeter by means of a nylon string, allowing the water to be forced into the bomb. Rotation was started at the time when 0.6 of the total temperature rise was noted and continued to the end of the experiment. The bomb was opened, and the aqueous solution was quantitatively recovered and analyzed for HF by potentiometric titration with standard base. Quantitative analyses for dissolved platinum and ammonium ion were at or below detection limits, well below thermally significant amounts. Mass spectrometer observation of the gaseous reaction products showed less than the detection limit of 0.03 mole % NF_3.

The bomb was calibrated with NBS 39h benzoic acid, using an amount (0.246 gram) such as to match the temperature rise of the NF_3–H_2 experiments. The bomb was charged with 1 ml. of water and 30.3 atm. of oxygen, and the final temperature was 25.0 ± 0.1° C. in all experiments. Under these conditions, the standard sample was calculated to have a heat of combustion of 6317.28 cal. per gram mass. The calorimeter equivalent when corrected to conditions for the NF_3 experiments was 3395.3 cal. per ° C. with a standard deviation of 1.6 cal. per ° C. The annular tank was closed off in the calibration experiments.

RESULTS

The results of six experiments are given in Table I. Molecular weights were calculated from the bomb volume, the measured pressure and temperature, and gas imperfection corrections using the Berthelot equation and the critical constants of Jarry and Miller (*4*). The agreement with theory is well within the estimated experimental error of 0.1%. Hydrogen fluoride recovery averaged 99.9% of theory although the precision on this measurement was poor. Miscellaneous corrections include calculations to ideal gas states and a heat of vaporization term for water entering the dry bomb.

Table I. Data for NF_3

Molecular Weight	HF Recovery, %	Sample Mass, Gram	Measured Calories, $-\epsilon\Delta t$	Misc. Corr., Cal.	$-\Delta E^{0}r/M$, Cal./Gram
71.05	100.5	0.5365	−1493.32	−4.45	2791.7
70.97	99.3	0.5303	−1476.75	−4.45	2793.1
71.10	100.1	0.5315	−1479.43	−4.45	2791.9
71.05	99.9	0.5354	−1489.35	−4.45	2790.1
71.10	99.9	0.5255	−1462.97	−4.45	2792.4
71.04	99.7	0.5323	−1483.51	−4.45	2795.3
				Av.	2792.4

The average value from Table I was corrected for 0.02 mole % CF_4 using −39.3 kcal. per mole as the energy of reaction of CF_4 and hydrogen. The corrected figure for $-\Delta E^0r/M$ is 2793.0 cal. per gram. Using atomic weights of 14.0067 for N and 18.9984 for F, the molar energy of reaction is $\Delta E^0r = -198.31$ kcal. per mole. The reaction to which this refers is:

$$NF_3(g) + \tfrac{3}{2}\,H_2(g) \rightarrow \tfrac{1}{2}\,N_2(g) + 3HF(1 \text{ in } 123\ H_2O)$$

Correcting to constant pressure conditions: $\Delta H^0r_{298} = -199.49 \pm 0.22$ kcal. per mole. The uncertainty is twice the over-all standard deviation.

Armstrong, Marantz, and Coyle (*1*) quoted −202.1 kcal. per mole based on NF_3 dosage and −208.4 kcal. per mole based on HF recovery, with the HF adjusted to infinite dilution. On the same basis for HF, the present work gives −208.40 kcal. per mole, in exact agreement with the value based on HF recovery. It would appear that the NF_3 used by Armstrong and coworkers was less pure than they estimated.

Ludwig and Cooper (*5*) measured the heat of reaction of boron and nitrogen trifluoride and derived $\Delta Hf_{298}(NF_3, g) = -30.4 \pm 1.2$ kcal. per mole. Employing this value and the present work yields $\Delta Hf_{298}(HF, 1 \text{ in } 123\ H_2O) = -76.63$ kcal. per mole. This is 0.94 kcal. per mole more negative than the value listed in Circular 500 (*7*). The heat of formation of ideal gaseous HF is also probably more negative than the value selected for Circular 500 (*2*). There is obviously a need for revision of the thermochemical values for gaseous HF and its aqueous solutions.

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Received for review February 17, 1965. Accepted June 1, 1965. This work was supported by the Advanced Research Projects Agency under Contract No. **AF04(611)-7554(2)**.

Vaporization and Sublimation of $SrCl_2$

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The sublimation and vaporization rates of $SrCl_2$ have been determined by means of the Langmuir and Knudsen techniques, respectively. The third-law heat of sublimation at 298° K. is 78.6 ± 1.0 kcal. mole^{-1}.

VAPOR PRESSURES and sublimation pressures for several alkaline earth dihalides are now available, but no extended Langmuir and Knudsen study or mass spectrometric characterization of the vapor over condensed $SrCl_2$ has been published. Neither has there been a careful consideration of the evaporation coefficient for any alkaline earth dihalide both above and below the melting point. A comparison of the torque-Knudsen, Langmuir, and mass spectrometric results for CaF_2 (*2, 3, 10, 13*) and BaF_2 (*1, 7, 8*) suggests that α_L, the Langmuir evaporation coefficient, may be 0.1 to 0.3 for CaF_2 (g) or BaF_2 (g) subliming from the solid fluorides. Burns (*5*) recently observed a discontinuous change in α_L for the vapor species over condensed Al_2O_3 at the melting point.

This paper reports Langmuir and Knudsen weight loss studies, a mass-spectrometric characterization of the vapor, and calculation of α_L for $SrCl_2$.

EXPERIMENTAL

The Langmuir studies were made with a sample of single-crystal $SrCl_2$ obtained from Semi-elements, Inc. The crystal was suspended from a tungsten support wire inside a quartz envelope mounted below one pan of an Ainsworth RVA-AU-2 semi-micro recording balance. A Kanthal wire-wound resistance furnace controlled by a West Model JP temperature controller was used to heat the sample. The rate of weight loss was automatically recorded while temperature measurements were made with a Pt-Pt 10% Rh

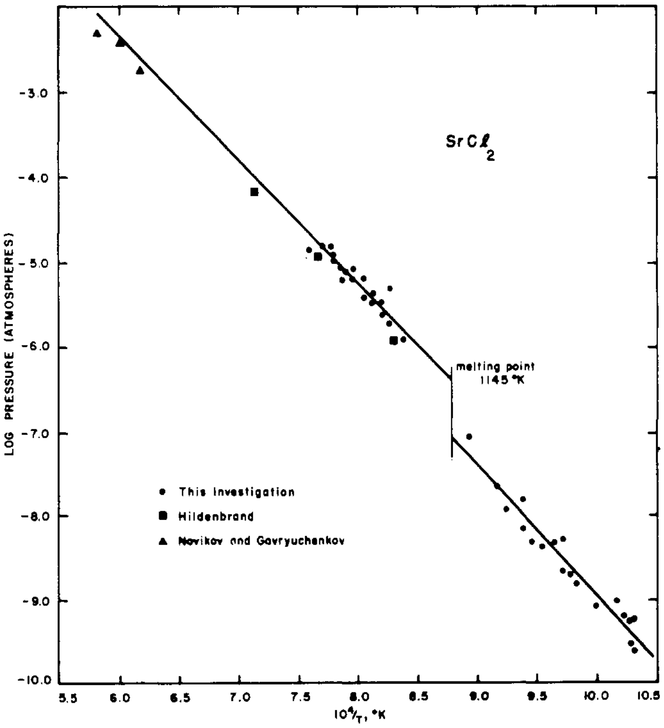

Figure 1. Vapor pressure of $SrCl_2$ by various investigators