

# NATIONAL BUREAU OF STANDARDS REPORT

6363

HEAT OF FORMATION OF NITROGEN TRIFLUORIDE

by

Sidney Marantz, Charles F. Coyle,  
and George T. Armstrong

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Technical Report  
to  
U.S. Navy Bureau of Ordnance



U. S. DEPARTMENT OF COMMERCE  
NATIONAL BUREAU OF STANDARDS

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Thermodynamics Section  
Heat Division

Technical Report  
to  
Navy Bureau of Ordnance  
Washington, D.C.

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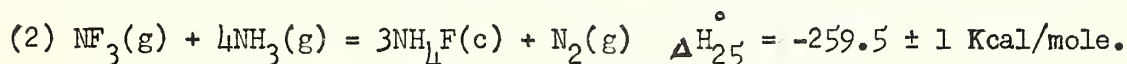
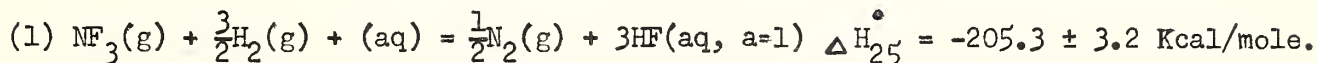




## The Heat of Formation of Nitrogen Trifluoride

## Abstract

By bomb calorimetric experiments the heats of the following reactions have been determined.



From the measurements the heat of formation of  $\text{NF}_3$  is found to be  $-29.7 \pm 1.8$  Kcal/mole. The mean bond energy  $E(\text{N-F})$  in  $\text{NF}_3$  is  $66.4 \pm 0.8$  Kcal/mole.

## 1. Introduction

With the growing interest in fluorine chemistry [1,2]<sup>a</sup> it has become increasingly desirable to understand the thermochemistry of fluorine-containing compounds. In general, it is known that the bond energies will be relatively small between fluorine and other non-metals of low atomic weight. The accuracy of some such bond energies is in doubt because of the limited amount of information on the heats of formation of the compounds. The present work was undertaken for the purpose of determining with greater certainty the energy of the nitrogen-fluorine bond,  $E(\text{N-F})$ , by a study of the heat of formation of nitrogen trifluoride.

The only previous measurements of the heat of formation of  $\text{NF}_3$  were made by Ruff and Wallauer in 1931 [3]. They ignited  $\text{NF}_3\text{-H}_2$  mixtures in a steel Mahler bomb. It is not customary practice to carry out completely gas phase reactions in a bomb, but Ruff and Wallauer resorted to this method after failing to achieve a dependable ignition in a flame calorimeter. (Preliminary experiments here confirmed that difficulty). They reported a value for  $\Delta H_{f25}^\circ$  of  $-26 \pm 2$  Kcal/mole,

<sup>a</sup>Numbers in brackets refer to references at end of this report.

which may be modified to -27.2 Kcal/mole on the basis of a better value for the heat of formation of hydrogen fluoride [4].

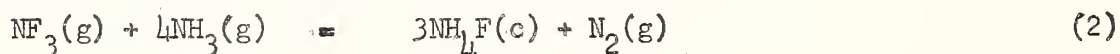
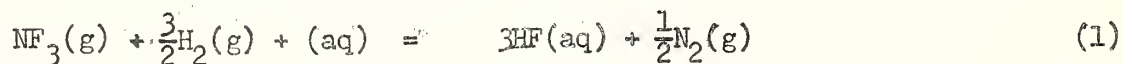
Aside from the fact that more accurate apparatus is available for thermal measurements, it was desirable to repeat the earlier work for two reasons.

1. The original investigators implicitly assumed that the reaction proceeded to completion without any side-effects. Because they did not confirm the chemistry of the process, some doubt must be associated with its "purity".

2. The value for the heat of formation of  $\text{NF}_3$  was based on only three determinations of a single reaction.

In preliminary experiments difficulty was experienced in attempting to repeat the earlier measurements. The Illium bomb was attacked in the reaction, corrosion occurring on the walls, the glass electrode insulator and the tin gasket. Placing about six ml. of water in the bomb to absorb the HF did not prevent scarring of the bomb. A gold lining reduced but did not eliminate completely the unwanted effect. In addition, there was a discrepancy of about 3 percent between the amount of product HF measured and that calculated from the amount of  $\text{NF}_3$  dosed into the bomb. The amount of HF measured was always low.

The dry reaction of  $\text{NF}_3$  with ammonia was then tried and proved to be more satisfactory. This latter reaction also yields the information sought. The results reported in this paper are based on the studies of the reaction of hydrogen with  $\text{NF}_3$  (Eq. 1) over water in a gold lined bomb, and of the dry reaction of ammonia with  $\text{NF}_3$  (Eq. 2) in the same bomb. They show that nitrogen trifluoride is slightly more stable than was determined by Ruff and Wallauer.



## 2. Experimental Work

### 2.1 Thermal Apparatus and Thermal Measurements

Thermal measurements were made with an isothermal jacket-type calorimeter very similar to that described by Dickinson [5]. The jacket temperature was maintained at  $28^{\circ}\text{C} \pm .002^{\circ}\text{C}$  by means of a mercury-toluene thermostat. Calculation of the corrected temperature rise was performed in the customary manner [5].

The bomb used is similar to, though not identical to one that has been described previously [6]. This bomb has a volume of 383.4 ml and has a groove in the lid for a metal or teflon gasket. In the lid are two needle valves, through one of which the loading of the bomb is accomplished. The needle valve is desirable because it permits exact pressure measurements inside the bomb to be made. On the basis of preliminary experiments some minor modifications of the bomb were made to make it more suitable in these experiments.

1. The interior of the Illium bomb was plated with a .001 in. lining of gold to prevent corrosion of it during the reactions.

2. The bomb was fitted with a teflon gasket after it became obvious that a tin gasket was easily attacked during an experiment. Besides being chemically resistant, the same teflon gasket could be used over and over, and one gasket sufficed for the experiments.

The bomb is fitted with platinum electrodes which are relatively heavy compared to the platinum wire fuse strung between them. A 12 volt A.C. transformer was used for ignition. In all of the  $\text{NF}_3\text{-H}_2$  runs and in the first four of the  $\text{NF}_3\text{-NH}_3$  runs a .012 in. diameter platinum wire was used. Use of this fuse necessitated a firing energy correction. On substitution of a .003 in. platinum wire for the .012 in. wire in the final experiments, the firing energy became insignificant.

## 2.2 Calibration

The calorimeter was calibrated in five experiments with benzoic acid (NBS Standard Sample 39h). The heating value used for the standardizing material was 26.4338 absolute kilojoules/g mass (weight in vacuo). The temperature to which the calibration reaction is referred is 28°C. Results of the runs are shown in table 1.

In runs 1 and 2 a 1.5 gram sample was used, resulting in a three degree temperature rise. Since the energy involved in an  $\text{NF}_3$  experiment corresponded only to about a one degree temperature rise, the three additional calibration experiments were carried out with 0.5 gram samples of benzoic acid.

The standard calorimeter chosen for these experiments was with the bomb completely empty except for fuse connections. To obtain the energy equivalent,  $E_s$ , of the standard calorimeter, the observed energy equivalent was corrected by a term,  $\Delta e$ , for the benzoic acid pellet, approximately 30 atm of oxygen, 1 ml of water and the platinum crucible which were present in the calibration experiments. The mean value of  $E_s$  for all five runs and the standard deviation of the mean are shown at the bottom of table 1.

In calculating a heat of reaction associated with the  $\text{NF}_3$  runs, the energy equivalent of the calorimeter was adjusted to include the materials in the initial bomb. The starting materials in the  $\text{NF}_3$  reactions with hydrogen were  $\text{NF}_3$  at about one atm pressure, hydrogen at about 3.5 atm pressure, and about 4.5 grams of water. The adjustment for these experiments amounts to about 0.05%. The starting materials in the  $\text{NF}_3$  reactions with ammonia were  $\text{NF}_3$  at about one atm pressure, and ammonia at about 6 atm for which the adjustment amounted to about 0.09%.

Table 1  
Calibration of Calorimeter

Run No.	Mass of Benzoic Acid. g	$\Delta e$ j/ohm	$\Delta R_c^*$ ohm	$(q_i + q_n)^{**}$	$E_s$ j/ohm
1	1.52309	173.1	0.297781	42.0	135176
2	1.51542	172.4	.296050	41.4	135136
3	0.54826	160.4	.107317	33.5	135195
4	0.53014	162.4	.103695	25.2	135219
5	0.53066	163.7	.103844	25.0	135158
mean					135177 $\pm$ 16

\*  $\Delta R_c$  is the corrected temperature rise.

\*\* This term includes energy corrections for ignition and the formation of  $\text{HNO}_3$  during combustion.



## 2.3 Materials

The  $\text{NF}_3$  used in the hydrogen reactions was obtained through the courtesy of Pennsalt Chemicals Corporation. By mass spectrometer analysis<sup>(b)</sup> the sample showed the following impurities in mole percent:  $\text{N}_2\text{O}$  or  $\text{CO}_2$ , 0.03; A, 0.02,  $\text{O}_2$ , 0.38;  $\text{COF}_2$  or  $\text{N}_2\text{F}_2$ , 0.07;  $\text{CF}_4$ , 0.02; and  $\text{N}_2$ , 2.00. Most of the nitrogen and oxygen were apparently introduced as air in the process of salvaging the material after the valve closing the sample container was found to be frozen. The assay of  $\text{NF}_3$  was taken to be 97.48%.

Some time after the experiments had been concluded, and nine months after the original analysis, a new analysis showed little change in the impurities except that the percent nitrogen had increased to 4.3. This suggests that  $\text{NF}_3$  was slowly reacting with the container walls which were iron.

The  $\text{NF}_3$  used in the ammonia reactions was supplied by E.I. duPont de Nemours and Company, Explosives Department. The mole percent composition was found by mass spectrometer analysis to be  $\text{N}_2$ , 0.5; Air, 0.55; HCN, 0.03,  $\text{N}_2\text{O}$  or  $\text{CO}_2$ , 0.04;  $\text{CF}_4$ , .01;  $\text{N}_2\text{F}_4$  or  $\text{COF}_2$ , 0.007.  $\text{NF}_3$  (by difference) 98.86%.

Because of the limited quantities available no effort was made in our laboratory to purify the  $\text{NF}_3$  samples.

The hydrogen was a commercial grade containing about 0.2% oxygen. The ammonia was a commercial grade with a nominal purity of 99.9 percent. A portion of the  $\text{NH}_3$  was distilled into a stainless steel container by evacuating the latter and placing it in a liquid nitrogen bath. After the transfer the frozen  $\text{NH}_3$  was pumped on to remove any volatile contaminants. This procedure of purification was

occasionally repeated during the experiments to insure the purity of the  $\text{NH}_3$ .

(b) Analyses were performed by S. Schuhmann and S. Bremer of the Molecular Structure and Properties of Gases Section.

Impurities in the starting materials which are reactive under the conditions of these experiments were accounted for by suitable corrections. The nature of these corrections is indicated in the calculations.

#### 2.4 Filling Apparatus and Filling Procedure

Description of the filling apparatus used in the  $\text{NF}_3\text{-H}_2$  and the  $\text{NF}_3\text{-NH}_3$  experiments will be clearer by referring to Figures 1 and 2, respectively, page 8. (The filling apparatus used in the  $\text{NF}_3\text{-H}_2$  experiments needed only minor changes to serve for the  $\text{NF}_3\text{-NH}_3$  experiments.)

The lines were constructed of 1/4 in. and 1/8 in. copper tubing. The open-end mercury manometer (A) was fitted with a glass scale, the back of which was silvered. On the front of the glass scale was an etched meter scale. The manometer was connected from one of its glass arms to the copper tubing by means of a Kovar seal. All valves and connectors, exclusive of those to the bomb, were of a design due to H.F. Stimson.

a.  $\text{NF}_3\text{-H}_2$ . (See Fig. 1). The monel U-tube (B) was filled with Dryerite and valves (5), (6), (7), and (8) were always adjusted in such a way that whenever the bomb, which initially contained about 6 ml of distilled  $\text{H}_2\text{O}$ , was being evacuated, the water which escaped from it was absorbed in the U-tube. The bomb was partially immersed in a water bath.

Bomb loading was accomplished as follows: The lines and the bomb were evacuated for about 10 minutes, flushed with approximately one atmosphere of impure  $\text{NF}_3$  and re-evacuated. The vacuum line was then closed, and  $\text{NF}_3$  was carefully introduced until the manometer indicated a pressure of about 87 cm, at which time the  $\text{NF}_3$  source was closed. Manometer readings as a function of time were taken during a 10 minute interval. During this time, barometer readings and temperature readings of the water bath were also noted.

Fig I.  $\text{NF}_3 - \text{H}_2$

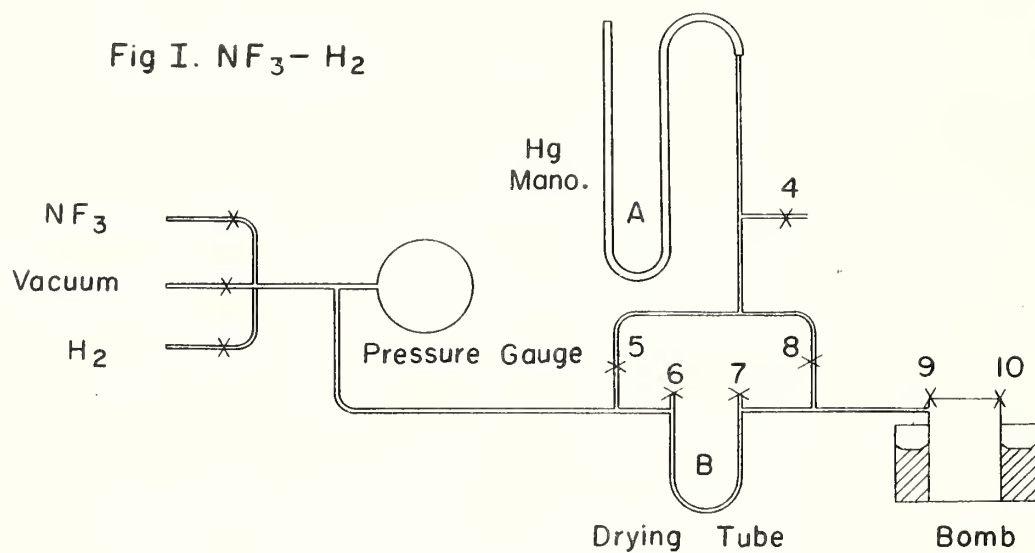
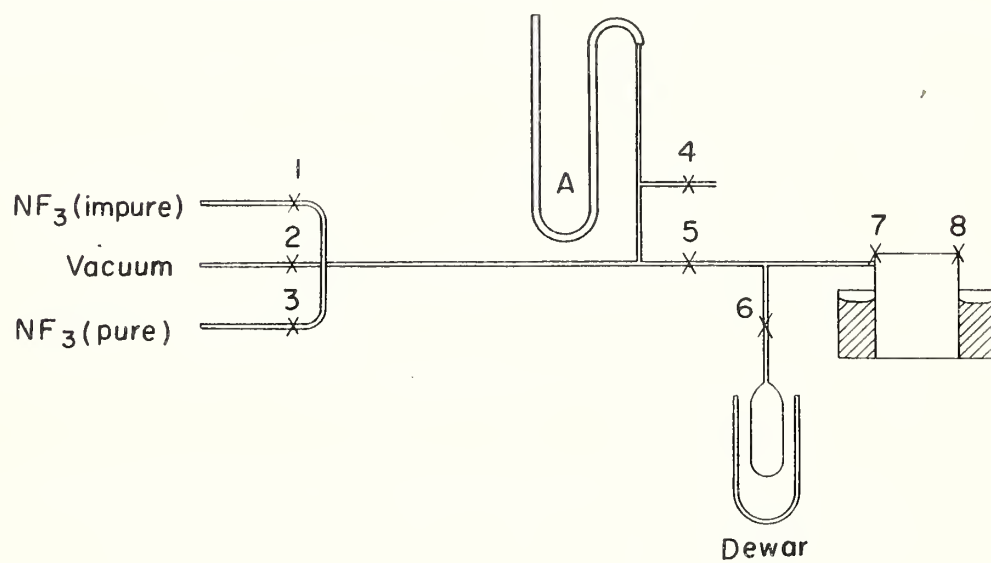


Fig II  $\text{NF}_3 - \text{NH}_3$





Valve (9) was closed and the lines were evacuated and flushed with about five atmospheres of  $H_2$ . (Valve (5) was closed previous to the  $H_2$  flushing so as to remove the mercury manometer from the lines). Hydrogen was then allowed to fill the lines until the pressure gauge indicated 55 lbs/in.<sup>2</sup>. Bomb valve (9) was cautiously cracked. This caused the pressure in the filling line to drop momentarily. About 10 seconds after the pressure had reached 55 lbs/in.<sup>2</sup> again, valve (9) was closed, and the bomb was disengaged and dried. The U-tube, which had been previously weighed, was also removed and weighed. The difference in weights was equal to the weight of water lost from the bomb during the charging process.

In some experiments the water vapor pressure in the bomb was measured with the manometer. This was done by closing valves (5) and (7) and opening (8). Since this pressure came reasonably close to that estimated from the bomb temperature, the water vapor pressure was usually determined the latter way.

b.  $NF_3-NH_3$  (See Fig. 2). The dosing procedure in this series of experiments was carried out in the following manner: The system was evacuated and flushed with impure  $NF_3$ . The lines were again evacuated and pure  $NF_3$  was introduced to a pressure of about 57 cm of Hg. Manometer, barometer, time and bomb temperature readings were taken over about a 10 minute interval. Valve (7) was closed and the lines were cleared of  $NF_3$ . Valve (5) was then closed and valve (6) was opened. Next, valve (7) was cracked slightly. This permitted gaseous  $NH_3$  to enter the bomb. Valve (7) was closed after about one minute. The Dewar surrounding the ammonia cylinder was filled with liquid nitrogen to draw back into the cylinder the ammonia contained in the lines between valves (5), (6), and (7). After the ammonia had been condensed and finally frozen, valve (6) was closed. The bomb was detached and dried. The Dewar was removed. After about four hours when the  $NH_3$  cylinder had attained

room temperature, it was detached and re-weighed to determine the amount of ammonia dosed into the bomb.

In the determinations of this series, the bomb, before being attached to the line, was weighed with an atmosphere of  $N_2$ . This was done with the purpose of weighing the amount of  $NH_4F$  formed during the combustion. In the last four experiments an additional check on the amount of  $NF_3$  used was obtained by weighing the bomb evacuated and again after introducing the  $NF_3$ .

## 2.5 Analysis of Products

In exploratory experiments the product gases were examined with the mass spectrometer. No residual  $NF_3$  was detected in either the  $NF_3-H_2$  or the  $NF_3-NH_3$  reactions.

a.  $NF_3-H_2$ : The amount of HF formed in the reaction was determined by titration.

Before disassembling the bomb, any HF still in the vapor phase was collected in a few ml of water by releasing the gases through a delivery tube extending below the surface of the water.

The resulting liquid was added to the bomb washings, which were then neutralized with a weighed amount of excess NaOH solution and back titrated potentiometrically with standard HCl solution to determine total HF present. The titration operations were carried out in a nitrogen atmosphere.

b.  $NF_3-NH_3$ : Upon completion of the thermal measurements, the bomb gases were released through an acid trap containing standard HCl, to collect the residual  $NH_3$ . The remaining product gases, nitrogen and hydrogen escaped into the room through a gas volume meter, as a secondary check on the total residual gas present.

Dry nitrogen gas was used to flush out the residual  $\text{NH}_3$ . At the conclusion of this procedure, the contents of the trap were transferred to a beaker, and the remaining acid was titrated with standard NaOH solution.

After being carefully dried and weighed, the bomb was opened. In every case,  $\text{NH}_4\text{F}$  had been deposited over the interior surface as a very white crystalline blanket. The  $\text{NH}_4\text{F}$  was collected as an aqueous solution by washing out the bomb deposit with distilled water, and the ammonia contained in it was determined by a standard Kjeldahl procedure. This determination served as a check on the weight of  $\text{NH}_4\text{F}$  deposited in the bomb during combustion.

An appreciable amount of ammonia was decomposed to nitrogen and hydrogen during each reaction. The amount of ammonia undergoing decomposition was calculated by subtracting the total ammonia found in the products from the amount of ammonia originally introduced.

## 2.6 Experimental Observations and Remarks

Because of the explosive nature with which the  $\text{NF}_3$  reactions proceed and the high momentary pressures resulting in the bomb, it was advisable as a safety measure to limit the energy release to about one third that in a conventional combustion reaction of a liquid or solid. This was accomplished by selecting a proper size sample of  $\text{NF}_3$ . Restricting the  $\text{NF}_3$  sample size also helped to conserve the small amount of material that was available.

The  $\text{NF}_3\text{-H}_2$  reaction was always accompanied by a distinctly audible "click" from the bomb about 1/2 second after the ignition circuit was completed, whereas the  $\text{NF}_3\text{-NH}_3$  reaction was attended by a fainter sound about one second afterwards.

a.  $\text{NF}_3\text{-H}_2$  (over water): Some effort was spent in finding means of preventing the Illium bomb surface from entering into the reaction. (That the bomb was participating

was indicated by the fluocculent precipitate which settled out when the bomb solution was neutralized and allowed to stand for awhile. The color of the precipitate varied from light green to black. Weight of this material was about 50 mg and spectrographic analysis of the precipitate showed contributions from all the elements present in the alloy--about a dozen in number).

The interior surface of the bomb was machined to a smoother finish to reduce the amount of reactive area. This brought no noticeable improvement.

By carrying out a reaction in the absence of water, it was hoped that a fluoride film would be formed that would serve as a protective coat in succeeding runs where water was present. There was a noticeable darkening and etching in the process, and the glass electrode insulator was attacked, but there was no appreciable improvement as a result of this procedure.

Finally, a light lining of gold electroplated on the surface gave promise, and an additional coat (about .001 in. in thickness) was added. This treatment indeed reduced the precipitate by a factor of about ten. It also added gold as one of the constituents of the precipitate. Since the precipitate was a mixture of many compounds, no certain correction could be made for the side-reaction, but an estimate based on an assumed heat of reaction indicated that the correction is probably insignificant for the amounts of precipitate observed.

In addition to the side-effect, there are other undesirable features of the experiment:

1. The use of water in the bomb involves several important corrections and complicates the filling procedure.

2. An average value for the heat of solution of HF must be assumed because the bomb is stationary and uniformity of solution cannot be assured.



3. Although  $\text{NF}_3$  is known to react with  $\text{H}_2\text{O}$  vapor when a mixture of the two is sparked, there is no simple way of determining whether this occurs in the  $\text{NF}_3\text{-H}_2$  reaction. The assumption was made that in the presence of excess hydrogen any oxides of nitrogen formed would immediately be reduced.

4. Hydrolysis of  $\text{NF}_3$  is assumed not to occur. This assumption is substantiated by pressure measurements of  $\text{NF}_3$  over water. However, the possibility of hydrolysis cannot be definitely ruled out.

5. The possibility of the formation of  $\text{NH}_4\text{F}$  in the reaction was not definitely ruled out, although it appears improbable because any correction made on the basis of its formation tends to separate the calculated heats of reaction more widely.

In spite of the disadvantages of having water in the bomb, which were recognized before the reactions were started, it was felt that the use of water was justified because it allowed corrections for HF gas imperfection to be avoided and it greatly curtailed the amount of corrosion caused by the HF.

Four completed experiments were carried out using the hydrogen reaction. The experimental results are shown in tables 2 and 3. In table 2,  $\Delta R_c$  is the corrected temperature rise;  $E_i$  is the energy equivalent of the initial calorimeter corrected for water, hydrogen, and nitrogen trifluoride contained in the bomb.

$\Delta E_b$  is the observed energy change of the bomb process. In table 3,  $n_1$  and  $n_2$  are the moles of reaction calculated on the basis of dosage of  $\text{NF}_3$  and of the amount of HF found in the products respectively. Further calculations are discussed in Section 3.

Table 2

Data and Calculations of  $\text{NF}_3\text{-H}_2$  Experiments

Run No.	$\Delta R_c \times 10^5$ ohms	$E_i$ j/ohm	$\Delta E_b$ j	$q_1$ j	$q_2$ j	$q_3$ j	$q_4$ j	$q_5$ j	$\Delta H_{j25}^\circ$
1	10248.7	135433	-13880.1	-667.21	-85.78	+120.84	+0.16	+15.0	-14497.1
2	10322.9	135392	-13976.4	-677.02	-86.23	+121.19	+0.16	+15.0	-14603.3
3	10186.3	135379	-13790.1	-666.65	-85.21	+120.42	+0.14	+15.0	-14406.4
4	8759.5	135387	-11859.2	-567.93	-73.17	+111.44	+0.23	+15.0	-12373.6

Table 3

Data and Calculations of  $\text{NF}_3\text{-H}_2$  Experiments (continued)

Run No.	$n_1$ moles	$n_2$ moles	$\Delta H_{25}^\circ$ ( $n_1$ ) Kcal/mole	$\Delta H_{25}^\circ$ ( $n_2$ ) Kcal/mole
1	.01705	.01666	-203.2	-208.0
2	.01731	.01675	-201.6	-208.4
3	.01701	.01652	-202.4	-208.4
4	.01471	.01417	-201.1	-208.7
		ave.	-202.1	-208.4
			$\pm 0.4$	$\pm 0.14$

b.  $\text{NF}_3\text{-NH}_3$ : No corrosion of the bomb was observed as a result of the  $\text{NF}_3\text{-NH}_3$  reactions. The  $\text{NH}_4\text{F}$  formed as a product was laid down almost uniformly over the interior of the bomb. Crystallization took place on the walls which presented a cool surface to the products.

In order to determine the amount of the reaction and to verify that the reaction was the one anticipated the following quantities were measured in the ammonia experiments: ( $n_1$ ) moles of  $\text{NF}_3$  introduced as determined from pressure volume, and temperature, ( $n_3$ ) weight of  $\text{NF}_3$  introduced, ( $n_2$ ) weight of solid product formed, ( $n_4$ ) moles of  $\text{NH}_3$  found in the solid product, as determined by Kjeldahl method. Eight completed reactions were carried out. The results are shown in Tables 4 and 5.

Table 4

Data and Calculations of  $\text{NF}_3\text{-NH}_3$  Experiments

Run No.	$\Delta R_c \times 10^5$ ohms	$E_i$ j/ohm	$\Delta E_b$ j	$q_1$ j	$q_2$ j	$q_3$ j	$q_4$ j	$q_5$ j	$\Delta H_{25}^\circ$ j
1	10318.6	135212	-13952.0	-71.8	-64.92	-944.5	-0.58	+30.0	-15003.8
2	10349.2	135211	-13993.3	-96.1	-57.13	-503.4	-0.40	+30.0	-14620.3
3	9117.9	135212	-12328.5	-5.6	-70.10	-2079.4	-1.06	+30.0	-14454.7
4	10178.6	135211	-13762.6	-74.4	-61.72	-873.9	-0.55	+30.0	-14743.2
5	10520.3	135216	-14225.1	-81.3	-80.08	-712.2	-0.50	0.0	-15099.2
6	10464.2	135216	-14149.3	-86.5	-80.51	-611.5	-0.44	0.0	-14928.2
7	10491.5	135216	-14186.2	-86.8	-80.12	-636.0	-0.46	0.0	-14989.6
8	10364.9	135217	-14015.1	-86.8	-80.83	-566.7	-0.41	0.0	-14749.8



Table 5

Data and Calculations of  $\text{NF}_3\text{-NH}_3$  Experiments (continued)

Run No.	$n_1$ moles	$n_2$ moles	$n_3$ moles	$n_4$ moles	$\Delta H_{25}^\circ$ ( $n_1$ ) Kcal/ mole	$\Delta H_{25}^\circ$ ( $n_2$ ) Kcal/ mole	$\Delta H_{25}^\circ$ ( $n_3$ ) Kcal/ mole	$\Delta H_{25}^\circ$ ( $n_4$ ) Kcal/ mole
1	.01378	.01387	--	.01374	-260.2	-258.5	--	-261.0
2	.01361	.01361	--	.01346	-256.7	-254.9	--	-259.6
3	.01338	.01343	--	.01321	-258.2	-257.2	--	-261.5
4	.01364	.01361	--	.01330	-255.2	-258.9	--	-264.9
5	.01381	.01383	.01385	.01370	-261.3	-260.9	-260.6	-263.4
6	.01369	.01378	.01382	.01359	-260.6	-258.9	-258.2	-262.5
7	.01382	.01397	.01380	.01360	-259.2	-256.4	-259.6	-263.4
8	.01367	.01350	.01352	.01335	-257.9	-261.1	-260.7	-264.1
mean					-259.1	-258.4	-259.8	-262.6
Std.dev.of mean					$\pm 1.7$	$\pm 0.8$	$\pm 0.6$	$\pm 2.0$

### 3. Calculation of the Results

#### 3.1 Corrections

The heat of reaction as obtained in the bomb process was corrected to obtain the heat of reaction in the standard state at 25°C. The following corrections were applied to the  $\text{NF}_3\text{-H}_2$  data: ( $q_1$ ) the difference between the internal energy change of the reaction as observed and the internal energy change of the reaction in the standard state; ( $q_2$ ) a term  $\Delta nRT$  for the difference  $\Delta H^\circ - \Delta E^\circ$ ; ( $q_3$ ) the energy contributed by reaction of the known impurities,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{CF}_4$  and  $\text{N}_2\text{F}_2$ ; ( $q_4$ ) a heat capacity term for the difference  $\Delta H_{25}^\circ - \Delta H_{28}^\circ$ ; ( $q_5$ ) the firing energy. The term  $q_1$  includes (a) the change in internal energy from zero pressure to the initial pressure for the reactants hydrogen and nitrogen trifluoride, (b) the change in internal energy from final bomb pressure to zero pressure for the products nitrogen and residual hydrogen, (c) the energy of evaporation of a small amount of water vapor condensed upon formation of the hydrogen fluoride aqueous solution, (d) the energy of condensation of a small amount of hydrogen fluoride remaining in the vapor phase, (e) the energy change on diluting the aqueous hydrogen fluoride solution formed to infinite dilution. The corrected values  $\Delta H_{25}^\circ$  in joules total heat change are shown in column 10 of table 4. The quantity  $\Delta H_{25}^\circ$  in kilocalories per mole for the reaction was calculated on the basis of the number ( $n_1$ ) of moles of  $\text{NF}_3$  dosed into the bomb (table 3, column 4) and also on the basis of the number ( $n_2$ ) of moles of  $\text{NF}_3$  corresponding to HF found by titration in the products (table 3, column 5). Corrections for the internal energy change of  $\text{NF}_3$  were made by means of the Berthelot equation of state, using values for  $T_c$  and  $P_c$  of  $\text{NF}_3$  reported by Jarry and Miller [7].

Partial pressures of water and HF over the aqueous solution were determined from the work of Brosher, Lenfesty and Elmore [8]. The heat of condensation of water into the HF solution was taken as that of pure water, while that of HF was taken as the difference between the heat of formation of gaseous HF (ideal) and aqueous HF of the concentration observed. For correction of the aqueous phase to infinite dilution, data on the heat of formation of HF solutions were taken from Rossini, Wagman et al [4]. In estimating the heat effects of side reactions all oxygen was considered to have been converted to water and fluorine to hydrogen fluoride. Carbon and nitrogen were presumed to have been reduced to the elements. An estimated value of +43 Kcal/mole was used for the heat of formation of  $N_2F_2$ , using an approximate N-F bond energy of 67.5 Kcal/mole and a N=N bond energy of 85.4 Kcal/mole suggested by Glockler and Dawson [9]. The total correction was approximately 0.4 percent of the final heat value.

Corrections for the  $NF_3-NH_3$  reaction were in part calculated differently. The following corrections were applied: ( $q_1$ ) the energy difference  $\Delta H_b - \Delta E_b$  determined from the PV products of the gases in the bomb at the beginning and end of the experiment, ( $q_2$ ) the difference between the enthalpy change of the reaction as observed and the enthalpy change of the reaction in the standard state, ( $q_3$ ) the energy contribution from side reactions, the largest part of which was contributed by decomposition of  $NH_3$ , ( $q_4$ ) a heat capacity term for the difference  $\Delta H_{25}^\circ - \Delta H_{28}^\circ$ , ( $q_5$ ) a term for the firing energy. The initial conversion of the bomb process energy  $\Delta E_b$  to an enthalpy change  $\Delta H_b$  was in part determined by the ready availability of enthalpy tables for nitrogen, hydrogen and ammonia and of  $\frac{PV}{RT}$  tables for nitrogen and hydrogen. PV corrections and enthalpy corrections for nitrogen and hydrogen were obtained from Hilsenrath, et al [10].

PV and enthalpy corrections for ammonia were determined from National Bureau of Standards tables [11]. Corrections for nitrogen trifluoride were determined here also by assuming it to follow the Berthelot equation of state.

Of corrections  $q_1$  and  $q_2$  for physical effects, the contributions from ammonia are by far the largest amounting to approximately 2 percent of the observed heat. Similarly the correction for decomposition of ammonia was much larger than for any other side reaction. The latter correction amounted from 500 to 2000 joules out of approximately 14,000 joules. Because of the large size of this correction, the final values for heat of the desired reaction were tested for correlation with the correction. Figure 3 shows a plot of the heat of reaction per mole as a function of the correction for ammonia decomposition. It is evident that there is no systematic error in the amount of this correction.

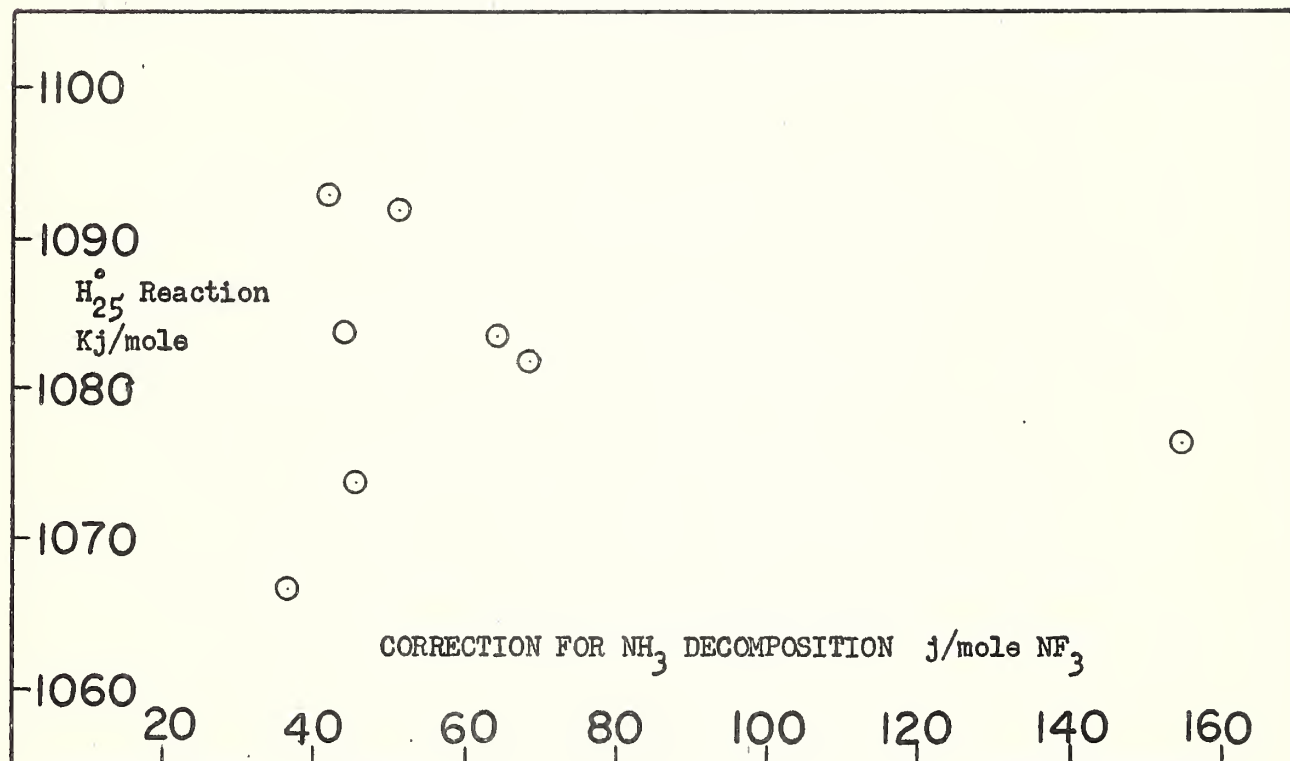
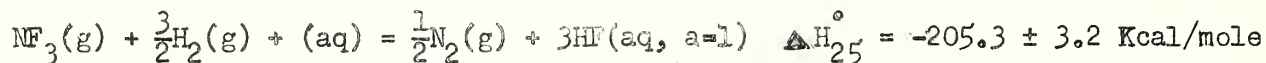


Figure 3. Variation of corrected heat of reaction with correction for  $NH_3$  decomposition.

3.2 Calculation of the Heat of Reaction and the Heat of Formation of  $\text{NF}_3$ 

Determination of the amount of reaction provided the greatest ambiguity in the results of the experiments, and provided difficulty of greater or less degree in both the hydrogen and the ammonia reactions. The behavior of the results in each case will be discussed briefly.

a.  $\text{NF}_3 - \text{H}_2$ : The extent of the reaction was determined in two ways: by the amount of nitrogen trifluoride dosed into the bomb, appropriately corrected for pressure, temperature and the presence of other materials as described in section 2.4; and by titration of the hydrofluoric acid solution formed. The number of moles found by each method is shown in table 3. The values differed by about three percent, with the HF titration giving lower values, and there was a tendency for the values to diverge as the experiments continued. The heats of reaction found on the basis of each method are shown in table 3, columns 4 and 5. Comparison shows that the values observed in this series lead to values for the heat of formation of nitrogen trifluoride which bracket those resulting from the measurements with ammonia, shown in table 5. These facts suggest that some factor was not under control in the experiments. This could have been a side reaction which was not detected such as a reaction of HF with the bomb, or a deterioration of the sample with time in a manner which was not detected. In the absence of a more justifiable procedure a value for the heat of reaction 1 was determined as the average of the two sets of results. This procedure gives:



The heat of formation of  $\text{NF}_3$  determined from this reaction depends upon the heat of formation of  $\text{HF}(\text{aq})$  at infinite dilution.  $\Delta H_{f25}^\circ(\text{HF}) = -78.66 \text{ Kcal/mole}$  [4]

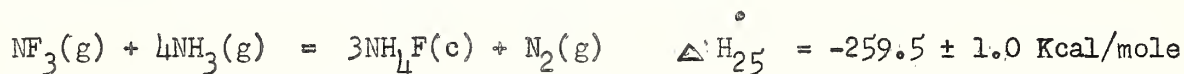


was used with an estimated uncertainty of 0.4 Kcal/mole, stemming principally from uncertainties in the gas phase imperfections of HF. The heat of formation of  $\text{NF}_3$  as determined from the hydrogen reactions is  $\Delta H_{f25}^\circ(\text{NF}_3) = -30.7 \pm 3.4$  Kcal/mole, the large uncertainty being due primarily to failure to achieve a satisfactory measure of the amount of reaction. Inhomogeneity of the HF solutions formed could have contributed a systematic bias to the measurements, but appears not to have done so because of the relatively good reproducibility of the experiments.

b.  $\text{NF}_3\text{-NH}_3$ :

For the ammonia experiments the amount of reaction is shown in table 5 as it was determined from the pressure and volume dosage of nitrogen trifluoride, the observed weight of nitrogen trifluoride, the weight of ammonium fluoride formed, and the amount of ammonia found in the product ammonium fluoride. With the exception of the value based on ammonia, the numbers of moles of reaction found by the different methods are in fairly good agreement. The agreement is best between values calculated from the weight of ammonium fluoride formed and from the weight of nitrogen trifluoride used, which are within the probable uncertainty of the weighings. The amount of reaction as determined from the ammonia bound in the solid product is substantially lower. In view of the generally close agreement between the weight of dosed  $\text{NF}_3$  and the weight of  $\text{NH}_4\text{F}$  product, the low value based on ammonia may be due to loss of ammonium fluoride in transfer to the titration vessel, rather than to incomplete reaction. We have been unable to devise a scheme whereby the low value for ammonia could be attributed to formation of ammonium bifluoride and still maintain the other observed weight or volume relationships. At the same time, the formation of ammonium bifluoride in an atmosphere containing excess ammonia seems improbable.

$\Delta H_{25}^\circ$  for reaction 2, determined using each of the molar quantities observed is shown in table 4 for each individual experiment, together with the four average values for all the experiments. The average values in kilocalories per mole are: (a) by volume of  $\text{NF}_3$ ,  $-259.1 \pm 1.7$ ; (b) by weight of  $\text{NF}_3$ ,  $-259.8 \pm 0.6$ ; (c) by weight of  $\text{NH}_4\text{F}$ ,  $-258.4 \pm 0.8$ ; (d) by titration of ammonia in  $\text{NH}_4\text{F}$ ,  $-262.6 \pm 2.0$ . The general average of these, weighted inversely as the square of the standard deviations of the means gives for the reaction



in which now the uncertainty is expressed as twice the standard deviation of the mean. In order to derive the heat of formation of  $\text{NF}_3$ ,  $\Delta H_{f25}^\circ(\text{NH}_3)$  was taken to be  $-11.04$  Kcal/mole [4] with an uncertainty of  $\pm 0.07$  Kcal/mole, and  $\Delta H_{f25}^\circ(\text{NH}_4\text{F})$  (c) was taken to be  $-111.0$  Kcal/mole [12]. In this calculation the heat of formation of  $\text{NH}_4\text{F}$  is important. Two independent determinations have been made which are in reasonably good agreement,  $-111.6$  Kcal/mole reported from the work of Guntz [13], 1884, and the above value reported by Higgins in 1957. A confirmation of the degree of validity of Higgins' measurements is provided by his measurement of the heat of formation of  $\text{NH}_4\text{HF}_2$ , in the same series of experiments, which agrees within  $0.6$  Kcal/mole with a value recently reported by Schutze, Euchen and Namsch [14]. The uncertainty attached to  $\Delta H_f^\circ(\text{NH}_4\text{F})$  therefore should not exceed  $0.6$  Kcal/mole.

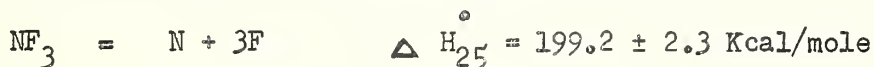
The heat of formation of  $\text{NF}_3$  calculated on this basis from the ammonia reactions is  $\Delta H_{f25}^\circ = -29.4 \pm 2.1$  Kcal/mole.

The weighted mean of the values for all experiments leads to  $\Delta H_{f25}^\circ = -29.7 \pm 1.8$  Kcal/mole.



## 4. Bond Energy Calculations

The bond dissociation energy of fluorine was recently recorelated by Evans, Munson and Wagman [15] and by Stamper and Barrow [16] on the basis of consistency with the third law of thermodynamics. The two correlations are in essential agreement and lead to a value of  $\Delta H_{f25}^{\circ}(2F) = 37.7 \pm 1$  Kcal/mole. Together with the  $\Delta H_{f25}^{\circ}(N) = 112.96 \pm 0.05$  Kcal/mole derived from the recently established value for the dissociation energy of nitrogen (see, for instance, Brewer and Searcy [17]), and the above value for the heat of dissociation of fluorine, the heat of formation of nitrogen trifluoride found by the experiments reported in this paper yields for the reaction



and an average bond energy,  $E(N-F) = 56.4 \pm 0.8$  Kcal/mole.

This is slightly greater than the bond energy derivable from the work of Ruff and Wallauer. In a recent informal communication Good, Scott Lacina and Waddington [19] reported the heat of formation of several perfluorinated cyclohexanes and piperidine. The compounds were carefully selected to allow an estimation of  $E(N-F)$  in perfluoropiperidine with a minimum amount of information about the other bonds in this compound. They reported a value of 73.2 Kcal/mole.

The bond energy values found by Good et al and those reported here are not necessarily inconsistent in view of the known variation of bond strength with environment. Reese and Dibeler [18] suggested the bond energy values  $D(NF_2-F) = 73$ ,  $D(NF-F) = 62$  and  $D(N-F) = 62$  Kcal/mole by analogy to the bond energies in ammonia, using a total bond energy of 197 Kcal/mole for  $NF_3$  derived from the data of Ruff and Wallauer. By similar analogy, but using the total bond energy value reported here, the individual bond energies would be slightly increased to 74.0, 62.6, 62.6 Kcal/mole.

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