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HIGH ENERGY OXIDIZERS IN SOLUTION (U)

By: W. E. TOLBERG    T. REWICK    R. S. STRINGHAM    M. E. HILL

AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
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By: W. E. TOLBERG  R. T. REWICK  R. S. STRINGHAM  M. E. HILL

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FOREWORD

This final report was prepared by Stanford Research Institute, Menlo Park, California, under Contract AF 04(611)-9370 for the Air Force Rocket Propulsion Laboratory, Edwards, California. The report covers the period from July 1, 1963, to August 15, 1966, with major emphasis on the research of the past year. The program was sponsored by the Advanced Research Projects Agency under ARPA Order 24, Amendment 64, Task 16, Program Code 391, Program Structure 920F, Project AFSC 4981. Scientists who worked on the program included Marion E. Hill, project supervisor; W.E. Tolberg and R.T. Rewick, principal investigators; R.S. Stringham, J.A. Neff, inorganic chemists; and C.A. Crutchfield, Anna Longwell, Ruth McNeely, and Ena Viale, analytical chemists. The technical consultation of Dr. Henry Taube of Stanford University is gratefully acknowledged.

The Air Force Rocket Propulsion Laboratory Contract Monitor is Dr. William Leahy/RPCL.

This technical report has been reviewed and is approved.

W.H. Ebelke, Colonel, USAF
Chief, Propellant Division
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I INTRODUCTION AND SUMMARY

This is the Final Report on Contract AF 04(611)-9370 which has been completed and has been succeeded by Contract F 04611-67-(C)-0002. The report, which contains unpublished work and four manuscripts for publication, summarizes research carried out in the period from July 1, 1963, to August 15, 1966, with major emphasis on the results obtained since May 1965. The highlight of this work was the discovery of the NF$_4^+$ cation described in Article 1, "The Synthesis of the Perfluoro Ammonium Cation, NF$_4^+$," a manuscript in process of publication in Inorganic Chemistry. Preliminary notice of the discovery of NF$_4^+$ was published in a communication to Inorganic and Nuclear Chemistry Letters, which is reproduced here as Article 2.

The research in this program had two objectives. The first was to determine whether energetic ionic species could be synthesized in chemical systems consisting of very weak bases such as NF$_3$ and very strong acids such as SbF$_5$. The new species, if formed, were expected to be energetic cations associated with the corresponding anions such as SbF$_6^-$. The second objective was to carry out the synthesis of highly energetic salts by coupling the new energetic cations with energetic anions through metathetical reactions in the solvent anhydrous HF.

The chemical system NF$_3$/F$_2$/SbF$_5$/HF was selected for study as being the most likely to be capable of forming the desired new cations. It was expected that, in the combinations of reagents containing NF$_3$, one or more of the ions, NF$_x^+$, could be synthesized. New information coincidental to these studies is reported in Article 3 "Evidence for the Existence of the Sb$_2$F$_{11}$ Anion" and in Article 4 "The Solubility of F$_2$, NF$_3$, and O$_2$ in Anhydrous Liquid HF" which will be submitted to Inorganic Chemistry and to Chemical and Engineering Data, respectively.
The quaternary system as well as its four ternary and six binary subsystems have been studied extensively and, as a result, a number of new salts containing energetic cations have been synthesized. The most important and most thoroughly characterized of these is the new salt, $\text{NF}_4\text{SbF}_6$, containing the energetic cation $\text{NF}_4^+$. It has been synthesized in greater than 10-gram quantities having purities from 96 to 99%. The salts $\text{NF}_4\text{Sb}_2\text{F}_{11}$, $\text{NF}_4\text{Sb}_3\text{F}_{13}$, and $\text{NF}_4\text{AsF}_6$ have also been synthesized and characterized. In addition, partial evidence for the formation of a very small quantity of the new salt $\text{NF}_2^+\text{Sb}_2\text{F}_{11}$ has also been obtained.

The above results have satisfied the first objective of the research. Additional results have established the feasibility of achieving the second. It has been shown that $\text{NF}_4\text{SbF}_6$ and $\text{KCLO}_4$ in solution in HF are not mutually destructive and therefore that the synthesis of $\text{NF}_4\text{ClO}_4$ is, in principle, possible.

The remainder of this report consists of one section containing classified information and four manuscripts intended for publication in various journals.
The Reaction of NF\textsubscript{3} with SbF\textsubscript{6}

Because the reaction of NF\textsubscript{3}, F\textsubscript{2}, and SbF\textsubscript{6} produces NF\textsubscript{4}SbF\textsubscript{6}, it was clearly possible that the reaction of NF\textsubscript{3} and SbF\textsubscript{6} would produce NF\textsubscript{2}SbF\textsubscript{5}. This possibility follows from the fact that the presence of NF\textsubscript{4}\textsuperscript{+} is implied in one of the two mechanisms that have been deduced as leading to the formation of NF\textsubscript{4}\textsuperscript{+}. The pertinent mechanism is:

\[
\text{NF}_3 + \text{SbF}_6 \rightarrow \text{NF}_2\text{SbF}_5
\]

The alternate route is:

\[
\text{F}_2 + \text{SbF}_6 \rightarrow \text{F}^+\text{SbF}_5^-
\]

\[
\text{NF}_3 + \text{F}^+\text{SbF}_5^- \rightarrow \text{NF}_4\text{SbF}_6
\]

The first of these two routes was studied by heating NF\textsubscript{3} and SbF\textsubscript{6} at 200\textdegree C and 2400 psi for 50 hours. The quantity of gas isolated from the reaction mixture was only slightly less than that initially present. The gas contained, however, a small amount of a material that was not condensable in liquid nitrogen. This appeared to be nitrogen because its vapor pressure at -210\textdegree C was higher than that of F\textsubscript{2}, the only possible alternative. It was also found that slightly more than 2\% of the NF\textsubscript{3} had disappeared. From this evidence it was clear that a reaction of NF\textsubscript{3} had occurred and that nitrogen gas had formed. We detected no N\textsubscript{2}F\textsubscript{4} or N\textsubscript{2}F\textsubscript{2} in the infrared spectra of the condensable fraction. These gases, if present, might have formed antimonate complexes in the presence of SbF\textsubscript{6}. The excess SbF\textsubscript{6} was removed from the reactor at 50\textdegree C, a temperature that would not decompose such complexes.

When the reactor was cut open in a dry box, a quantity of a white solid was found on the walls of the lower part of the vessel. This material was hydrolyzed and the gas evolved was analyzed by mass spectrometry. The gas contained O\textsubscript{2}, NF\textsubscript{3}, NO\textsubscript{2}, NO, and N\textsubscript{2}O. The
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hydrolysate contained a substantial quantity of nickel and copper salts, implying the presence of Ni(II) and Cu(II) antimonates in the white product.

The presence of NF₃ and O₂ in the gas evolved on hydrolysis indicated the presence of NF₄⁺. The oxides of nitrogen formed indicated the possible presence of the antimonate complexes of N₂F₄ and N₂F₂ and of NF₂⁺ whose reaction with water would produce oxides of nitrogen of the same valence state.

We regarded it as highly unlikely that NF₃ would disproportionate to the elements and to N₂F₄ and N₂F₂ in a heavily passivated vessel at 200°C. Thus it appeared likely that the first step in the observed reaction was:

$$\text{NF}_3 + 2\text{SbF}_5 \rightarrow \text{NF}_2^+ \text{Sb}_2\text{F}_{11}^-$$

From the unusually large amount of monel salts formed, it was concluded that a second reaction was:

$$\text{NF}_2^+ + \text{Ni} \rightarrow \text{NiF}_2 + \frac{1}{2}\text{N}_2$$

The formation of NF₄⁺ could be accounted for as follows:

$$\text{NF}_3 + \text{NF}_2^+ \rightarrow \text{NF}_4^+ + \frac{1}{2}\text{N}_2\text{F}_2$$

On the basis of these reactions and with the assumption that disproportionation of NF₃ did not occur, we concluded but did not prove that NF₂⁺ had been formed. The study of this reaction was not pursued further because of the apparent lower stability of the product formed as compared with NF₄⁺.

Interaction of a Perchlorate with NF₄SbF₆

We attempted to determine whether the synthesis of NF₄ClO₄ is possible, first by observing the stability of a mixture of the solids NF₄SbF₆ and KClO₄, and second by observing the behavior of these two solids in solution in liquid HF. Because no apparent mutual destruction of the perchlorate and NF₄SbF₆ was detected, in our opinion synthesis of NF₄ClO₄ should be possible.
It has been reported\(^1\) that attempts to prepare \(\text{NF}_2\text{O}^+\text{ClO}_4^-\) resulted in mutual destruction of \(\text{NF}_2\text{O}^+\) and \(\text{ClO}_4^-\) to form \(\text{FClO}_3\) and \(\text{FNO}_2\). In our experiments involving \(\text{NF}_4\text{SbF}_6\) and \(\text{KClO}_4\), we searched the contents of the reaction vessel for evidence that would indicate the occurrence of such a decomposition. No molecules containing the species \(\text{F-Cl-O} \equiv \text{F-H-O}\) were found either in the gas phase or in successive fractions obtained by vaporizing the HF solvent. The solid remaining after removal of solvent was hydrolyzed; no evidence for the presence of nitrogen oxides could be observed, although evolved gas (presumably \(\text{NF}_3\) and \(\text{O}_2\)) indicated the presence of the \(\text{NF}_4^+\) cation in the residue.

\(^1\)Allied Chemical Corporation, General Chemical Division, Quarterly Report No. PR-25, Contract No. DA-01-021-AMC-12264(Z), June 1965.
THE SYNTHESIS OF THE PERFLUORO AMMONIUM CATION, NF$_4^+$

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THE SYNTHESIS OF THE PERFLUORO AMMONIUM CATION, NF$_4^+$

W.E. Tolberg, R.T. Rewick, R.S. Stringham, and M.E. Hill

ABSTRACT

When a mixture of nitrogen trifluoride, fluorine, and antimony pentafluoride is heated under pressure, the salt NF$_4^+$ SbF$_6$ is formed. This is the first derivative of the perfluoroammonium cation NF$_4^+$ to be observed. It was characterized by evidence obtained from thermal decomposition, hydrolysis, elemental analyses, and fluorine nmr spectra. The salt is stable in a very dry atmosphere and at 200°C in vacuo but decomposes rapidly above 300°C to NF$_3$, F$_2$, and SbF$_5$. Elemental analysis was carried out by determination of the quantity and identity of the gases evolved on hydrolysis followed by analysis of the hydrolysate. Hydrolysis of NF$_4^+$ quantitatively produces NF$_3$ and O$_2$ in a two to one mole ratio. These analyses showed that the empirical composition of the solid was NSbF$_{10}$, and that the oxidation number of nitrogen in the compound is five. The product is from 96 to 99% pure as isolated from the monel reactor, the balance consisting mainly of Ni(SbF$_6$)$_2$. The fluorine nmr spectra were obtained from the salt dissolved in anhydrous HF and were consistent with the presence of SbF$_5^-$ and of a species of the type NF$_x$$. From this and other evidence the structure of the salt was shown to be NF$_4^+$ SbF$_6^-$ . Because the nmr spectra showed that all fluorines attached to nitrogen are equivalent, the NF$_4^+$ ion is almost certainly tetrahedral.

The salt NF$_4$AsF$_6$ was also synthesized in a similar reaction and was characterized by thermal decomposition, hydrolysis, and elemental analysis. These results were quite analogous to those of the antimonate salt except that the thermal decomposition temperature was slightly lower and the purity was only about 95%.
INTRODUCTION

In a recent communication, the synthesis of the new cation \( \text{NF}_4^+ \) was described as resulting from the reaction of nitrogen trifluoride, fluorine, and antimony pentafluoride in liquid HF, at 200°C and up to 85 atmospheres pressure in a monel metal vessel. The product consisted of a mixture of \( \text{NF}_4 \text{SbF}_6 \) and the antimonate and fluoride salts of metals from the reaction vessel.

This synthesis resulted from a systematic study of the \( \text{NF}_3/F_2/SbF_5/HF \) system in which it was thought that one or more of the possible \( \text{NF}_x^+ \) cations might be formed from \( \text{NF}_3 \). We have studied extensively a number of combinations of the components of the above quaternary system and have found, in addition to the reaction reported earlier, a second reaction in which the \( \text{NF}_4^+ \) cation is formed. These two reactions differ in that, in the first, a liquid phase of HF was present while, in the second, no HF was added to the system. The new reaction is:

\[
\text{NF}_3 + F_2 + \text{SbF}_5 \rightarrow \text{NF}_4 \text{SbF}_6
\]

Price et al., on considering the \( \text{NF}_4^+ \) cation theoretically, concluded from its calculated electron affinity and size that it could not form crystalline salts. Wilson estimated the heat of formation of \( \text{NF}_4^+ \) by comparing the isoelectronic series \( \text{CF}_3/\text{CF}_4/\text{CF}_5 \) and \( \text{NF}_2^+/\text{NF}_3^+/\text{NF}_4^+ \). From this and other considerations, he concluded that it was not unlikely that \( \text{NF}_4^+ \) could be prepared by a suitable ion-molecule reaction and observed in the gas phase. He also discussed the stability of hypothetical perfluoroammonium fluoride, perchlorate, sulfate, and fluoborate. Of these, only the latter was thought possibly capable of existence and this only at low temperatures. He did not discuss the antimonate or arsenate salts in his paper but privately stated that these might very well be stable.

Prior to our experimental studies of the \( \text{NF}_3/F_2/SbF_5/HF \) system, we concluded that, if the series, \( \text{BF}_4^- \), \( \text{CF}_4^- \), \( \text{NF}_4^+ \), and their trifluoride precursors had consistent properties, \( \text{NF}_4^+ \) might be considerably more
stable than predicted. We also estimated the heat of reaction to form
the hypothetical salt \( \text{NF}_4^+ \text{F}^- \) in liquid \( \text{HF} \). These conclusions and cal-
culations encouraged us to attempt the preparation of \( \text{NF}_4 \text{SbF}_6 \).

Nearly pure \( \text{NF}_4 \text{SbF}_6 \) can be obtained under certain conditions.
Variation of temperature and heating periods has produced salts having
the compositions \( \text{NF}_4 \text{Sb}_2 \text{F}_{11} \) and \( \text{NF}_4 \text{Sb}_3 \text{F}_{16} \). It is likely that the complex
anions \( \text{Sb}_2 \text{F}_{11}^- \) and \( \text{Sb}_3 \text{F}_{16}^- \) exist in these salts, since the fluorine nmr
spectrum of \( \text{Sb}_2 \text{F}_{11}^- \) has been observed in other systems.\(^5,\,^6,\,^7\) \( \text{NF}_4 \text{SbF}_6 \)
can be obtained from these salts, however, by heating them in vacuo.

The following describes the preparation, characterization, and some
reactions of \( \text{NF}_4 \text{SbF}_6 \) and \( \text{NF}_4 \text{AsF}_6 \).

**EXPERIMENTAL SECTION**

**Apparatus.** The vacuum system used in this work consisted of a
metal manifold to which a number of subsystems were attached. These
were: (1) a multipurpose line for handling, measuring, and transferring
reactants; (2) a line for purifying and storing fluorine; and
(3) a similar line for nitrogen trifluoride. The multipurpose subsystem
(1) with a monel metal reaction vessel attached is shown in Figure 1 and
the fluorine line in Figure 2.

All valves are Hoke M-482-M bellows valves. The fluorine line
consists of copper lines and vessels fabricated with silver/copper
eutecic solder. The multipurpose line is of monel metal assembled by
means of heliarc welding. Demountable joints were made from fittings
having FEP Teflon ferrules.

The 60-cc reaction vessel is shown in detail in Figure 3. The
vessels were fabricated by means of heliarc welding and were tested
under vacuum with a helium leak detector, treated with fluorine gas,
and later tested at 200 atmospheres with nitrogen gas. The welds are
made the full thickness of the tubing for strength.
FIG. 1 MULTIPURPOSE LINE
Fig. 2 Fluorine Purification Line
FIG. 3 MONEL REACTION VESSEL
Reagents. Nitrogen trifluoride was obtained 99.9% pure from Air Products Company. Because about 0.1 mole or 7 grams were required for each preparation, the NF$_3$ was transferred within the vacuum system by a method designed to prevent contamination and to remove the nitrogen impurity originally present. Two and one fourth liter-atmospheres was condensed at liquid nitrogen temperature, warmed to -130°C, and transferred to the calibrated volume at -196°C and pumped on.

Fluorine with a typical analysis of 98% purity was obtained from Allied Chemical Corporation. Three liter-atmospheres was condensed into a trap packed with nickel spirals and cooled to -196°C. The gas remaining in the metering volume was isolated from the trap, and the contents of the trap volatile at -196°C were transferred to a 1-liter volume cooled to -210°C. On isolation from the trap, the liquid was pumped on at -210°C (solid nitrogen/liquid nitrogen slush), warmed to -196°C, and transferred into the calibrated volume at -210°C.

Antimony pentafluoride was obtained 99.5% pure from Allied Chemical Corporation. It was transferred directly from the supply vessel into an FEP Teflon buret by trap-to-trap distillation. The contents of the buret were pumped on at -44°C and used without further purification.

Hydrogen fluoride was obtained in excellent purity from Olin Corporation. Because HF reacts slowly with its container forming hydrogen gas, the hydrogen must be removed both to facilitate vacuum transfer and to avoid reaction with fluorine on subsequent fluorination of the HF. In addition, solid HF expands rapidly on melting, and at 23°C the resulting liquid occupies a volume about 1.5 times that of the solid. Therefore, an enclosed container filled with solid HF will burst as the HF melts. Figure 4 shows the apparatus used to obtain about 200 cc of solid HF in a double trap that is pumped on while cooled with liquid nitrogen. The HF is transferred successively from the trap to the buret and to the storage vessel where it is treated with fluorine gas. The fluorine is removed by pumping on the HF cooled to -196°C.

Experimental Techniques. The volumes of all sections of the multipurpose line were measured by expansion of a known pressure of nitrogen.
FIG. 4 HF LINE
from a known volume. The vacuum system was maintained leak-free by testing with a helium leak detector. The combination of reagents H\textsubscript{2}, N\textsubscript{2}, and SbF\textsubscript{5}, although highly corrosive, appears to passivate the system. If exposed to air containing water vapor, the system corrodes and the bellows deteriorate rapidly. Thus, the bellows are never needlessly exposed to air and are installed so that they are in vacuum. All sections are treated with fluorine gas after each exposure to air.

Fluorine behaves as a perfect gas relative to its behavior at one atmosphere up to a pressure of 13 atmospheres (gauge limit), and was measured in the calibrated volume at sufficient pressure to obtain about 0.13 mole.

Nitrogen trifluoride does not behave as a perfect gas at pressures up to 13 atmospheres relative to its behavior at one atmosphere. Consequently, its deviation from perfect gas law behavior was determined and used to obtain measurement of the quantity of NF\textsubscript{3} supplied to the reaction vessel.

Antimony pentafluoride was measured only approximately by volume because in a metal system treated with fluorine much SbF\textsubscript{5} is lost by reaction with metal fluorides to form antimonate salts. The monel reaction vessel also absorbed several grams of SbF\textsubscript{5} when exposed to fluorine at high pressure and 200°C.

In a typical preparation, 0.07 mole SbF\textsubscript{5} and 0.05 mole NF\textsubscript{3} were condensed into the reaction vessel at -196°C while 0.13 mole of F\textsubscript{2} was condensed from the calibrated volume at -196°C into the reaction vessel at -210°C. The reaction vessel was placed in a vertical tube furnace surrounded by Fiberglas and enclosed in a steel safety shield. The temperature was obtained from an iron-constantan thermocouple. The reaction mixtures were heated at 100°C or at 200°C for from 24 to 124 hours.
ANALYSES

The procedure is here outlined for safely removing unreacted starting materials from the reactor on completion of the heating period and for subsequent analysis of the $\text{NF}_4^+$ salts formed in the reaction. After 50 hours heating at 200°C, the reaction vessel is cooled and installed as shown in Figure 1. The sections of tubing exposed to the atmosphere are repassivated with fluorine gas, evacuated, and tested with a helium leak detector. The pressure of unreacted $\text{F}_2$ and $\text{NF}_3$ in the reaction vessel is in excess of 30 atmospheres. Because fluorine at pressures greater than two atmospheres cannot always be released through a small valve into an evacuated system without the occurrence of a fluorine fire in the valve, the reactor is cooled to $-196^\circ\text{C}$, the valve is opened, and the reactor is warmed to $-130^\circ\text{C}$. The $\text{F}_2$ and $\text{NF}_3$ are transferred into the 500-cc vessel and warmed to room temperature, and the pressure is recorded.

The mixture is condensed again in the 500-cc volume at $-210^\circ\text{C}$ and the fluorine is removed by pumping on the system. The fluorine is disposed of slowly through the scrub vacuum line which is equipped with a Sodasorb trap. Complete separation of fluorine requires repeated warming of the mixture to room temperature, measurement of pressure, cooling to $-210^\circ\text{C}$, and pumping. When a constant pressure is observed (usually after the third extraction), the gas remaining is $\text{NF}_3$ containing a small but detectable quantity of both $\text{CF}_4$ and $\text{SiF}_4$. Since neither are detectable by infrared spectra of the starting materials, it is assumed that they are derived from the reaction vessel. The impurities present, however, do not contribute appreciable error to the determination of $\text{F}_2$ and $\text{NF}_3$ from pressure readings obtained as described above.

The reactor is cut open with a hack saw within the dry box and the $\text{NF}_4^+$ antimonate and complex antimonate salts (> 15 grams) are safely removed from the reactor by breaking up the melt and scraping it out.

Reaction with $\text{SiO}_2$. Because water and the elements of water are extremely difficult to remove from glass, it was necessary to observe
the interaction of $\text{NF}_4\text{SbF}_6$ with glass to determine the feasibility of obtaining X-ray powder diffraction patterns in glass capillaries. As expected, the reaction of very dry glass with $\text{NF}_4\text{SbF}_6$ resembled hydrolysis until the elements of water were depleted. When the temperature was increased to 85°C, a different reaction occurred, yielding $\text{I}^-$ and $\text{SiF}_4$ but no oxygen. It was assumed that $\text{Os}_2\text{SbF}_6$ was formed. At higher temperatures, the monel vessel was attacked and metal oxides were formed. Thus it appears that X-ray spectra can be obtained only with special treatment of the glass capillaries to avoid partial decomposition of the sample.

**Reaction with Halides.** Attempts to obtain infrared spectra in KBr, KCl, and AgCl showed that $\text{NF}_4^+$ reacts with bromide but not with these chlorides in the solid state.

**NMR Spectra.** $\text{F}^{19}$ resonance spectra were obtained from $\text{NF}_4\text{SbF}_6$ dissolved in HF and contained in an FEP Teflon capsule. The capsule fits inside a standard nmr tube and had an i.d. of 0.100 in. The capsule permits diffusion of water vapor through its walls such that half the $\text{NF}_4^+$ is hydrolyzed after five weeks. The spectrometer is a Varian Associates Model HA-100, operated in the HR mode at 94.1 Mc/s.

**Solubility in HF.** $\text{NF}_4\text{SbF}_6$ is quite soluble in HF, 0.75 gram having completely dissolved in 1 gram of HF in an FEP Teflon vessel. The salt precipitated from solution, however, when exposed to a passivated monel vessel, indicating that it easily forms supersaturated solutions. Relative intensities of nmr lines show that solubility decreases with decreasing temperature.

**Thermal Decomposition.** $\text{NF}_4\text{SbF}_6$ is thermally stable at 200°C but decomposes rapidly above 300°C according to the reaction:

$$\text{NF}_4\text{SbF}_6 \rightarrow \text{NF}_3 + \text{F}_2 + \text{SbF}_6$$

The decomposition was carried out in a monel vessel heavily passivated with respect to $\text{F}_2$ and $\text{SbF}_6$. The $\text{F}_2$ and $\text{NF}_3$ were recovered quantitatively in a 1:1 mole ratio (approximately 49% $\text{NF}_3$ and 48% $\text{F}_2$) but only a small quantity of the $\text{SbF}_6$ was observed, the balance having been taken up by the metal vacuum lines.
The number of moles of \( \text{NF}_3^+ \) formed is equal to the number of moles of \( \text{NF}_3 \) consumed, because no other products from other reactions involving \( \text{NF}_3 \) have been detected.

In preparations involving the quantities of reactants given above at 200°C and 50 hours, about 41% of the \( \text{NF}_3 \) initially present is consumed. The consumption of \( \text{NF}_3 \) drops to 11% at 100°C for 50 hours. The amount of \( \text{F}_2 \) consumed always exceeds the amount of \( \text{NF}_3 \) consumed because of reaction of \( \text{F}_2 \) with the container.

The \( \text{NF}_3^+ \) salts react readily with moisture in the atmosphere but are stable indefinitely in the nitrogen atmosphere provided by a Vacuum Atmospheres Corporation dry box equipped with a recirculation system that removes both oxygen and water.

**Hydrolysis.** Weighed samples (0.5 gram) of the product were hydrolyzed in one to two cc of water. The hydrolysis is a smooth reaction proceeding according to the equation:

\[
\text{NF}_4^+ + \text{H}_2\text{O} \rightarrow \text{NF}_3 + \text{H}_2\text{O} + \text{H}_2\text{F}^+
\]

The \( \text{NF}_3 \) and \( \text{O}_2 \) were determined by the method described for \( \text{NF}_3 \) and \( \text{F}_2 \). The ratio of \( \text{NF}_3 \) to \( \text{O}_2 \) was 2 to 1 with a precision of 2 parts in 200. Mass spectrometric analysis of the gases evolved showed only \( \text{NF}_3 \) and \( \text{O}_2 \); no other gases such as nitrogen oxides were detectable. The hydrolysis of the anion(s) is complex and is complete in strong base.\(^9\) The hydrolysate was later analyzed for antimony by bromate titration,\(^9\) with the modification that borate was added to eliminate interference by fluoride ion. Fluoride was determined colorimetrically.\(^10\) Because the product is contaminated with salts from the monel metal container, the sample is also analyzed for \( \text{Ni}^{+2} \) and \( \text{Cu}^{+2} \). The contamination by copper which might reasonably be expected to occur in a monel vessel is usually negligible.

The elemental analysis performed as above indicates the presence of complex fluoantimonate anion. When the mixtures from various preparations were heated at 200°C for three days, they analyzed quantitatively from 96.0 to 99.5% \( \text{NF}_4\text{SbF}_6 \) and the balance \( \text{Ni} \)\( (\text{SbF}_6)^{+2} \). These purities
represent a range observed in 12 preparations, and the quality of preparations improved as our work progressed.

Calc. for NF₄SbF₆:  N = 4.30  Sb = 58.33  F = 37.37
Found:  N = 4.27±0.04  Sb = 57.85±0.06  F = 37.64±1.5  i.i < 0.30

Preparation of NF₄AsF₆. NF₃, F₂, and AsF₅ were heated at an initial pressure of 2000 psi for 260 hours at 125°C. About 12% of the NF₃ was converted to a solid product that, when heated to 300°C, decomposed to yield approximately equimolar quantities of the starting reagents. Hydrolysis of 0.5 gm of the salt yielded NF₃ and O₂ in an approximately 2 to 1 mole ratio. No oxides of nitrogen were detectable by mass spectrometry. The sample was about 95% pure.

RESULTS AND DISCUSSION

The interaction of NF₃, F₂, and SbF₅ has been studied in several reactions under varying conditions of temperature, pressure, and proportion of starting materials. The product is NF₄SbF₆ contaminated with a small percentage of metal antimonate salts from the reaction vessel. This conclusion is based on elemental analysis, identity and quantity of products from hydrolysis, thermal decomposition, and nmr spectra.

The results from elemental analysis rule out empirical formulas other than NSbF₁₀.

The F¹⁹ nmr spectra of the reaction product dissolved in HF (Figure 5) consisted of a triplet at -214.7 ppm from PCCI₃ and a broad line obscured by the sidebands downfield from HF. The latter appears to be characteristic of SbF₆⁻, while the triplet differs from any known NF compound. The triplet was assigned to NF₄⁺ as follows:

1) The resonance triplet having lines of equal intensity can arise from the interaction of F¹⁹ with a nucleus having unit quadrupole moment.
2) The triplet no longer appeared after the product had been thermally decomposed and had evolved equivalent quantities of both NF₃ and F₂.
FIG. 5 NMR SPECTRUM OF NF₄SbF₆
Thus since nitrogen has a quadrupole moment of one, the triplet is due to the presence of a structure of the type \( NF_x^+ \). Exclusion of paramagnetic structures and those having more than eight electrons in the bonding orbitals allows only \( NF, NF_2^-, NF_2^+, \) and \( NF_4^+ \). (3) The hydrolysis of the product evolves \( NF_3 \) and \( O_2 \) while \( NF_3, N_2F_2 \), and the ionic complexes \( N_2F_{12}F_6 \) (Ref. 11) and \( N_2F_3Sb_2F_{11} \) all produce oxides of nitrogen. (The hydrolysis of the gases is slow, while that of the ionic compounds is rapid, \( N_2F_3Sb_2F_{11} \) hydrolyzing explosively at room temperature.) In addition, evolution of \( NF_3 \) and \( O_2 \) in a ratio of 2 to 1 on hydrolysis shows that the oxidation number nitrogen in the allowed NF species is five. \( NF_4^+ \) is the only one of the allowed structures that has the proper valence and that could produce \( NF_3 \) on hydrolysis. If \( NF_4^+ \) is present as shown above, the compound has the structure \( NF_4^+SbF_6^- \).

The existence of the \( NF/F_19 \) triplet and no other resonance attributable to an NF structure shows that all fluorines in \( NF_4^+ \) are equivalent and that the structure of the ion is almost certainly tetrahedral as expected.

Fluorine nmr spectra were obtained on numerous reaction products as well as on products converted to \( NF_4SbF_6 \) by heating in vacuo.\(^\text{15}^\) No resonance lines other than those attributable to \( NF_4^+ \) in the form of its antimonate or complex antimonate salts have been observed. The combined evidence from nmr spectra, hydrolysis, and analysis of unreacted starting materials shows that \( NF_3 \) undergoes no reactions other than those leading to formation of \( NF_4^+ \). The reaction mechanism leading to \( NF_4^+ \) is not known, although it might involve either the heterolytic dissociation of \( F_3 \) to form \( F^+SbF_6^- \), formation of \( NF_2SbF_6 \), or both.

The stability of \( NF_4SbF_6 \) in vacuo at 200°C and its decomposition at 300°C implies that the ion, at least in this salt, is quite stable. The former indicates an activation energy (possibly 30 to 50 kcal/mole) for the decomposition of \( NF_4^+ \) that is higher than we expected and much higher than anticipated by Wilson.\(^8\) Consequently, the hypothetical salts he discussed might very well have sufficient stability to be preparable.
ACKNOWLEDGMENTS

Research reported in this paper was supported by the Advanced Research Projects Agency through the Air Force Rocket Propulsion Laboratory, Edwards, California, Contract AF 04(611)-9370. The Project Monitor is Dr. William Leahy, RPCL. The authors express their appreciation to Dr. Henry Taube, Stanford University, for many valuable discussions and suggestions.
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(12) After learning that we had synthesized the NF₄⁺ ion in the form NF₄SbF₆, Christe et al.¹ requested that we obtain NMR spectra from two samples of a powdery solid that had been prepared in a glow discharge reaction involving NF₃, F₂, and AsF₅ in a glass reaction vessel. When HF was added to the first of these, part of the white powder dissolved forming a colorless solution and a dark brown residue that appeared to be copper fluoride. The colorless solution was decanted into an FEP Teflon NMR tube, and the spectra showed no NF species were present. A broad, intense resonance line due to AsF₆⁻ was observed upfield from HF, however, indicating the presence of a substantial quantity of AsF₆⁻ salts.

The second sample prepared subsequently from quantities of reactants exposed to glow discharge for several weeks was dissolved in HF and, as before, formed a colorless solution and a dark residue. The NMR spectrum contained, at very low intensity, the triplet we had shown earlier to be characteristic of NF₄⁺. We estimated from

*See Article 4 of this report.*
the ratio of the area of the hexafluoroarsenate line to that of
the triplet (about 100 to 1) that this particular sample almost
certainly contained about $1\frac{1}{2}$ NF$_4$AsF$_6$. The balance of the arsenic
salts were thought to be NOAsF$_6$ and NO$_2$AsF$_6$, formed by reaction
of fluorine with glass during the glow discharge. It was later
reported$^{13}$ that hydrolysis of the discharge product yielded nitrogen
oxides alone with NF$_5$. The hydrolysis of NOAsF$_6$ could explain
the evolution of NO, while that of NF$_4$AsF$_6$ could not. This
difference in properties of NF$_4$AsF$_6$ indicates that the glow discharge
produced impurities at least in the samples we examined. These
observations, however, comprise a partial confirmation of our
conclusions in that the glow discharge synthesis is a third method
of preparing the NF$_4^+$ cation.

ILLUSTRATIONS

Figure 1  Multipurpose Line
Figure 2  Fluorine Purification Line
Figure 3  Monel Reaction Vessel
Figure 4  HF Line
Figure 5  NMR Spectrum of $\text{NF}_4\text{SbF}_6$
Article 2

THE SYNTHESIS OF THE PERFLUORO AMMONIUM CATION, NF₄⁺
THE SYNTHESIS OF THE PERFLUORO AMMONIUM CATION, $\text{NF}_4^+$

W.E. Tolberg, R.T. Rewick, R.S. Stringham, and M.E. Hill

Stanford Research Institute
Menlo Park, California

The purpose of this note is to report the first synthesis of the tetrafluoroammonium ion, $\text{NF}_4^+$. The ion was synthesized in the form of its salt, $\text{NF}_4\text{SbF}_6$, during research directed toward determining conditions under which the ionic species, $\text{NF}_x^+$, can be made to exist. The approach included studies of the system $\text{NF}_3/\text{F}_2/\text{SbF}_5/\text{HF}$ and its six binary and four ternary subsystems, whose reactions forming solid salts in these systems possibly involved the following:

1. $\text{NF}_3 + \text{SbF}_5 \xrightarrow{\text{HF}} \text{NF}_2\text{SbF}_6$
2. $\text{NF}_3 + \text{HSbF}_6 \xrightarrow{\text{HF}} \text{HNF}_2\text{SbF}_6$
3. $\text{NF}_3 + \text{F}_2 + \text{SbF}_5 \xrightarrow{\text{HF}} \text{NF}_4\text{SbF}_6$

At ambient and lower temperatures and at pressures up to 12 atmospheres, we observed no new N-F-containing species in the systems containing $\text{NF}_3$ either by means of conductivity and solubility measurements or by means of NMR and EPR spectra. In addition, thermochemical estimates indicated that the heat of reaction to form the hypothetical crystal, $\text{NF}_4^+/\text{F}^-$, would be endothermic by about 50 kcal. More significant, perhaps, is that the several mechanisms through which $\text{NF}_4^+$ itself might be formed involved processes considerably more endothermic than indicated by the net heat of reaction.

From prior experimental observations, thermochemical estimates, and the calculations of Curtis and Wilson on the estimated entropy and stability of the $\text{NF}_4^+$ cation, it seemed reasonable that the synthesis of...
NF₄SbF₆ could be accomplished by heating the quaternary system, NF₃/F₂/SbF₅/HF, at moderate temperatures and relatively high pressures. The synthesis occurred as expected when equimolar quantities of NF₃, F₂, and SbF₅ were heated in a monel tube reactor for about 2-1/2 days at 200°C and at pressures up to 85 atmospheres. A liquid phase of HF and SbF₅ was present at a concentration of 0.2 mole fraction of SbF₅ relative to HF at room temperature. On completion of the reaction and removal and analysis of unreacted starting materials, the solids remaining in the reactor exhibited a vapor pressure not in excess of a few microns at 200°C. The product was decomposed at 350°C in vacuo yielding approximately 0.01 mole of gas containing equimolar quantities of NF₃ and F₂. In this first experiment, no attempt was made to observe SbF₅. The evolution of equimolar quantities of NF₃ and F₂ was expected from the thermal decomposition of NF₄SbF₆ formed as shown in reaction (3).

Reaction parameters have been studied, and it appears that a satisfactory preparation is obtained when 0.1 mole each of NF₃, F₂, and SbF₅ (the latter 0.2 mole fraction in HF) are heated at 200°C for two to three days in a 60 cc monel tube reactor and at pressures up to 18 atmospheres. The crude product also contains salts formed by the reaction of monel metal with F₂ and SbF₅. We have, in fact, been unable to obtain any evidence that the crude product contains other than a mixture of NF₄SbF₆ and the salts from the reaction with monel metal.

From material balances on a number of preparations, the consumption of NF₃, F₂, and SbF₅ was best accounted for by the formation of NF₄SbF₆ along with Ni(II) and Cu(II) hexafluoroantimonates. In a typical preparation, more than 40% of the NF₃ charged is converted to a solid. The crude product of the reaction contains about 0.035 mole of NF₄SbF₆ and is approximately 75% pure by weight, the remainder consisting of metal salts. The crude (75%) NF₄SbF₆ was characterized without further purification by means of thermal decomposition, hydrolysis, and F¹⁹ NMR spectra. Above 300°C thermal decomposition proceeded according to the following reaction:

\[
\text{NF}_4\text{SbF}_6 \xrightarrow{\Delta} \text{NF}_3 + \text{F}_2 + \text{SbF}_5
\]
The hydrolysis reaction was:

\[ \text{NF}_4\text{SbF}_6 + 7\text{H}_2\text{O} \rightarrow \text{NF}_3 + \frac{3}{2}\text{O}_2 + \text{HSb'O}_2\text{F}_6 + 7\text{HF} \]

Hydrolysis proceeds smoothly to yield a colorless solution. Data from these reactions agreed within experimental error with the product composition indicated by the material balance. The NMR spectra of the HF solution of the product contained a triplet resonance, centered at -214.7 ppm from FCCl₃. The lines of the triplet were equally intense with a coupling constant, J\(_{\text{N-F}}\), of 231 cps. The chemical shift and splitting differ from any known N-F species. These observations and others not included in this note are consistent with the synthesis, reactions, and properties of the salt, NF₄SbF₆.

Subsequently, the salt, NF₄AsF₆, was synthesized by the same method used for the synthesis of NF₄SbF₆. The conversion of NF₃ was substantially less, apparently because of the volatility of Ni(AsF₆)₂ at 200°C. The product decomposed at 300°C to yield NiF₂ and AsF₅.

It was most gratifying to have certain of the results reported here confirmed in research conducted at the Stauffer Chemical Company by Christe, Guertin, and Pavlath. At their request, we obtained NMR spectra from samples of two solids which they had prepared in a glow discharge in the presence of NF₃, F₂, and AsF₅. The N-F resonance which we had earlier shown to be characteristic of NF₄⁺ was observed at low intensity in the HF-soluble portion of one of the two samples. Their glow discharge product almost certainly contained NF₄AsF₆.

ACKNOWLEDGEMENTS

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3. Private communications. See also the note by Karl O. Christe, Jacques P. Guertin, and Attila E. Pavlath in this issue of Inorganic and Nuclear Chemistry Letters.
Article 3

EVIDENCE FOR THE EXISTENCE OF THE $\text{Sb}_2\text{F}_{11}^-$ ANION

To be submitted as a note to Inorganic Chemistry.
EVIDENCE FOR THE EXISTENCE OF THE Sb$_2$F$_{11}^-$ ANION

Stanford Research Institute
Menlo Park, California

ABSTRACT

In a study of the strongly acid system HF/SbF$_5$, F$^{19}$ nmr spectra consistent with the presence of H$_2$F$^+$, SbF$_6^-$, and the structure Sb$_2$F$_{11}^-$ were obtained on mixtures that were about 0.2 mole fraction SbF$_5$. The Sb$_2$F$_{11}^-$ structure is that of two octahedra joined by a common apex. The resonance lines assigned to Sb$_2$F$_{11}^-$ were resolved at a temperature just above the freezing point of the mixture near -50°C. A stable salt of this anion, NFnSb$_2$F$_{11}$, was also synthesized and characterized.

NOTE

In a study of the system HF/SbF$_5$, by means of conductivity measurements and infrared and Raman spectra, Hyman et al. established the equilibrium reaction

$$2\text{HF} + \text{SbF}_5 \rightleftharpoons \text{H}_2\text{F}^+ + \text{SbF}_6^-$$

They also concluded from their evidence that another discrete species was present and suggested that it might be the ion pair H$_2$F$^+$SbF$_6^-$. We
have obtained evidence from \( \text{P}^{19} \) nmr spectra of the HF-SbF\(_5\) system that this species is probably Sb\(_2\)F\(_{11}\). The \( \text{P}^{19} \) nmr spectra of this system were observed elsewhere independently, and the Sb\(_2\)F\(_{11}\) ion was similarly deduced.\(^2\) These independent results have not, however, been published. In addition, we have observed the formation of a salt NF\(_4\)Sb\(_2\)F\(_{11}\) that contains this anion. A similar salt N\(_2\)F\(_3\)Sb\(_2\)F\(_{11}\) also appears to have this structure.\(^2\)

Fluorine resonance spectra were obtained on mixtures that were approximately 0.05, 0.2, and 0.5 mole fraction SbF\(_5\) in polychlorotrifluoroethylene nmr tubes at ambient temperature and at temperatures just above the freezing point of each mixture. For the samples that were 0.2 mole fraction in SbF\(_5\), this temperature was about -50°C. In normal operation, the Varian Associates HA-60 Spectrometer produced spectra having sidebands that overlapped and obscured the observed resonance lines of the HF/SbF\(_5\) system. The sidebands were eliminated by disconnecting the integrator, and it then became necessary to record data by photographing the spectra displayed on the oscilloscope screen.

The spectra of all mixtures at ambient temperature consisted of very broad lines, but at just above the freezing point of the mixture that was 0.2 mole fraction SbF\(_5\), five relatively sharp lines were observed: three of these had fine structure. Data derived from these spectra are given in Figure 1. The chemical shifts of the lines were obtained by calibrating the horizontal scale of the oscilloscope grid in parts per million per division. This was done by using the chemical shifts of pure antimony pentafluoride\(^3\) and pure HF from FCCl\(_3\) as references. We estimated that the shifts of the observed lines were obtained within four ppm.

In view of the presence of SbF\(_6\)\(^-\) and \( \text{H}_2\text{F}^+ \) as shown by Hyman et al., two of the five lines were attributed to these species. In Figure 1, peak I was most probably due to SbF\(_6\)\(^-\) and peak II to the exchange between HF and \( \text{H}_2\text{F}^+ \).

The spin coupling splittings in the fine structure observed in the three remaining peaks were determined with the aid of a 100 cps sideband. These splittings, shown in Figure 1, indicate that the three lines are
related to a single species. The areas of the three lines are best expressed in terms of the ratio 1:8:2, corresponding to peaks labeled \( A_1, M_8, \) and \( X_2 \) in Figure 1. While the areas could not be determined with sufficient precision to rule out other closely related ratios, the ratio 1:8:2 was consistent with the species \( \text{Sb}_2\text{F}_{11}^- \) in the form of two octahedra joined by a common apex. The quartet labeled \( M_8 \) resembled a pair of overlapped doublets and was consistent with eight equivalent fluorines split by two types of non-equivalent fluorine. The quintet \( X_2 \) appeared as a regular binomial distribution and was consistent with two equivalent fluorines split by four. Finally, although \( A_1 \) was observed as a seven-fold multiplet instead of the nine-fold array required by this structure, it is still consistent with the splitting of a single fluorine by eight equivalent ones. This follows from the binomial distribution of intensities that predicts the first and last lines of a multiplet of nine to be 1/168 of the intensity of the central line. Thus, in this method of obtaining spectra from the oscilloscope screen, sufficient amplification could not be used to observe them.

While this evidence satisfactorily indicated the presence of \( \text{Sb}_2\text{F}_{11}^- \) in the \( \text{HF}/\text{SbF}_5 \) systems, it remained to observe the existence of salts having this anion. This occurred in studies which followed the synthesis\(^4\) of \( \text{NF}_4\text{SbF}_6 \) from the reaction of \( \text{NF}_3, \text{F}_2, \) and \( \text{SbF}_5 \) under high pressure and at 100 to 200°C. At 100°C and in the presence of excess \( \text{SbF}_5 \), the product formed in this reaction is \( \text{NF}_4\text{Sb}_2\text{F}_{11} \) as shown by elemental analysis. It is stable at 100°C in vacuo but loses \( \text{SbF}_5 \) to form \( \text{NF}_4\text{SbF}_6 \) at 200°C.

The synthesis of the salt \( \text{NF}_4\text{Sb}_2\text{F}_1 \), and the nmr spectra consistent with the \( \text{Sb}_2\text{F}_{11}^- \) structure taken together comprise substantial evidence for the existence of the \( \text{Sb}_2\text{F}_{11}^- \) ion.
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(2) Private Communication from R.J. Gillespie.


FIGURE LEGEND

Fig. 1. Fluorine nmr spectra of the HF/SbF₅ system.
CHEMICAL SHIFTS IN HF/SbF₅ SOLUTION

42 ± 3 cps

A₁

68 ± 3 cps

X₂

SPIN COUPLING SPLITTING IN Sb₂F₁₁

A₂MₓX₂ STRUCTURE OF Sb₂F₁₁

FIG. 1 FLUORINE nmr SPECTRA OF THE HF/SbF₅ SYSTEM
THE SOLUBILITY OF F₂, AND O₂ IN ANHYDROUS LIQUID HF

Presented in part at the 149th Meeting of the American Chemical Society, Detroit, Michigan, April 1965; submitted to Journal of Chemical and Engineering Data.
THE SOLUBILITY OF F$_2$, NF$_3$, AND O$_2$ IN ANHYDROUS LIQUID HF

W.E. Tolberg, R.T. Revick, M.E. Hill
Stanford Research Institute, Menlo Park, California

ABSTRACT

The solubilities of F$_2$, NF$_3$, and O$_2$ in anhydrous liquid HF have been measured at several temperatures. The solubility of F$_2$ passes through a minimum between 0 and 20°C. The solubility of NF$_3$ exhibited no such minimum in the temperature range studied but deviated appreciably from ideal behavior at dry ice temperature and above one atmosphere pressure. The solubility of O$_2$ was measured at 0 and 20°C. and was, as expected, virtually identical with that of F$_2$. In contrast, the solubilities of O$_2$ in HF at 0 and 20°C. were factors of ten and five, respectively, larger than the literature values of the solubility of O$_2$ in H$_2$O at the corresponding temperatures.

Solubilities of gases in liquids are of theoretical interest, and when measured with sufficient precision and sensitivity, can be used along with other information such as conductivity to infer the presence or absence of interaction of the gas with the solvent. In the study of the chemistry of NF$_3$ and F$_2$ in liquid HF, it was of interest to determine their solubilities in this solvent. The solubility of O$_2$ in HF was also determined in order to permit comparison between solubilities in HF and in H$_2$O. A similar comparison of the solubilities of F$_2$ in the two solvents would have little value because of the reaction of F$_2$ with water.

The solubility of BF$_3$ in liquid HF is the only recently reported$^1, 2, 3$ gas solubility in HF. Thus, this paper is the first report of the solubilities of F$_2$, NF$_3$, and O$_2$ in HF. The method used in this work was
similar to that used by Kilpatrick and Luborsky,\textsuperscript{1} and the measurements were made at several temperatures from 19.85 to -77.2°C.

EXPERIMENTAL SECTION

The apparatus used is shown in Figure 1. All parts were fabricated from Monel metal and were assembled by brazing with silver solder. All valves were Hoke M-482-M bellows valves. The volumes of vessels were determined from the weight and density of distilled water that completely filled them. Volumes of the remainder of the system were calculated from PV changes of argon. Two Wallace and Tiernan pressure gages were used: a 0-1520 mm. gage and a dual-scale gage, 0-200 pria and 0-1035 cm. Hg. Both had calibrations traceable to the Bureau of Standards but were tested as follows: the low pressure gage agreed exactly with a mercury barometer at atmospheric pressure. Successive quantities of argon measured at one atmosphere were then condensed into the high pressure gage volume. Assumption of the perfect gas law permitted calculation of the pressures that should have resulted. The standard deviation of the pressures observed from those calculated was 0.7 cm. Hg.

Anhydrous hydrogen fluoride was obtained in excellent purity from Olin Corporation. It was condensed into a copper trap at liquid nitrogen temperature and pumped on to remove hydrogen. The HF was then distilled slowly into a Kel-F conductivity cell having platinum electrodes and was found to have a conductivity of \(3 \times 10^{-5}\) ohm.\textsuperscript{-1} cm.\textsuperscript{-1}, indicating relatively high purity. The HF was then distilled into the 450 cc. vessel and weighed: 212.9 grams were present.

Fluorine was obtained from Allied Chemical Corporation with a typical analysis of 98\% purity. It was purified by condensing a known quantity of gas into a trap packed with nickel spirals and cooled to -190°C. Gases volatile at -190°C were then transferred to a receiver at -196°C. The significant impurity remaining is approximately 1\% air. A substantial part of the remaining air was removed by extractions of the vapor above the liquid fluorine into an evacuated volume. The fluorine obtained in this manner was used without further purification or analysis.
FIG. 1 SOLUBILITY APPARATUS
RESULTS

The solubility of $F_2$ in HF at five temperatures is given in Figure 2. The straight line plots are given by a Henry's law expression, $p = kM$, wherein the pressure of fluorine in the vapor phase equals a constant times the molality of fluorine in solution. The solubility apparently goes through a minimum between 0 and 20°C, but between 0 and -77.2°C, the solubility can be calculated from the temperature coefficient. Values calculated from the latter agree within 3% of the values determined in single point measurements at -23 and -65°C.

The solubility of NF$_3$ at three temperatures is shown in Figure 3. Straight line plots were obtained at ice temperature and above. At dry ice temperature, a curved plot was observed. Its limiting slope was very nearly equal to that predicted from the temperature coefficient from which the calculated curve was derived. From this fact, it seems clear that NF$_3$ does not have a solubility minimum in the temperature range observed and that the nonlinearity of the solubility at dry ice temperature might be due to other effects such as hydrogen bonding between HF and NF$_3$, or to interactions of NF$_3$ with itself at a temperature and pressures close to critical. The latter seems most likely.

The solubility of O$_2$ in HF is given by $p = 3.4 \times 10^3M$ at 293.0°C and $3.320 \times 10^3M$ at 272.9°C, where $p$ is in cm Hg, $M$ is in moles per 1000 grams, and $k$ in corresponding units.

The solubilities of O$_2$ and F$_2$ in HF are very similar at ice temperature and 20°C. Because the solubility of O$_2$ was not studied at additional temperatures, no conclusions as to the existence of a solubility minimum can be made, nor is it likely that solubilities can be estimated reliably by extrapolation of the temperature coefficient.

Comparison of the solubility of O$_2$ in HF and in H$_2$O shows that it is a factor of ten less soluble in H$_2$O at 0°C. The solubility of F$_2$ in water is probably similarly a factor of ten less.
FIG. 2 SOLUBILITY OF FLUORINE IN HF AT FIVE TEMPERATURES
FIG. 3 SOLUBILITY OF NF₃ IN HF AT THREE TEMPERATURES
LITERATURE CITED


FIGURE LEGEND

Figure 1. Solubility Apparatus
Figure 2. Solubility of Fluorine in HF at Five Temperatures
Figure 3. Solubility of NF$_3$ in HF at Three Temperatures
When a mixture of nitrogen trifluoride, fluorine, and antimony pentafluoride in heated under pressure, the salt NF₄SbF₆ is formed. This is the first derivative of the perfluoroammonium cation NF₄⁺ to be observed. It was characterized by evidence obtained from thermal decomposition, hydrolysis, elemental analyses, and fluorine nmr spectra. The salt is stable in a very dry atmosphere and at 200°C in vacuo but decomposes rapidly above 280°C to NF₃, F₂, and SbF₅. Elemental analysis was carried out by determination of the quantity and identity of the gases evolved on hydrolysis followed by analysis of the hydrolysate. Hydrolysis of NF₄⁺ quantitatively produces HF₃ and C₂ in a two to one mole ratio. These analyses showed that the empirical composition of the solid was N8SbF₂₀, and that the oxidation number of nitrogen in the compound is five. The product is from 96 to 99% pure as isolated from the monel reactor, the balance consisting mainly of Ni(SbF₆)₂. The fluorine nmr spectra were obtained from the salt dissolved in anhydrous HF and were consistent with the presence of SbF₅⁻ and of a species of the type NF₄⁺SbF₅⁻. From this and other evidence the structure of the salt was shown to be NF₄⁺SbF₅⁻. Because the nmr spectra showed that all fluorines attached to nitrogen are equivalent, the NF₄⁺ ion is almost certainly tetrahedral.

The salt NF₄AsF₆ was also synthesized in a similar reaction and was characterized by thermal decomposition, hydrolysis, and elemental analysis. These results were quite analogous to those of the antimonate salt except that the thermal decomposition temperature was slightly lower and the purity was only about 95%.

(Abstracts continued)
NF₄⁺ cation

Sb₂F₁₁ anion

HF Solution Chemistry

Solubility of gases in liquid HF

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Article 3
In a study of the strongly acid system HF/SbF$_5$, $^n$H nmr spectra consistent with the presence of H$_2$F$,^-$, SbF$_5^-$, and the structure Sb$_2$F$_{11}^-$ were obtained on mixtures that were about 0.2 mole fraction SbF$_5$. The Sb$_2$F$_{11}^-$ structure is that of two octahedra joined by a common apex. The resonance lines assigned to Sb$_2$F$_{11}^-$ were resolved at a temperature just above the freezing point of the mixture near -50°C. A stable salt of this anion, NF$_4$Sb$_2$F$_{11}$, was also synthesized and characterized.

Article 4
The solubilities of F$_2$, NF$_3$, and O$_2$ in anhydrous liquid HF have been measured at several temperatures. The solubility of F$_2$ passes through a minimum between 0 and 20°C. The solubility of NF$_3$ exhibited no such minimum in the temperature range studied but deviated appreciably from ideal behavior at dry ice temperature and above one atmosphere pressure. The solubility of O$_2$ was measured at 0 and 20°C, and was, as expected, virtually identical with that of F$_2$. In contrast, the solubilities of O$_2$ in HF at 0 and 20°C were factors of ten and five, respectively, larger than the literature values of the solubility of O$_2$ in H$_2$O at the corresponding temperatures.