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AFRPL-68-47

March 25, 1968

Technical Progress Report No. 4 — Final

SYNTHESIS OF ENERGETIC OXIDIZERS (U)

By: W. E. TOLBERG R. T. REWICK G. R. ZEILENGA
J. A. NEFF M. P. DOLDER M. E. HILL

Prepared for:

AIR FORCE ROCKET PROPULSION LABORATORY-
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE, CALIFORNIA

CONTRACT F 04611-67-C-0002

MAR 29 1968

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SRI Project FRU-6200

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FOREWORD

This final report was prepared by Stanford Research Institute, Menlo Park, California, for the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base, California. The report covers work from August 1, 1966 to September 30, 1967, under Air Force Contract F 04611-67-C-0002. This is a continuation of the work begun under Contract AF 04(611)-9370. Scientists working on the program include M. E. Hill, project supervisor, W. E. Tolberg, R. T. Rewick, G. R. Zeilenga, J. A. Neff, and M. P. Dolder; C. A. Crutchfield and Anna Longwell are responsible for analytical work. The technical consultation of Dr. H. Taube, of Stanford University, is gratefully acknowledged.

The Air Force Rocket Propulsion Laboratory Contract Monitor is Dr. Frank Roberto/RPCS.

This technical report has been reviewed and is approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

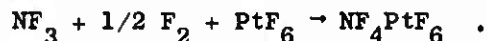
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ABSTRACT

(C) Synthesis of NF_4^+ salts has been carried out by two general methods. Direct synthesis reactions of NF_3 , F_2 , and a series of Lewis acids at high pressure and moderately elevated temperatures have been used to produce a series of NF_4^+ salts having fully fluorinated anions. Metathesis reactions in liquid HF have been used to produce a number of new NF_4^+ salts including some with oxygen-containing anions.

(C) The rate of reaction to form NF_4^+ salts in direct synthesis depends on the acidity of the Lewis acid. Thus, SbF_5 forms NF_4SbF_6 in good yield, AsF_5 produces the arsenate in moderate yield, PF_5 forms NF_4PF_6 in very low yield, and BF_3 produces only a trace of NF_4BF_4 . It was concluded that compounds less acidic than BF_3 in HF would be unlikely to form NF_4^+ salts by direct synthesis. This was confirmed when ClF_3 and ClF_5 did not yield the corresponding salts, NF_4ClF_4 , or NF_4ClF_6 , on heating NF_3 , F_2 , ClF_3 , and ClF_5 at high pressure for extended periods of time.

(C) In addition to NF_4SbF_6 , NF_4AsF_6 , and NF_4PF_6 , a fourth salt, NF_4PtF_6 , was formed by direct synthesis in the reaction:

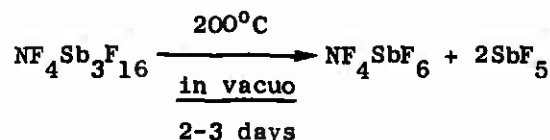
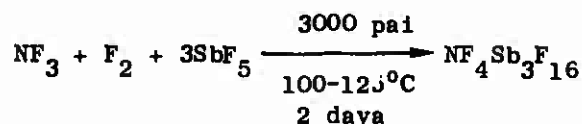


This salt was characterized by nmr and infrared spectroscopy, hydrolysis, and elemental analysis of the hydrolysate.

(U) NF_4SbF_6 has proved to be the most useful in metathesis reactions. Its synthesis is complicated by the formation of varying amounts of the complex fluoroantimonate anions, $\text{Sb}_2\text{F}_{11}^-$ and $\text{Sb}_3\text{F}_{16}^-$, as well as formation of contaminants formed by reaction of F_2 and SbF_5 with the Monel reaction vessel. The optimum conditions found for synthesis of NF_4SbF_6 involve:

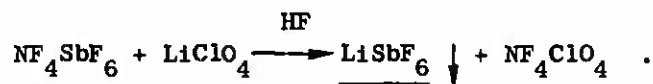
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Products ranging in purity from 96 to 99.5% have been obtained. Monel-antimonate impurities were removed by dissolving NF_4SbF_6 in HF and filtering out the insoluble metal salts. Monel antimonate impurities are mainly $\text{Ni}(\text{SbF}_6)_2$ and $\text{Cu}(\text{SbF}_6)_2$. Other components in Monel metal comprise 2.5% or less of the metal and their presence in the impurities (except for Si which has been detected as small amounts of SiF_4) has not been confirmed by us.

(C) Fully characterized NF_4SbF_6 has been used as a reagent in a number of metathesis reactions forming new salts. A typical reaction is:



Similar reactions have been used to form NF_4HF_2 , $\text{NF}_4\text{SO}_3\text{F}$, NF_4NO_3 , and NF_4BF_4 . The perchlorate decomposes to NF_3 and FClO_4 above -27.5°C , the bifluoride is unstable at -44°C and above, the fluorosulfonate is unstable at -78°C and above, the nitrate is decomposed in HF solution, but NF_4BF_4 is quite stable.

(C) NF_4CN could not be formed owing to decomposition of the alkali metal cyanide to HCN in liquid HF and to the reaction of cyanide with the inter-halogen solvent BrF_5 . The similar decomposition of K_2SiF_6 in HF led to an attempt to synthesize $(\text{NF}_4)_2\text{SiF}_6$ in BrF_5 . No reaction occurred on mixing NF_4SbF_6 with K_2SiF_6 in BrF_5 . The lack of reaction may indicate that one or both of the starting reagents dissolved without dissociation into ionic species.

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(C) Several alkali metal salts of the ClF_4^- and BrF_6^- anions were synthesized. In HF, these decompose to form alkali metal bifluorides and the corresponding interhalogen. They are, however, moderately soluble in BrF_5 . It is expected that this solvent will permit determining whether the salts NF_4ClF_4 and NF_4BrF_6 can be synthesized.

(C) An effort was made to synthesize NF_4BF_4 in a purity sufficient for determining heats of formation. The highest purity obtained was a sample containing 92% NF_4BF_4 and 8% NF_4SbF_6 .

(U) A number of solubility studies were carried out in support of work on metathesis reactions. Solubilities of a number of pertinent compounds in HF, BrF_5 , IF_5 , and BrF_3 are reported and discussed.

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I INTRODUCTION

(U)This report summarizes progress between August 1, 1967, and September 30, 1967, on research concerned with the synthesis of energetic oxidizers. The objectives of the work are to study the chemistry of the NF_4^+ cation and to apply this chemistry to the synthesis of solid inorganic oxidizers.

(U)This program is a continuation of research carried out under Contract AF 04(611)-9370, which involved studies of the interactions of NF_3 and F_2 with the fluoride acceptors SbF_5 , AsF_5 , and HF . The results of these studies included the synthesis and characterization of the salts NF_4SbF_6 , $\text{NF}_4\text{Sb}_2\text{F}_{11}$, $\text{NF}_4\text{Sb}_3\text{F}_{16}$, and NF_4AsF_6 , as well as the probable synthesis of $\text{NF}_2^+\text{Sb}_2\text{F}_{11}^-$. Because of the high yields of reactions that form NF_4^+ salts and the apparent high stability of NF_4^+ compared with NF_2^+ , study of the chemistry of NF_4^+ has been emphasized in this continuing work.

(U)During the current contract period, we have studied the synthesis of NF_4^+ salts by means of two general approaches. The first of these, the direct synthesis approach, involved the temperature/pressure activated reactions of NF_3 and F_2 with a series of Lewis acids. The second, metathesis reactions in liquid HF , were used to synthesize more or less energetic salts. In addition, we have studied a number of systems in the interhalogen solvents BrF_5 and IF_5 in which it is possible that metathetical reactions can take place.

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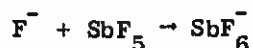
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II DISCUSSION

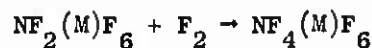
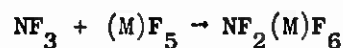
A. Direct Synthesis Reactions of NF_4^+ Salts

(C)The first reaction in which an NF_4^+ salt was synthesized was the reaction of NF_3 and F_2 with SbF_5 to form NF_4SbF_6 . From this it seemed clear that a series of NF_4^+ salts could be directly synthesized from NF_3 , F_2 , and a series of Lewis acids. This conclusion is true provided that the Lewis acid involved is sufficiently acidic. In the series SbF_5 , AsF_5 , PF_5 , BF_3 , ClF_5 , and ClF_3 , we found that acidity with respect to HF was the key factor in the rate of production of NF_4^+ salts. Thus the rate of formation fell off rapidly as we proceeded from SbF_5 to ClF_3 . Good yields were obtained only with SbF_5 and AsF_5 , while PF_5 yielded a few tenths of a gram and BF_3 yielded only a trace. Attempts to form NF_4ClF_4 and NF_4ClF_6 produced no evidence of NF_4^+ salt formation. This is consistent with the fact that ClF_3 and ClF_5 are basic or slightly basic in HF.

(C)In a direct synthesis reaction which differed from the above, PtF_6 was used as the anion precursor and was found to form NF_4PtF_6 very slowly. The anion-forming reaction is essentially $\text{PtF}_6 + e^- \rightarrow \text{PtF}_6^-$ and thus differs from the classical Lewis acid concept wherein, for example,



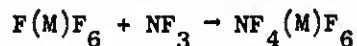
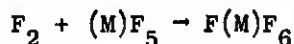
(C)We are not certain of the mechanism by which NF_4^+ is formed. Two alternatives occur and either can account for the relatively slow formation of NF_4^+ salts:



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or



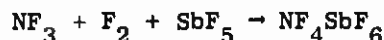
where M may be antimony, arsenic, phosphorus, or boron.

(U)The concentration of either intermediate must be small during reaction. The system NF_3/SbF_5 was heated at 200°C for two days and resulted in formation of a very small amount of solid product. The product contained NF_4^+ salt as well as a material that hydrolyzed to yield nitrogen oxides. Formation of the latter could have been due to the presence of an NF_2^+ salt. It could also have been the result of disproportionation of NF_3 into N_2F_4 and F_2 , the N_2F_4 forming a complex with SbF_5 . Thus no clearcut evidence as to the formation of NF_2^+ salts was obtained from this brief study, but the implication was clear that the NF_2^+ salt could serve as the limiting reagent in the reaction. We have not studied the possible F_2/SbF_5 interaction.

(C)Because the systems involving reaction of NF_3 , F_2 , and a Lewis acid differ, each will be described below.

1. (U) NF_4SbF_6

(U)The reaction to form NF_4SbF_6 can be written:



However, this reaction is complicated by the behavior of SbF_5 , which tends strongly to associate with itself or with SbF_6^- . As a result, depending on the temperature and heating time, the product may consist of NF_4SbF_6 , $\text{NF}_4\text{Sb}_2\text{F}_{11}$, $\text{NF}_4\text{Sb}_3\text{F}_{16}$, or mixtures of these.

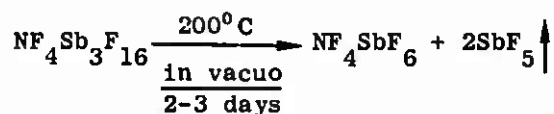
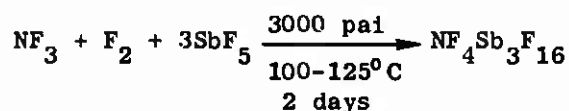
(U)At 80°C , 2000-3000 psi, and a heating time of two days, the product is $\text{NF}_4\text{Sb}_3\text{F}_{16}$ with some unreacted SbF_5 . At 100° to 125°C with the same pressure and heating time, the product is almost exclusively $\text{NF}_4\text{Sb}_3\text{F}_{16}$. At higher temperatures, the product contains $\text{NF}_4\text{Sb}_2\text{F}_{11}$ and NF_4SbF_6 . The

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product obtained at 200°C, 2000-3000 psi, and a heating time of one day, is largely $\text{NF}_4\text{Sb}_2\text{F}_{11}$ with a few percent of NF_4SbF_6 .

(U) From analysis of a large number of preparations, we have concluded that the method of preparation yielding the purest final product of NF_4SbF_6 is the following:



(U) The product from the first step of the reaction sequence is isolated from the reactor by cutting it open with a hacksaw within a drybox and scraping out the salt, which forms as a melt in the bottom of the reactor. The product is not sensitive to impact nor to any of these manipulations.

(U) The $\text{NF}_4\text{Sb}_3\text{F}_{16}$ is ground to a fine powder in a sapphire mortar and placed in a flanged vessel. Conversion to NF_4SbF_6 is carried out by heating the vessel to 200°C while evacuating it through a dry ice-cooled trap. When SbF_5 is no longer collected in the trap, the reaction is complete.

(U) Occasionally, NF_3 is evolved during the heating procedure. This has been attributed to reaction of the NF_4^+ salt with the Monel vessel. The metal vessel is usually pretreated with F_2 under one to two atmospheres of pressure at 200°C. The pretreatment minimizes the reaction of NF_4^+ salt with the container.

(U) The NF_4SbF_6 prepared according to the above procedure is found on analysis to be from 96 to 99.5% pure, the impurities being Monel- SbF_6^- salts. These impurities are relatively insoluble in HF and can be removed by extracting the very soluble NF_4SbF_6 with liquid HF. The amount of impurities has been reduced to about 0.5% by weight by this extraction procedure.

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2. (U) NF_4AsF_6

(U)Initially, both NF_4SbF_6 and NF_4AsF_6 were prepared in reactions that included liquid HF along with NF_3 , F_2 , and the Lewis acid. The presence of liquid HF resulted in extensive corrosion of the reaction vessels and in products that contained large amounts of Monel fluorides and hexafluoroarsenates and antimonates. In the NF_4AsF_6 synthesis, there was an additional problem in that, at the reaction temperature of 200°C , the Monel arsenates appeared to be volatile and sublimed to cooler portions of the reactor, plugging the inlet line. This sublimation also resulted in removal of the otherwise passive coating of Monel salts from the heated portion of the reactor, causing continued exposure of reactive metal surface. This behavior resulted in formation of a large amount of Monel-arsenate salts during the reaction. From these observations it was clear that the reaction temperature should be held below the temperature at which sublimation occurred. In addition, it was obvious that since NF_4SbF_6 formed in relatively high purity in the absence of HF, liquid HF should be omitted from the reaction.

(U)For these reasons, a mixture of NF_3 , F_2 , and AsF_5 was heated at a temperature of 125°C at an initial pressure of 2500 psi for ten days. In contrast to the preparation of NF_4SbF_6 which is formed at the bottom of the reactor, NF_4AsF_6 is found uniformly distributed on the walls of the reactor. The fine white powder is scraped off the walls and isolated. A typical preparation yields about six grams of product.

(U)Because the product is formed on the walls and must be isolated by scraping it out, more impurities from the vessel have been found in the NF_4AsF_6 . The product is typically about 93% pure, the balance consisting of Monel arsenates.

(U)The product was characterized by the same methods used to establish the structure and composition of NF_4SbF_6 . These were hydrolysis, elemental analysis of the hydrolysate, and nmr spectra. This information, as well as other data pertaining to NF_4AsF_6 and NF_4SbF_6 , is given in a recent publication.¹

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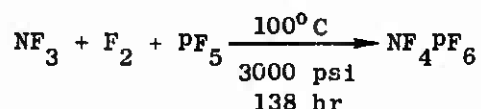
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(U)We have found that extractions with liquid HF lead to no improvement in purity of NF_4AsF_6 . Thus it appears that while NF_4AsF_6 is about half as soluble in HF as is NF_4SbF_6 , the Monel-arsenate impurities are more soluble than the Monel antimonates. As a result of our inability to purify the NF_4AsF_6 , we have found little use for it except in one experiment that will be described later.

(U)The rate of formation of NF_4AsF_6 was deduced from the 17% of NF_3 converted into solid in ten days of reaction at 125°C . Under similar conditions of temperature and pressure and in two days, a 22% conversion of NF_3 into NF_4^+ antimonates was observed. Thus the rate of formation of NF_4AsF_6 is at least a factor of five slower.

3. (C) NF_4PF_6

(C)The salt NF_4PF_6 was synthesized by the reaction:



On completion of the heating period, the residual starting materials were removed from the reactor and measured. From our experience in previous reactions of this type, we expected some fluorine would have reacted with the Monel vessel to form more fluoride than already present from the passivation procedure. We also expected the Lewis acid, in this case PF_5 , to react with the fluorides to form Monel- PF_6^- salts. Thus the only reliable index to the extent of NF_4^+ salt formation was the consumption of NF_3 . Approximately 1.6% less NF_3 was recovered than was originally present. This indicated the possible presence of about 0.4 g of NF_4PF_6 . When the reactor was cut open, a thin layer of product was observed uniformly distributed on the inner surface. Some of the product was hydrolyzed and yielded NF_3 and O_2 , as expected from NF_4PF_6 .

(C)The rate of this reaction was a factor of at least 50 slower than the antimonate reaction. The rate implied that it would be necessary to heat the reaction mixture for about 50 days to prepare sufficient compound with which to undertake complete characterization.

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4. (C) NF₄BF₄

(C) From the results on the syntheses of NF₄PF₆, it was expected that the formation of NF₄BF₄ by direct synthesis would be extremely slow. It was also expected that NF₄BF₄ might be much less thermally stable than the NF₄⁺ salts having larger anions. Thus the synthesis might be adversely affected by too high a reaction temperature. As a result we chose to heat the reaction mixture at 100°C. The reaction was carried out for 185 hours at an initial reactant pressure of 3000 psi.

(C) Isolation and analysis of residual starting materials indicated that as much as 0.7 g of product might be present. However, later observations showed that this could not be true. We used the apparent consumption of NF₃ as an indicator of the extent of NF₄⁺ salt formation. BF₃ was separated from NF₃ by absorbing BF₃ in aqueous base. This procedure evidently resulted in hydrolysis of some NF₃, leading to an incorrect determination of NF₄⁺ salt present.

(C) After residual starting materials had been removed, the reactor was cut open and a small quantity of solid was scraped out. We chose to employ thermal decomposition as the method of characterization. In this case, we expected that heating the isolated solids would result in evolution of NF₃, F₂, and BF₃ if NF₄BF₄ were present. A portion of the isolated solids was heated slowly to above 300°C in an evacuated vessel that had been passivated with fluorine. Only a few millimeters of gas were evolved. The gas contained F₂, NF₃, and SiF₄, but no BF₃ was observed. The small amount of BF₃ to be expected from the thermal decomposition could have been absorbed by Monel metal fluorides. This conclusion was based on the fact that in a separate observation, BF₃ was absorbed by a passivated copper surface but none of the SiF₄ present in the BF₃ was removed. Nevertheless, the above experiment was inconclusive with respect to the direct synthesis of NF₄BF₄ but lent substance to the hypothesis that the rate of formation of NF₄⁺ salts in these direct synthesis reactions is strongly influenced by the acidity of the Lewis acid involved.

(C) The presence of SiF₄ in the gases evolved during thermal decomposition, along with the presence of both NF₃ and F₂, can be explained if the salt

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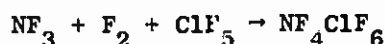
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(NF_4)₂ SiF_6 was present. This seems very unlikely in view of the relative acidity of SiF_4 in HF. The SiF_4 arose from reaction of F_2 with the silicon present in Monel metal.

(C) In a later experiment, a mixture of NF_3 , F_2 , and BF_3 was heated at 150°C and high pressure for three weeks. (The decomposition of NF_4BF_4 is detectable in a mass spectrometer experiment at 176°C ,² thus 150°C was selected as the reaction temperature.) On completion of the heating period, the reactor was evacuated, weighed and heated to 300°C . The system was passivated with respect to BF_3 . The reactor lost 4 mg and the gas evolved contained NF_3 , BF_3 , CF_4 , and possibly a trace of F_2 . There were no more than 4 mg of NF_4BF_4 formed in this experiment. However, the synthesis of NF_4BF_4 has been accomplished by means of a metathesis reaction that will be described in a later section of this report.

5. (C) Attempted Direct Synthesis of NF_4ClF_4 and NF_4ClF_6

(C) From experience with the weaker Lewis acids PF_5 and BF_3 , it seemed unlikely that ClF_3 and ClF_5 would form the hypothetical salts NF_4ClF_4 and NF_4ClF_6 in direct synthesis reactions of the following type:



These reactions were, however, attempted. In the first of these, the F_2 and ClF_3 combined to form the equilibrium concentration of ClF_5 . Thus, the study of the mixture of NF_3 , F_2 , and ClF_3 was essentially the study of both of the hypothetical reactions.

(C) The mixture was heated at 100°C and 3000 psi initial pressure for 65 hours. The reaction vessel was passivated first with respect to fluorine and next with respect to SbF_5 to avoid possible reactions of the interhalogens with metal fluorides. Unfortunately, our analysis

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of reaction products later showed that excess SbF_5 was present in the vessel and that it had reacted to form NF_4^+ antimonate salts.

On completion of reaction, the starting materials were removed and the presence of NF_3 , F_2 , ClF_3 , and ClF_5 was confirmed. The evacuated vessel was then heated slowly up to 350°C and the pressure of evolved gas was observed. Above 225°C the pressure rose from several millimeters to about one atmosphere. The gas contained NF_3 , F_2 , SiF_4 , and about 2% ClF_5 . At first, we attributed the presence of ClF_5 to the decomposition of the hypothetical salt NF_4ClF_6 , but later experiments in which we heated mixtures of NF_3 , F_2 , and ClF_5 in vessels having no SbF_5 present showed that no ClF_5 was evolved on thermal decomposition. Thus, the ClF_5 found in the gas from the first experiment was due to an interaction with SbF_5 . This interaction could have been



However, a separate study of this mixture indicated the occurrence of a complicated reaction system that gave no clear-cut evidence for the formation of the ClF_6^+ cation. The interaction of ClF_5 and SbF_5 could also have been simply the formation of the well-known complex formed by these two reagents and its thermal decomposition above 300°C to yield an observable amount of ClF_5 . It is necessary to assume that the similar complex formed by ClF_3 and SbF_5 did not decompose in the temperature range studied, since no ClF_3 was found in the products of thermal decomposition. Because later experiments provided no evidence for evolution of either ClF_3 or ClF_5 on thermal decomposition, it is necessary to conclude, as expected, that no NF_4ClF_4 nor NF_4ClF_6 had been formed by the direct synthesis route.

6. (C) NF_4PtF_6

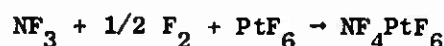
(C)The systems NF_3/PtF_6 and $\text{NF}_3/\text{F}_2/\text{PtF}_6$ were tested for interactions that might form solid salts. A vessel containing solid and about 90 mm of gaseous PtF_6 as well as NF_3 at about 1250 psi was allowed to stand for 137 hours at room temperature. Since all the NF_3 originally present could be recovered from the reaction vessel, it was clear that no interaction occurred at room temperature. The system was not studied at higher temperatures.

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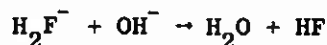
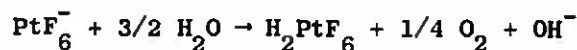
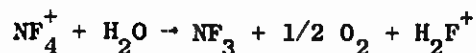
(C) The system $\text{NF}_3/\text{F}_2/\text{PtF}_6$ was examined at three temperatures. There was no reaction at 2000 psi and after 143 hours at room temperature; there was little if any reaction after 400 hours at 50°C. The mixture was then heated at 125°C for 1700 hours, during which time all of the PtF_6 present reacted to form a solid product. Since this reaction was not monitored closely, the rate of reaction could not be determined, and it is possible that the reaction was complete in a much shorter time.

(C) The mixture that formed the solid product contained 214 mmole of NF_3 , 132 mmole of F_2 , and 45 mmole of PtF_6 . The consumption of the three components was consistent with the reaction:



The F^{19} nmr spectrum was obtained on a dilute solution of the salt in liquid HF. The NF triplet characteristic of NF_4^+ was observed at -214.3 ppm from FCCl_3 . This chemical shift is identical within experimental error to that observed for $\text{NF}_4^+\text{SbF}_6^-$ and $\text{NF}_4^+\text{AsF}_6^-$. There was no line or lines between the positions of HF and F_2 that could be attributed to PtF_6^- . The HF line was sharp; the sharpness indicated that very little fluoride exchange was occurring.

(C) Hydrolysis of the salt was consistent with the reactions:



In addition, the presence of an insoluble precipitate in the hydrolysate indicated that some hydrated PtO_2 had formed in accord with reported observations on the hydrolysis of O_2PtF_6 .³

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(C)Elemental analysis was in reasonably good agreement with a product composition of NF_4PtF_6 contaminated with $\text{Ni}(\text{PtF}_6)_2$ from the nickel reactor:

	Calc	Found
N	3.51	3.40
F	48.88	45.27
Pt	47.61	45.58
Ni	-0-	0.88

(C)The infrared spectrum was obtained from a sample of the product dispersed in KCl and pressed into a transparent pellet. The spectrum contained the intense line of NF_4^+ at 1155 cm^{-1} and the PtF_6^- absorption⁴ at 647 cm^{-1} .

(C)During preparation of the nmr sample, it was observed that most of the sample of the impure NF_4PtF_6 had dissolved in HF while a small amount of insoluble material appeared in the bottom of the Kel-F tube. By analogy with impure NF_4SbF_6 , in which the impurities are only slightly soluble in HF, it seemed possible that the NF_4PtF_6 could be purified by extraction in HF. The attempted purification was carried out in an apparatus developed for use in metathetical reactions. The apparatus consists of two Kel-F tubes joined to a common fitting through flexible FEP Teflon lines. The common fitting is also connected to a valve and through the valve to the vacuum system. One of the Kel-F tubes is fitted with a filter having a fine grade of Zitex Kel-F/Teflon filter paper. Insoluble material can be separated by pouring the solution through the filter and through the flexible line to the second vessel.

(C)During the attempted purification, the Kel-F tubes formed deep stress cracks and began to leak HF vapor. The separation was completed and the HF removed as rapidly as possible. Before the vessels failed, however, we obtained a very approximate value for the solubility of NF_4PtF_6 in HF. This was about 0.5 g/ml of HF. We also noted that the color of the insoluble residue differed from that of the crude NF_4PtF_6 and from the presumably purified material. We concluded that a separation of impurities had been accomplished.

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(C) Stress cracking of Kel-F has occurred on several occasions, and the only factor common to all vessel failures seems to be length of time in use. During use, the vessels are generally cooled many times to liquid nitrogen temperature and warmed to room temperature with a hot air gun. Quite possibly, this temperature cycling is the major cause of stress cracking. We have not been able to show that any chemical or chemical mixture is the cause. In view of the above, we concluded that crude NF_4PtF_6 could be purified in a new Kel-F/Teflon apparatus.

B. Metathesis Reactions

(C) It was obvious that the synthesis of many possibly interesting NF_4^+ salts, especially those containing oxyanions, would not be possible under the conditions of the temperature/pressure activated reactions. Consequently, we sought to find the proper reagents and conditions for metathesis reactions. The problem was clearly one of obtaining starting reagents that were soluble in the solvent of choice and that would form double decomposition products whose solubilities differed substantially. We have found a number of such systems.

(C) The solvent of choice was liquid HF, in which NF_4^+ salts are quite soluble and which does not react with them. The solubilities of a number of inorganic compounds in HF are given by Simons.⁵ Solubility data on a number of metal fluorides⁶ and on two alkali metal hexafluoroantimonates^{7,8} were also available. From these data, it seemed clear that the SbF_6^- anion could be removed from solution by precipitating it as a relatively insoluble alkali metal salt. The solubility behavior of the new NF_4^+ salt formed on metathesis could only be estimated. For this estimation, we used the hypothesis that the NF_4^+ ion could be treated as though it were an extension of the alkali metal ions, NF_4^+ being much larger than Cs^+ . Thus, the alkali metal fluorides which increase in solubility and in size from LiF through CsF could be used as an indicator for the solubility of the hypothetical salt NF_4^+F^- . In HF, the fluoride ion would necessarily be present in the solvated form. These considerations suggested that the desired product of the metathesis reaction, the NF_4^+ salt, would be

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present in solution, while the co-product of metathesis, for example, LiSbF_6 , would be present as a precipitate.

(C) These conclusions were proved correct. However, the solubilities of the alkali metal fluorides are the only ones we have studied that follow the correlation of increased solubility with larger size. Other alkali metal salts show either a minimum or a maximum solubility of the potassium salt, and the solubility of the NF_4^+ salt cannot be estimated by this qualitative extrapolation. Fortunately, all NF_4^+ salts are quite soluble and are reasonably separable from the insoluble products of metathesis.

1. (C) NF_4HF_2

(C) The first metathesis reaction studied was that of NF_4SbF_6 with LiF as follows:



The reaction was carried out in the apparatus shown in Fig. 1. Six mmole of the reactants were placed in separate vessels. This operation was carried out in a drybox to avoid reaction of the NF_4^+ salt with water vapor and to avoid introducing water as a contaminant in the reaction. The apparatus was then connected to the vacuum line and about 2.5 cc of HF was condensed into each tube. The nearly saturated solution of LiF was poured into the vessel containing the NF_4SbF_6 in HF. A white precipitate formed immediately. This was later shown to be LiSbF_6 from its X-ray powder pattern.

(C) About 2.5 cc of HF was removed from the mixture to concentrate the NF_4^+ salt and to precipitate additional LiSbF_6 . Part of the solution remaining was decanted into a Kel-F nmr tube and part into the empty tube from which the LiF solution had been removed.

(C) The nmr tube was sealed off and an nmr spectrum of the contents was obtained. The NF_4^+ triplet was present at very substantial intensity. No SbF_6^- line was detectable, while the HF line was shifted downfield a few ppm from its normal position. This shift was taken to indicate

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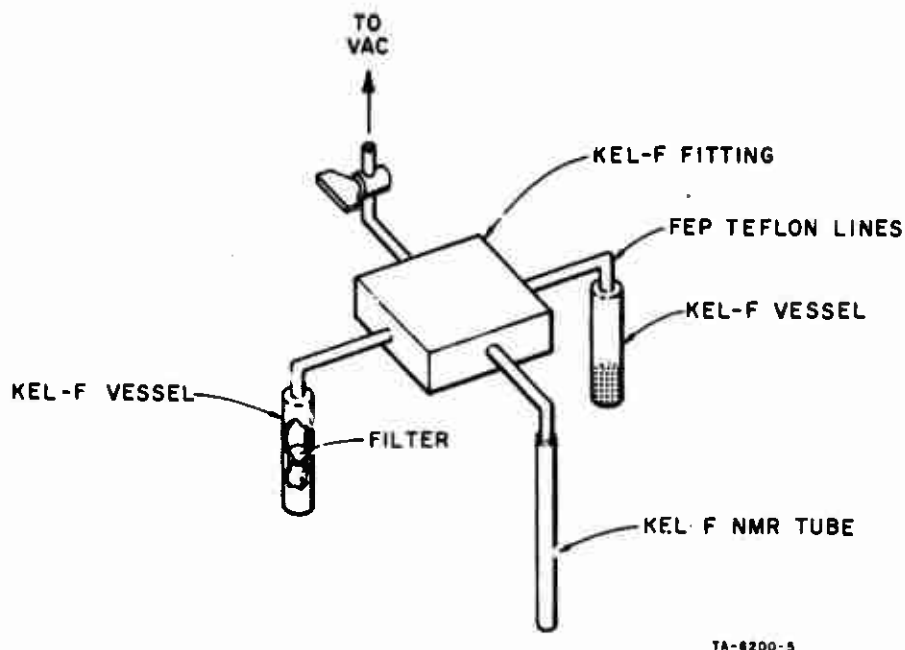


FIG. 1 METATHESIS REACTION APPARATUS

fluoride ion exchange with HF as might be expected from the presence of HF_2^- . Subsequent nmr spectra taken over a period of three weeks showed no change in the concentration of NF_4^+ , indicating that the salt was stable in HF solution.

(C)The solvent remaining in solution in the metathesis apparatus was removed at room temperature. A white solid was isolated that was initially thought to be the expected product NF_4HF_2 . Later, however, the white solid was shown to be the fraction of LiSbF_6 that is soluble in HF. All attempts to isolate NF_4HF_2 resulted in decomposition of the salt into NF_3 , F_2 , and HF at temperatures of -44°C and above.

(C)Solvent could be removed at -78°C only very slowly. After a week of pumping on the solution at this temperature, there remained a product that had the appearance of a wet solid. When the product was warmed to -44°C , NF_3 , F_2 , and HF were evolved. The quantity of NF_3 evolved was almost equivalent to the amount of NF_4^+ originally present. Thus NF_4HF_2

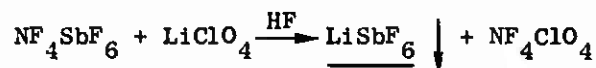
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was found to be unstable at -44°C and above. The instability of the bifluoride was taken to indicate that the fluoride, if a system could be found in which to synthesize it, would also be unstable.

2. (C) NF_4ClO_4

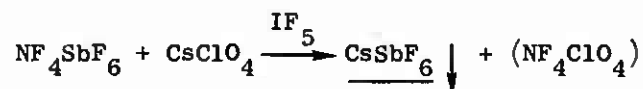
(C)The salt NF_4ClO_4 was synthesized in the reaction:



The reaction was carried out in the metathesis apparatus and the HF solution of NF_4ClO_4 was isolated as described above. During removal of solvent at room temperature, it immediately became obvious that the salt was decomposing by evolution of gas. The first sample of gas taken for infrared analysis contained only NF_3 and HF. Later, however, the gas contained both NF_3 and FClO_4 as would be expected from the decomposition of NF_4ClO_4 . When decomposition was complete and the evolved gases and solvent were removed, the weight loss was equal to that expected for the complete decomposition of NF_4ClO_4 into NF_3 and FClO_4 .

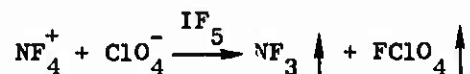
(C)In subsequent experiments we showed that NF_4ClO_4 was stable up to -27.5°C , but that above this temperature it decomposed as given above.

(C)It was thought at first that the decomposition might be catalyzed by the small amount of HF undoubtedly still present in the solid NF_4ClO_4 isolated at reduced temperatures. The preparation of NF_4ClO_4 in a solvent other than HF could verify this. We selected IF_5 as the solvent, determined compatibility and solubility of NF_4SbF_6 and some perchlorates in IF_5 , and carried out the reaction. It should be noted that LiClO_4 reacts in IF_5 to form FClO_3 among other products, while CsClO_4 is unreactive and reasonably soluble. (A later section of this report contains a summary of solubility studies carried out in support of work on metathesis reactions in HF, BrF_5 , and IF_5 .) Thus, the reaction carried out was:

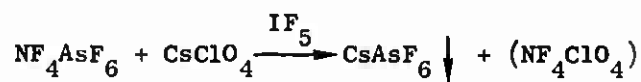


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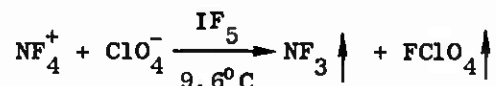
However, the product decomposed as soon as the IF_5 melted at about 9.6°C . The reaction was:



(C) It was reported by workers at Stauffer⁹ that NF_4AsF_6 and CsClO_4 were stable in IF_5 at room temperature. In view of the above results on NF_4SbF_6 and CsClO_4 in IF_5 , we carried out the similar experiment:



and the result was:



These reactions were carried out both in quartz and in Kel-F vessels. The results were not affected by the type of vessel used. The IF_5 used in these studies was water white. This material was obtained only after extensive passivation of the reaction system and vacuum lines with IF_5 and F_2 . The IF_5 was stored in a large Kel-F vessel containing finely divided KF and a magnetic stirring bar; the KF was present to remove HF. IF_5 transferred from the cylinder to the storage receiver was usually colored a light yellow-red. The color disappeared on addition of fluorine. IF_5 purified by treatment with KF and F_2 did not react with either NF_4SbF_6 or NF_4AsF_6 , the weight of sample being unchanged on addition and subsequent removal of solvent.

(C) From the evidence we have obtained on metathesis in HF and on the reactions of NF_4SbF_6 and NF_4AsF_6 with CsClO_4 in purified IF_5 , it seems clear that NF_4ClO_4 is intrinsically unstable at temperatures above -27.5°C . This conclusion is based on strong evidence and clearly contradicts the report of the Stauffer workers.

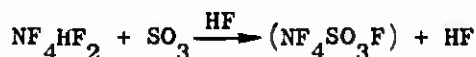
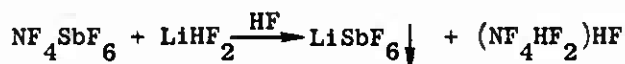
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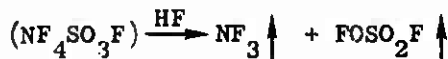
(C) In one experiment, we tested the sensitivity of NF_4ClO_4 by striking it repeatedly with a hammer on a steel plate cooled to -35°C . There was no evidence of sensitivity. Both NF_4SbF_6 and NF_4AsF_6 are also insensitive in this test carried out at room temperature. Unfortunately, the observed instability of NF_4ClO_4 makes it of little use as a solid oxidizer.

3. (C) Attempted Preparation of $\text{NF}_4\text{SO}_3\text{F}$

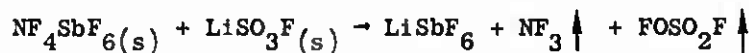
(C) We attempted preparation of $\text{NF}_4\text{SO}_3\text{F}$ in the following set of reactions:



However, the reaction



occurred rapidly at room temperature and slowly at -78°C . In addition, the reaction:



occurred at room temperature. Thus the salt $\text{NF}_4\text{SO}_3\text{F}$ is unstable at -78°C and is probably unstable at lower temperatures.

4. (C) Attempted Preparation of NF_4NO_3

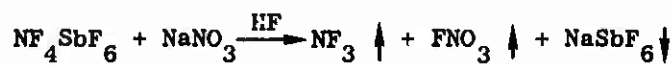
(C) Because NF_4ClO_4 was unstable, it seemed quite likely that the corresponding nitrate would also be unstable. Nevertheless, experiments were carried out to determine whether NF_4NO_3 could be made. The interaction of nitrate with anhydrous HF is complex⁵ and there is some question⁸ concerning the species actually present. The reaction of nitrate with HF may involve protonation to form HONO_2 or H_2NO_3^+ or it might involve formation of H_3O^+ , NO_2^+ , and HF_2^- . It is also possible that an equilibrium exists that involves all these species.

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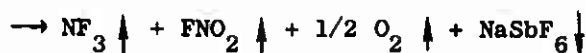
(C) Our results on dissolving NF_4SbF_6 and NaNO_3 in HF at room temperature indicated that the species formed from nitrate in HF were probably not simply the protonated ones. The attempted reaction was:



On separation of NaSbF_6 and removal of HF, the desired NF_4NO_3 could be recovered if the system were stable. Instead, the HF solution evolved NF_3 steadily at room temperature. When the evolution of gas ceased and the solvent was removed, the observed weight loss was that to be expected from

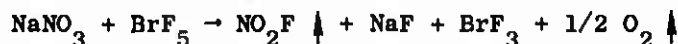


or



However, we observed none of the NOF compounds; only NF_3 and some non-condensable gas were present. Our results could be explained if FNO_2 were present in the form NO_2^+ and HF_2^- . On evaporation of solvent, the FNO_2 would also be removed, thus accounting for the observed weight loss. Whether FNO_2 was present in the HF was not determined because it was obvious that NF_4NO_3 could not be prepared in this system.

(C) We also explored the possibility that NF_4NO_3 could be formed in a metathesis reaction in a solvent other than HF, in this case BrF_5 . BrF_5 is an adequate solvent for NF_4SbF_6 , but when BrF_5 was placed in contact with sodium or cesium nitrates, the following reaction occurred:



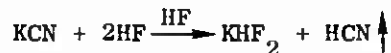
This reaction along with the reaction in HF rules out the possibility of forming NF_4NO_3 .

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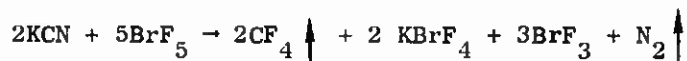
(C)To obtain some information on the possible stability of NF_4NO_3 , we studied the interaction of the two solids NaNO_3 and NF_4SbF_6 in the temperature range from room temperature to 215°C . If the two finely divided and well mixed solids react at room temperature or even at some moderately elevated temperature, it is most probable that the NF_4^+ salt derivable by means of double decomposition in solution will be unstable. On the other hand, if the two solids react only at some elevated temperature, it is possible to conclude only that the NF_4^+ salt derivable on metathesis might be stable. Thus, on examining the solid/solid interaction of NaNO_3 and NF_4SbF_6 , we found that the two solids gave off NF_3 and noncondensables very slowly at room temperature and evolved NF_3 and NO_2 plus noncondensables also very slowly up to 215°C . From this we concluded that NF_4NO_3 , if formed, would very probably be unstable.

5. (C) Observations on CN^-

(C)In view of the reaction:



we concluded that it would not be possible to carry out the synthesis of NF_4CN in HF. We thought it might be possible to carry out the synthesis in BrF_5 . It soon became apparent, however, that KCN was unstable in BrF_5 and reacted as follows:



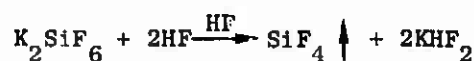
(C)The solid/solid reaction of KCN and NF_4SbF_6 was also studied from 25 to 110°C . The mixture continuously but slowly evolved gas. At 110°C , the reaction rate increased appreciably and gave off NF_3 , CF_4 , and noncondensables. We concluded that even if NF_4CN could be synthesized, it would probably be unstable.

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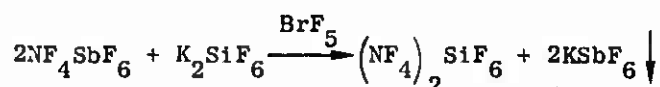
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6. (C) Observations on SiF_6^-

(C) Analogous to the cyanides, the hexafluorosilicates also decompose in HF, i.e.:



Consequently, we attempted the synthesis of $(\text{NF}_4)_2\text{SiF}_6$ by the reaction:



It was first determined that the starting reagents were soluble in BrF_5 while KSbF_6 was relatively insoluble. We expected that $(\text{NF}_4)_2\text{SiF}_6$ would be quite soluble in view of the generally high solubility of NF_4^+ salts in the solvents we have studied.

(C) When these reagents were dissolved in BrF_5 , no KSbF_6 was formed. We also observed that there was no adverse decomposition of the starting materials. The latter indicates that the hypothetical salt $(\text{NF}_4)_2\text{SiF}_6$ will probably be stable, but the fact that no KSbF_6 was formed showed that no reaction occurred to form the desired products. The lack of reaction was surprising in view of the solubility relationships which were ideal for the occurrence of a metathesis reaction. We can understand the lack of reaction if one or both of the starting materials dissolved without dissociation into ionic species. We are currently studying other solvents, including BrF_3 and IF_5 , in which a metathesis reaction might possibly occur.

7. (U) Preparation of Tetrafluorochlorate and Hexafluorobromate Salts

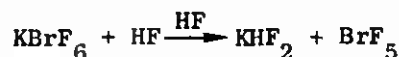
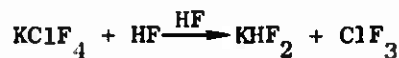
Among the energetic anions with which it might be possible to associate the NF_4^+ cation in a stable compound are ClF_4^- , BrF_4^- , and BrF_6^- . KBrF_4 forms readily from KF and BrF_3 at room temperature,¹⁰ while other

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metal salts of this anion have not been well defined and some lose BrF_3 at ordinary temperatures. Certain alkali metal (K^+ , Rb^+ , and Ca^+) salts of ClF_4^- and BrF_6^- have been synthesized and are reportedly quite stable.¹¹ We have prepared the potassium and cesium salts of these anions by modifying the method of Whitney et al., who reported only partial conversion of the alkali metal fluorides to the complexes at 100°C and a reaction time of one hour.¹¹ Increased reaction time and improved stirring yielded 97% conversions. We later found that the reaction also occurs at room temperature. The conversion was about 16 to 19% in one to two hours.

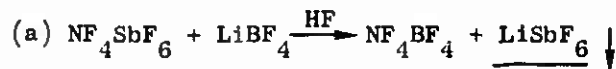
(C) We have tested the alkali metal ClF_4^- and BrF_6^- salts in HF. The reactions



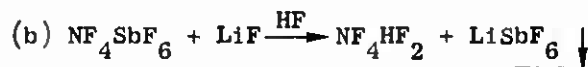
occur slowly at room temperature. These reactions rule out the use of HF as a solvent, and we have carried out some experiments to determine whether BrF_5 and IF_5 are suitable solvents for these salts. The solubilities of these salts are given in Section D of this report. The cesium salts are sufficiently soluble to show whether a metathesis reaction can occur with NF_4SbF_6 in BrF_5 and will permit us to show whether the NF_4^+ /interhalogen anion salts can be prepared and are stable.

C. (C) Preparation of Purified NF_4BF_4

(C) The preparation of NF_4BF_4 has been achieved by carrying out metathetical reactions in liquid HF:



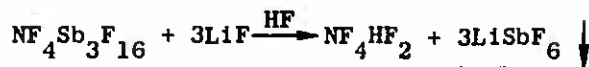
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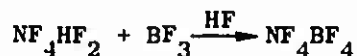
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or



followed by



(C)The purity of the NF_4BF_4 that is obtained is limited by the dissolved LiSbF_6 that accompanies the NF_4BF_4 or NF_4HF_2 on filtration.

(C)The solubilities of Li, Na, K, Rb, and Cs tetrafluoroborates in liquid HF were determined to be 5.27, 3.14, 0.76, 2.2, and 9.2 molar, respectively. If NF_4^+ behaves in solution as an alkali metal ion larger than Cs^+ , NF_4BF_4 should be more soluble than CsBF_4 . Assuming that NF_4BF_4 is as soluble as CsBF_4 and using the solubility of LiSbF_6 in HF (0.22 molar), calculations showed that NF_4BF_4 with a maximum of 97% purity might be obtained. Since NF_4HF_2 is probably more soluble than NF_4BF_4 , somewhat higher purities should be obtained when a saturated NF_4HF_2 solution is filtered.

(C)Actual purity of the NF_4BF_4 obtained in these metathesis reactions in HF was never higher than 88%, with the major impurity being LiSbF_6 , as expected. The large difference between the calculated and the actual purity is probably the increased solubility of LiSbF_6 due to the high ionic strength in the concentrated solutions. Another possible source of impurity is finely divided solid LiSbF_6 passing through the medium-porosity Teflon filter paper.

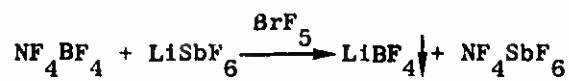
(C)Since NF_4SbF_6 and NF_4AsF_6 are soluble in liquid BF_3 , NF_4BF_4 was also expected to have an appreciable solubility. LiBF_4 has a solubility of less than 1.25 mg/g of BrF_5 . Thus it appeared that extraction of the NF_4BF_4 - LiSbF_6 mixture should yield pure NF_4BF_4 .

(C)When a sample consisting of NF_4BF_4 and LiSbF_6 was treated with BrF_5 , the soluble fraction contained very little lithium. The antimony content, however, was almost the same as in the original sample, the overall NF_4^+ content indicated a mixture of NF_4BF_4 and NF_4SbF_6 . Another sample,

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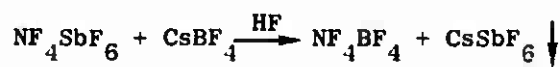
prepared using excess LiF and thus consisting of a mixture of NF_4BF_4 , LiSbF_6 , and LiBF_4 , was treated with three successive portions of BrF_5 . LiBF_4 is insoluble in BrF_5 and should filter out with the LiSbF_6 . Analyses again indicated that the soluble fractions were mixtures of NF_4BF_4 and NF_4SbF_6 . The antimony content was almost the same in each fraction.

(C) Thus it appears that the following reaction occurred:



This reaction must occur as the material dissolves, since the antimony is not preferentially dissolved. The NF_4^+ may be removed from the lattice with the closest SbF_6^- or BF_4^- , leaving behind the insoluble LiBF_4 or LiSbF_6 .

(C) Since CsSbF_6 was found to have a lower molar solubility in HF than LiSbF_6 , treatment of the NF_4SbF_6 - NF_4BF_4 mixture with CsBF_4 in HF should convert much of the NF_4SbF_6 into CsSbF_6 :



The soluble fraction, after filtering, should contain less SbF_6^- than the product after the LiBF_4 reaction, and the exchange of SbF_6^- in BrF_5 might not occur with CsSbF_6 . CsSbF_6 and CsBF_4 are insoluble in BrF_5 and will filter out. The NF_4SbF_6 - NF_4BF_4 mixture was therefore treated with excess CsBF_4 in HF , the saturated solution filtered, and the soluble product extracted with BrF_5 . The purity of the final product was 90.2% as indicated by gas evolution on hydrolysis which was only slightly higher than the original mixture, but antimony content was only 2.13% compared with almost 10% originally. The remainder of impurity may have been finely divided CsBF_4 which passed through the filter.

(C) Consequently, another metathesis reaction was carried out using NF_4SbF_6 and CsF , filtering the concentrated solution, adding BF_3 , and extracting the solid product with BrF_5 . An extra fine porosity Teflon filter paper was used to reduce the chance of solid passing through.

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Data from hydrolysis, pyrolysis, and analysis for Cs^+ indicate the sample was 92% NF_4BF_4 and 8% NF_4SoF_6 .

D. (U) Solubility Studies

(U)A number of solubility studies on pertinent compounds have been carried out in support of our work on metathesis reactions. The solubility data have been used to determine whether a metathesis reaction is possible and to estimate to what extent a separation of products can be achieved.

(U)All the solids used in this study were either prepared by standard procedures or purchased, the highest commercial purity available being obtained. In addition, all the samples were thoroughly dried and then stored before use in a Vacuum Atmospheres Corp. dry box. The infrared spectra of many of the salts were obtained as an additional purity check.

(U)The same rigorous conditions were also applied to the solvents that were used. Vapor pressure and the infrared spectrum verified the purity of the particular sample.

(U)The HF solubilities of the various compounds listed in Table I were necessarily run in Kel-F vessels, while those in other solvents were determined in quartz tubes.

(U)In a typical solubility determination, the salt under study was transferred into a solubility vessel in the dry box, weighed, and then connected to the vacuum line. Enough purified solvent was added to completely dissolve the solute, which was easily visible with the aid of a strong illumination source placed behind the solubility tube. Solvent was then slowly removed with stirring to the first sign of a permanent precipitate. The vessel was then reweighed to determine the quantity of solvent present.

(U)The procedure is estimated to be accurate within 6% based on a similar determination of the solubility of KCl in H_2O using this method. However, the accuracy of the method decreases with decreasing solubility. Thus, for materials of very low solubility, the results are only indicative.

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Table I
SOLUBILITIES OF PERTINENT COMPOUNDS

Compound	Solubility (mg/g)	Temperature (°C)	Compound	Solubility (mg/g)	Temperature (°C)	
in HF			in BrF ₅			
LiSbF ₆	56.2	27	LiSbF ₆	<1.25	27 ↓	
NaSbF ₆	108	30	KSbF ₆	<0.2		
KsOF ₆	210	30	CsSbF ₆	8.1		
RbSbF ₆	87.3	30	NF ₄ SbF ₆	152		
CsSbF ₆	55.5	30	LiBF ₄	<0.2		
NF ₄ SbF ₆	2800	30	CsBF ₄	<0.45		
LiBF ₄	522	25	LiClO ₄	Rx		
NaBF ₄	366	27	KClO ₄	<3.84		
KBF ₄	101	26	CsClO ₄	<8.08		
RbBF ₄	402	28	AgClO ₄	<3.25		
CsBF ₄	2140	25	CsClF ₄	1.1		
LiClO ₄	857	27	KBrF ₆	<1.4		
KClO ₄	211	30	CsBrF ₆	8.1		
CsClO ₄	169	27	LiF	<1.60		
NF ₄ AsF ₆	1370	26	Na ⁺	<1.98		
LiAsF ₆	421	30	KF	Rx		
NF ₄ PtF ₆	<549	26	CsF	Rx		
NF ₄ BF ₄	~758	27	K ₂ SiF ₆	>100		
in IF ₅			NF ₄ AsF ₆	<66.5		↓
NF ₄ SbF ₆	~450	27 ↓	NF ₄ BF ₄	~76		
KSbF ₆	<6.28		in BrF ₃			
CsClO ₄	112.9		NF ₄ SbF ₆	31.2	27	
K ₂ SiF ₆	<21.99					

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E. Conclusions and Recommendations

(C) It is important to note that the series of salts, NF_4SbF_6 , NF_4AsF_6 , NF_4PF_6 , and NF_4BF_4 , has been shown to exist during this work. It is also important that these salts, as well as NF_4PtF_6 , are thermally quite stable. NF_4SbF_6 and NF_4PtF_6 decompose rapidly under the conditions of a vacuum thermal stability test only above 300°C . NF_4AsF_6 decomposes rapidly above 250°C , and NF_4BF_4 decomposes rapidly above 200°C . The decomposition of NF_4PF_6 was not studied. All of these salts except NF_4PtF_6 decompose in the same manner, forming NF_3 , F_2 , and the anion precursor. NF_4PtF_6 also decomposes into the starting reagents but, in addition, some of the PtF_6 formed on initial decomposition decomposes further into PtF_4 and F_2 .

(C) The decomposition reaction can be understood if the cation and anion are written NF_3^+-F^- and MF_x^--F^- , where M may be Sb, As, P, or B. When the bonds to F^+ and to F^- are broken, these entities can then form F_2 . In the case of NF_4PtF_6 , the anion must be written $\text{PtF}_6^--\text{e}^-$, and the electron reacting with F^+ to form F and subsequently F_2 completes the description. This mode of decomposition permits us to speculate on the stability of salts such as the hypothetical NF_4ClF_4 or NF_4BrF_6 . The alkali metal salts of ClF_4^- and BrF_6^- decompose in HF, while the similar salts of BF_4^- do not. This indicates that the fluoride ion is less strongly held in ClF_4^- and BrF_6^- than in BF_4^- . Consequently, we can conclude that the NF_4^+ salts of the interhalogen anions will be less stable than NF_4BF_4 , but how much less stable is certainly not known nor is it possible to predict this from presently known data. It can be argued, however, that the alkali metal ClF_4^- and BrF_6^- salts are quite stable thermally,¹¹ and that this thermal stability is a sufficient basis for expecting the corresponding NF_4^+ salts to be satisfactorily stable. Thus it is our recommendation that experimental efforts to synthesize NF_4ClF_4 , NF_4BrF_6 , and possibly other interhalogen-containing anions be undertaken.

(C) The decomposition of NF_4ClO_4 above -27.5°C and the observed instability of $\text{NF}_4\text{SO}_3\text{F}$ at -78°C and above can be understood, at least in part, by invoking the structure NF_3^+-F^+ . The reactions form either FClO_4

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or FOSO_2F as though F^+ were reacting directly with a localized negative charge on the anion. We have concluded that this decomposition behavior below room temperature probably is to be expected of most, if not all, other oxyanions. We therefore do not recommend further work on coupling NF_4^+ with an oxyanion in the near future.

(C)One of the indices we have used to predict stability of an anion in the presence of NF_4^+ is the relative ease of directly fluorinating the anion in the form of its salts or as the acid. Our results on NF_4^+ and oxyanions have led us to believe that salts or acids fluorinated by fluorine will be much more easily fluorinated by NF_4^+ . Conversely, it appears that ionic compounds not easily fluorinated by fluorine might contain anions that will be stable when coupled with NF_4^+ . On the basis of this simple index, we have selected several compounds containing anions that might very well be stable when coupled with NF_4^+ and have recommended further study of these.

(C)The metathesis reactions in which NF_4ClO_4 and NF_4HF_2 were synthesized should be viewed as a generally applicable method for synthesis of energetic oxidizers. This type of reaction in liquid HF or in interhalogens may very well find application to syntheses involving energetic cations other than NF_4^+ and to anions not yet studied during our search for new NF_4^+ compounds. We intend to use the solubility information and knowledge of compatibility of various pertinent compounds in HF and in interhalogen solvents to pursue the synthesis of solid oxidizers.

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III EXPERIMENTAL SECTION

A. Direct Synthesis Reactions

(C) Experimental procedures for the synthesis of NF_4^+ salts from NF_3 , F_2 , and Lewis acids were described in our report AFRPL-TR-66-326, November 14, 1966, and in a published paper.¹ The report includes drawings of apparatus not given in the paper.

(U) These articles discuss the handling of NF_3 and F_2 in the vacuum line and describe a safe procedure for dealing with F_2 under high pressure, but little comment is devoted to the manipulation of SbF_5 and the other anion precursors used in the preparation of NF_4^+ salts. SbF_5 has a low vapor pressure and can be transferred only very slowly. It also reacts with fluorides on the walls of the vacuum system and forms SbF_6^- and, we feel certain, $\text{Sb}_2\text{F}_{11}^-$ and possibly $\text{Sb}_3\text{F}_{16}^-$ salts. These salts can plug the line, hydrolyze when water is introduced as a reactant, probably interact with HF, and in general yield a system that is difficult to evacuate and may require cleaning. Thus, SbF_5 should be distilled from its container into a buret and from the buret into the reactor through the shortest path. This can be done in a small subsystem that can be easily cleaned.

(U) AsF_5 forms arsenate salts in an F_2 passivated Monel metal line but forms no complex arsenate salts analogous to the antimony system. In addition, these simple hexafluoroarsenates resist hydrolysis. Thus AsF_5 could be handled in the vacuum line without difficulty. Its quantity was determined by PV measurements which were adequate for our purposes.

(C) PtF_6 was synthesized by burning electrically heated platinum wire in an atmosphere of fluorine contained in a vessel cooled to liquid nitrogen temperature.¹² The excess F_2 was removed and discarded, and the PtF_6 was isolated, weighed, and transferred to the reaction vessel. The transfer was made through the shortest path possible, the system having been thoroughly passivated whenever the line or parts of the line were exposed to the atmosphere. We observed no decomposition of the PtF_6 during manipulation.

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(C) PF_5 and BF_3 were handled by the same technique used for AsF_5 . It seems unlikely, however, that these two reagents are of interest in preparing NF_4^+ salts by the direct synthesis method because of the low yields.

B. Metathesis Reactions

(C) Experimental details of importance in metathesis reactions include handling of solvents and the nature of the apparatus. The solvents used in the present work were HF and several interhalogens. Extensive effort was required, with each solvent, to obtain pure material suitable for use with NF_4^+ salts. When purified, HF, ClF_3 , ClF_5 , BrF_5 and IF_5 are colorless; BrF_3 is yellow.

(U) Preparation of anhydrous HF involves several steps that can be hazardous. The first of these steps in which difficulty might be encountered is the isolation of the desired quantity from the steel container in which the HF is received. HF reacts with the container to form hydrogen which must be removed to facilitate vacuum transfer and to avoid possible reaction at a later stage when the HF is treated with fluorine. In this work, HF and H_2 are passed into a specially designed copper trap cooled with liquid nitrogen. HF is frozen out, while most of the hydrogen is pumped away. The trap is built so that the inlet line from the HF container extends halfway to the bottom of the trap. When the HF level in the trap rises to the bottom of the inlet tube, the inlet tube is plugged with frozen HF and the transfer stops. Another hazard is avoided by the design of the trap. The HF expands by a factor of about 1.5 on warming from -196° to room temperature; thus if the HF were melted in an enclosed volume too small to contain the resulting volume of liquid, enormous pressure would develop and burst the container. Use of the metal trap also permits rapid heat transfer, rapid and apparently complete condensation and freezing of the HF, and a high rate of transfer.

(U) When melted, a portion of the HF in the trap is transferred slowly into a Kel-F vessel at -196°C . Transfer must be sufficiently slow that no liquid forms in the metal lines. If liquid forms, impurities are

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entrained in the HF and collect in the Kel-F vessel. Frost on the lines indicates the probable presence of liquid HF. However, if the transfer is carried out so that HF is vaporized in the trap, passes through the line in the vapor phase, and is recondensed only in the Kel-F vessel, the product should be colorless. Again, care should be taken to assure that only about half the volume of the vessel is filled with HF. Although the Kel-F vessel is cooled with liquid nitrogen, the rate of heat transfer is sufficiently low and the rate of input of HF is high enough that the HF condenses as a liquid and is frozen only after transfer is stopped and the vessel has been allowed to stand at -196°C for about half an hour. Pumping on the frozen HF apparently removes any hydrogen that might remain.

(U)To avoid possible contamination with water that can diffuse through the walls of the Kel-F vessel, the HF is transferred immediately to a copper vessel in which it is treated with fluorine. The mixture is allowed to stand overnight, and the fluorine and other volatiles are removed by pumping on the HF solid at -196°C .

(C)Small amounts of HF for use in metathesis reactions are transferred as needed from the copper storage vessel. However, if the vacuum line has been passivated with respect to an interhalogen, a new effect is observed. The HF interacts with the passivation products in the line and the liquid in the receiver is colored. We have assumed that the colored HF contains impurities that would probably react with NF_4^{+} salts. To avoid this, we have treated the vacuum line with HF and F_2 until the liquid HF isolated is colorless. The treatment requires several batch-wise additions of HF and F_2 and may consume as much as a day's work. Colorless liquid HF, when obtained as outlined above, reacts negligibly or not at all with NF_4^{+} salts.

(C)To obtain interhalogens suitable for metathesis reactions requires passivation of the system with respect to the interhalogen and subsequent removal of products of the passivation reactions. We have noted that a system apparently passivated with respect to fluorine is not passive toward an interhalogen. In addition, a system passive with respect to one interhalogen is not necessarily passive with respect to another.

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However, we have worked out a technique that enables us to obtain solvent that does not react with NF_4^+ salts and that can be used for all the interhalogens we have studied. The technique involves batchwise addition of, for example, IF_5 to the vacuum line until no non-condensables are formed. When this condition is achieved, products of the passivation reaction are still in the line. These products are removed sufficiently well by treatment with fluorine and evacuation of the system.

(C) On passivation of the system and removal of impurities, IF_5 or other interhalogen is condensed into a Kel-F storage vessel. This vessel is equipped with a stirring magnet and contains an excess of KF to remove HF. BrF_3 forms a stable, solid salt with KF but not with CsF. This will be discussed below. The storage vessel is enclosed in a polyethylene bag containing a desiccant to prevent diffusion of water into the system. The interhalogen is condensed into a reaction vessel containing NF_4^+ salt and does not react with the NF_4^+ .

(C) BrF_3 , in our work contaminated with BrF_5 , was purified (in part at least) by trap-to-trap distillation and was subsequently mixed with an excess of CsF. CsBrF_4 and CsBrF_6 formed on standing with stirring for 48 hours, after which the BrF_3 was recovered by warming the salts with a heat gun. CaBrF_4 decomposed readily on warming and BrF_3 was recovered. NF_4SbF_6 was soluble in and did not react with BrF_3 obtained in this manner.

(U) The apparatus for the metathesis reactions is shown schematically in Fig. 1, and has been discussed briefly in Section II. Details of the apparatus involve the type of fittings and connectors used and the design of the filter system.

(C) The filter system was evolved in stages throughout this work. We found that Chemplast Company Zitex brand paper, composed of Kel-F and Teflon, was compatible with NF_4^+ salts in HF solution and with BrF_5 . The first paper available was a coarse grade; finer grades were later obtained. The filter paper was supported on a perforated Kel-F disk and held in place by a snap ring. Pressure drops across the filter paper developed when the vacuum system was pressurized with nitrogen to

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check for gross leaks or when HF was admitted. Occasionally, the filter paper was pulled out of the snap ring by the pressure change. When finer grades of paper were used, the pressure drops almost invariably caused displacement of the paper and a new design was required. When the paper was supported between two perforated Kel-F disks, the filter remained intact and filtered adequately as well.

(U)Figure 2 shows the fittings and vessels used for the apparatus. The Kel-F must be machined very slowly with spray cooling to prevent overheating the plastic. One vessel, which was machined without such cooling, formed deep stress cracks when placed in liquid nitrogen. Vessels made subsequently with cooling have not cracked except after extensive use. It should be noted that the metathesis reaction assembly was quite expensive.

(C)The procedure for using this apparatus is described in the following outline of the preparation of NF_4BF_4 . The parts of the subsystem are thoroughly degreased with trichloroethylene, assembled, attached to the vacuum line, filled with 2 atm of nitrogen, and tested for leaks with a soap solution. When leak-free under these conditions, the unit is tested with a helium leak detector. It should be noted that helium diffuses slowly through the FEP Teflon Tubing (1/4" o.d., 1/8" i.d.). This may be observed by placing a plastic bag around the subsystem and filling the bag with helium. After one to two minutes, the leak detector registers an enormous leak. When the plastic bag and thus the source of helium is removed, the helium in the system is removed only very slowly. This is due in part, at least, to the slow rate of diffusion through Teflon. Consequently, helium leak testing of this system must be carried out rather quickly, avoiding long exposure of the Teflon to the stream of helium.

(U)When leak-free, the T system was placed in the dry box.

(C)A 5 g sample of NF_4SbF_6 was added to the filter tube in the dry box, and a 3 g sample of CsF was added to the receiving tube. Both tubes contained Teflon-coated stirring bars. The 3 g of CsF was a 29% excess. The tubes were attached to the T and HF was added using the vacuum line.

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About 5 ml of HF was added to each sample. After stirring, the CsF solution was added to the NF_4SbF_6 solution. A heavy white precipitate formed. Some HF was distilled back to wash the receiving tube. Part of the HF was distilled off, concentrating the NF_4HF_2 solution to reduce the total CsSbF_6 content in solution. The solution was filtered through the extrafine-grade Teflon filter paper. About 3 ml of solution passed through the filter.

(C) Another 5 ml of HF was distilled into the NF_4HF_2 solution. An excess of BF_3 at 50 psi was placed above the solution and the solution was stirred for 30 min. The solution was cooled to -78°C and stirred for a few minutes, then allowed to warm and stirred further. The cooling and stirring process was carried out two more times after which the BF_3 and HF were removed and the solids were pumped on to remove traces of HF.

(C) The receiving tube had collected 2.19 g of product (theory: 2.71 g).

The T system was returned to the dry box and a filter cap was added to the tube with the NF_4BF_4 . A receiving tube, prepassivated with BrF_5 , as was the filter cap, was attached to the T.

(C) The vacuum system was passivated with BrF_5 before BrF_5 was added to the sample. A sample of BrF_5 was added to the NF_4BF_4 and the mixture was stirred for 1-1/2 hrs. Some solid remained undissolved. The solution was filtered, yielding a clear filtrate. Total BrF_5 in the solution was 5.3 ml.

(C) The BrF_5 was distilled off and the solid was pumped on overnight. The recovery was 0.99 g of NF_4BF_4 ; also, some was lost in the arms of the T.

(C) Both hydrolysis and pyrolysis indicate that the final product consisted of about 92% NF_4BF_4 with 8% of NF_4SbF_6 .

C. Infrared Spectra

(C) The infrared spectra of NF_4SbF_6 , NF_4AsF_6 , and NF_4PtF_6 are given in Figs. 3, 4, and 5, respectively. These spectra were obtained on a few milligrams of the salt dispersed in 350 mg of finely divided salt;

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this mixture was then pressed in a pellet die into a transparent plate. Either KCl or KF was used. NF_3 appears in all spectra we have obtained by this technique. Its presence is the result of decomposition of the NF_4^+ salt during the pressing of the pellet. Since the pellet, while being pressed, cannot be expected to reach temperatures at which thermal decomposition can occur, the NF_3 must arise from reaction with impurities in the KF or KCl or with KCl itself. We obtained some spectroscopic-grade KF, compared spectra of NF_4SbF_6 obtained in KCl and in KF, and observed that much less NF_3 was present in the KF matrix.

(C) The KCl was reagent-grade salt that was precipitated rapidly from a saturated solution with concentrated HCl, dried in a vacuum oven for a week, and stored in the dry box. Spectra of blank KCl pellets showed that a small amount of water was present if the die was not leak-free. The same was true of KF. In addition, when spectra of NF_4^+ salts were studied, several bands due to bifluoride were observed, which indicated reaction with H_2O . These bands were less significant in KF, corresponding to the smaller amount of NF_3 present in these pellets.

(C) The bifluoride absorption bands are quite intense, and we estimate that if 0.5% of the NF_4^+ salt were converted to bifluoride by hydrolysis, the bifluoride band at 1220 to 1230 cm^{-1} would be easily seen. This band has been assigned by Christie et al.,¹³ to NF_4^+ , but we feel this is open to question.

(U) The die used in pressing pellets is a specially hardened unit with 0.5" diameter pistons. The driver piston is tungsten carbide alloy, which occasionally splits under the pressure employed, i.e., 45,000 pounds of thrust in a press with a 2" diameter ram. The die containing the pressed plate is returned to the dry box where the pellet is removed. The pellet is placed in a sealed cell to prevent contact with atmospheric moisture. The cell consists of a holder containing two silver chloride windows separated by a washer having O-rings on each face. The pellet fits inside the washer.

(U) Sample preparation includes grinding a weighed quantity of the salt matrix to a very fine powder in a mortar, grinding the sample to a fine

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powder in a separate mortar, weighing the sample, and then grinding the sample and matrix together.

D. NMR Spectra

(U) NF_4^+ salts are generally quite soluble in HF and give good F^{19} nmr spectra in this solvent. With HF, glass or quartz tubes cannot be used; it is common practice to employ a Kel-F nmr tube. In this work, these are machined from 8" long Kel-F tubing, 1/4" o.d., 1/8" i.d. Seven inches of this length is reduced in diameter to 0.190 inch. The narrow end is sealed with the aid of a small flame.

(U)The tubing is degreased, attached to a valve, connected to the vacuum line, and passivated. After passivation, the assembly is leak-tested to be certain that the heat-sealed end is properly sealed. The assembly is then placed in the dry box where a weighed sample of salt is placed in the tube. On reassembly and removal from the dry box, the unit is attached to the vacuum line and leak-tested again, and HF is added to the desired level. The tube is cooled to -196°C and is heat-sealed well above the level of the HF. When the HF melts, a leak in the new seal can be easily detected as a stream of white vapor. Refreezing the solution permits further attempts to seal the tube. When a seal has been obtained the ends of the tube, which may have become distorted during the sealing process, can be reduced to the proper diameter either by filing or by working the melted plastic. The latter method is best carried out with the contents frozen.

(U)These tubes are spinnable in the nmr spectrometer. However, the spectroscopist should handle the sample carefully in view of its contents.

(C)Spectra as illustrated in Figs. 6, 7, and 8 were obtained on a Varian Associates HA-100 spectrometer at 94.6 Mc. The field was usually scanned from the HF line to the F_2 line. However, only the portion showing HF, CFCl_3 , and NF_4^+ is included. In the spectrum of NF_4AsF_6 , the quadruplet due to AsF_6^- is detectable at about 70 ppm from CFCl_3 . No lines due to SbF_6^- or PtF_6^- were seen. When the salt is largely $\text{NF}_4\text{Sb}_2\text{F}_{11}$, the HF and SbF peaks merge to give a very broad line. Thus, if the SbF_6^- concentration were very high, we expect that it would appear

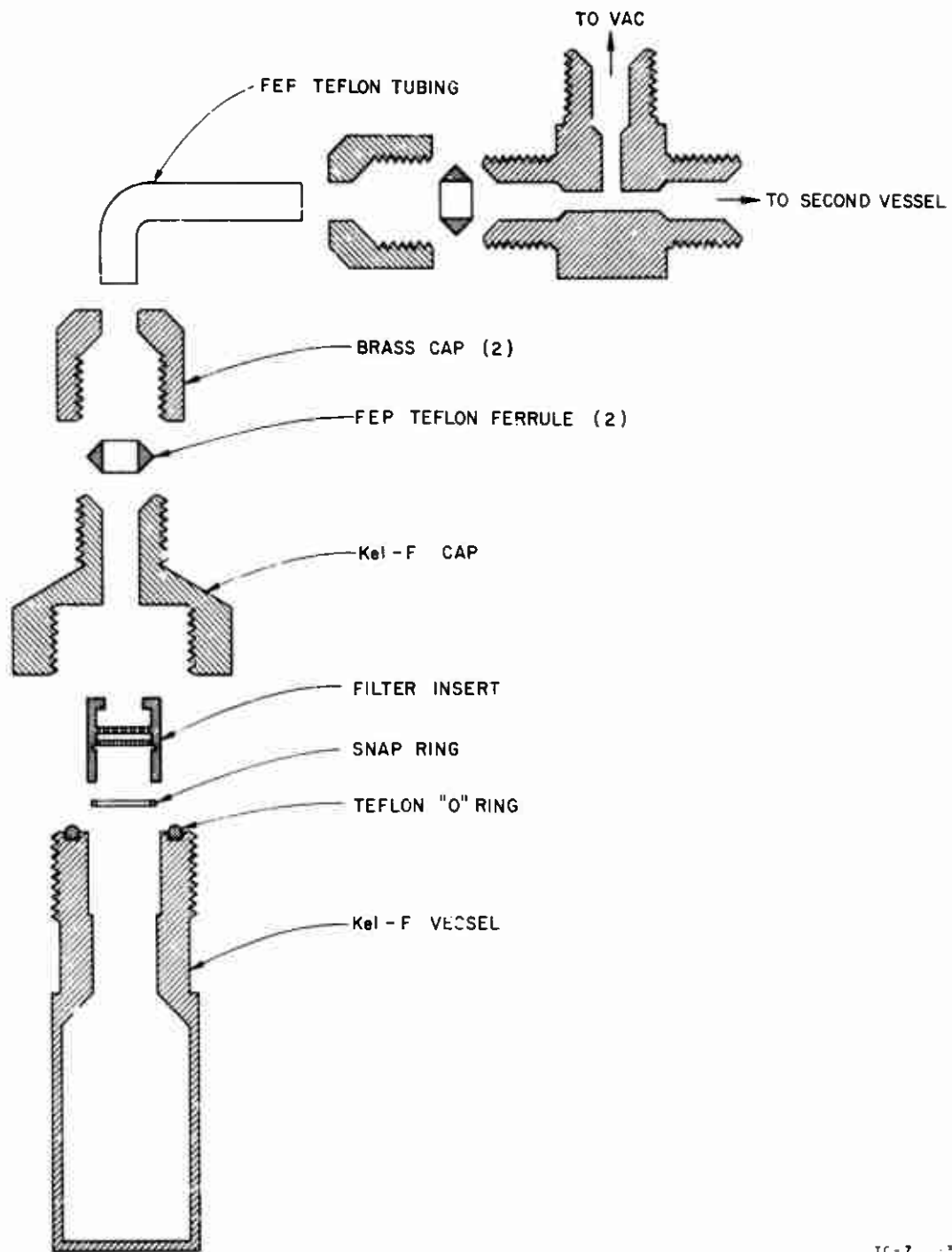
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under the sidebands downfield of HF. The CFCl_3 line was obtained by the substitution method. Spectra were usually scanned both with and without CFCl_3 reference in order to determine whether weak lines could be observed in the vicinity of the CFCl_3 line.

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FIG. 2 1:1 SCALE DRAWING OF METATHESIS REACTION VESSEL AND FILTER

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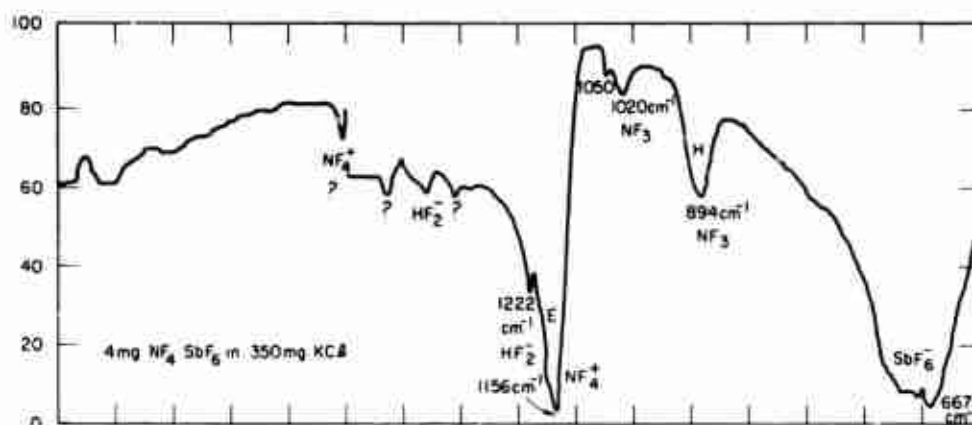


FIG. 3 INFRARED SPECTRUM OF NF_4SbF_6

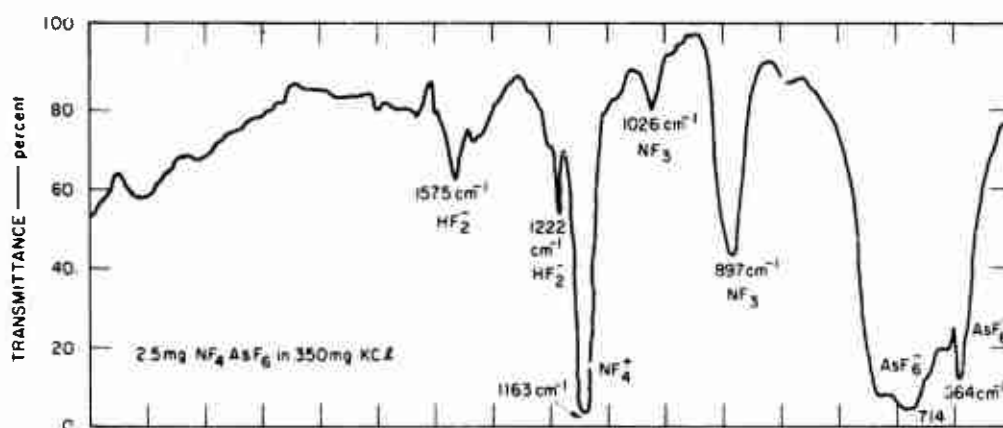


FIG. 4 INFRARED SPECTRUM OF NF_4AsF_6

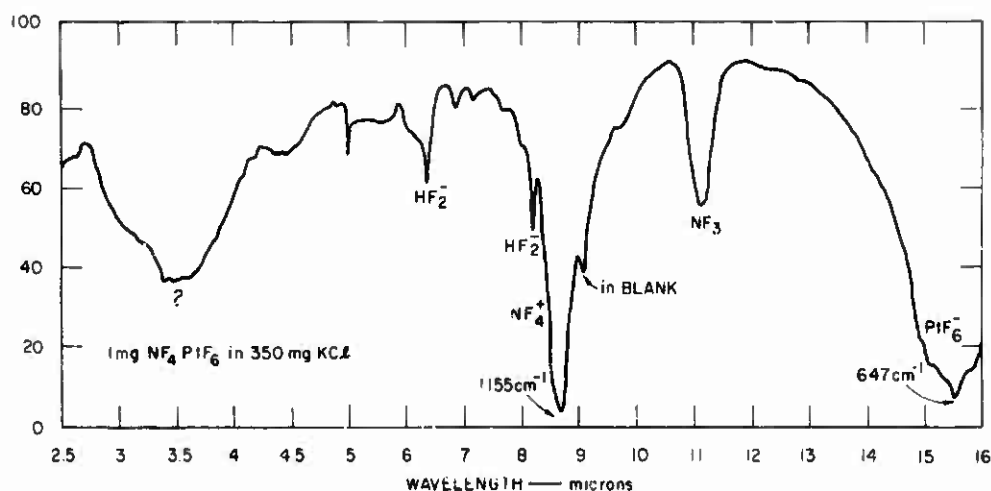


FIG. 5 INFRARED SPECTRUM OF NF_4PF_6

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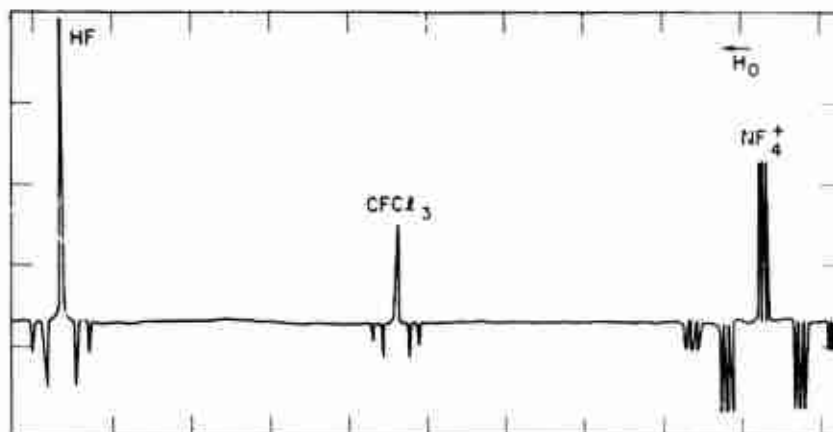


FIG. 6 ^{19}F nmr SPECTRUM OF NF_4SbF_6 (37.5 wt% in HF)

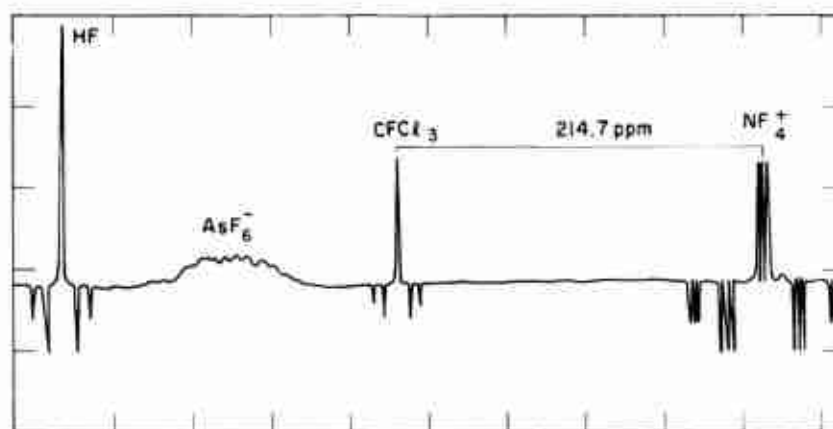


FIG. 7 ^{19}F nmr SPECTRUM OF NF_4AsF_6 (ca 0.5 gm/cc of HF)

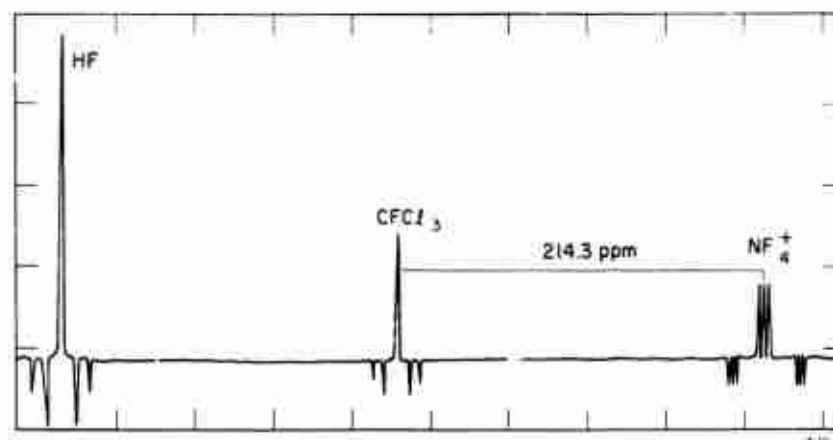


FIG. 8 ^{19}F nmr SPECTRUM OF NF_4PF_6 (concentration ca 100 mg/cc of HF)

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Synthesis of NF_4^+ salts has been carried out by two general methods. Direct synthesis reactions of NF_3, F_2, and a series of Lewis acids at high pressures and moderately elevated temperatures have been used to produce a series of NF_4^+ salts having fully fluorinated anions. Metathesis reactions in liquid HF have been used to produce a number of new NF_4^+ salts including some with oxygen-containing anions.(C) The rate of reaction to form NF_4^+ salts in direct synthesis depends on the acidity of the Lewis acid. Thus, SbF_5 forms NF_4SbF_6 in good yield, AsF_5 produces the arsenate in moderate yield, PF_5 forms NF_4PF_6 in very low yield, and BF_3 produces only a trace of NF_4BF_4, if any. It was concluded that compounds less acidic than PF_5 in HF would be unlikely to form NF_4^+ salts by direct synthesis. This was confirmed when ClF_3 and ClF_5 did not yield the corresponding salts, NF_4ClF_4, or NF_4ClF_6, on heating NF_3, F_2, ClF_3, and ClF_5 at high pressure for extended periods of time. (C) In addition to NF_4SbF_6, NF_4AsF_6, and NF_4PF_6, a fourth salt, NF_4PtF_6, was formed by direct synthesis in the reaction: $\text{NF}_3 + 1/2 \text{F}_2 + \text{PtF}_6 \rightarrow \text{NF}_4\text{PtF}_6 \quad (\text{C})$ This salt was characterized by nmr and infrared spectroscopy, hydrolysis, and elemental analysis of the hydrolysate. (C) NF_4SbF_6 has proved to be the most useful in metathesis reactions. Its synthesis is complicated by the formation of varying amounts of the complex fluoroanti-		

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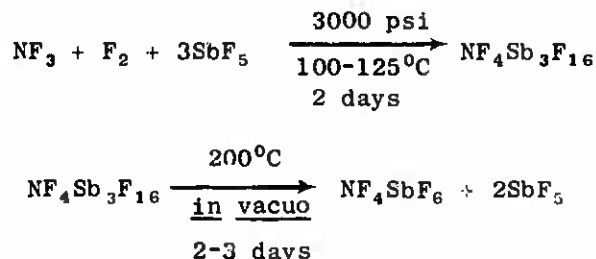
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NF_4SbF_6 Metathetical Reactiona in Liquid HF and Interhalogens Solubilities Inorganic Oxidizers						

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monate anions, $\text{Sb}_2\text{F}_{11}^-$ and $\text{Sb}_3\text{F}_{16}^-$, as well as formation of contaminants formed by reaction of F_2 and SbF_5 with the Monel reaction vessel. The optimum conditions found for synthesis of NF_4SbF_6 involve:



Products ranging in purity from 96 to 99.5% have been obtained. Monel-antimonate impurities were removed by dissolving NF_4SbF_6 in HF and filtering out the insoluble metal salts. (C)

Fully characterized NF_4SbF_6 has been used as a reagent in a number of metathesis reactions forming new salts. A typical reaction is:



Similar reactions have been used to form NF_4HF_2 , $\text{NF}_4\text{SO}_3\text{F}$, NF_4NO_3 , and NF_4BF_4 . The perchlorate decomposes to NF_3 and FClO_4 above -27.5°C , the bifluoride is unstable at -44°C and above, the fluorosulfonate is unstable at -78°C and above, the nitrate is decomposed in HF solution, but NF_4BF_4 is quite stable. (C)

NF_4CN could not be formed owing to decomposition of the alkali metal cyanide to HCN in liquid HF and to the reaction of cyanide with the interhalogen solvent BrF_5 . The similar decomposition of K_2SiF_6 in HF led to an attempt to synthesize $(\text{NF}_4)_2\text{SiF}_6$ in BrF_5 . No reaction occurred on mixing NF_4SbF_6 with K_2SiF_6 in BrF_5 . The lack of reaction indicated that one or both of the starting reagents dissolved without dissociation into ionic species. (C)

Several alkali metal salts of the ClF_4^- and BrF_6^- anions were synthesized. In HF, these decompose to form alkali metal bifluorides and the corresponding interhalogen. They are, however, moderately soluble in BrF_5 . It is expected that this solvent will permit determining whether the salts NF_4ClF_4 and NF_4BrF_6 can be synthesized. (C)

An effort was made to synthesize NF_4BF_4 in a purity sufficient for determining heats of formation. The highest purity obtained was 96.1%. The impurities have not yet been determined. (C)

A number of solubility studies were carried out in support of work on metathesis reactions. Solubilities of a number of pertinent compounds in HF, BrF_5 , IF_5 , and BrF_3 are reported and discussed. (U)