Translated from *Uspekhi Khimii*, 54, 722-740 (1985) U.D.C. 546.161 + 661.48

Tetrafluoroammonium Salts

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The methods of synthesis, structure, thermal and chemical properties, and possible applications of tetrafluoroammonium salts have been reviewed.
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I. INTRODUCTION

Until the early nineteen-sixties, apparently, there were no theoretical or experimental indications of the possible existence of the NF_4^+ cation in the gas phase or in salt crystal lattices. The formula NF_4^+ appeared for the first time in Ref.1, where the dissociation energies and ionisation potentials of various fluorides were estimated, and it was concluded that salts of the NF_4^+ cation could not be obtained. Three years later, Wilson[2] devoted a special paper to the estimation of the stability of the NF_4^+ cation and its salts. He used the method of analogies, isoelectronic series, and the bond energy and ionisation potential values then available to estimate the crystal lattice energies of tetrafluoroammonium fluoride, perchlorate, sulphate, and tetrafluoroborate. The calculations showed that the first three salts should be extremely unstable relative to their possible decomposition products ($NF_3 + F_2$, $NF_3 + FClO_4$, $2NF_3 + F_2O + SO_3$ respectively) and cannot exist, and that the tetrafluoroborate may be stable at temperatures below 120 K. The possible stabilisation of the NF_4^+ cation in compounds with other polyatomic fluoro-anions was not examined,[2] although it was assumed that tetrafluoroammonium fluoroantimonate or fluoroarsenate might be more stable.[3]

Nitrogen trifluoride is extremely inert towards Lewis acids. An infrared spectroscopic study[4] of the reaction of nitrogen fluorides with Lewis acids established only weak association in the systems $NF_3 + BF_3$ (at temperatures below 148 K) and $NF_3 + BCl_3$ (below 173 K) and no association or reaction in the $NF_3 + PF_5$ system (as far as 145 K). The possible reaction $NF_3 + F_2 \rightleftharpoons NF_4^+ + F^-$ between NF_3 and fluorine in anhydrous hydrogen fluoride was noted in Ref.5. The authors of Ref.6, who studied the action of the bremsstrahlung of electrons on a number of compounds of fluorine, nitrogen, and oxygen, including a mixture of NF_3 and BF_3, were apparently close to the synthesis of NF_4^+.

In 1966, two groups of American authors[7,8] simultaneously reported the synthesis of two tetrafluoroammonium salts, the fluoroarsenate and the fluoroantimonate. In 1970, a method for preparing tetrafluoroammonium tetrafluoroborate was patented[9] in the USSR, and a paper[10] published in the same year described the properties of this compound, whose thermal stability was found to be much higher than that predicted in Ref.2. New methods for synthesising NF_4BF_4, NF_4AsF_6, and NF_4SbF_6 have since been found, and methods have been developed for preparing other tetrafluoroammonium salts. The synthesis of NF_4ClO_4 was reported[11] in 1980. The existence of this salt contradicts the predictions of Ref.2; it decomposes slowly only at 273 K.

The names "perfluoroammonium", "tetrafluoroammonium", "tetrafluoronitrogen", and "tetrafluoronitronium" have been proposed for the NF_4^+ cation. None of them can be regarded as satisfactory, but most authors prefer to call this ion the tetrafluoroammonium ion. This name will be used in the present work, but it must be borne in mind that the NF_4^+ ion cannot be obtained by replacing the hydrogen atoms in the ammonium ion, and that the formal oxidation state of nitrogen in NF_4^+ is +5, whereas that in NH_4^+ is -3. In the text, the name of the NF_4^+ ion will be abbreviated to TFA. The synthesis and properties of TFA salts were examined briefly in Refs.12 and 13.

II. SYNTHESIS OF TETRAFLUOROAMMONIUM SALTS

As shown below, the synthesis of TFA salts involves considerable experimental difficulties, and a special method of synthesis has to be developed for almost every new compound. This probably explains why TFA salts have as yet been prepared in only a few laboratories. In the present work, the experimental conditions for the synthesis of TFA salts will be examined in more detail than is usual in review papers; the "key" compounds, that is the hexafluoroarsenate, hexafluoroantimonate, and tetrafluoroborate, will be considered first, followed by the others in order of increasing atomic number of the central atom of the anion. The "key" TFA salts were synthesised first, and subsequently used to obtain various other TFA salts. The total number of TFA salts synthesised by mid-1983 was greater than 30.

$NF_4^+AsF_6^-$. This salt was first obtained[8,14] by the action of an electrical glow discharge on a mixture with the molar ratio $NF_3:AsF_5:F_2 = 1:1:2$. The method of synthesis is described in more detail in Ref.15. A mixture of NF_3, AsF_5, and F_2 was passed into a glass electrical-discharge reaction vessel, supplied from a transformer and fitted with a circulating pump, to an initial pressure of not more than 80 mmHg, after which the discharge was switched on and the reaction carried out under circulation conditions at a temperature of the walls of the reaction vessel of 195 K. The apparatus used had a low efficiency, and the synthesis of 1 g of salt took ~40 h. The same paper[15] described an unsuccessful attempt to obtain NF_4AsF_6 from NF_3, AsF_5, and an excess of F_2 by heating the reagents to 758 K at a pressure of ~168 atm in a Monel metal vessel for 12 h. Instead of the expected product, this gave $Ni(AsF_6)_2$, formed by corrosion of the walls of the autoclave.

According to Ref.3, however, when a mixture of NF_3, F_2, and AsF_5 was heated for a longer time (260 h) at 398 K, 95% pure NF_4AsF_6 was obtained. It was later established[16] that the NF_4AsF_6 specimens obtained by the high-temperature method do not have a uniform composition and contain appreciable quantities of nickel and copper salts, formed by corrosion of the walls of the Monel metal reaction vessel; salts of the $As_2F_{11}^-$ anion are not formed under these conditions.

TFA hexafluoroarsenate can be obtained photochemically.[17] Irradiation of an equimolar mixture of NF_3, F_2, and AsF_5, placed in a sapphire reaction vessel at room temperature, with a high-pressure mercury lamp (without a filter) gives NF_4AsF_6 in less than 1% yield. This low yield can be attributed to the deposition of a layer of product on the walls of the reaction vessel, leading to the absorption of ultraviolet radiation, and the low thermal stability of possible intermediate products of the photosynthesis. In an improved procedure,[18] NF_4AsF_6 was obtained by the ultraviolet irradiation of NF_3, AsF_5, and F_2 (3:3:1) in a special quartz reaction vessel which made it possible to carry out the synthesis at 77 K. The product is highly pure, and is formed at a rate of more than 1 g h^{-1}. The ultraviolet irradiation of a mixture of CF_3NF_2, AsF_5, and F_2 gives the hexafluoroarsenates of NF_4^+, $N_2F_3^+$, and N_2F^+.[18] $^{15}NF_4AsF_6$ has been obtained photochemically[18] from $^{15}NF_3$, F_2, and AsF_5; the $^{15}NF_3$ required was synthesised from $^{15}N_2$ and F_2 in an electrical glow discharge.[19]

$NF_4^+SbF_6^-$. TFA fluoroantimonate was first obtained by the reaction of NF_3 with F_2 and SbF_5 in hydrogen fluoride.[7,20] When an equimolar mixture of the starting materials was heated in a Monel metal reaction vessel at 473 K and a pressure of up to 185 atm for 2–3 d, more than 40% of the NF_3 added to the autoclave was used up. The product contained up to 25% impurities—metal salts formed by corrosion of the walls of the reaction vessel.

It was also found[7] that the TFA salt can be obtained in the absence of hydrogen fluoride.[3,20] A mixture with $NF_3:SbF_5 \approx 1:1$ with a slight excess of F_2 was placed in a heated Monel metal vessel and kept in it at 373–473 K for several days.[3] The reaction took place comparatively slowly; the degree of transformation of NF_3 after 50 h was 11% at 373 K, and 41% at 473 K. Under these conditions, the product is apparently a mixture of TFA salts containing the SbF_6^- anion and the $Sb_2F_{11}^-$ and $Sb_3F_{16}^-$ polyanions. When the TFA fluoroantimonate specimens are heated for a long time in a vacuum at 473 K, the polyanions decompose to give NF_4SbF_6.[5] Similarly, for example, $O_2^+Sb_2F_{11}^-$ is converted into $O_2^+SbF_6^-$ by heating in a vacuum to a temperature above 403 K.[21]

Further refinements[22] showed that the reaction of NF_3 with F_2 and SbF_5 at 373–397 K and a pressure of ~210 atm gives $NF_4Sb_3F_{16}$, which in a vacuum at 473 K over a period of 2–3 d gives up SbF_5 and is converted into NF_4SbF_6. It was later found[22,23] that the reaction of NF_3 with F_2 and SbF_5 at 388 K with subsequent thermal decomposition of the product in a vacuum at 473 K gives a substance with composition close to $NF_4Sb_2F_{11}$, which is converted into NF_4SbF_6 in a vacuum at a higher temperature (523–533 K). After heating for 1–1.5 h at 523–533 K in a vacuum with removal of the volatile decomposition products, the specimen is completely converted into NF_4SbF_6, and in this time interval not more than 3% of the NF_4SbF_6 obtained decomposes. Appreciable decomposition of the NF_4SbF_6 formed in this operation takes place only at 548–573 K. From these results it was concluded[23] that the reaction of NF_3 with F_2 and SbF_5 at 388–473 K and a pressure of up to 200 atm gives a product $NF_4SbF_6.nSbF_5$, where n = 2.1–3.2, depending on the reaction conditions. Thermal decomposition in a vacuum at 473 K lowers the value of n to 0.8–1.1, and thermal decomposition at 533 K gives pure NF_4SbF_6.

Thus the synthesis of NF_4SbF_6 by heating a mixture of NF_3, F_2, and SbF_5 is fairly laborious and time-consuming, but it can be used to obtain the salt in large quantities. In a simpler version[24] of the "thermal" synthesis of the salt, antimony pentafluoride is replaced by the trifluoride:

$$NF_3 + 2F_2 + SbF_3 \rightarrow NF_4SbF_6 .$$

The process is carried out at 523 K and 30–70 atm over a period of several days, and gives pure NF_4SbF_6 containing no significant quantities of polyfluoroantimonates.

The salt NF_4SbF_6 can be obtained by the reaction of NF_3 with $KrF^+SbF_6^-$ at room temperature, or by the reaction of equimolar quantities of KrF_2, NF_3, and SbF_5 in hydrogen fluoride at 295 K,[25] but this method requires krypton fluoride, which is not readily available. In addition, $NF_4SbF_6.nSbF_5$ is also formed when a mercury lamp is used to irradiate a mixture of SbF_5, NF_3, and F_2 in a quartz vessel at room temperature.[17] The reaction is slow, and the product consists of a mixture of dioxygenyl and TFA fluoroantimonates. The reaction of fluorine with quartz liberates oxygen, which is oxidised to O_2^+ in the presence of fluorine and under the influence of ultraviolet radiation:

$$5F_2 + 2SiO_2 + 4SbF_5 \rightarrow 2SiF_4 + 2O_2^+Sb_2F_{11}^- .$$

TFA fluoroantimonates can apparently also be obtained by a plasmochemical method, for example from SbF_5, NF_3, and F_2 or from SbF_5, N_2, and F_2 using an electrical glow discharge, but the reaction is difficult, because of the low volatility of SbF_5.

$NF_4^+BF_4^-$. Attempts to obtain this salt by analogy with NF_4AsF_6 and NF_4SbF_6, that is by activating the system NF_3 + F_2 + BF_3, appear quite natural, and were probably made during the search for methods for synthesising the salts of TFA with the AsF_6^- and SbF_6^- anions. Thus in 1969, an unsuccessful attempt to synthesise NF_4BF_4 in a glow discharge from NF_3, F_2, and BF_3 at a temperature of the walls of the reaction vessel of 193 K was reported.[26] Instead of the expected compound, the product obtained was $O_2^+BF_4^-$ and other salts, which were hydrolysed with the liberation of oxides of nitrogen. A later paper[27] reported that one of the authors of Ref.8 in 1967 had subjected a mixture of NF_3 with F_2 and BF_3 to an electric discharge, but obtained $N_2F^+BF_4^-$, and not NF_4BF_4. An attempt was made[7] to obtain NF_4BF_4 by the double decomposition of salts of the NF_4^+ cation and salts of the BF_4^- anion (see Ref.27). After NF_4BF_4 was synthesised in 1969[9] from NF_3, F_2, and BF_3 in an electrical glow discharge, it became clear that the authors of Refs.8 and 26 had been very close to success, and had failed because the temperature of the walls of the reaction vessel at which the experiments in the discharge were carried out was not sufficiently low.

The synthesis of NF_4BF_4 is carried out in a quartz discharge tube immersed in liquid nitrogen; a mixture of NF_3 and BF_3 in almost equimolar proportions with a slight excess of NF_3 is first condensed, after which the discharge is switched on and fluorine is slowly introduced into the reaction vessel to maintain a pressure of 30–55 mmHg in it.[9,10,28] When one of the reagents (NF_3 or BF_3) is used up, the pressure begins to increase in the apparatus in proportion to the rate of supply of fluorine; when the supply of fluorine is stopped, the pressure remains constant, indicating that the reaction is complete. The efficiency of this method of synthesis corresponds to tens of grams of product per hour in a reactor volume of 50–100 cm^3.

The photochemical method[17,18] for synthesising NF_4BF_4 has a lower efficiency than the plasmochemical method. The salt is obtained in a yield of less than 1% when a mixture of NF_3 with F_2 and BF_3 is irradiated with ultraviolet light at room temperature.[17] The low-temperature photolysis of mixtures of the same reagents is more efficient;[18] when a high-pressure mercury lamp is used as the source of ultraviolet radiation, a yield of NF_4BF_4 greater than 3 g h^{-1} is achieved. During the photolysis, it is necessary to introduce fresh portions of the reagents into the reaction vessel at intervals, to prevent the formation of a screening layer of the product on the surface of the condensed reagents. The same precautions should also be taken in the plasmochemical preparation of the salt if the process is carried out for a long time.[10,28]

TFA fluoroborate has also been synthesised by the action of bremsstrahlung on a mixture of NF_3 with F_2 and BF_3 (1:6:1) cooled to 77 K; the yield of the product in the reaction vessel with mixing of the contents was over 100 mg h^{-1} for a radiation power of 100 Mrad h^{-1}.[27]

A method for preparing NF_4BF_4 by the action of a laser on a mixture of NF_3 and BF_3 with a different gaseous source of fluorine, namely SF_6, has been patented.[29]

According to data reported in Ref.22 (see note 3 of Ref.22), the following method was developed for the synthesis of NF_4BF_4:

$$CsF + HF \rightarrow CsHF_2,\ NF_4SbF_6 + CsHF_2 \rightarrow CsSbF_6 + NF_4HF_2,$$
$$NF_4HF_2 + BF_3 \rightarrow NF_4BF_4 + HF$$

(all the reactions are carried out in HF). The NF_4BF_4 formed is extensively contaminated by $CsSbF_6$, which is removed by treating with bromine pentafluoride; in BrF_5, however, the reaction $NF_4BF_4 + CsSbF_6 \rightarrow CsBF_4 + NF_4SbF_6$ takes place, and the NF_4BF_4 is contaminated with NF_4SbF_6. The replacement of CsF by silver fluoride[30] in this process eliminated the stage involving treatment with bromine pentafluoride, but did not lead to an appreciable increase in the purity of the product. Further improvement[22,31] of this method gave NF_4BF_4 specimens with a purity exceeding 99%. It has been suggested that $CsBF_4$ be used instead of $CsHF_2$, and that the reaction

$$CsBF_4 + NF_4SbF_6 \rightarrow CsSbF_6 + NF_4BF_4$$

be carried out in HF at 195 K in the presence of a 10–15% excess of NF_4SbF_6, which decreases the solubility of $CsSbF_6$ in HF.

The preparation of NF_4BF_4 by the reaction of an equimolar mixture of KrF_2, NF_3, and BF_3 at 295 K in HF has been reported.[25]

Of all the methods examined for the synthesis of NF_4BF_4, the plasmochemical method appears to be the most accessible, simple, and efficient.

$NF_4^+HF_2^-.nHF$. The synthesis of this salt can be regarded as resulting from attempts to prepare TFA fluoride $NF_4^+F^-$, which, if it were stable, would be a unique compound containing 87% active fluorine. An attempt might be made to obtain $NF_4^+F^-$, for example, by a double decomposition of the type

$$NF_4^+SbF_6^- + M^+F^- \rightarrow NF_4^+F^- + MSbF_6.$$

Work by a research group (see note 4 in Ref.11) showed that the double composition of LiF and NF_4SbF_6 in HF at room temperature gives an $LiSbF_6$ precipitate and a solution containing NF_4^+ cations, but attempts to isolate the TFA salt from the solution were unsuccessful, since the salt decomposed to NF_3, F_2, and HF.

The authors cited[11] used CsF as the ionic fluoride, but it was found that the reaction of NF_4SbF_6 with CsF in HF at 195 K does not give $NF_4^+F^-$, but leads to the formation of the unstable solid compound $NF_4^+HF_2^-.nHF$. For the synthesis of this salt, equimolar quantities of NF_4SbF_6 and CsF are placed in HF, the mixture is kept at room temperature and then cooled to 195 K, and the $CsSbF_6$ precipitate is filtered off. The excess of solvent is removed almost completely by distilling at 228 K; the residue consists of a transparent liquid, which solidifies at 195 K. The compound dissociates at 298 K:

$$NF_4HF_2 \cdot nHF \rightarrow NF_3 + F_2 + (n+1)HF$$

and the molar ratio NF_3:HF is ~10.1 at the start of the decomposition, and 1.54 at the end. It is extremely difficult to remove the solvating HF molecules completely, since the salt decomposes. Solutions of NF_4HF_2 in HF are stable at room temperature, and can be used to synthesise other TFA salts.

$NF_4^+Be_2F_5^-.BeF_2$, prepared by the thermal decomposition of $(NH_4)_2BeF_4$, reacts with a concentrated solution of NF_4HF_2 in HF. The reagents are kept for 65 h at 298 K to give $NF_4.Be_2F_5$, containing ~16% impurities.[32]

$NF_4^+AlF_4^-$. A specimen of NF_4AlF_4 containing ~17% impurities was synthesised by analogy with $NF_4Be_2F_5$, by the reaction of AlF_3 with NF_4HF_2 in HF.[32] The reaction

$$M_3AlF_6 + 3NF_4SbF_6 \rightarrow 3MSbF_6 + (NF_4)_3AlF_6$$

(M = Cs or Na) could not be carried out in BrF_5 at 298 K, or in HF at 195 K, or in molten NF_4SbF_6 at 548 K at an increased pressure of NF_3 and F_2.[32]

$(NF_4^+)_2SiF_6^{2-}$. Attempts to obtain the TFA salt with the SiF_5^- anion by low-temperature photolysis[18] were unsuccessful, as were attempts to synthesise TFA hexafluorosilicate by the double decomposition of NF_4SbF_6 and Cs_2SiF_6 in anhydrous HF.[33] Success was achieved by the reaction of SiF_4 with $NF_4HF_2.nHF$, previously freed (as far as possible) from excess HF:

$$2NF_4HF_2 \cdot nHF + SiF_4 \rightarrow (NF_4)_2SiF_6 + 2(n+1)HF.$$

This reaction gave a 95.5% pure specimen of $(NF_4)_2SiF_6$. The reaction of $(NF_4)_2SiF_6$ with an excess of SiF_4 does not give NF_4SiF_5, in contrast to $(NF_4)_2GeF_6$, which reacts with an excess of GeF_4 to give NF_4GeF_5.[33]

$NF_4^+PF_6^-$. Low-temperature photolysis[18,34] has proved suitable for the synthesis of this salt from a mixture of NF_3, PF_5, and F_2 in the ratio 3:3:1. The rate of formation of the product was only 10 mg h^{-1}. NF_4PF_6 can be obtained in larger quantities by the replacement reaction

$$NF_4BF_4 + PF_5 \rightarrow NF_4PF_6 + BF_3.$$

When a mixture of NF_4BF_4 with an excess of PF_5 is kept for 64 h at 298 K, the NF_4BF_4 is practically completely converted into NF_4PF_6.[18,35] In the reaction of NF_4BF_4 with an excess of PF_5 in HF at room temperature, the conversion of NF_4BF_4 into NF_4PF_6 is only partial (8–17%).[18] The salt can also be obtained by the reaction of NF_3 with KrF_2 and PF_5 (1:1:1) in HF at 295 K.[25]

$NF_4^+SO_3F^-$. This salt is obtained[36] by the double decomposition of NF_4SbF_6 and $CsSO_3F$ in anhydrous HF at room temperature with subsequent cooling to 195 K and filtration

at this temperature; the solvent is removed by distilling at 243 K. Solutions of NF_4SO_3F in HF are stable at 298 K for several days. TFA sulphate cannot be obtained by the analogous reaction of NF_4SbF_6 with Cs_2SO_4, since caesium sulphate reacts with HF to give $CsSO_3F$.

$NF_4^+ClO_4^-$. TFA perchlorate was synthesised[11] by the reaction of equimolar quantities of NF_4SbF_6 and $CsClO_4$ in anhydrous HF. The mixture of reagents is kept for 15 h at 195 K and for 2 h at 228 K, after which the $CsSbF_6$ precipitate is separated at 195 K, and the solvent distilled off. The purity of the product reaches 95%. Attempts to synthesise NF_4BrO_4 and NF_4IO_4 by analogous methods were unsuccessful: $NF_4.BrO_4$ is extremely unstable in HF, and decomposes explosively when isolated from solution, and IO_4^- is readily fluorinated to $IF_4O_2^-$ in HF or BrF_5.

$(NF_4^+)_2TiF_6^{2-}$ and TFA polyfluorotitanates. $(NF_4)_2TiF_6$ was obtained[37] by the reaction of saturated solutions of NF_4SbF_6 and Cs_2TiF_6 in HF (molar ratio $NF_4SbF_6:Cs_2TiF_6 = 2:1$) at room temperature, followed by filtration of the solution at 195 K and distillation of the volatile products at 323 K. Fluorotitanates containing polyanions are formed[37] by displacing BF_3 from NF_4BF_4 using titanium tetrafluoride:

$$NF_4BF_4+nTiF_4\rightarrow NF_4TiF_5\cdot(n-1)TiF_4+BF_3.$$

The reaction of NF_4BF_4 with TiF_4 in anhydrous HF at room temperature gives $NF_4Ti_2F_9$ and $NF_4Ti_3F_{13}$, and the composition of the products depends on the preliminary treatment of the TiF_4 taken for the reaction; if a specimen previously treated with fluorine at 523 K and 70 atm is used, the product is $NF_4Ti_3F_{13}$. The reaction of NF_4BF_4 with TiF_4 without a solvent at 443 K gives $NF_4Ti_2F_9$. Heating TiF_4 with an excess of NF_3 and F_2 at 453–468 K and a pressure of up to ~160 atm gives a product with a composition close to $NF_4Ti_6.F_{25}$:

$$NF_3+F_2+6TiF_4\rightarrow NF_4Ti_6F_{25}.$$

According to Ref. 25, $(NF_4)_2TiF_6$ is formed by the reaction of NF_3 with KrF_2 and TiF_4 (2:2:1) in HF at 295 K; the vibrational spectra of the product given in Ref. 25, however, differ from the spectra of $(NF_4)_2TiF_6$ given in Ref. 37.

$(NF_4^+)_2MnF_6^{2-}$. The fluorination of a mixture of $MnCl_2$ and CsF at 673 K was used to obtain Cs_2MnF_6, which then reacted with NF_4SbF_6.[38] The mixture of Cs_2MnF_6 and NF_4SbF_6 (1:2) in anhydrous HF was kept for 30 min at 298 K, after which the solution was cooled to 195 K. The solvent was then distilled off, to give 91.27% pure $(NF_4)_2MnF_6$. The salts $(NF_4)_3MF_6$ (M = Mn, Co, Cu) could not be synthesised in this way, because of the solvolysis of MF_6^{3-} in HF. The salt $(NF_4)_3CoF_6$ similarly could not be obtained by the reaction of CoF_3 with NF_4HF_2 in HF at 228 K.[38]

$(NF_4^+)_2NiF_6^{2-}$. The double decomposition of Cs_2NiF_6 and NF_4SbF_6 (1:2) in anhydrous HF at 298 K gives $(NF_4)_2.NiF_6$,[39,40] which is separated from $CsSbF_6$ by filtration at 195 K, and freed from solvent by distillation at 298 K.

$NF_4^+GeF_5^-$, $(NF_4^+)_2GeF_6^{2-}$. NF_4GeF_5 was obtained by the low-temperature photolysis[18] of a mixture of NF_3 with GeF_4 and F_2 (3:3:1). The rate of formation of the salt was only 25 mg h^{-1}, so that a different method was proposed[18] for preparing NF_4GeF_5, based on the reaction of NF_4BF_4 with a large excess of GeF_4. At room temperature without a solvent, GeF_4 displaces BF_3 from NF_4BF_4; after 64 h, the degree of conversion of NF_4BF_4 into NF_4GeF_5 was 65%, and complete conversion required repeated treatment of NF_4BF_4 with germanium tetrafluoride. The reaction of NF_4BF_4 with GeF_4 in anhydrous HF at 298 K gives 85% conversion of NF_4BF_4, but the product is a mixture of NF_4GeF_5 and $(NF_4)_2.GeF_6$. Germanium tetrafluoride is a weaker Lewis acid than AsF_5, so that it does not displace AsF_5 from NF_4AsF_6 in HF.

The salt $(NF_4)_2GeF_6$, the first TFA salt to be synthesised with a doubly-charged anion, can be obtained in quantitative yield by keeping NF_4GeF_5 in an excess of HF at 298 K. Treatment of $(NF_4)_2GeF_6$ with a large excess of GeF_4 at 298 K gives NF_4GeF_5 in quantitative yield.[18]

$NF_4^+NbF_6^-$. This compound was obtained[25] by the reaction of KrF_2 with NF_3 and NbF_5 (1:1:1) in anhydrous HF at room temperature.

$NF_4^+SnF_5^-$, $(NF_4^+)_2SnF_6^{2-}$. When mixtures of NF_3 with F_2 and SnF_4 are heated (573 K, ~150 atm), a TFA salt is not formed.[41] $(NF_4)_2SnF_6$ was synthesised from Cs_2SnF_6 and NF_4SbF_6 (1:2) in anhydrous HF at room temperature, followed by filtration of the solution at 193 K.[41] The reaction of equimolar quantities of NF_4BF_4 and SnF_4 in anhydrous HF at 298 K gives practically pure NF_4SnF_5. If however a two-fold excess of NF_4BF_4 is taken, the product is not NF_4SnF_5 but only a small quantity of $(NF_4)_2SnF_6$, even after prolonged reaction.[41]

$NF_4^+XeF_7^-$, $(NF_4^+)_2XeF_8^{2-}$. The reaction of XeF_6 with NF_4HF_2 in HF gives 98% pure NF_4XeF_7.[42,43] Prolonged exposure of a specimen to laser radiation with a wavelength of 4880 Å at room temperature leads to the decomposition of NF_4XeF_7 to give $(NF_4)_2XeF_8$ and XeF_6.

$NF_4^+WF_7^-$. A specimen of NF_4WF_7 containing 1.61% $CsSbF_6$ was synthesised[44] by the reaction of WF_6 with NF_4HF_2.

$NF_4^+WOF_5^-$, $NF_4^+W_2O_2F_9^-$. NF_4WOF_5 was synthesised by the reaction of WOF_4 with a concentrated solution of NF_4HF_2 in HF at 298 K.[45] When heated in a sapphire reaction vessel in a vacuum, NF_4WOF_5 is completely converted into $NF_4W_2O_2F_9$:

$$3NF_4WOF_5\rightarrow 2NF_3+OF_2+WF_6+NF_4W_2O_2F_9.$$

In anhydrous HF, solvolysis of NF_4WOF_5 takes place, again giving $NF_4W_2O_2F_9$.

$NF_4^+BiF_6^-.nBiF_5$. Heating equimolar quantities of NF_4BF_4 and α-BiF_5 at 448–453 K leads to the liberation of BF_3 and the formation of NF_4BiF_6.[23] The same reaction can be carried out at room temperature in anhydrous HF. As in the synthesis of TFA fluoroantimonate, the direct synthesis of TFA fluorobismuthate from NF_3, F_2, and BiF_5 gives salts of polyanions, chiefly $Bi_2F_{11}^-$. Heating a mixture of NF_3 with F_2 and BiF_5 at 448 K and a pressure of 167 atm gives a product having the formula $NF_4BiF_6.0.6BiF_5$. The thermal decomposition of $NF_4BiF_6.nBiF_5$ in a vacuum at 553 K gives $NF_4.BiF_6$.[23] A study[46] of the properties of NF_4BiF_6 as a possible replacement for NF_4SbF_6 in the preparation of TFA salts by double decomposition with alkali metal salts showed that NF_4BiF_6 has no advantages over NF_4SbF_6.

$NF_4^+UF_7^-$. A specimen of NF_4UF_7 containing small quantities of NF_4SbF_6 and $CsSbF_6$ was obtained[44] by the reaction of UF_6 with NF_4HF_2 in 88% yield relative to NF_4HF_2.

$NF_4^+UOF_5^-$. This salt was synthesised[47] from UOF_4 and NF_4HF_2 in anhydrous HF. The possible synthesis of NF_4UOF_5 by the double decomposition of NF_4SbF_6 and the corresponding alkali metal salt is inapplicable in this case, because of

the very low solubility of NF_4UOF_5 in HF. It was also impossible to synthesise the salt from UOF_4, CsF, and NF_4SbF_6 in HF.

Synthesis of other TFA salts. An unsuccessful attempt to prepare NF_4ClOF_4 and NF_4BrOF_4 by the double decomposition of NF_4SbF_6 and the corresponding caesium salts in BrF_5 at room temperature has been described.[11] The reaction of NF_4SbF_6 with $CsBrOF_4$ gives NF_3, fluorine, $BrOF_3$, and $CsSbF_6$, and $CsClOF_4$ reacts with BrF_5 to give $CsBrF_6$ and $ClOF_3$. Anhydrous HF cannot be used as solvent, since it reacts with $CsBrOF_4$. TFA nitrate cannot be obtained by double decomposition in HF, since $CsNO_3$ reacts with HF to give NO_2^+. It was also impossible to carry out F—Cl exchange between NF_4^+ and BCl_3 or between NF_2O^+ and BCl_3 to obtain salts of NCl_4^+ and NCl_2O^+ cations.[11] The double decomposition of $CsIO_2F_4$ and NF_4SbF_6 in HF does not give $NF_4IO_2F_4$, but gives *cis*- and *trans*-OIF_4OF.[11,48] The synthesis of NF_4MF_6, where M = Ru, Rh, Pt, and Au, using KrF_2 has been described[49] (without any experimental details), as has the preparation of NF_4MnF_5, formed in the HF + KrF_2 + MnO_3F + NF_3 (or N_2F_4) system.[50]

The Possible Existence of NF_5

The NF_4^+ cation can be regarded formally as an ion formed by the removal of a fluoride ion from the hypothetical higher fluoride of nitrogen NF_5. The existence of this fluoride as a sufficiently stable compound is unlikely.[12] Nevertheless, the possible existence of a compound with the empirical formula NF_5, for example as the solvated ion pair $NF_4^+F^-$ at low temperatures in an inert medium, cannot be completely excluded.

The formation of a new unstable nitrogen fluoride was noted[51] in a study of the products obtained by the radiolysis of a mixture of NF_3 with F_2 using uranium fission products. Reliable identification of the compounds was practically impossible, since the quantity of substance formed was 1–10 μmole; the authors[51] suggested, however, that they had synthesised NF_5 or F_3NNF_3. The formation of an unstable unidentified nitrogen fluoride was also observed when liquid NF_3 was irradiated at 77 K with electrons with an energy of 800 keV.[52] The formation of small quantities of a white solid substance was observed[27] as a result of the action of bremsstrahlung with a dose of 100 Mrad on a mixture of NF_3 with an excess of fluorine at 77 K. This substance decomposed at 143 K to give NF_3. The condensation of BF_3 into the mixture of the products after irradiation at 77 K, and subsequent heating of this mixture, gave a small quantity of NF_4BF_4, possibly confirming the decomposition

$$NF_4^+F^- + BF_3 \rightarrow NF_4BF_4.$$

The Mechanism of the Reactions Involved in the Synthesis of TFA Salts

A general method for preparing salts of fluorocations involves the action of a fluoride ion acceptor EF_n on a covalent fluoride RF:

$$RF + EF_n \rightarrow R^+[EF_{n+1}]^- \quad (1)$$

where E represents an atom of B, P, V, As, Sb, etc., and R a group such as ONF_2, $OClF_2$, ClF_4, etc. In a number of cases, polyatomic cations made up of non-metal atoms are formed by the action of EF_n on a mixture of two compounds

$$RF + Z + EF_n \rightarrow [RZ]^+[EF_{n+1}]^-$$

where Z = Cl_2, H_2S, etc.[12] Reaction (2), describing the formation of TFA salts, is usually referred to as the direct synthesis of TFA salts:

$$NF_3 + F_2 + EF_n \rightarrow [NF_4]^+[EF_{n+1}]^-. \quad (2)$$

A second route to NF_4^+ cation is based on the oxidation of nitrogen trifluoride, which can be carried out only using an extremely strong oxidising agent, such as a krypton salt:

$$NF_3 + [KrF]^+[EF_{n+1}]^- \rightarrow [NF_4]^+[EF_{n+1}]^- + Kr. \quad (3)$$

Since nitrogen pentafluoride as starting material does not exist, reaction (1) cannot be used to synthesise NF_4^+, and the direct synthesis of the NF_4^+ cation is achieved by the action of heat or other source of energy on the NF_3 + F_2 + EF_n system (reaction (2)). The methods for obtaining TFA salts described above show that the NF_4^+ ion can be synthesised either by heating the starting materials or by plasmochemical, photochemical, or radiation-chemical methods.

The direct synthesis of TFA salts is possible when EF_n is a fairly strong Lewis acid, monomeric, volatile, and stable under the conditions of the reaction. These requirements are completely or partly satisfied by BF_3, PF_5, GeF_4, AsF_5, SbF_5, and BiF_5. The Lewis acid taken for the direct synthesis accepts a fluoride ion and forms a stable anionic fluoro-complex.

The action of a stronger Lewis acid on a TFA salt with an anion formed by a weaker Lewis acid (for example NF_4BF_4) can displace the weaker acid (BF_3) and give a new salt with the fluoro-anion of the stronger acid. This method has been used to obtain salts of TFA and the corresponding anionic fluoro-complexes by the action of PF_5, TiF_4, GeF_4, SnF_4, and BiF_5 on NF_4BF_4. Boron trifluoride can displace HF from NF_4HF_2 to give NF_4BF_4.

The third group of reactions used for the synthesis of TFA salts involves the double decomposition of NF_4SbF_6 and caesium salts in anhydrous HF. The chief requirement of these reactions is that the starting materials should be soluble, and one of the products ($CsSbF_6$) insoluble, in HF; when this condition is satisfied, it is possible to isolate a new TFA salt, which however entrains appreciable quantities of impurity. This method has been used to prepare NF_4HF_2, NF_4SO_3F, NF_4ClO_4, $(NF_4)_2TiF_6$, $(NF_4)_2MnF_6$, $(NF_4)_2NiF_6$, and NF_4SnF_5.

A unique group of reactions for synthesising TFA salts is formed by those based on TFA hydrogen fluoride. The use of this compound is appropriate when double decomposition is impossible because the starting materials are insoluble or react with the solvent, or when the Lewis acid EF_n is polymeric and non-volatile. Salts of TFA with the corresponding anionic fluoro-complexes have been synthesised by the reactions of NF_4HF_2 with BeF_2, AlF_3, SiF_4, XeF_6, WF_6, WOF_4, UF_6, and UOF_4.

NF_4SbF_6, NF_4PF_6, $(NF_4)_2TiF_6$, NF_4NbF_6, and various other TFA salts have been obtained by oxidising nitrogen trifluoride (reaction (3)).

The mechanism of formation of the NF_4^+ cation was first represented as a set of elementary stages, without any firm experimental proof of the possibility of these stages. For the synthesis of NF_4^+ in an electrical discharge, for example, the following scheme was proposed:[8]

$$NF_3^+ + F_2 \rightarrow NF_4^+ + F,\ NF_3^+ + F \rightarrow NF_4^+,\ NF_3 + F_2^+ \rightarrow NF_4^+ + F,$$
$$NF_3 + F^+ \rightarrow NF_4^+.$$

The formation of NF_3^+, F_2^+, and F^+ ions is possible in the plasma of a glow discharge, which is a highly non-equilibrium

system, as a result of the presence of electrons with energies sufficient to ionise NF_3, F_2, or F. This ionisation cannot take place, however, on thermal or photochemical excitation of the reagents. This led[17] to an examination of the possible formation of the AsF_6 radical as an intermediate product of the direct synthesis of NF_4AsF_6. The AsF_6 radical might be formed by the reaction of F atoms with AsF_5 molecules, and, in the opinion of the authors cited,[17] should be a very strong oxidising agent, comparable with PtF_6 and capable of oxidising NF_3:

$$NF_3 + AsF_6 \rightarrow NF_3^+AsF_6^-,\ NF_3^+AsF_6^- + F_2 \rightarrow NF_4^+AsF_6^- + F.$$

This idea of the role of AsF_6 radicals might be extended to the synthesis of other TFA salts, and also dioxygenyl or xenon salts. The possibility of this mechanism for the formation of NF_4^+ was confirmed[30] when EPR recorded both stable pyramidal radical-cations NF_3^+ and unstable radicals AsF_6, SbF_6, and Sb_2E_{11}, produced by the γ-irradiation of specimens of NF_4AsF_6 and $NF_4SbF_6.0.8SbF_5$, cooled to 77 K. The formation of NF_3^+ radical-cations was also observed[53] by EPR in the low-temperature photolysis of NF_3–F_2–AsF_5 and NF_3–F_2–BF_3 mixtures. The EPR spectra of $^{14}NF_3^+$ and $^{15}NF_3^+$ radical-cations, generated by the γ-irradiation of TFA salts or by low-temperature ultraviolet photolysis, have also been studied.[54]

More detailed studies[55] of the thermal decomposition of NF_4BF_4 and NF_4AsF_6 showed, however, that the mechanism for the synthesis of salts based on radicals of the AsF_6 type is inapplicable. EPR was unable to detect any signs of the reaction of F atoms with AsF_5 to give AsF_6 radicals. Moreover, a kinetic study of the thermal decomposition of NF_4BF_4 and NF_4AsF_6 made it possible[55] to exclude from consideration a number of proposed stages in the decomposition or synthesis of these salts, and to conclude that the only scheme describing the formation and decomposition of NF_4AsF_6 and not contradicting any available experimental data must include the following reversible reactions:

$$F_2 \rightleftharpoons 2F$$
$$F + NF_3 \rightleftharpoons NF_4$$
$$NF_4 + AsF_5 \rightleftharpoons NF_3^+AsF_6^-$$
$$NF_3^+AsF_6^- + F \rightleftharpoons NF_4^+AsF_6^-.$$

In the opinion of the authors cited,[55] this scheme is applicable to other TFA salts, except those for which oxidative fluorination of the anion takes place during the decomposition. The scheme does not include reactions involving NF_5, whose existence has not been proved, but it assumes the participation of the NF_4 radical, whose existence also has not been proved experimentally. According to calculations[55] based on a Born–Haber cycle, the stage $F + NF_3 \rightarrow NF_4$ should be thermally neutral, and probably takes place without an activation energy.

The degree of dissociation of fluorine molecules under the conditions of the experiments of Ref. 55 on the synthesis of NF_4SbF_6 from NF_3, F_2, and SbF_5 is $\sim 10^{-7}$. It is difficult to decide whether the fairly low concentration of F atoms can ensure the comparatively high rate of formation of NF_4SbF_6, observed by the authors cited,[55] if account is taken of only the reaction of atomic fluorine with NF_3 and the NF_3^+ salt, without assuming the possibility of reactions involving molecular fluorine. The scheme proposed in Ref. 55 for the synthesis and decomposition of TFA salts apparently requires more detailed examination and further experimental justification.

Monofluoroammonium and Difluoroammonium Salts

Of the three possible mixed-ligand fluoroammonium cations H_nNF_{4-n} (n = 1–3), H_3NF^+ and $H_2NF_2^+$ have been obtained. $H_3NF^+X^-$ were synthesised by the action of strong proton acids HX on alkyl fluorocarbamates:[56,57]

$$NHFCO_2R + 2HX \rightarrow H_3NFX + CO_2 + RX.$$

where R = ethyl or isopropyl, and X = ClO_4^-, $CH_3SO_3^-$, or $CF_3SO_3^-$. Weaker inorganic acids such as hydrochloric acid decompose fluoro-carbamates. The reaction of the acids with $NHFCO_2R$ takes place rapidly at temperatures equal to or slightly above room temperature in a solvent (methylene chloride). The extremely hygroscopic H_3NFClO_4 and $H_3NFSO_3CH_3$ melt and decompose at 373–378 K; they attack glass, and decompose on standing. The less hygroscopic and more stable $H_3NFSO_3CF_3$, which melts with partial decomposition at 437–438 K, does not react with glass, and is soluble in ethers and nitriles.

The difluoroammonium salts $H_2NF_2^+AsF_6^-$ and $H_2NF_2^+SbF_6^-$ were obtained[58] by the usual method for synthesising fluorocations, by the action of EF_5 (E = As, Sb) on difluoroamine and HF in a medium of HF at 195 K. The salts are stable at 223 K, but at room temperature they decompose rapidly to give HF, EF_5, F_2, NF_3, and small quantities of *trans*-N_2F_2. An attempt to obtain fluoroammonium cations by the action of fluorine on the ammonium salt NH_4AsF_6 in HF was unsuccessful.[58] Similarly, adduct formation was not observed in the NF_3 + HF + SbF_5 system.[58]

III. PROPERTIES OF TETRAFLUOROAMMONIUM SALTS

The earliest studies[3,7,8,15] established that TFA compounds are ionic. The tetrahedral structure of the NF_4^+ ion is confirmed by the vibrational and ^{19}F NMR spectra. For the NF_4^+ structure with T_d symmetry, there are four forms of normal vibration: $A_1 + E + 2F_2$. All the vibrations are active in the Raman spectrum, and the A_1 line is polarised; in the infrared spectrum, only the triply degenerate vibrations are active. The laser Raman spectrum of NF_4AsF_6 [16] shows the vibrational wavenumbers of the (NF_4^+) groups at 847 cm^{-1} (ν_1, A_1), 445 cm^{-1} (ν_2, E), 1160 cm^{-1} (ν_3, F_2), and 611 cm^{-1} (ν_4, F_2). Intense absorption at 1159 cm^{-1} (ν_3, F_2) and absorption of medium intensity at 611 cm^{-1} (ν_4, F_2) are observed in the infrared spectrum of NF_4AsF_6.[59] A detailed study[19] of the vibrational spectra of $^{14}NF_4AsF_6$ and comparison with $^{15}NF_4$. .AsF_6 gave for the normal vibrations of $^{14}NF_4^+$ the values ν_1 = 848.2, ν_2 = 443.3, ν_3 = 1158.95, and ν_4 = 611.15 cm^{-1}; for $^{15}NF_4^+$, the same vibrations appear at 848.2, 443.3, 1129.7, and 609.35 cm^{-1}. The force constant of the NF stretches of the NF_4^+ ion (6.15 mdyne Å^{-1}) is much greater than the force constants 2.15 mdyne Å^{-1} for FNO or 4.31 mdyne Å^{-1} for NF_3, indicating that the strength of the NF bond in the NF_4^+ ion is unusually high for nitrogen fluorides. The estimated interatomic distance N–F in NF_4^+ is 1.24 Å (1.512 Å for FNO and 1.365 Å for NF_3).[19] The anions of the salts have practically no influence on the vibrational spectra of the NF_4^+ ion. The normal vibrations of NF_4^+, recorded in the spectra of all the salts synthesised, lie in a narrow wavenumber range of ~20 cm^{-1}, and this range is possibly determined not so much by the properties of the salts as by the quality of the experimental spectra.

The ^{19}F NMR spectra of TFA salts show that the fluorine atoms in NF_4^+ are equivalent, and that the ion has tetrahedral symmetry. The spectrum of NF_4AsF_6 (solution in HF, 298 K, 94.6 MHz) contains a triplet of very narrow bands of equal

intensity, corresponding to the NF_4^+ ion, with a chemical shift of −213.5 p.p.m. ($CFCl_3$) and a spin–spin coupling constant of 234 Hz.[59] The band width at half-height does not exceed 10 Hz, indicating that there is no N–F quadrupole coupling. Analogous ^{19}F NMR spectra were obtained for other TFA salts.

TFA tetrafluoroborate has been studied by X-ray electron spectroscopy.[28] The energy of the removal of the 1s electron of the N atom for NF_4BF_4 is 417.3 eV, which is much greater than all known values for nitrogen compounds. The energy of the removal of the 1s electron of the F atom for NF_4^+ (694.4 eV) is also greater than all known values. From these data it follows that the negative charge on the F atoms in NF_4^+ is a minimum, and that the N–F bond is less polar than the C–F or B–F bonds. From an analysis of the intensities of the ν_1 line in the Raman spectrum of NF_4BF_4,[27] it was concluded that the bonds in NF_4^+ are more covalent than those in BF_4^-.

The crystal structures of various low-temperature forms of TFA salts have been determined from the X-ray powder diffraction patterns. The salts have a tetragonal lattice with $Z = 2$. The unit cell parameters and values of the calculated density ρ are given in Table 1. The calculated[18,37,39,41] values of the parameters a and c for the lattices of $(NF_4)_2EF_6$, where E = Ge, Ti, Ni, or Sn, were corrected in Ref.38, and the corrected values are given in Table 1. The density of NF_4AsF_6, measured in a perfluorinated amine, is 2.98 g cm^{-3} at 298 K.[15]

Table 1. Crystallographic data for TFA salts.

Salt	Cell parameters, Å		ρ, g cm^{-3}	Refs.
	a	c		
NF_4BF_4	7.01	5.22	2.29	[27]
NF_4BF_4	9.944	5.229	2.27*	[18]
NF_4PF_6	7.577	5.653	2.41	[18]
NF_4AsF_6	7.70	5.73	2.72	[15]
NF_4SbF_6	7.903	5.806	2.98	[23]
NF_4BiF_6	8.006	5.821	3.68	[23]
$(NF_4)_2TiF_6$	6.99	9.28	2.51	[38]
$(NF_4)_2MnF_6$	6.90	9.23	2.64	[38]
$(NF_4)_2NiF_6$	6.828	9.270	2.71	[60]
$(NF_4)_2GeF_6$	6.92	9.25	2.75	[38]
$(NF_4)_2SnF_6$	7.05	9.41	2.93	[38]

* $Z = 4$.

Crystallographic studies[60] of powders and single crystals of 98.9% pure $(NF_4)_2NiF_6$ showed that the compound has a body-centred tetragonal cell, space group $I4/m$. The salt is made up of octahedral NiF_6^{2-} ions and tetrahedral NF_4^+ cations, and has the antifluorite structure. The calculated interatomic distance N–F in the NF_4^+ tetrahedra is 1.30–1.40 Å, and the F...F distance is ~2.2 Å.[60]

TFA salts are colourless crystalline substances, except for the bright-red compound $(NF_4)_2NiF_6$ and the yellow compounds $(NF_4)_2MnF_6$, NF_4XeF_7, NF_4UF_7, and NF_4UOF_5. The salts do not sublime, and almost all decompose without melting. The melting points are ~591 K for NF_4SbF_6 and 614 K for NF_4BiF_6; $NF_4Sb_2F_{11}$ melts at 451 K, and the melt solidifies at 434 K. The melting point of $NF_4HF_2.nHF$ increases with decrease in the number of solvating HF molecules, and approaches room temperature as $n \to 0$.

TFA salts are soluble to different extents in anhydrous HF; the solubility of $(NF_4)_2MnF_6$ is greater than 1.30 g per g HF at 297 K, the solubilities of NF_4SbF_6 and NF_4BiF_6 are 259 mg and 173 mg per g HF at 195 K, and NF_4UOF_5 is sparingly soluble. Bromine pentafluoride, in which TFA salts are less soluble than in HF, can also be used as solvent. The salts are extremely hygroscopic, and react vigorously with water, and also with common organic solvents.

1. The Thermal and Thermochemical Properties of TFA Salts

TFA salts have an unusually high thermal stability. Although the stability of the fluoroantimonate and fluoroarsenate might have been predicted by analogy with other salts of fluoro-cations, the existence of the extremely stable tetrafluoroborate was completely unexpected. The synthesis of each new TFA salt was naturally followed by a study of its thermal stability. Unfortunately, the published results are not standardised, and the data must be regarded as only approximate, particularly because of the strong catalytic influence of the walls and impurities present in the salts on the rate of decomposition. Table 2 gives the temperatures of the start of the decomposition of various TFA salts, recorded by DTA or DSC, and also manometrically or by visual observation of the behaviour of the substance when heated in a sealed capillary. Although these values are understandably inaccurate, they are useful for estimating the relative stability of the salts.

Table 2. Temperatures of the start of the decomposition of TFA salts (T, K).

Salt	T	Salt	T
NF_4BF_4	513	$(NF_4)_2SiF_6$	363
NF_4GeF_5	522*	$(NF_4)_2TiF_6$	473
NF_4SnF_5	543	$(NF_4)_2MnF_6$	373
NF_4PF_6	518*	$(NF_4)_2NiF_6$	383
NF_4AsF_6	543	$(NF_4)_2GeF_6$	511*
NF_4SbF_6	>573	$(NF_4)_2SnF_6$	513
NF_4XeF_7	348	NF_4SO_3F	283
NF_4WF_7	>398**	NF_4ClO_4	273
NF_4UF_7	>398**	NF_4WOF_5	358
		NF_4UOF_5	333

*Temperature of the start of rapid decomposition.
**In a vacuum.

The salt NF_4HF_2 is stable in HF up to room temperature, and decomposes rapidly at 328 K; $NF_4Sb_2F_{11}$ at 523–533 K in a vacuum gives up SbF_5 and is converted into NF_4SbF_6;[23] the salt NF_4BiF_6 is apparently the most stable, and melts at ~614 K.[23] Table 2 shows that the stability of the salts depends markedly on the nature of the anions. Salts with oxygen-containing anions decompose at temperatures below 373 K, whereas salts with the anionic fluoro-complex BF_4^- and anions of the type EF_{n+1}^- ($n = 4–6$) or EF_6^{2-} are much more stable, and even the salt of the weak Lewis acid SiF_4 is stable up to ~363 K. According to recent data[61] obtained by DSC, the decomposition of NF_4BF_4, NF_4PF_6, NF_4AsF_6, NF_4SbF_6, NF_4GeF_5, and $(NF_4)_2GeF_6$ begins at 435, 446, 518, 578, 374, and 440 K respectively, and the maxima of the effects are observed at 530, 533, 596, 655, 475, and 481 K. For NF_4GeF_5, the temperature of the start of the decomposition (374 K) was taken as the temperature of the transformation of the salt into $(NF_4)_2GeF_6$ according to the scheme

$$2NF_4GeF_5 \rightarrow (NF_4)_2GeF_6 + GeF_4$$

and the maximum of the effect (475 K) corresponds to the decomposition stage

$$(NF_4)_2GeF_6 \rightarrow 2NF_3 + 2F_2 + GeF_4 .$$

According to Ref.38, a specimen of $(NF_4)_2NiF_6$ after 6 h at 373 K decomposes to the extent of 9%, but in Ref.62 it is stated that the temperature of the start of the decomposition of this salt is 407 K. The decomposition of $(NF_4)_2MnF_6$ at 373 K for 20 min takes place with acceleration, after which the pressure of the gaseous decomposition products increases linearly.[38] At 373 K after 17 h, 0.17% of the $(NF_4)_2MnF_6$ taken decomposes, whereas at 403 K after the same time interval the degree of decomposition is 0.66%. In a vacuum, NF_4XeF_7 decomposes at rates of 1.6% and 28% per hour at 348 K and 373 K; NF_4WF_7 at 418 K in a vacuum after 1 h decomposes to the extent of 1.4%, and NF_4UF_7 to the extent of 25%.[44] At 358 K, NF_4WOF_5 decomposes at a rate of ~0.03% per hour, and at 428 K after 6.5 h the degree of conversion into $NF_4W_2O_2F_9$ is 90%.[45]

The decomposition of TFA salts with the anions EF_{n+1}^- (n = 3–6) and EF_6^{2-} gives NF_3, F_2, and the corresponding fluorides EF_n, for example $NF_4BF_4 \rightarrow NF_3 + F_2 + BF_3$. The decomposition of $(NF_4)_2NiF_6$ gives non-stoichiometric nickel fluoride, and is described by the equation $(NF_4)_2NiF_6 \rightarrow 2NF_3 + (3 - x/2)F_2 + NiF_{2+x}$. The decomposition of $(NF_4)_2MnF_6$ gives MnF_3 according to the scheme: $2(NF_4)_2MnF_6 \rightarrow 4NF_3 + 5F_2 + 2MnF_3$.

The decomposition of salts with oxygen-containing anions is accompanied by the reaction of fluorine with the anions to give a different set of decomposition products. The decomposition of NF_4UOF_5 is described by the equations $NF_4UOF_5 \rightarrow NF_3 + F_2 + UOF_4$, $2UOF_4 \rightarrow UF_6 + UO_2F_2$; the decomposition products contain a mixture of UOF_4 and UO_2F_2, and the decomposition of NF_4UOF_5 gives OF_2 (in small quantities). At 453 K in a vacuum, NF_4WOF_5 is converted into the more stable $NF_4W_2O_2F_9$ according to the scheme: $3\,NF_4WOF_5 \rightarrow 2NF_3 + OF_2 + WF_6 + NF_4W_2O_2F_9$. The thermal decomposition of NF_4ClO_4 and NF_4SO_3F provides a new method for synthesising the corresponding hypofluorites: $NF_4ClO_4 \rightarrow NF_3 + FOClO_3$, $NF_4SO_3F \rightarrow NF_3 + FOSO_2F$. The decomposition of NF_4ClO_4 can be used to obtain very pure $FOClO_3$, which does not decompose when handled.[63] The hypofluorite $FOIOF_4$ has been obtained[48] as a mixture of *cis*- and *trans*-isomers by the thermal decomposition of the compound $NF_4IO_2F_4$, formed as an intermediate product of the reaction of $CsIO_2F_4$ with NF_4SbF_6 in HF.

The first paper devoted to the study of the kinetics of the thermal decomposition of TFA salts[64] described the decomposition of NF_4AsF_6 specimens in a Monel metal vessel. The specimens were synthesised from NF_3, F_2, and AsF_5 in an electrical glow discharge by the method described in Ref.15. It was found that the dependence of the total pressure p of the gaseous decomposition products of NF_4AsF_6 on time t in the temperature range 448–495 K is given by the equation $p^{3/2} = At + B$, where A and B are coefficients. It was suggested that the decomposition of the salt is described by the equations $NF_4AsF_6 \rightleftharpoons NF_5 + AsF_5$, $NF_5 \rightarrow NF_3 + F_2$, but it was impossible to isolate the suggested intermediate product NF_5 in an Ne matrix to record its infrared spectrum.

The results of Ref.64 appear doubtful, since the decomposition of the salt was studied at 448–495 K, whereas DTA indicates that decomposition begins at a higher temperature, for example ~543 K;[8] this lack of agreement was noted in Ref.12. The authors cited[64] apparently used NF_4AsF_6 specimens containing considerable quantities of impurities; moreover, the walls of the Monel metal vessel react with Lewis acids in the presence of fluorine at high temperatures, so that these vessels are unsuitable for kinetic studies.

The kinetics of the thermal decomposition of NF_4BF_4 and NF_4AsF_6 have been studied[55] in a vessel of synthetic sapphire, which is stable to mixtures of F_2 with BF_3 or AsF_5. The decomposition of NF_4AsF_6 was studied at 473–511 K, and that of NF_4BF_4 at 455–488 K. The time dependence of the total pressure of the decomposition products of the salts obeyed a law analogous to that in Ref.64, but the decomposition was much slower than in Ref.64. A special experiment with a small quantity of NF_4BF_4 at 526 K showed that the decomposition is not autocatalytic, and the linear dependence of $p^{3/2}$ on t is preserved as far as a degree of decomposition of the salt of ~25%. The addition of helium to the system has practically no influence on the rate of decomposition of the salts, the addition of fluorine and NF_3 decreases the rate slightly, and the addition of BF_3 to NF_4BF_4 or of AsF_5 to NF_4AsF_6 leads to a marked decrease in the rate of decomposition.

The decomposition of the salts is characterised by fairly high activation energies: 36.6 ± 0.8 kcal mole^{-1} for NF_4BF_4, and 44.7 ± 4.2 kcal mole^{-1} for NF_4AsF_6.[55] Preliminary studies[39] of the thermal decomposition of $(NF_4)_2NiF_6$ in the range 353–401 K showed that the decomposition of this salt is not autocatalytic, and takes place with an activation energy of 35.161 kcal mole^{-1}. The decomposition of $(NF_4)_2SiF_6$ in the temperature range 361.5–372.5 K has an activation energy of 26.6 kcal mole^{-1}.[33]

Phase transformations have been detected for various TFA salts: for NF_4BF_4 at 493–503 K[10] or at 507 K[18] or at 509 K;[27] for NF_4PF_6 at 398 K;[18] for NF_4AsF_6 at 406 K;[18] and for NF_4GeF_5 at 402 K.[18] The results of a DSC study of various salts, obtained in Ref.61, are given in Table 3. In $NF_4.SbF_6$, the phase transformation almost coincides with the start of the decomposition, and cannot be recorded accurately; the estimated temperature of the start of the transformation is 598 K.[61]

Table 3. Phase transformations in TFA salts.

Salt	Temperature of the start of the effect, K	Temperature of the maximum of the effect, K	ΔH, kJ mole^{-1}	ΔS, J mole^{-1} K^{-1}
NF_4BF_4	497	510	7.58	15.27
NF_4PF_6	404	415	5.90	14.50
NF_4AsF_6	418	428	4.62	10.96

The X-ray powder diffraction pattern of the high-temperature form of NF_4AsF_6, obtained in Ref.61, shows that at 439 K the salt has a cubic lattice with parameter 9.13 Å. For one of the NF_4SbF_6 specimens, a cubic lattice with a = 5.66 Å was found at room temperature.[61]

Until recently, there were no published data on the thermodynamic characteristics of TFA salts. By 1979, the only data were for NF_4BF_4, for which the enthalpy of decomposition had been used to determine experimentally the standard enthalpy of formation, equal to −337.4 kcal mole^{-1} (unpublished data, see Refs.27, 55, and 61), from which it follows that the enthalpy of the reaction $F_2(gas) + NF_3(gas) + BF_3(gas) \rightarrow NF_4^+BF_4^-(solid)$ is −34.6 kcal mole^{-1}.[55] From the estimate in Ref.55, $\Delta H_f^0(NF_4AsF_6) \cong -372$ kcal mole^{-1}. In a DSC study of the thermal decomposition of $(NF_4)_2NiF_6$ and NF_4SbF_6, the values −247 kcal mole^{-1} and −393 kcal mole^{-1} respectively were obtained for the standard enthalpies of formation of these salts.[62] The enthalpy of formation of $(NF_4)_2NiF_6$ had previously[39] been estimated as ~−230 kcal mole^{-1}.

DSC and measurement of the heats of hydrolysis of various TFA salts by water and various aqueous solutions were used[61] to find the enthalpies of formation of the salts. The follow-

ing values of ΔH_f^0 (kJ mole^{-1}) for the solid salts were recommended:

NF_4BF_4	-1410 ± 5	NF_4SbF_6	-1669 ± 12
NF_4AsF_6	-1538 ± 11	NF_4PF_6	-1841 ± 7
NF_4GeF_5	-1473 ± 1	$(NF_4)_2GeF_6$	-1606 ± 5

The affinity of NF_3 for the F^+ ion was estimated as -845 kJ mole^{-1}, and the enthalpy of formation of NF_4^+(gas) as 784 kJ mole^{-1}.[61] From the estimate in Ref. 27, the enthalpy of formation of NF_4^+(gas) is 204 kcal mole^{-1} (853 kJ mole^{-1}). Examination of a Born–Haber cycle with the assumption that the crystal lattice energy of $NF_4^+F^-$ is -630 kJ mole^{-1} gave for the enthalpy of the reaction NF_3(gas) + F_2(gas) → $NF_4^+F^-$ (solid) the value 36 ± 40 kJ mole^{-1}.[61] From a comparison of the enthalpies of formation of TFA salts and other fluorine–nitrogen compounds, it was suggested[65] that the formation of $NF_4^+F^-$ may be exothermic.

2. The Chemical Properties of TFA Salts

TFA salts, like the salts of other fluoro-cations,[12] have an extremely high chemical activity. They react vigorously with water, alcohols, hydrocarbons, and other organic compounds, but in the absence of moisture they can be kept for a long time in Teflon, steel, or quartz containers; they are not sensitive to shock if they are not in contact with a substance capable of being oxidised.

Hydrolysis of the salts leads to the quantitative liberation of NF_3, which is extremely stable to hydrolysis and practically insoluble in water. Measurement of the quantity of NF_3 liberated has been made the basis of a method of elemental analysis which has been used repeatedly in all studies of the synthesis of TFA salts. To avoid a vigorous reaction, several millilitres of water are condensed at 77 K into a vessel containing a specimen of the salt with a mass of 0.5–1.0 g, after which the contents of the vessel are slowly heated to room temperature. The gaseous hydrolysis products are either separated by fractional condensation or analysed chromatographically.[56] The quantitative liberation of oxygen in the molar ratio $NF_3:O_2 = 2:1$ when TFA salts are hydrolysed apparently takes place only for NF_4AsF_6.[61] In the hydrolysis of, for example, NF_4SbF_6, 0.45 mole of O_2 is liberated per mole of NF_3.[23] The decrease in the quantity of oxygen liberated is due to the formation of hydrogen peroxide:

$$NF_4^+ + OH^- \rightarrow NF_3 + HOF,\ 2HOF \rightarrow 2HF + O_2,\ HOF + H_2O \rightarrow HF + H_2O_2$$

The ratio $H_2O_2:O_2$ can vary from one experiment to another, depending on the conditions. A different picture is observed in the hydrolysis of NF_4BiF_6, where 0.86 mole O_2 is liberated per mole of NF_3.[21] The BiF_6^- anion oxidises water according to the equation:

$$BiF_6^- + H_2O \rightarrow BiF_3 + HF_2^- + HF + {}^1/_2O_2$$

and this reaction may also be accompanied by the formation of H_2O_2.

The salt $(NF_4)_2NiF_6$ represents a combination of a fluoro-cation with a fluoro-anion, both of which are strong oxidising agents. The neutral compound NiF_4 corresponding to the NiF_6^{2-} anion is unstable, and decomposes to lower fluorides of nickel with the liberation of fluorine. The hydrolysis of the salt is described approximately by the equation

$$2(NF_4)_2NiF_6 + 5H_2O \rightarrow 4NF_3 + 10HF + 2O_2 + OF_2 + 2NiF_2$$

and the ratio $O_2:OF_2$ varies from one experiment to another. An interesting feature is that OF_2 is formed only when NF_4^+ and NiF_6^{2-} are present together, and is not observed in the hydrolysis of NF_4^+ or NiF_6^{2-} taken separately.[39] The appearance of OF_2 in the hydrolysis products may be due to the fluorination of the intermediate product HOF by the NiF_6^{2-} anion:

$$NF_4^+ + 2H_2O \rightarrow HOF + H_3O^+ + NF_3$$
$$HOF + NiF_6^{2-} \rightarrow OF_2 + HF + NiF_4^{2-}$$

In addition to hydrogen peroxide, ozone in quantities of several mole % is always formed as a side product in the hydrolysis of TFA salts by water, even when the hydrolysis is carried out very carefully.[61]

X-Ray electron spectroscopy has detected the formation of ONF_2^+ and NO_3^- in the reaction of NF_4BF_4 with atmospheric moisture:[28]

$$NF_4^+ + H_2O \rightarrow ONF_2^+ + 2HF$$
$$ONF_2^+ + 3H_2O \rightarrow HNO_3 + 2HF + H_3O^+$$

Up to the present, research workers have been interested chiefly in developing methods for the synthesis of TFA salts, so that a fairly large number of these compounds has been obtained. Subsequent studies will probably be directed towards the investigation of the chemical properties of the salts. TFA salts have a fairly high thermal stability, contain a large quantity of active fluorine, and decompose with the liberation of fluorine over a wide temperature range, and their reactions can be carried out at a controlled rate. These features make it possible to regard TFA salts as promising fluorinating agents in inorganic and organic synthesis. Unfortunately, reactions involving TFA salts have been little studied up to the present.

An early study[67] showed that NF_4SbF_6 in HF fluorinates chlorine to give ClF_3 at room temperature. The thermal decomposition of TFA salts with oxygen-containing cations can be used to synthesise hypofluorites.[36,48,63] The reaction of TeF_5OH with NF_4HF_2 at 250 K gives the stable hypofluorite $FOTeF_5$, whose possible existence was previously doubted.[68]

The reactions of NF_4BF_4 with various aromatic compounds have been studied.[69] The choice of NF_4BF_4 as fluorinating agent is determined, in particular, by the fact that its decomposition products NF_3 and BF_3 are inert towards organic compounds at low temperatures. The reactions of NF_4BF_4 take place by an electrophilic substitution mechanism. Benzene, toluene, and nitrobenzene react rapidly with NF_4BF_4 in anhydrous HF at 273 K to give fluoro-substituted derivatives. In the rapid stage, up to four hydrogen atoms are replaced, and the methyl group of toluene is not fluorinated. After the stage involving the rapid replacement of hydrogen atoms, a much slower stage involving the addition of fluorine atoms at the aromatic bonds begins. The reaction of NF_4BF_4 with hexafluorobenzene at 298 K in HF gives C_6F_8 (yield 94%), in which the added F atoms are in the *para*-position to one another.

3. Application of TFA Salts

TFA salts are solid sources of so-called "available fluorine", which is liberated as F_2 and NF_3 on thermal decomposition. The term "available fluorine" is preferable to the term "active fluorine", since the latter refers only to F_2, and not to fluorine in NF_3. Of the TFA compounds known at present, the following have the highest concentrations of available fluorine (%):

$(NF_4)_2XeF_8$	65.6	NF_4XeF_7	59.0
$(NF_4)_2NiF_6$	64.6	$(NF_4)_2TiF_6$	55.6
$(NF_4)_2MnF_6$	59.9	NF_4BF_4	53.7
$(NF_4)_2SiF_6$	59.0		

In the thermal decomposition of 1 cm^3 of solid $(NF_4)_2NiF_6$, the quantity of available fluorine formed is 12% greater than that from the same quantity of liquid fluorine at 86 K.[39] It is only for NF_4XeF_7 and $(NF_4)_2XeF_8$, however, that complete utilisation of the fluorine present is possible; in other cases, some of the fluorine after the decomposition of the salt remains firmly bound to the element present in the anion.

TFA salts have attracted attention as possible components of solid rocket fuels[70] and gas generators for chemical HF–DF lasers.[23,71,72] The high-density fuel mass[70] contains 25–70% TFA salt, 5–50% high-molecular-weight polytetrafluoroethylene, and 10–25% low-molecular-weight polytetrafluoroethylene. The mixture of these components is dispersed in a suitable fluorinated solvent, after which the solvent is removed and the homogenised mass is pressed or extruded.

The operation of the gas generator[23,73] is based on the liberation of F_2 and NF_3 on the combustion of granules containing a TFA salt with a small quantity of fuel, such as Teflon powder. The heat liberated by the combustion of the Teflon brings about the thermal decomposition of the TFA salt and the dissociation of NF_3 to F atoms and F_2 molecules. The decomposition of TFA salts with anionic fluoro-complexes based on volatile and completely or partly monomeric Lewis acids leads to the liberation of these acids into the gas phase, and hence to contamination of the generated mixture. The liberation of the Lewis acid into the gas phase can be prevented by introducing into the mixture a strong Lewis base such as KF, to bind the acid in a complex; the presence of KF, however, leads to a deterioration in the properties of the mixture. An alternative solution to this problem is to create self-sintering compositions. $(NF_4)_2SnF_6$, which on decomposition gives non-volatile polymeric SnF_4,[41,74] and also $N_2F_3SnF_5$,[75] have been proposed as a basis for these mixtures. TFA salts have also been proposed for increasing the detonation pressure of organic explosives.[76]

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