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The Properties and Reactions of Ammonium Fluorides

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The most important thermal properties of ammonium fluorides and fluorometallates, and the reactions of ammonium fluorides with elements, other simple fluorides, oxides, and salts have been reviewed.
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I. INTRODUCTION

Inorganic fluorides play an important role in modern technology. The principal methods for their preparation are based on the use of anhydrous hydrogen fluoride, fluorine, and hydrofluoric acid, and, on a smaller scale, halogen fluorides.[1] The original raw materials for the production of all these reagents are fluorite concentrates, which are treated with sulphuric acid to give hydrogen fluoride or hydrofluoric acid; hydrogen fluoride is decomposed electrolytically to give fluorine, and fluorine is used to synthesise halogen fluorides.[2]

This is not the only scheme, however. Phosphorite and apatite concentrates, which are raw materials for the phosphorus fertiliser industry,[3] are used in addition to fluorite concentrates as an industrial source of fluorine on every scale. A technical by-product (ammonium "fluoride–hydrogen fluoride"), consisting of a mixture of NH_4HF_2 and NH_4F, is now being obtained from the waste gases from the production of superphosphates.[4–8] Pure and technical grade ammonium fluorides can be used to obtain anhydrous hydrogen fluoride and hydrofluoric acid, and also directly for fluorination. They have been used, for example, to extract metals from beryl,[9] ilmenite,[10] pyrochlore,[11] monazite,[12] and scheelite,[13–15] to dissolve metals,[16] to purify fluorides,[17] and to obtain the fluorides of aluminium,[18] zinc,[19] cadmium,[20] and many other metals.

As a result of the exhaustion of rich fluorite deposits, the increase in the production of phosphoric acid and phosphorus fertilisers, and the need to obtain more complete utilisation of fluorine compounds, the volume of fluorides obtained from natural phosphorites, and the importance of ammonium fluorides as fluorinating agents, are increasing continuously.

Ammonium fluorides (anhydrous or in aqueous solution) react with many substances. These reactions are specific, and are accompanied by the formation of ammonium fluorometallates or oxofluorometallates. Increase in the temperature of synthesis or the action of heat on the fluorometallates lead to their thermal decomposition. The characteristic regular features of these reactions and the thermal properties of fluorometallates are important for optimising the conditions for the synthesis of fluorides using ammonium fluorides. Since published data on these topics have not been summarised before, the aim of the present review was to fill this gap.

A special section of the review is devoted to a brief description of the properties of ammonium fluorides, since these properties to a large extent determine the thermal characteristics of ammonium fluorometallates,[21] and it is necessary to supplement the last review, published about 10 years ago.[22]

II. PROPERTIES OF AMMONIUM FLUORIDES

Two compounds of ammonia with hydrogen fluoride, stable under ordinary conditions, are known: NH_4F and NH_4HF_2.

Ammonium fluoride is a colourless substance which forms hexagonal crystals with the wurtzite lattice (space group $P6mc$).[23–27] This distinguishes it from other ammonium halides, which have cubic structures, and is related to the formation of strong hydrogen bonds by NH_4F [28] and is responsible for the fact that the NH_4^+ groups are immobile in the crystal.[29,30] At 23°, the crystal lattice of NH_4F has the parameters: $a = 0.4439$ nm, $c = 0.7165$ nm, $z = 2$.[23,31] The measured and calculated values of the density are 1.002 g cm^{-3} and 1.006 g cm^{-3} respectively.[31]

The boiling point of NH_4F is not known. When heated, NH_4F decomposes according to the equation

$$2\,NH_4F(\text{crystalline}) \rightarrow NH_4HF_2(\text{crystalline}) + NH_3(\text{gas}) \qquad (1)$$

and this also distinguishes it from other ammonium halides. In the temperature range 343–383 K, the decomposition pressure (the equilibrium pressure of the gaseous products) is given by the expression[32]

$$\lg p\ [\text{mmHg}] = -8.82996 + 3022.966/T + 6.87415 \lg T$$

and in the range 404.2–438.9 K it is given by the equation:[33]

$$\lg p\ [\text{mmHg}] = 47.863 - 6582/T - 11.365 \lg T$$

The temperature at which the NH_3 pressure becomes equal to 760 mmHg is ~167 °C.[33–35]

The standard enthalpy of reaction (1), determined calorimetrically, is 19.7 kcal, and the value calculated from tensimetric data is 19.1 kcal.[36] The enthalpy of the reaction

$$NH_4F(\text{crystalline}) \rightarrow NH_3(\text{gas}) + HF(\text{gas})$$

at 298 K is 35.8 ± 0.9 kcal (calorimetry) or 35.1 ± 1.0 kcal (tensimetry).[36] The standard enthalpy of formation of NH_4F [37] is 110.8 ± 0.6 kcal $mole^{-1}$, and the Gibbs free energy $\Delta G^0_{\text{formation}}$ (298 K, NH_4F, crystalline) = −83.28 kcal $mole^{-1}$. The values were obtained assuming that $\Delta H^0_{\text{formation}}$ (298 K, HF, gas) = −64.8 kcal $mole^{-1}$, although the absolute value accepted at present is larger (−65.32 kcal $mole^{-1}$).[38]

The standard heat capacity and entropy of crystalline NH_4F are 15.60 ± 0.02 cal $mole^{-1}$ K^{-1} and 17.20 ± 0.05 cal $mole^{-1}$ K^{-1}.[39] The heat capacity data in Ref.40 do not agree with those in Ref.39, and are apparently erroneous.

Ammonium fluoride is readily soluble in water; its solubility at 25 ° is 45.38%.[41] It is unstable in aqueous solution, and when heated it decomposes with the liberation of NH_3, so that it cannot be obtained by evaporating its solutions;[4,6,7,41] NH_4F is readily soluble in liquid HF, and with NH_4HF_2 it forms a eutectic melting at 109.3°.[35,43]

Ammonium hydrogen fluoride (bifluoride) is a colourless slightly hygroscopic substance, which forms an orthorhombic crystal lattice with parameters $a = 0.840$, $b = 0.816$, $c = 0.367$ nm, $z = 4$, space group *Pman*, calculated density 1.505 g cm^{-3}.[23] The NH_4^+ group is joined to the F atom by hydrogen bonds: each fluorine atom forms two hydrogen bonds with nitrogen atoms, and one with another fluorine atom.[44] The melting point of NH_4HF_2 is 126.45°, and the enthalpy of fusion 4.564 ± 0.002 kcal mole^{-1}.[45]

The decomposition pressure of solid NH_4HF_2 at 343–383 K is given by the equation:[32]

$$\lg p\ [\text{mmHg}] = 5.42446 - 3424.363/T + 1.60995 \lg T$$

Over a wider temperature range (209–399.3 K), the decomposition pressure is given by the expression:[33]

$$\lg p\ [\text{mmHg}] = 6.723 - 3295/T + 6.915 \lg T - 0.00547\,T.$$

The decomposition pressure of liquid NH_4HF_2 in the range 392.5–411.7 K is given by the equation:[33]

$$\lg p\ [\text{mmHg}] = 20.809 - 4256/T - 3.6 \lg T + 0.00028\,T$$

The boiling point of NH_4HF_2 is ~238 °C.[6,7,33,35,46] Liquid NH_4HF_2 has an anomalously high compressibility, compared with the solid phase.[47]

The standard enthalpy of the reaction

$$NH_4HF_2(\text{crystalline}) \rightarrow NH_3(\text{gas}) + 2HF(\text{gas})$$

is 51.9 ± 0.2 kcal mole^{-1} [36] or 51.4 kcal mole^{-1} [48] from calorimetric data, or 51.1 kcal mole^{-1} [32,36] from tensimetric data. In Ref. 37, the value of $\Delta H^0_{\text{formation}}$ (298 K, NH_4HF_2, crystalline) was taken as −191 ± 1 kcal mole^{-1}. From calorimetric data, C_p^0(298 K) = 25.48 cal mole^{-1} K^{-1}, and S^0(298 K) = 27.61 cal mole^{-1} K^{-1}.[23,37,49]

Ammonium hydrogen fluoride is readily soluble in water. At 25° its solubility is 41.50 mass %[41] or 41.08 mass %,[48] and the enthalpy of solution to give a saturated solution is 5.12 ± 0.06 kcal mole^{-1}.[48] The soluion is accompanied by the absorption of heat. The density of the saturated solution at 25° is 1.1273 g cm^{-3}.[50] NH_4HF_2 is also readily soluble in liquid HF. In the NH_4HF_2–HF system, the compounds $NH_4H_3F_4$ and $NH_4H_5F_6$, which melt congruently (melting points 23.2° and −8.0°) and decompose readily with the liberation of HF, are formed.[43]

Thus ammonium hydrogen fluoride is of greatest interest as a fluorinating agent. Ammonium fluoride, when heated to medium temperatures, decomposes to ammonium hydrogen fluoride, and at temperatures above 165–170° it can exist only at an ammonia pressure greater than 1 atm. The "vapours" of ammonium fluorides, that is their thermal decomposition products, contain hydrogen fluoride, and can therefore take part in reactions characteristic of HF.

The properties of ammonium fluorides are such that in the thermal decomposition of ammonium fluorometallates, in addition to the absorption of heat as a result of decomposition to simple fluorides, at temperatures above 165–170° (and more particularly above 235–240°) absorption of heat takes place as a result of the highly endothermic decomposition of ammonium fluoride itself.

III. THERMAL PROPERTIES OF AMMONIUM FLUORO- AND OXOFLUOROMETALLATES

All the transition elements except the heavy actinides, and also beryllium, magnesium, and the non-transition elements of groups III–V except carbon and nitrogen, can form ammonium fluorometallates. Transition elements from the central part of the periodic system (mainly metals of groups V–VII), and also uranium and the non-transition elements of group V, also form oxofluorometallates.

Subsequent sections examine the compositions of the compounds and give the sequence of stages in the thermal decomposition, the temperatures of the separate stages, and the enthalpies of formation and other thermodynamic parameters of ammonium fluoro- and oxofluorometallates, except for the characteristics of the low-temperature phase transformations.

1. Compounds of Non-Transition Elements

Beryllium forms $(NH_4)_2BeF_4$, NH_4BeF_4, and $NH_4Be_2F_5$.[51–53] The tetrafluoroberyllate decomposes with the successive formation of NH_4BeF_3, $NH_4Be_2F_5$, and BeF_2; the minima of the endothermic effects on the differential thermal analysis (DTA) curves for the first two stages lie at 300° and 360°;[53] under isothermal conditions, the decomposition can be carried out at lower temperatures.[52] The standard enthalpy of formation of $(NH_4)_2BeF_4$ is −475.7 ± 1.5 kcal mole^{-1},[54,55] the Gibbs free energy $\Delta G^0_{\text{formation}} = 413.1$ kcal mole^{-1},[55] $S^0 = 59.8 \pm 0.6$ cal mole^{-1} K^{-1}, and $C_p^0 = 50.4 \pm 0.5$ cal mole^{-1} K^{-1}.[55,56]

Magnesium forms $MgF_2.2NH_4F.2H_2O$, $MgF_2.2NH_4F$, and $MgF_2.NH_4F$. Dehydration takes place at 110°;[57] $MgF_2.2NH_4F$ decomposes to $MgF_2.NH_4F$ and then to MgF_2 at 215–220° and 280–285° respectively.[57–59]

The fluoroborates NH_4BF_4 and $NH_4BF_4.NH_4F$,[60] and a large number of oxofluoro- and hydroxofluoroborates, for example $NH_4B(OH)_2F_2$, $NH_4B(OH)_3F$, NH_4BOF_4 or $(NH_4)_3B_3O_3F_{12}$, $(NH_4)_2BOF_3$, $(NH_4)_2B_3O_3(OH)F_4$, and $(NH_4)_2B_4OF_{12}$,[61,62] have been synthesised.

The thermogram of ammonium tetrafluoroborate shows endothermic effects with minima at 176 and 346°, corresponding to its polymorphic transformation and decomposition (sublimation).[61] According to Refs. 63 and 64, the temperature of the transformation is 205 ± 3°, and according to Ref. 65 it is 208 ± 2°. The enthalpy of the transformation is 2.4 ± 0.1 kcal mole^{-1}.[65] The decomposition pressure is given by the equation[66]

$$\lg p\ [\text{mmHg}] = 6.82 - 2469/T$$

so that the decomposition temperature is close to 354°, and the enthalpy of decomposition is close to 33.9 kcal mole^{-1}. The standard values of C_p^0 and S^0 for NH_4BF_4 are 32.09 cal mole^{-1} K^{-1} and 46.77 cal mole^{-1} K^{-1}.[67] According to Refs. 65 and 66 and the estimates of the present authors, $\Delta H^0_{\text{formation}}$ (298 K, NH_4BF_4, crysallline) ≦ −381.4 kcal mole^{-1}, $\Delta G^0_{\text{formation}}$ (298 K, NH_4BF_4, crystalline) ≦ −341 kcal mole^{-1}.

The reaction

$$(NH_4)_2B_3O_3(OH)F_4 \rightarrow NH_4BF_4 + B_2O_3 + NH_3 + H_2O$$

takes place at 200–250°.[68]

Aluminium, gallium and indium form higher fluorometallates with the same composition, $(NH_4)_3MF_6$. The hexafluoroaluminate decomposes in two stages with the successive formation of NH_4AlF_4 and γ-AlF_3.[69,72] It has been reported[7] that the thermal decomposition also gives the compound $NH_4AL_2F_7$, and

the compound $(NH_4)_2HAlF_6.H_2O$ has been described in a patent.[73]

The reactions

$$(NH_4)_3AlF_6(\text{crystalline}) \rightarrow NH_4AlF_4(\text{crystalline}) + 2NH_3(\text{gas}) + 2HF(\text{gas})$$
$$NH_4AlF_4(\text{crystalline}) \rightarrow \gamma\text{-}AlF_3 + NH_3(\text{gas}) + HF(\text{gas})$$

give endothermic effects at 305° and 450°; the equilibrium constants of these reactions are given by the equations:[71,72]

$$\lg K_p = 30.455 - 18182/T \quad (507 \leqslant T \leqslant 578\ \text{K})$$
$$\lg K_p = 17.240 - 13071/T \quad (663 \leqslant T \leqslant 731\ \text{K})$$

The mean enthalpies of decomposition of $(NH_4)_3AlF_6$ and NH_4AlF_4 are 83 ± 1 kcal mole^{-1} and 60 ± 1 kcal mole^{-1}, and the enthalpies of formation −731.3 kcal mole^{-1} and −496.6 kcal mole^{-1} respectively.[64]

According to Refs.74 and 75, $(NH_4)_2GaF_5.H_2O$ is dehydrated at 100–150°, and decomposes with the successive removal of two NH_4F molecules at 350° and 450°. Ammonium hexafluoroindate is converted at 280° into the pentafluoroindate, which then decomposes in two stages at 320° and 400°.[76] In Ref.77, much lower temperatures are given for the start of the separate stages (120, 170, and 185°). These data are less accurate, since if NH_4F were removed at such low temperatures, the thermograms would also have shown the effect at 238° corresponding to the "boiling" of NH_4HF_2. $(NH_4)_5In_3F_{14}$, $NH_4In_2F_7$, and $NH_4In_3F_{10}$ have been obtained directly from the simple fluorides.[78] $(NH_4)_2Ga(OH)_2F_3$ and $(NH_4)_2In(OH)_2F_3$ have also been described.[79]

Silicon forms the double salt $(NH_4)_2SiF_6.NH_4F$, which according to thermographic data decompose above 190°, and also ammonium hexafluorosilicate, which decompose above 300°.[80,81] The vapour pressure over $(NH_4)_2SiF_6$ at 532–592 K is given by the equation:[81]

$$\lg p\ [\text{mmHg}] = 9.94 - 4170/T$$

If it is assumed that $(NH_4)_2SiF_6$ decomposes to SiF_4, NH_3, and HF, the values of the enthalpies of decomposition and formation of $(NH_4)_2SiF_6$ from the elements are 95.4 kcal mole^{-1} and −633.1 kcal mole^{-1} respectively. The standard enthalpy of formation, determined calorimetrically, is −642.6 kcal mole^{-1}, the Gibbs free energy is −567.4 kcal mole^{-1}, $S^0 = 68.0$ cal mole^{-1} K^{-1}, and $C_p^0 = 59.25$ cal mole^{-1} K^{-1}.[82,83]

Germanium forms compounds similar to the silicon compounds: $(NH_4)_2GeF_6.NH_4F$ and $(NH_4)_2GeF_4$.[64] The hexafluorogermanate decomposes in a single stage with a minimum on the DTA curve at 400°.[85]

Tin(II) forms the fluorostannate $(NH_4)_2SnF_4.2H_2O$,[86] described as early as 1886, and also NH_4SnF_3 and $NH_4Sn_2F_5$.[87] The last two compounds decompose in an evacuated vessel at 160–200°.

Tin(IV) forms the fluorides $(NH_4)_4SnF_8$, $(NH_4)_2SnF_6$ (described in 1859),[86] $(NH_4)_2SnF_6.NH_4F$, $(NH_4)_2Sn(OH)F_5$, $(NH_4)_2Sn(OH)_2F_4.H_2O$, $(NH_4)_4Sn_2OF_{10}$, and $(NH_4)_3HSn_2OF_{10}$.[88] The thermal decomposition of $(NH_4)_2SnF_6.NH_4F$ takes place at 320°, and $(NH_4)_2SnF_6$ decomposes in two stages, at 410° and 500°[85] (according to Ref.89, the hexafluorostannate(IV) decomposes at 210°). The hydroxofluorostannates(II) decompose in three stages in the range 80–360°.[88]

Phosphorus(V) forms the fluoro-acids hexafluorophosphoric acid HPF_6, difluorophosphoric acid HPO_2F_2, and monofluorophosphoric acid H_2PO_3F, all of which form ammonium salts;[86] $NH_4PF_6.NH_4F$ has also been described.[90] Ammonium difluorophosphate and monofluorophosphate are thermally stable at 135°; the monofluorophosphate decomposes at 220° to NH_4HPO_3F, which melts at ~226°.[91,92]

Arsenic(V) gives similar compounds: NH_4AsF_6,[93] $NH_4As.(OH)F_5$, $NH_4As(OH)_2F_4$,[94] and $(NH_4)_2AsO_2F_2$.[95]

Antimony(III) gives the following compounds with alkali metal and ammonium cations: M_2SbF_5, $MSbF_4$, MSb_2F_7, and MSb_4F_{13};[96,97] *antimony(V)* forms M_2SbF_7 and $MSbF_6$. The compound $(NH_4)_2SbF_5$ undergoes phase transformations at temperatures between −23° and 17°.[98]

Bismuth(III) forms NH_4BiF_4.[86]

The melting point of NH_4SO_3F is 245°.[96]

2. Compounds of the Transition Elements

Copper(II) forms the compounds $(NH_4)_2CuF_4$ and NH_4CuF_3, which separate from aqueous solutions as the hydrates,[86] but which can also be obtained anhydrous.[99] The decomposition of NH_4CuF_3 gives a minimum on the DTA curve at 250°, and is accompanied by the absorption of 34.2 kcal mole^{-1}.[100]

Zinc and cadmium form the fluorides $(NH_4)_2ZnF_4.2H_2O$, $(NH_4)_2CdF_4.2H_2O$,[101] NH_4ZnF_3, NH_4CdF_3;[99,100] the anhydrous fluorides $(NH_4)_2CdF_4$ and $(NH_4)_3Cd_2F_7$ have also been described.[102] The decomposition temperatures of the trifluorometallates of zinc and cadmium are 250° and 205°, and the enthalpies of decomposition are 33.9 kcal mole^{-1} and 33.3 kcal mole^{-1} respectively.[100] As in the case of the fluorocuprate, the values obtained for the enthalpy of decomposition are lower than the value for the decomposition of NH_4F itself, so that they must be regarded with caution.

Scandium forms complex compounds with compositions corresponding to those of the aluminium compounds. Ammonium hexafluoroscandate decomposes at 260–290° and 340–350° with the successive formation of NH_4ScF_4 and ScF_3.[103–105]

The equilibria for the reactions

$$(NH_4)_3ScF_6(\text{crystalline}) \rightarrow NH_4ScF_4(\text{crystalline}) + 2NH_3(\text{gas}) + 2HF(\text{gas})$$
$$NH_4ScF_4(\text{crystalline}) \rightarrow ScF_3(\text{crystalline}) + NH_3(\text{gas}) + HF(\text{gas})$$

at 448–492 K and 563–605 K respectively are described by the equations:[106]

$$\lg K_p = 29.8 - 15400/T$$
$$\lg K_p = 16.0 - 10200/T$$

The mean enthalpies of decomposition of $(NH_4)_3ScF_6$ and NH_4ScF_4 are 70.5 kcal mole^{-1} and 46.7 kcal mole^{-1} respectively. Since they are independent of temperature, and $\Delta H^0_{\text{formation}}(298\ \text{K}, ScF_3, \text{crystalline}) = -394 \pm 2$ kcal mole^{-1},[107] the standard enthalpies of formation of the corresponding ammonium fluoroscandates can be found (−737 ± 7 kcal mole^{-1} and −517 ± 5 kcal mole^{-1}).

Yttrium forms the compound $NH_4Y_2F_7.NH_4F$, which decomposes in two stages, at 260° and 380°, to give $NH_4Y_2F_7$ and YF_3.[106] The equilibrium for the reaction

$$NH_4Y_2F_7(\text{crystalline}) \rightarrow 2YF_3(\text{crystalline}) + NH_3(\text{gas}) + HF(\text{gas})$$

at 601–653 K is described by the equation:

$$\lg K_p = 12.9 - 9000/T$$

Thus the mean enthalpy of decomposition is ~41 kcal mole^{-1}.

In the systems LnF_3–NH_4F–H_2O (Ln = lanthanum or a lanthanide), crystalline phases with the most varied compositions have been detected.[108,109] The compounds identified

most reliably are $(NH_4)_3LnF_6$, $(NH_4)_3Ln_2F_9$, NH_4LnF_4 (or $(NH_4Ln_2F_7.NH_4F)$, and $NH_4Ln_2F_7$.[110–114] According to Ref. 110, many lanthanides also form the compounds $(NH_4)_3Ln_2F_9.H_2O$. La, Pr, Nd, Sm, Eu, Gd, and Tb form tetrafluorometallates NH_4LnF_4, which decompose directly to LnF_3; Dy, Ho, Er, Tm, Yb, and Lu form $NH_4Ln_2F_7.NH_4F$ or $(NH_4)_3.Ln_2F_9$, which decompose at 250–270° to $NH_4Ln_2F_7$, and at 350° to LnF_3.[110,111]

Table 1. Characteristics of the decomposition of NH_4LnF_4.

Ln	T, K	$\lg K_p = A - B/T$		ΔH_T^0, kcal mole^{-1}
		A	B	
Pr	478—516	18.556	9 980	45.6
Nd	478—523	18.551	10 201	46.7
Sm	500—528	17.070	9 780	44.7
Gd	497—545	19.150	10 858	49.7

The decomposition pressures and enthalpies of decomposition of various Ln compounds are given in Table 1.[111]

The equilibrium for the reaction

$$NH_4Dy_2F_7(\text{crystalline}) \rightarrow 2DyF_3(\text{crystalline}) + NH_3(\text{gas}) + HF(\text{gas})$$

at 584–614 K is described by the expression:

$$\lg K_p = 32.003 - 20122/T$$

The enthalpy of the reaction is 46.0 kcal mole^{-1}.[111]

The thermal decomposition of NH_4EuF_4 takes place at 258° with the absorption of 21.8 ± 0.1 kcal mole^{-1}.[114] The enthalpy of the process was found in Ref.114 by differential scanning calorimetry, and is apparently too low.

The compounds $(NH_4)_3Ln_2F_9.H_2O$, where Ln = La, Pr, Sm, and Er, are dehydrated at 100°, and then decompose to $NH_4Ln_2F_7$ (at 200–215° for Sm and Eu) or to NH_4LnF_4 (at 170–185° for La and Pr). For the La Salt, the dehydration and the removal of NH_4F take place simultaneously.[109] According to Ref.109, the compounds $(NH_4)_2Ln_3F_{11}.H_2O$, where Ln = Dy, Ho, and Er, also exist, and at 60–120° decompose to $(NH_4)_2Ln_3F_{11}$ and then to $NH_4Ln_3F_{10}$ (at 204° for Ho) or to the trifluorides (at 159° for Dy and at 316° for Er). These data are apparently contradictory. For example, it is not clear why the trifluoride is formed from $(NH_4)_3Dy_2F_7$ at temperatures above 350°, but is formed from $NH_4Dy_3F_{10}$ even at 159°.

According to Ref.113, $(NH_4)_3NdF_6$ decomposes to NH_4NdF_4 at 350–400° and to NdF_3 at ~500°. The decomposition of $(NH_4)_3Ce_2F_9$ at 430° in a vacuum leads to the successive formation of NH_4CeF_4 and CeF_3.[115] According to Ref.116, NH_4CeF_4 decomposes to CeF_3 at 400–450°.

Cerium is unique among the lanthanides in its ability to form Ce^{IV} compounds. $(NH_4)_4CeF_8$, $(NH_4)_3CeF_7$, $(NH_4)_2CeF_6$, NH_4CeF_5, and $(NH_4)_7Ce_6F_{31}$ are known.[117–119] The decomposition of the most complex compounds begins at 108°, and is complete at 430° with the formation of CeF_3. Anhydrous CeF_4 may be formed at 300°.[118]

The actinides(IV) Th, Pa, U, Np, Pu, and Am have properties similar to those of Ce^{IV}. For each of these elements, the most complex ammonium fluorometallates are $(NH_4)_4AnF_8$ (where An = actinide), which decompose successively to $(NH_4)_2AnF_6$, $NH_4Th_2F_9$, $NH_4Th_2F_9.H_2O$,[125] and $7NH_4F.2ThF_4.H_2O$.[126]

Thorium forms $(NH_4)_4ThF_8$, which gives slightly different decomposition products. $(NH_4)_3ThF_7$,[124] $(NH_4)_2ThF_6$, $NH_4Th_2F_9$, $NH_4Th_2F_9.H_2O$,[125] and $7NH_4F.2ThF_4.H_2O$ [126] have been described.

Uranium forms the fluorometallate series $UF_6.nNH_4F$, $UF_5.nNH_4F$, and $UF_4.nNH_4F$. Ammonium oxofluorouranates(VI), or ammonium uranyl fluorides, are also known.

Only one ammonium fluorouranate(VI) has been obtained: NH_4UF_7.[124–126] According to Ref.127, its thermal decomposition takes place in three stages, involving the exothermic reduction of U^{VI} to U^V at 100–130°, the decomposition of NH_4F at 200–320°, and reduction to UF_4 at 350–450°. NH_4UF_6 is formed in the first stage.[128]

The UF_5–NH_4F system gives $(NH_4)_3UF_8$, $(NH_4)_2UF_7$, and NH_4UF_6.[128,129] According to Ref.130, the last compound is stable in a vacuum at 150°, although in Refs.131 and 132, vigorous exothermic decomposition is reported. In Ref.131, the mechanism of the decomposition was described by the equation

$$NH_4UF_6 \rightarrow UF_4 + NH_4F + {}^1/_2F_2$$

which has not been rigorously proved, however, since fluorine and NH_4F are incompatible (see section IV).

U^{IV} compounds have been most extensively studied. Studies of the system UF_4–NH_4F and UF_4–NH_4F–H_2O [121,133,134] have made it possible to characterise $(NH_4)_4UF_8$, $(NH_4)_2UF_6$, $7NH_4F.6UF_4$, NH_4UF_5, and $NH_4F.3UF_4$. The reported[135] existence of anhydrous $(NH_4)_3UF_7$, $NH_4U_2F_9$, $NH_4U_4F_{17}$, and $NH_4U_6F_{25}$ is not sufficiently well-founded.

The octafluorouranate(IV) is stable in air to ~100°,[121] the hexafluorouranate(IV) to 225–250°, the pentafluorouranate(IV) to 350°, and $NH_4F.3UF_4$ to 450°.[136] In a vacuum, $(NH_4)_2UF_6$, NH_4UF_5, and $NH_4F.3UF_4$ decompose at 180, 290, and 400°.[121] The reported formation of HUF_5 from NH_4UF_5 at 320–360° [137] has not been confirmed.

The enthalpies of formation of $(NH_4)_4UF_8$, $(NH_4)_2UF_6$, $7NH_4F.6UF_4$, and $NH_4F.3UF_4$ are −941 ± 4, −413 ± 20, and −1510 ± 10 kcal mole^{-1}. The results[138] were calculated using the most reliable value for the standard enthalpy of formation of UF_4.[107]

The estimated values of the Gibbs free energy of formation of the compounds, given in Ref.119, are inaccurate. According to more reliable data,[139] for the formation of $(NH_4)_4UF_8$, $(NH_4)_2UF_6$, and $7NH_4F.6UF_4$ from the simple crystalline fluorides, the values of the change in the Gibbs free energy are −23.5, −20.9, and −97.1 kcal mole^{-1} respectively.

In the systems UO_2F_2–NH_4F–H_2O [140,141] and UO_3–NH_4F–H_2O,[142,143] the most stable complex compound is $(NH_4)_3UO_2F_5$. Its thermal decomposition takes place in two stages

$$(NH_4)_3UO_2F_5(\text{crystalline}) \rightarrow {}^1/_2NH_4(UO_2)_2F_5(\text{crystalline}) + {}^5/_2NH_3(\text{gas}) + {}^5/_2HF(\text{gas})$$

$$^1/_2NH_4(UO_2)_2F_5(\text{crystalline}) \rightarrow UO_2F_2(\text{crystalline}) + {}^1/_2NH_3(\text{gas}) + {}^1/_2HF(\text{gas})$$

and the decomposition pressures are given by the equations:[144]

$$\lg p, [\text{atm}] = 8.01 - 4468/T \quad (516 \leqslant T \leqslant 558\ \text{K})$$

$$\lg p, [\text{atm}] = 6.927 - 4878/T \quad (647 \leqslant T \leqslant 703\ \text{K})$$

The mean enthalpies of decomposition are 102 ± 3 kcal mole^{-1} and 22 ± 2 kcal mole^{-1}.

The enthalpies of formation of $(NH_4)_3UO_2F_5$ and $NH_4.(UO_2)_2F_5$, found from tensimetric data,[144] are −749.4 kcal mole^{-1} and −918.0 kcal mole^{-1}, and coincide with the

calorimetric data (−748.9 ± 2.2 kcal mole^{-1} and −921.5 ± 2.8 kcal mole^{-1} from Refs.107 and 145, or −753 kcal mole^{-1} and −919 kcal mole^{-1} from Ref.138). The above values of the enthalpies of formation of oxofluorouranates(VI) were refined slightly by the present authors using published data[107] for UO_2F_2.

Under certain strictly defined conditions, ammonium oxofluorouranates(VI) can apparently sublime, and this has been made the basis of a method for extracting uranium from its ores.[146] These conditions cannot be determined from the thermal characteristics of salts and UO_2F_2 available at present.[147]

The hydrate $NH_4(UO_2)_2F_5.4H_2O$ melts at 64.5° and decomposes to give the trihydrate, which melts at 98.7° and decomposes to the anhydrous salt.[141] The enthalpies of formation of the hydrates have been measured.[148]

The data in Ref.149 on the formation of $NH_4UO_2F_3$ have not been confirmed experimentally by other workers, and are unreliable; the existence of an exothermic effect in the decomposition of pure $NH_4(UO_2)_2F_5$ [150] appears unlikely.

Neptunium forms fluorometallates in which the oxidation state of the metal is +4,[122] although the existence of neptunium(V) compounds is possible. The thermal decomposition begins at ~120° for $(NH_4)_4NpF_8$, 220° for $(NH_4)_2NpF_6$, 280° for $7NH_4F.6NpF_4$, and 300° for NH_4NpF_5. The most stable compound (up to ~600–650°) is $NH_3Np_3F_{13}$, which decomposes to the tetrafluoride.

Plutonium fluorides have properties similar to those of uranium fluorides. The thermal decomposition of ammonium octafluoroplutonate(IV) in air at 160° gives the hexafluoroplutonate, and at 210° the compound $7NH_4F.6PuF_4$; the latter is converted into NH_4PuF_5 in oxygen at 220°, into $NH_4F.3PuF_4$ in a vacuum at 290°, and into PuF_4 in a vacuum at 330°.[121] The formation of PuF_4 in the decomposition of ammonium fluoroplutonates(IV) has been confirmed;[151,152] the hydrate $NH_4PuF_5.2H_2O$ was not detected. Other workers,[119,153], however, report that the decomposition is complete with the formation of plutonium trifluoride. PuF_4 can apparently be reduced by ammonia, and the composition of the final product depends on the thermal decomposition conditions.

Published data[154] indicate that the thermal decomposition of ammonium fluorocurates(IV) also gives the trifluoride.

The transition metals of group IV in the oxidation state +4 do not form such a wide variety of fluorometallates as the actinides.

Titanium(IV) forms the compounds $(NH_4)_2TiF_6.NH_4F$,[155,156] $(NH_4)_2TiF_6$,[157] and NH_4TiF_5,[158] the first two of which were described in the middle of the last century by Marignac. Their decomposition in an inert medium is accompanied by the transfer of titanium to the gas phase (to the extent of 75% from published thermogravimetric curves,[85] 85% according to Ref.157, more than 95% according to Ref.158, and 100% according to Ref.159). The differences in the values obtained are due to differences in the moisture content of the gases surrounding the specimens, and the tendency of fluorotitanates to undergo hydrolysis.[160–162] Ammonium heptafluorotitanate decomposes slowly at temperatures above 150°, the hexafluorotitanate above 250°, and the pentafluorotitanate above 280°.

The enthalpy of formation of $(NH_4)_2TiF_6$ from the simple crystalline fluorides at 25° is −30.0 ± 1.0 kcal mole^{-1},[163] and that from the elements (using published data[164] for TiF_4) is −645.8 ± 2.6 kcal mole^{-1}.

Ammonium oxofluorotitanate $(NH_4)_2TiOF_4$,[158] peroxofluorotitanate $(NH_4)_3Ti(O_2)F_5$,[163,166] and fluorotitanate(III) NH_4TiF_4 also exist. The last compound decomposes to non-volatile titanium trifluoride at 600° in a stream of Ar or H_2.[167]

Zirconium(IV) and hafnium(IV) form $(NH_4)_3MF_7$, $(NH_4)_2MF_6$, and NH_4MF_5, whose thermal decomposition has been studied in detail.[157,168–173] The DTA curves show endothermic effects with minima at 315, 365, and 435° for $(NH_4)_3ZrF_7$, and at 300, 360, and 430° for $(NH_4)_3HfF_7$. Each minimum corresponds to the removal of 1 mole of ammonium fluoride. The equilibrium values of the decomposition pressures and enthalpies of decomposition of the zirconium and hafnium compounds are given in Table 2.

Table 2. Characteristics of the decomposition of Zr and Hf salts.[172]

Reactions	T, K	$\lg K_p = A - B/T$		ΔH^0_T, kcal mole^{-1}
		A	B	
3:1 → 2:1	525–567	13.79	8 330	38.1
2:1 → 1:1	578–625	12.72	8 500	38.8
1:1 → ZrF_4	640–687	14.42	10 500	48.1
3:1 → 2:1	518–565	16.28	8 710	44.4
2:1 → 1:1	578–625	14.60	9 750	44.6
1:1 → HfF_4	630–688	18.85	11 270	51.5

Note. 3 : 1, 2 : 1, and 1 : 1 represent respectively the formulae $(NH_4)_3MF_7$, $(NH_4)_2MF_6$, and MH_4MF_5, where M = Zr or Hf.

The enthalpies of the successive addition of crystalline NH_4F to crystallise ZrF_4, found from these values, are −12.9, −3.6, and 3.0 kcal mole^{-1}, which show satisfactory agreement with the calorimetric data (−13.5, −5.4, and −0.9 kcal mole^{-1}).[174] Thus the standard enthalpies of formation of $(NH_4)_3ZrF_7$, $(NH_4)_2ZrF_6$, and NH_4ZrF_5 −809.2 ± 0.7, −697.5 ± 0.7, and −581.2 ± 0.7 kcal mole^{-1} respectively. The Gibbs free energies are −703.6, −619.0, and −529.9 kcal mole^{-1} respectively (the absolute values of these quantities given in Ref. 164 are lower by ~5 kcal mole^{-1}).

For hafnium, the mean enthalpies of the successive addition of NH_4F to the tetrafluoride are −16.8, −9.4, and −8.6 kcal mole^{-1},[172] and the enthalpies of formation of $(NH_4)_3HfF_7$, $(NH_4)_2HfF_6$, and NH_4HfF_5 are −829.2, −709.6, and −589.2 kcal mole^{-1} respectively.

The enthalpy of the phase transformation of $(NH_4)_2ZrF_6$ at 138 °C is 1.7 kcal mole^{-1},[174,175] and the enthalpies of the transformations of $(NH_4)_2HfF_6$ at 140 °C and 240 °C are −1.39 kcal mole^{-1} and 1.18 kcal mole^{-1}.[175] The existence of the transformations influences the kinetics of the thermal decomposition.[173] The hydrate $NH_2ZrF_5.H_2O$ is also known; its standard enthalpy of formation is −651.97 ± 0.6 kcal mole^{-1}.[176]

The transition elements of group V have three characteristic oxidation states: +5, +4, and +3, so that in principle they can form compounds of the series $MF_5.nNH_4F$, $MOF_3.nNH_4F$, $MO_2F.nNH_4F$, $MF_4.nNH_4F$, $MOF_2.nNH_4F$, and $MF_3.nNH_4F$.

Vanadium forms compounds of all the series except $VF_4.nNH_4F$. Ammonium hexafluorovanadate(V) is very hygroscopic, and apparently thermally unstable.[177] Ammonium dioxotetrafluorovanadate is extremely unstable, and decomposes even at 50–60°. When this compound is heated,

$(NH_4)_2VO_2F_3$ is formed at 140°, $(NH_4)_3V_2O_4F_5$ at 160°, and $NH_4VO_2F_2$ at 180°.[178] The last compound begins to decompose at 150°[179] to give first an unidentified oxofluorovanadate, and then at 360° an oxide fluoride in which the oxidation state of vanadium is lower than +5[178] (the decomposition in air is complete with the formation of a product which does not contain fluorine).[180]

According to Ref.85, the oxofluorovanadate(IV) $(NH_4)_3VOF_5$ decomposes to give $(NH_4)_2VOF_4$, NH_4VOF_3, and VOF_2 successively at 250–300, 320–360, and 390–430°. The compound $NH_4V_3O_6F$ is also known;[181] the thermal decomposition of $(NH_4)_3VF_6$ begins at 250°, passes through stages involving the formation of $(NH_4)_2VF_5$, $VF_3.0.3NH_4F$, and VF_3, containing 0.1–1.5% NH_4^+, and is complete at 650–700° with the formation of the trifluoride.[182]

Niobium forms only ammonium oxofluoroniobates(V). The thermal decomposition of $(NH_4)_3NbOF_6$ gives $(NH_4)_2NbOF_5$, NH_4NbOF_4, and NbO_2F successively at 255, 320, and 420°.[183] It was also suggested[183] that the decomposition of NH_4NbOF_4 gives the oxide fluoride $NbOF_3$, which then decomposes to NbO_2F and NbF_5.

The most complex ammonium fluorometallate formed by tantalum is $(NH_4)_3TaF_8$, which is unstable even at 100°.[184] The more stable $(NH_4)_2TaF_7$ decomposes at 310° and 390° to give NH_4TaF_6, and then a mixture of TaF_5, NH_3, and HF.[184] The presence of water vapour leads to hydrolysis to TaO_2F and to a decrease in the quantity of tantalum volatilised. The enthalpies of formation of $(NH_4)_2TaF_7$ from the crystalline fluorides and from the elements at 298.15 K are −31.4 kcal mole^{-1} and −708.1 ± 0.4 kcal mole^{-1} respectively.[185]

According to Ref.183, the course of the thermal decomposition of $(NH_4)_3TaOF_6$ is similar to that described above for niobium, except that the separate stages take place at 175, 290, and 465°. It was suggested[183] that crystalline $TaOF_3$ exists in the temperature range 320–465°, but this appears unlikely, since attempts by other workers to isolate this compound have been unsuccessful. Heating moist NH_4TaOF_4 in air at 1000° gives mainly Ta_2O_5.[186] More complex oxofluoroniobates and oxofluorotantalates have also been isolated.[183]

Chromium forms NH_4CrO_3F,[187,188] $(NH_4)_3CrF_6$, $(NH_4)_2CrF_5.2H_2O$,[189,190] and NH_4CrF_4.[191] Ammines of chromium trifluoride are also known.[192]

Molybdenum forms the compounds NH_4MoF_7,[124,193,194] $NH_4Mo_2F_{13}$,[194] NH_4MoF_6, NH_4MoF_5, $(NH_4HF_2)_2MoF_5$,[196] NH_4MoOF_5,[194] $6NH_4F.7MoOF_4$,[195] $(NH_4)_3MoO_2F_5$, $(NH_4)_2MoO_2F_4$, $NH_4MoO_2F_3$,[196–199] $(NH_4)_3MoO_3F_3$, and $(NH_4)_2MoO_3F_2$.[200–201] The properties of many of the compounds have been reviewed.[202]

NH_4MoF_7 decomposes at 70, 145, and 380° according to the scheme:[203]

$$NH_4MoF_7 \rightarrow NH_4MoF_6 \rightarrow NH_4MoF_5 + MoF_5 + NH_4F \rightarrow MoF_3 + Mo_2N_3$$

The compound $6NH_4F.7MoOF_4$ (and probably NH_4MoOF_5) is stable up to 190°, although the most intense endothermic effect on the DTA curve is observed at 420°;[195] its decomposition products were not identified. The salt $(NH_4)_3MoO_2F_5$ is unstable, and decomposes even at 90–115° to give $(NH_4)_2.MoO_2F_4$; the latter is converted into $NH_4MoO_2F_3$ at 210° to 230°,[196] and at temperatures above 270–300° into a non-volatile molybdenum oxide fluoride containing 64.2% Mo, 10.9% F, and 2.0% N.[204]

Data on the thermal decomposition of $(NH_4)_2MoO_3F_2$ and $(NH_4)_3MoO_3F_3$ indicate that they have a high thermal stability; the first compound decomposes at 375°, and the second at 300°.[202]

Tungsten forms fewer ammonium fluorometallates than molybdenum. NH_4WF_7,[124] $(NH_4)_3WO_2F_5$, $(NH_4)_2WO_2F_4$, $(NH_4)_3W_2O_4F_7$,[197,198] $(NH_4)_3WO_3F_3$, $(NH_4)_2WO_3F_2$, $9NH_4F.5WO_3$, and NH_4WO_3F[205] have been characterised.

The thermal decomposition of $(NH_4)_3WO_2F_5$ gives $(NH_4)_2.WO_2F_4$, $(NH_4)_3W_2O_4F_7$, and $NH_4W_2O_2F_7$ successively at 240, 285, and 330°. The last compound decomposes at 380° to give an oxide fluoride, which was first assigned the composition WOF_2,[197,198] and then $W_2O_4F.n(N_mOF)$.[204,206] It is most probably an oxide fluoride bronze AW_2O_4F, in which the inserted cations A are NH_4^+, H_3O^+, and H_2F^+.[207]

Ammonium peroxofluoromolybdates(VI) and peroxofluorotungstates(VI) are also known.[208,209]

Manganese forms the fluorides $(NH_4)_3MnF_6$, $(NH_4)_2MnF_5$, and NH_4MnF_4,[210–212] and also NH_4MnF_3.[100] When heated, $(NH_4)_3MnF_3$ gives endothermic effects at 92, 115, and 203°. The last of these is due to decomposition to $(NH_4)_2MnF_5$, which in turn decomposes at 240–285° and 305–320° to NH_4MnF_4 and MNF_2. NH_4MnF_3 decomposes at 310° with the absorption of 38.5 ± 0.5 kcal mole^{-1}.[100]

Technetium and rhenium form the compounds $(NH_4)_2MF_6$, which decompose in an inert medium or in a vacuum at 300°.[213] The formation of nitride fluorides in the decomposition, postulated in Ref.213, was refuted by other workers.[214]

Stable compounds are formed by iron in two oxidation states: +3 and +2. The thermal decomposition of $(NH_4)_3FeF_6$ gives NH_4FeF_6 at 280°, and iron trifluoride at 410°.[69] In addition, the appearance of phases with the composition $(NH_4)_xFeF_{3+x}$, where $x = 0.7–0.8$ and 0.1–0.2, has been observed. The standard heat capacity of $(NH_4)_3FeF_6$ is 70.5 ± 1.7 cal mole^{-1} K^{-1}.[215]

The composition of ammonium hexafluoroferrate(III), isolated from aqueous solutions, does not correspond to the traditionally accepted formula. According to Ref.216, this compound has the composition $(NH_4)_{2.6}FeF_{5.6}.0.4H_2O$. The thermal properties of NH_4FeF_3[217,318] have not been studied. The existence of $NH_4Fe^{2+}Fe^{3+}F_6$ is possible.

The decomposition of $(NH_4)_2CoF_4$ gives an endothermic effect at 260°.[219] The NH_4CoF_3 formed decomposes at 290,[100] 310,[192] of 335°[219] to give CoF_2. The enthalpy of decomposition of NH_4CoF_3 is 30.4 ± 0.5 kcal mole^{-1}.[100]

Nickel forms the compounds $(NH_4)_2NiF_4$[219,220] and NH_4NiF_3. The first compound decomposes at 270°,[219] and the second at 290°[100] or 370°.[219] The enthalpy of decomposition of NH_4NiF_3 is 35.0 ± 0.5 kcal mole^{-1}.[100]

IV. REACTIONS OF AMMONIUM FLUORIDES

1. Reactions with Elements

The reactions with many elements can be described by the following equations:

$$E + nHF(gas) \rightarrow EF_n(crystalline) + \frac{n}{2}H_2 \quad (2)$$

$$E + \frac{n}{2}NH_4HF_2(crystalline) \rightarrow EF_n(crystalline) + \frac{n}{2}H_2 + \frac{n}{2}NH_3 \quad (3)$$

$$E + nNH_4F(crystalline) \rightarrow EF_n(crystalline) + \frac{n}{2}H_2 + nNH_3 \quad (4)$$

Table 3 shows that each of these reactions is probable for the alkali and alkaline earth metals, and also beryllium.

When the products are not simple fluorides, but fluorometallates, for example ammonium fluoroberyllates, the absolute values of ΔG^0 for the reactions are greater than those characteristic of reactions (2)–(4). The most negative values are observed for the reaction of a mixture of gaseous NH_3 and HF.

Table 3. Gibbs free energies ($-\Delta G^0$, kcal mole^{-1} for reactions (2)–(4) for non-transition elements of groups I and II (at 298 K).[23,55]

Reaction	Li	Na	K	Rb	Cs	Be	Mg	Ca	Sr	Ba
(2)	75.4	65.0	65.3	59.8	60.3	103.5	125.4	149.9	146.8	141.9
(3)	65.2	58.8	53.3	49.6	50.1	83.1	105.0	129.5	126.4	121.5
(4)	61.3	50.9	49.4	45.7	46.2	75.3	97.2	124.7	118.6	109.8

The results of the calculations given in Table 3 are confirmed by experimental data. Metallic beryllium is readily soluble in aqueous NH_4F solutions, and the rate of solution has the values 0.6 mg cm^{-2} min^{-1} and 2.4 mg cm^{-2} min^{-1} at 50° and 97°.[221] NH_4F solutions can be used to remove the beryllium coverings of fuel elements, and for the selective solution of beryllium from UBe_{13} alloy.[222]

With increase in the group number, the probability of reactions (2)–(4) for non-transition elements decreases (Table 4).

Carbon should obviously be inert with respect to all the reagents examined; phosphorus is probably stable to ammonium fluorides; arsenic and the group VI elements should also be inert.

Aluminium and silicon give high negative values of the Gibbs free energy. The formation of ammonium hexa- and tetrafluoroaluminates from a mixture of gaseous HF and NH_3 and crystalline NH_4HF_2 and NH_4F is highly exothermic. This is also true of the reactions

$$Si + 6HF(gas) + 2NH_3(gas) \rightarrow (NH_4)_2SiF_6(crystalline) + 2H_2$$
$$Si + 3NH_4HF_2(crystalline) \rightarrow (NH_4)_2SiF_5(crystalline) + 2H_2 + NH_3(gas)$$
$$Si + 6NH_4F(crystalline) \rightarrow (NH_4)_2SiF_6(crystalline) + 2H_2 + 4NH_3(gas)$$

for which the enthalpies at 298 K are −232, −81, and −22 kcal mole^{-1}, and the Gibbs free energies −168,0, −106.0, and −83.2 kcal mole^{-1}.[23,37,81,83] This explains why exothermic reactions of NH_4HF_2 with aluminium and silicon (at 120° and 80° respectively) were observed.[223] Since aluminium is kinetically relatively stable towards anhydrous HF,[224] NH_4HF_2 apparently dissolves the fluoride film on the metal surface. It is apparently because of these properties that mixtures containing NH_4HF_2 have been recommended for the cleaning and chemical polishing of aluminium and its alloys.[225–227]

Of the non-transition elements of groups VI and VII, oxygen and fluorine react with the ammonia present in ammonium fluorides. These reactions are used to isolate hydrogen fluoride[228,229] or nitrogen trifluoride.[230]

The regular features of the change in the probability of fluorination are slightly different for transition metals. Table 5 shows that reactions (2)–(4) are most probable for the elements of the central part of the periodic system, that is in groups III, IV, and V. Copper, silver, gold, mercury, molybdenum, tungsten, the group VII metals, and the platinum metals should be stable towards HF and ammonium fluorides. The values of ΔG^0 for the formation of Fe, Co, and Ni difluorides are −17.2 −17.8, and −15.3 kcal mole^{-1} respectively for reaction (2), and +11.0, +10.4, and +12.9 kcal mole^{-1} respectively for reaction (4).[23,164]

Table 4. Gibbs free energies (ΔG^0, kcal mole^{-1}) for reactions (2)–(4) for non-transition elements of groups III–VI (at 298 K).

Reaction	B	Al	In	C	Si	Ge	P	As	S	Se	Te
(2)	−71.9	−146.2	−34.1	48.9	−114.9	−13.6	−36.1	46.3	128.1	148.9	99.8
(3)	−41.3	−115.6	−3.5	89.7	−73.8	27.2	14.9	97.3	189.3	201.1	161.0
(4)	−29.6	−103.9	8.2	105.3	−58.2	42.8	34.4	116.8	212.7	233.5	184.4

Note. The calculation was carried out for the higher fluorides, which in all cases except Al and In were gaseous; the data from Refs.23, 37, 83, and 64 were used.

Table 5. Gibbs free energies (ΔG^0, kcal mole^{-1}) for reactions (2)–(4) for transitions elements (at 298 K).

Reaction	Cu^I	Ag^I	Zn	Cd	Hg	Sc	Y	La	Ti	Zr	Hf	V	Nb	Ta	Mo	W
(2)	9	20.4	−39.9	−24.6	42	−179	−197	−199	−111.4	−171.4	−176.2	−2.9	−79.5	−101	39.8	1.0
(3)	19	30.6	−19.5	−4.2	62	−148	−166	−168	−70.6	−130.6	−135.4	48.1	−28.5	−50	101.0	62.2
(4)	23	34.5	−11.7	3.6	70	−137	−155	−157	−55.0	−115.0	−119.8	67.6	−9.0	−31	124.4	85.6

Note. The calculation was carried out for the higher fluorides; the fluorides of V, Mo, and W were assumed to be liquid; the data from Refs.23, 107, and 164 were used.

The reactions of various transition metals may stop at the stage of lower fluoride formation. This is characteristic, for example, of titanium, which forms the trifluoride only on prolonged contact with gaseous HF in the absence of oxidising agents and moisture.[224,231]

The probability of fluorination increases if fluorometallates are formed. For the reaction

$$Zr + 6HF(gas) + 2NH_3(gas) \rightarrow (NH_4)_2ZrF_6(crystalline) + {}^3/_2H_2$$

$$Zr + 3NH_4HF_2(crystalline) \rightarrow (NH_4)_2ZrF_6(crystalline) + {}^3/_2H_2 + NH_3(gas)$$

$$Zr + 6NH_4F(crystalline) \rightarrow (NH_4)_2ZrF_6(crystalline) + {}^3/_2H_2 + 4NH_3(gas)$$

The absolute values of the standard free energies ΔG^0 are greater than those given in Table 5, and are −518, −230, and −135 kcal mole^{-1} (from Ref.164 with allowance for the corrections described in section III of the present review). Thus the reaction with ammonium fluorides to give fluorometallates is unlikely only for copper, mercury, vanadium, molybdenum, and tungsten. The other transition metals of groups II–V (including scandium, yttrium, lanthanum, the lanthanides, and the actinides), in the absence of kinetic restrictions, can react readily under ordinary conditions with ammonium fluorides to give fluorometallates.

Thus NH_4HF_2 is used to etch zirconium and its alloys,[232] and aqueous NH_4F solutions can be used to dissolve titanium, zirconium, and hafnium.[233]

Niobium and tantalum dissolve in liquid NH_4HF_2 and react with it.[16] The enthalpies of the reactions

$$2M + 5NH_4HF_2(liquid) \rightarrow (NH_4)_2MF_7(crystalline) + 3NH_4F(crystalline) + MH_{0.8}(crystalline) + 2.1H_2$$

$$MH_{0.8}(crystalline) + {}^7/_2NH_4HF_2(liquid) \rightarrow (NH_4)_2MF_7(crystalline) + {}^3/_2NH_3(gas) + 2.9H_2$$

are close to −49 kcal mole^{-1} and −24 kcal mole^{-1} for niobium, and close to −64 kcal mole^{-1} and −54 kcal mole^{-1} for tantalum.[16] Niobium and tantalum react with gaseous hydrogen fluoride to form the pentafluorides,[234,235] so that their reactions with "gaseous" ammonium fluorides are quite problabe.

2. Reactions with Other Simple Fluorides

Many ammonium fluorometallates can be obtained by the direct reaction of the simple fluorides. Thus UF_4 and PuF_4 add on NH_4F at 80–130°,[121] UF_5 at 80–85°,[128,130] $TiOF_2$ at 80°,[158] and UF_6 at room temperature.[125] Stoichiometric mixtures of the simple fluorides have been used to obtain NH_4MgF_3,[58] NH_4CdF_3,[102] NH_4MnF_3,[211] $(NH_4)_2NiF_4$,[220] NH_4CoF_3,[236] and ammonium fluoroindates.[78] Compounds more highly saturated in NH_4F can be obtained by the reaction of the less saturated compounds with NH_4F. Thus heating equimolar mixtures of $(NH_4)_2SiF_6$ or $(NH_4)_2TiF_6$ with NH_4F at 90° to 95° gives the heptafluorometallates.[81,158]

Solid-phase syntheses using NH_4F are generally time-consuming, however (complete reaction takes from several hours to several days), and to avoid the loss of NH_3 and the partial loss of HF they must be carried out in closed vessels. To increase the reaction rates, mixtures of the powdered reagents can be compressed or heated under pressure[236] (liquid NH_4F is an ionic conductor[237]), but it is better to use solvents.

The most widely used solvent is water. The equilibrium solubility in metal fluoride (fluorometallate)–NH_4F–H_2O systems has been studied for BeF_2,[238,239] NH_4BF_4,[60] AlF_3,[240] GaF_3,[74,241] InF_3,[76] TlF,[242,243] $(NH_4)_2SiF_6$,[244] SnF_2,[87] CuF_2,[245] CdF_2,[246] CeF_4,[117] UF_4,[133,134] UO_2F_2,[140–142], CoF_2,[245] and NiF_2.[245] The NH_4BF_4–NH_4HF_2–H_2O system has been studied.[60]

Anhydrous HF,[194,247] ClF_3,[124] methanol,[99] polymerised trifluoroethylene,[248] etc. have also been used as solvents. HF, however, decomposes many fluorometallates, ClF_3 reacts with NH_4F (sometimes explosively) on slight heating, and the solubility of NH_4F in organic solvents is low (in Ref.125, a suspension of NH_4F in trichloroethylene was used).

Table 6 gives the enthalpies of formation of fluorometallates, and shows that the maximum values of $-\Delta H^0_{formation}$ are observed for $(NH_4)_4UF_8$, $(NH_4)_2UF_6$, $(NH_4)_3AlF_6$, $(NH_4)_3HfF_7$, and $(NH_4)_2SiF_6$. If however the enthalpy is related to 1 mole of NH_4F, it decreases in a slightly different order: NH_4AlF_4, $(NH_4)_2UF_6$, NH_4HfF_5, $(NH_4)_2TaF_7$, $(NH_4)_2TiF_6$, etc., although in this case also the compounds of the elements of groups III–V are among the energetically most stable compounds. Comparison of the enthalpies of addition in the series $MF.nNH_4F$–$MF_2.nNH_4F$–$MF_3.nNH_4F$–$MF_4.nNH_4F$–$MF_5.nNH_4F$–$MF_6.nNH_4F$, where M represents a given metal in different oxidation states or metals from the same row of the periodic system, shows that the enthalpy tends first to increase and then to decrease.

Table 6. Enthalpies of formation of fluorometallates (at 298 K).

Substance	$-\Delta H^0_{formation}$, kcal mole^{-1}		Substance	$-\Delta H^0_{formation}$, kcal mole^{-1}	
	I	II		I	II
$(NH_4)_2BeF_4$	8.6	78.6	$(NH_4)_3UF_8$	39	109
NH_4BF_4	−1	33.9	$7NH_4F.6UF_4$	525	770
$(NH_4)_3AlF_6$	38	143	$NH_4F.3UF_4$	9.4	44
NH_4AlF_4	25	60	$(NH_4)_3UO_2F_5$	17.7	122.7
$(NH_4)_2SiF_6$	35	105	$NH_4(UO_2)_2F_5$	13.1	48
NH_4CuF_3	−1	34	$(NH_4)_2TiF_6$	31	101
NH_4ZnF_3	−1	34	$(NH_4)_3ZrF_7$	19.8	125
NH_4CdF_3	−2	33	$(NH_4)_2ZrF_6$	18.9	89
$(NH_4)_3ScF_6$	13	117	NH_4ZrF_5	13.5	48.5
NH_4ScF_4	12	47	$(NH_4)_3HfF_7$	36	141
$NH_4Y_3F_7$	6	41.2	$(NH_4)_2HfF_6$	26	96
NH_4PrF_4	10.6	45.6	NH_4HfF_5	17	51
NH_4NdF_4	11.7	46.7	$(NH_4)_2TaF_7$	31.4	101
NH_4SmF_4	9.7	44.7	NH_4MnF_3	4	39
NH_4GdF_4	14.7	49.7	NH_4CoF_3	−5	30
$NH_4Dy_3F_7$	11	46.0	NH_4NiF_3	0	35
$NH_4)_4UF_8$	40	180			

Note. I) from the simple crystalline fluorides; II) from MF_n(crystalline), HF(gas), and NH_3(gas). For references see Section III.

Fluorometallates with the maximum number of coordinated fluorine atoms have a lower thermal stability and a lower enthalpy of formation from the simple fluorides (calculated for 1 mole of NH_4F) than the compounds of the same metal with a smaller number of added NH_4F molecules.

NH_4HF_2 can also react with simple fluorides to give ammonium fluorometallates. $(NH_4)_2NiF_4$ has been obtained from NiF_2,[249] and $(NH_4)_2NiF_4$ and $(NH_4)_2CoF_4$ from NiF_2 and CoF_2 dihydrates.[219]

The reactions

$$MF_n(crystalline) + mNH_4HF_2(crystalline) \rightarrow (NH_4)_mMF_{n+m}(crystalline) + mHF(gas)$$

take place with a much smaller liberation of heat (by 15.4m kcal mole^{-1})[23] than the reactions

$$MF_n(crystalline) + mNH_4F(crystalline) \rightarrow (NH_4)_mMF_{n+m}(crystalline)$$

The difference in the Gibbs free energies for the reactions of NH_4HF_2 and NH_4F is smaller, and amounts to 8.8m kcal mole^{-1}. At the same time, the values of ΔH^0 and ΔG^0 for the

reactions of "gaseous" NH_4F and NH_4HF_2 should not be different. Thus the reactions

$$\underbrace{MF_n + mNH_3(gas) + 2mHF(gas)}_{\text{vapour over } NH_4HF_2} \rightarrow (NH_4)_mMF_{n+m}(crystalline) + mHF(gas)$$

can be used to obtain hydrogen fluoride from NH_4HF_2. This method was first patented by Sudarikov and co-workers;[250] silicon tetrafluoride is used, and the reaction is carried out at 140° with liquid NH_4HF_2 or at 200° with "gaseous" NH_4HF_2. A wider range of fluorides is listed in other patents,[251–253] which mention, in particular, the fluorides of copper, magnesium, calcium, zinc, aluminium, indium, thorium, germanium, tin, titanium, zirconium, vanadium, bismuth, chromium, iron, and nickel, and also fluorometallates not saturated in NH_4F. The preferred temperature range for carrying out the reactions is 125–200°.

Processes for obtaining hydrogen fluoride, based on the formation and thermal decomposition of alkali metal hydrogen fluorides, are of much greater practical importance. Usually, an aqueous solution of NH_4F and the sodium salt is heated to give $NaHF_2$, which is filtered off, dried, and heated. Ammonia, the mother-liquor, and sodium fluoride are returned to the same or another stage of the process. Sodium hydrogen fluoride can also be obtained by the reaction of anhydrous NH_4HF_2 and NaF, which begins at 105°.[254] Different versions of the method have been described and patented;[255–263] it can also be applied to potassium salts.[275, 264–267]

Ammonium hydrogen fluoride forms compounds and mixed crystals with the alkali metal hydrogen fluorides.[268–270]

The reaction of gaseous SiF_4 with NH_4F solution has been proposed for preparing $(NH_4)_2SiF_6$[271] and for trapping SiF_4 from gas streams.[4,8,272]

3. Reactions with Oxides and Hydroxides

Reactions with oxides and hydroxides, which are widely encountered in nature and are involved in many technological processes, are of considerable practical importance.

For the hydroxides of the alkali and alkaline earth elements (and also Be and Mg), the following reactions are of interest:

$$M(OH)_n(crystalline) + nHF(gas) \rightarrow MF_n(crystalline) + nH_2O(gas) \quad (5)$$

$$M(OH)_n(crystalline) + \frac{n}{2}NH_4HF_2(crystalline) \rightarrow MF_n(crystalline) + nH_2O(gas) + \frac{n}{2}NH_3(gas) \quad (6)$$

$$M(OH)_n(crystalline) + nNH_4F(crystalline) \rightarrow MF_n(crystalline) + nH_2O(gas) + nNH_3(gas) \quad (7)$$

The final products for the alkali metal hydroxides can apparently be hydrogen fluorides:

$$MOH(crystalline) + 2HF(gas) \rightarrow MHF_2(crystalline) + H_2O(gas) \quad (8)$$

$$MOH(crystalline) + NH_4HF_2(crystalline) \rightarrow MHF_2(crystalline) + H_2O(gas) + NH_3(gas) \quad (9)$$

$$MOH(crystalline) + 2NH_4F(crystalline) \rightarrow MHF_2(crystalline) + H_2O(gas) + 2NH_3(gas) \quad (10)$$

Table 7 shows that all these processes are probable. The same is true of many reactions involving the fluorination of oxides:

$$MO_{n/2}(crystalline) + nHF(gas) \rightarrow MF_n(crystalline) + \frac{n}{2}H_2O(gas) \quad (11)$$

$$MO_{n/2}(crystalline) + \frac{n}{2}NH_4HF_2(crystalline) \rightarrow MF_n(crystalline) + \frac{n}{2}H_2O(gas) + \frac{n}{2}NH_3(gas) \quad (12)$$

$$MO_{n/2}(crystalline) + nNH_4F(crystalline) \rightarrow MF_n(crystalline) + \frac{n}{2}H_2O(gas) + nNH_3(gas) \quad (13)$$

Table 7. Gibbs free energies (ΔG^0, kcal mole^{-1}) for reactions (5)–(7) for non-transition elements of groups I and II and for reactions (8)–(10) for the alkali metals (at 298 K).

Reaction	Li	Na	K	Be	Mg	Ca	Sr	Ba
(5)	−24.4	−28.1	−27.2	−18.3	−35.5	−43.4	−48.5	−46.1
(6)	−14.2	−17.9	−17.0	2.1	−15.1	−23.0	−28.1	−25.7
(7)	−10.3	−14.0	−13.1	9.9	−7.3	−15.2	−20.3	−14.9
(8)	−26.5	−26.8	−28.8	—	—	—	—	—
(9)	−6.0	−6.3	−8.3	—	—	—	—	—
(10)	1.7	1.4	−0.6	—	—	—	—	—

Note. The data from Refs. 23, 55, and 273 were used in the calculation.

Table 8. Gibbs free energies (ΔG^0, kcal mole^{-1}) for reactions (11)–(13) for non-transition elements of groups II–VI (at 298 K).

Reaction	Be	Mg	Ca	Sr	Ba	B	Al	C	Si	Ge	P	As	S
(11)	−19.7	−44.1	−59.1	−69.5	−71.5	−11.1	−138.9	33.8	−19.2	1.8	−13.5	1.3	40.9
(12)	0.7	−23.7	−38.7	−49.1	−51.1	20.6	−107.1	74.8	21.8	42.8	37.8	52.6	102.4
(13)	8.5	−15.9	−30.9	−41.3	−40.3	31.2	−96.6	90.2	37.2	58.2	57.0	71.8	125.5

Note. The calculation was carried out for the higher oxides and fluorides; the latter, for B, C, Si, Ge, P, As, and S were gaseous; the data from Refs. 23, 37, 64, 83, and 274 were used.

The data in Table 8 show that the reactions of the oxides of all non-transition elements of group II are probable. The higher oxides of the non-transition elements of groups III–V, except carbon, can react with HF to form higher fluorides, but with increase in the group number, the values of ΔG^0 for the reactions become more positive, and the reactions become less probable.

In many cases, the fluorination is characterised by larger absolute negative ΔG^0 values or smaller absolute positive ΔG^0 values, because of fluorometallate formation. Thus the reactions of α-quartz with crystalline NH_4HF_2 and NH_4F to give $(NH_4)_2SiF_6$ take place with $\Delta G^0 = -10.8$ kcal mole^{-1} and +12.3 kcal mole^{-1}.[83] There is also a high probability that oxide fluorides, and not fluorides, will be formed. For example, the values of ΔG^0 for the fluorination of P_2O_5 (crystalline) and SO_3 (gas) to gaseous POF_3 and SO_2F_2 are −18.5 kcal mole^{-1} and −29.5 kcal mole^{-1}.[23,37,274]

Many processes have been well studied by experimental methods. Thus BeO and moist $Be(OH)_2$ react with NH_4HF_2 on heating to 50–100°.[52,80,275] Different versions of the fluorination of alkali and alkaline earth metal oxides have been described.[276–281]

The fluorination of boric acid by anhydrous ammonium fluorides or their aqueous solutions gives NH_4BF_4,[61,62,65,282–284] but with a deficit of fluorinating agent and a short contact time the products are mixtures of $(NH_4)_2BOF_3$, $(NH_4)_3B_3O_3F_6$, and other ammonium oxo- and hydroxofluoroborates.[61,62,68,285]

A detailed study[286] showed that the reactions of $Al(OH)_3$ and Al_2O_3 with NH_4HF_2 begin at 20–130°, take place with considerable liberation of heat, and give $(NH_4)_3AlF_6$. Increase in the alumina heating temperature from 500° to 1200°, leads to a sharp decrease in its activity: a specimen obtained at 1200° is inert towards NH_4HF_2. Different versions of the process have been described.[287–291]

The reaction in a mixture of SiO_2 and NH_4HF_2 begins at a temperature of ~100° and takes place exothermally to give $(NH_4)_2SiF_6.NH_4F$.[80,81] Quartz dissolves relatively rapidly in aqueous NH_4HF_2 solutions.[292] Ammonium fluorides and their solutions have therefore been recommended for the removal of oxides from semiconductor surfaces[293] and for the removal of quartz from fluorite concentrates.[294–299] Silica is also soluble in alkaline and neutral NH_4F solutions,[300,301] and the rate of solution on heating is relatively high.[302] NH_4F solutions at 150–400° can be used for the hydrothermal preparation of single crystals of quartz and amethyst.[303]

The reaction of P_2O_5 with NH_4HF_2 or NH_4F takes place rapidly at 135° with the liberation of a large quantity of heat, to give $NH_4PO_2F_2$ or $(NH_4)_2PO_3F$.[91,304,305] Heating As_2O_3 with concentrated NH_4HF_2 solution for 1 h gives NH_4AsO_2.[94]

Table 9 shows that the regular features of the change in ΔG^0 for the fluorination of higher oxides to fluorides are slightly different for the transition elements than for non-transition elements. With increase in the group number, the probability of fluorination at first increases, reaching a maximum for the group III elements, and then decreases. In this case also, the reaction products for the metals of group V and VI may be oxide fluorides or ammonium oxofluorometallates, and this may lead to a considerable change in the ΔG^0 values.

Ammonium fluoride and more particularly ammonium hydrogen fluoride are fairly powerful fluorinating agents for many transition metal oxides. Thus ZnO reacts rapidly with molten NH_4HF_2 [278] or its "vapour" at 300°.[19]

The reaction of Sc_2O_3 with NH_4HF_2 begins at 60°, takes place with exothermic and endothermic effects, and is complete at 180° with the formation of $(NH_4)_3ScF_6$.[306] Y_2O_3 is fluorinated by ammonium hydrogen fluoride with an exothermic effect at 80° and an endothermic effect at 170°.[106,307,308] With an excess of NH_4HF_2, the initial product is $NH_4Y_2F_7.NH_4F$, which decomposes to YF_3. With a deficit of the fluorinating agent, yttrium oxide fluoride is formed.[309,310] It has also been suggested that the fluorination involves the formation of ammines of the trifluoride in intermediate stages.[309,310]

The fluorination is similar for La_2O_3, which is converted into NH_4LaF_4 or $NH_4La_2F_7$,[110,112,114] but which may also give the oxide fluoride or ammine.[309,310] The oxides of all the lanthanides are fluorinated with an exothermic effect at 80–180°; Eu_2O_3 is converted into NH_4EuF_4.[114] It has been concluded[110,112] that for Pr, Nd, Sm, and Gd, the first stage of the reaction gives the compounds NH_4LnF_4. According to Ref. 111, Dy_2O_3 is first converted into $NH_4Dy_2F_7$, and according to Refs. 110 and 112, the oxides of Dy, Ho, Er, Tm, Yb, and Lu give the compounds $(NH_4)_3Ln_2F_9$ in the initial stages of the fluorination. With a relatively small quantity of NH_4HF_2 at temperatures of 300–360°, hexagonal oxide fluorides were detected[111] in the fluorination products of the oxides of Pr, Nd, Sm, and Gd.

Table 9. Gibbs free energies (ΔG^0, kcal mole^{-1}) for reactions (11)–(13) for transition element (at 298 K).

Reaction	Cu^{II}	Ag^{I}	Zn	Cd	Hg	Sc	Y	La
(11)	−9.7	−9.5	−17.9	−24.4	1.0	−43.9	−62.0	−77.3
(12)	10.7	4.7	2.5	−4.0	21.4	−13.3	−31.4	−46.7
(13)	18.5	8.6	10.3	3.8	29.3	−1.6	−19.7	−35.0
	Tl	Zr	Hf	V	Nb	Ta	Mo	W
(11)	2.7	−31.4	−31.9	21.1	−15.2	−19.5	35.6	19.8
(12)	43.5	9.4	9.1	72.1	35.8	31.5	96.8	81.0
(13)	59.1	25.0	24.5	91.6	55.3	51.0	120.2	104.4

Note. The calculation was carried out for the higher oxides and fluorides; the latter, for V, Mo, and W, were liquid; the data from Refs. 23 and 107 were used.

The fluorination of CeO_2 gives $(NH_4)_3CeF_7$ at 60° [117,118] and $(NH_4)_{0.6}CeF_{4.45}$ at 200°.[115]

NH_4F solutions at 200–300° can be used for the hydrothermal synthesis of single crystals of ammonium fluorometallates of erbium.[311]

The oxides of the light actinides (thorium, uranium, neptunium, plutonium, americium, and, apparently, protactinium) are fluorinated by ammonium fluoride or ammonium hydrogen fluoride at relatively low temperatures. Thus the conversion of $Th(OH)_4$ into ThF_4 by the action of NH_4F,[12] the fluorination of NpO_2,[122] the fluorination of PuO_2,[151–153] and the preparation of CmF_3 by the action of an excess of NH_4HF_2 on CmO_2 [154] have been described; in all cases, the reactions began at 110–125°. The fluorination of uranium dioxide has been studied in most detail. As early as 1943, it was shown that the reaction takes place at 150–200°;[312] higher temperatures are required to increase the degree of fluorination.[312–314] The reaction of UO_2 with NH_4HF_2 is exothermic[315] and takes place at 150–170° to give $(NH_4)_2.UF_6$.[136,316] The product of the reaction of UO_3 with concentrated NH_4HF_2 solutions is $(NH_4)_3UO_2F_5$.[142,143] UO_3 can also be fluorinated in the absence of a solvent.

The reaction of TiO_2 with NH_4HF_2 begins at a temperature of ~100° [158] to give $(NH_4)_2TiF_6.NH_4F$.

Zirconium dioxide reacts with NH_4HF_2 to give $(NH_4)_3ZrF_7$ [317] or $(NH_4)_2ZrF_6$.[160,318,319] The reaction is most vigorous after the NH_4HF_2 melts.[282,320,321] Treatment with ammonium hydrogen fluoride reduces the concentration of oxygen in ZrF_4 to 0.25%.[322]

NH_4F solution at temperatures of 450–700° and pressures of 800–3000 atm can be used to grow single crystals of TiO_2, ZrO_2, and HfO_2.[323]

The reaction of V_2O_3 with NH_4HF_2 in the ratio 1 : 8 or 1 : 2 at 185–200° for 2 h gives the green compound $(NH_4)_3VF_6$.[182] A mixture of V_2O_5 and NH_4HF_2 reacts at 95° to give $(NH_4)_3VO_2F_4$.[178]

Stoichiometric mixtures of Ta_2O_5 or TaO_2F with NH_4HF_2, with gentle heating, give $(NH_4)_2TaF_7$.[184] Under analogous conditions, the niobium compounds form $(NH_4)_3NbOF_6$.

According to Ref.324, the reaction of CrO_3 with NH_4F in aqueous solution gives $(NH_4)_2Cr_2O_7$ and HF.

The reaction of MoO_3 with NH_4HF_2 at a molar reagent ratio of 1 : 2 and a temperature of 105–110° leads to the exothermic formation of $(NH_4)_2MoO_2F_4$.[196,199] At lower temperatures, $(NH_4)_3MoO_2F_4$ is formed.[196] A stoichiometric mixture of WO_3 and NH_4HF_2 at 190–200° is converted into $(NH_4)_3WO_2F_5$.[197] The reactions of molybdenum and tungsten trioxides with aqueous NH_4F solutions give the salts $MO_3.nNH_4F$.[200,205]

The reaction of ReO_3 with NH_4HF_2 has been studied only qualitatively; its products are volatile oxide fluorides.[325]

The reaction of Fe_2O_3 with NH_4HF_2 takes place at 170° to give $(NH_4)_3FeF_6$.[69] NH_4HF_2 apparently reacts readily with other iron oxides, since ammonium fluorides have been recommended for the simultaneous removal of rust and sand from the surface of iron tubes.[326]

The higher oxides of other transition metals (manganese, cobalt, nickel, etc.) also apparently react with ammonium fluorides. Alumina heated at high temperatures is apparently the oxide most resistant to the action of ammonium fluorides. Oxides can be fluorinated using fluorometallates. This process has been described for Al_2O_3 [71,327] and BeO.[328]

The above data confirm the conclusions reached in Ref.329: NH_4HF_2 begins to react with oxides at 70–130°, the reactions are most vigorous after the NH_4HF_2 melts, and the reactivity of NH_4HF_2 (to give fluorometallates) is often greater than that of anhydrous hydrogen fluoride.

4. Reactions with Salts

A large number of reactions of ammonium fluorides with salts have been reported. For example, the conversion of calcium chloride into the fluoride by boiling an aqueous solution containing NH_4F,[330,331] of MgCl solution into $(NH_4)_2.MgF_4$,[58] of cadmium salt solutions into CdF_2,[20] and of solutions of lanthanide chlorides into the trifluorides[332] have been described. Phosphorus chlorides and oxide chlorides, and arsenic and silicon chlorides, although not salts, are fluorinated when boiled under reflux with NH_4F.[333]

The ammonium fluorometallates of many metals can be obtained by the reactions of the bromides or nitrates with NH_4F in methanol.[99,334,335] The conversion of $Th(NO_3)_4$ solution into ammonium fluorometallates[125] and the conversion of $NaNO_3$ into $NaHF_2$ [260] have been described.

Carbonates are often used as the starting materials for preparing fluorides. The carbonates and ammonium fluorides have been used to prepare lithium fluoride,[336] cerium trifluoride,[387] fluorides for luminophors,[338] and $(NH_4)_2MgF_4$,[58] and the hydroxide carbonates have been used to prepare fluoro-complexes of cobalt and nickel.[219] Treatment with anhydrous NH_4F or its solutions can be used to remove traces of $CaCO_3$ from CaF_2.[294,298] (The mechanism and kinetics of this process have been described.[338–341]) NH_4HF_2 can be used to obtain lanthanide fluorides from concentrates containing carbonates,[342] and also KHF_2 from K_2CO_3.[343]

Ammonium fluorides have also been used to fluorinate sulphates,[344–347] silicates,[9,348] phosphates,[349,350] magnesium acetate,[351] beryllium oxide acetate,[352] sodium aluminate,[346] ammonium vanadate,[178] ammonium tungstate,[197] calcium tungstate,[13–15] ammonium molybdate,[197] lithium hydroborate,[353] cerium(III) oxalate,[337] and various minerals and concentrates with complex compositions.[10–12,354]

The salts of most acids probably react with ammonium fluorides to give the corresponding fluorides. The formation of double salts is a somewhat unique phenomenon; they are few in number, however, and are known only for ammonium nitrate and perchlorate.[60,355–358]

V. CONCLUSION

In the research literature, including recent publications, it is still possible to find ammonium fluoride regarded as a complete analogue of other ammonium halides. Because of the formation of strong additional hydrogen bonds, however, many of the properties of ammonium fluoride differ sharply from those of compounds of NH_3–HX systems, where X = Cl, Br, or I. The most characteristic difference shown by the fluorides is the ability of the NH_3–HF system to form stable hydrogen salts: ammonium hydrogen fluoride even has a higher thermal stability than ammonium fluoride.

Ammonium fluorides also differ considerably from other ammonium halides in their reactivity, due to the specific properties of inorganic fluorides, namely the high strength of element–fluorine bonds (high enthalpy of bond rupture), and the consequent high values of the enthalpies and Gibbs free energies for many fluorination reactions.

In the series of traditional fluorinating agents (fluorine, halogen fluorides, anhydrous hydrogen fluoride, and hydrofluoric acid), ammonium fluorides, in particular ammonium hydrogen fluoride, occupy an intermediate position between fluorine and anhydrous hydrogen fluoride, often giving higher values than the latter for the equilibrium constants and rates of fluorination.

As shown above, ammonium fluorides can be used to fluorinate various elements, many oxides, and a very large number of salts (metallates).

The fluorination of the oxides of the non-transition elements of groups II–IV gives the higher fluorides or the corresponding fluorometallates, whereas the fluorination of the oxides of the non-transition elements of group V gives the oxide fluorides or oxofluorometallates. For the higher oxides of the transition metals, the "boundary" between the tendency to form completely fluorinated products (fluorides and fluorometallates) and the tendency to give oxide fluorides or oxofluorometallates corresponds to the centre of the periodic system; the oxides of the group IV metals form fluorometallates, and the oxides of the group VI metals form oxofluorometallates. An interesting feature is that V_2O_5, Nb_2O_5, and Ta_2O_5 under identical conditions react with NH_4HF_2 to give compounds of different types: $VO_2F.nNH_4F$, $NbOF_3.nNH_4F$, and $TaF_5.nNH_4F$. A decrease in the oxidation state of the metal in the oxide brings it closer to the elements of groups with a smaller number. Thus on fluorination, V_2O_3 behaves like a group III element and gives derivatives of VF_3; UO_3 is converted into $(NH_4)_3UO_2F_5$, resembling to some extent MoO_3 and WO_3, whereas the behaviour of UO_2 (which is converted into UF_4 derivatives) is closer to that of ZrO_2.

The thermal decomposition of fluoro-derivatives of Ce^{IV}, Mn^{III}, Pu^{IV}, and Cm^{IV}, and also oxofluoro-derivatives of V^{V}, Mo^{VI}, and W^{VI}, involves partial reduction in the last stages. This phenomenon should also be characteristic of salts of Cr^{IV}, Re^{VIII}, Re^{VI}, and other metals of group VII, and also of all the actinides following plutonium.

In an excess of NH_3, reduction may be accompanied by the ammonolysis of the simple fluorides. The question of the possibility of ammonolysis during thermal decomposition remains open. Heating simple fluorides in an ammonia atmosphere up to 300–900° gives nitrides or nitride fluorides.[359–364] A mixture of molybdenum nitride and trifluoride was detected in the thermal decomposition products of ammonium fluoromolybdate,[203] although these data require confirmation.

The behaviour of nitrogen in the last stages of the thermal decomposition has been little studied. The removal of small quantities even as ammonia is kinetically hindered (this is characteric, for example, of vanadium(III) [182]) because of mechanical blocking, the formation in a number of cases of solid solutions of the fluorometallates in the fluorides, or, as in the case of the lower oxide fluorides of tungsten and molybdenum, because of the introduction of ammonium ions into the cavities of the crystal lattice. These effects possibly also lead to erroneous conclusions about the formation of "new phases", with lower ammonium fluoride concentrations (see for example Refs.7 and 135). An increased concentration of residual nitrogen lowers the quality of the fluorides obtained, and is particularly undesirable when fluorides are used to prepare metals.

An interesting and little studied problem concerns the preparation of volatile fluorides using ammonium fluorides. The action of heat on many ammonium fluorometallates leads to the transfer of the metal fluorides (for example titanium, niobium, tantalum) to the gas phase, and the problem reduces to the separation of mixtures of these fluorides, ammonia, and hydrogen fluorides, which on simple cooling react again to re-form fluorometallates with the same or different compositions. The selective trapping of TiF_4 on CaF_2 at 300–350° has been proposed[365] for the separation of TiF_4 from its mixtures with NH_3 and HF.

The available published thermodynamic data on ammonium fluoro- and oxofluorometallates are unfortunately as yet insufficient for making any generalisations, predictions, or estimations.

Although various reactions of ammonium fluorides and properties of ammonium fluorometallates still require further study, it may be concluded that a fairly wide range of inorganic fluorides can be synthesised using ammonium fluorides.

The most urgent problems in further research in this direction are related primarily to the measurement of the enthalpies of formation, decomposition pressures, and heat capacities of fluoro- and oxofluorometallates, the study of the mechanism and kinetics of all the stages (particularly the last stages) of the thermal decomposition of fluoro- and oxofluorometallates, and the study of the reactions of ammonium fluorides with oxides, metallates, and minerals.

While the present manuscript was being prepared for publication, a number of publications related to its various sections appeared. Thus an indirect method has been used[366] to measure the degree of decomposition of NH_4F in the gas phase, and it has been shown that at 288.9 K, when the total vapour pressure is 0.40 Pa, the degree of decomposition is only 0.97. Strange as it may seem, even lower values were obtained for other ammonium halides. At the same time, a new measurement of the enthalpy of decomposition of NH_4HF_2[367] gave a result (about 51.5 kcal $mole^{-1}$) differing little from the value previously adopted.

The study of the fusion diagram of the NH_4F–HF system has been repeated, a number of new ammonium hydrogen fluorides have been detected, and the crystal structures of $NH_4H_3F_4$, $NH_4H_4F_5$, and $NH_4H_7F_8$ have been studied.[368] The enthalpies of solution of NH_4F and NH_4HF_2 in water have been measured again.[369]

Published calorimetric data on the enthalpies of formation of NH_4ZnF_3 and NH_4CdF_3 (−295.3 kcal $mole^{-1}$ and −286.8 kcal $mole^{-1}$)[370,371] make it possible to eliminate the contradiction noted in the text of the present review, and indicate that the results obtained in Ref.100 are too low. The enthalpies of the separate stages of the thermal decomposition of $(NH_4)_3WO_2F_5$ and the overall enthalpy of decomposition to W_2O_4F (109 kcal $mole^{-1}$) have been determined.[372]

Hydrothermal synthesis in NH_4HF_2 has been used to synthesise $NH_4Fe^{2+}Fe^{3+}F_6$, NH_4MnFeF_6, and NH_4MnCrF_6,[373–375] which are isostructural with one another and have a previously unknown structure. The thermal properties of these unusual fluorometallates have been studied.

New data on the reactions of ammonium fluorides have been published. Thus the reaction of an equimolar mixture of CrO_3 and NH_4HF_2 in the presence of small quantities of water has been used to synthesise NH_4CrO_3F;[376] the thermal decomposition of this compound is accompanied by the reduction of Cr^{6+} to Cr^{3+}.

The reaction of nickel and cobalt oxide carbonates and hydrated fluorides with ammonium fluorides has been studied in more detail.[377] The reactions of NH_4F with XeF_2, XeF_6, and KrF_2[378] give N_2, HF, and Xe (or Kr). In the presence of metals (Fe, Cr), the compounds NH_4MF_4 are also formed.

According to Ref.379, the reaction of NH_4HF_2 with $NaVO_3$ and NH_4VO_3 gives $(NH_4)_2NaVO_2F_4.H_2O$ and $(NH_4)_3VO_2F_4.0.5H_2O$. The published[379] thermal decomposition schemes assume that the compounds give up NH_4F in three stages, but retain water of crystallisation. This does not agree with the general regular features of processes of this kind (ammonium fluorometallates have a higher thermal stability than the metal fluoride crystalline hydrates), X-ray diffraction data (the presence of water of crystallisation would change the structures of the compounds), and the results of earlier studies.[178,180] The process proposed in Ref.178, however, also requires refinement, with allowance for the observed[379] reversible phase transformation of $(NH_4)_3VO_2F_5$ (408 K; ~0.6 kcal $mole^{-1}$).

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