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# A STUDY OF THE FLUORIDES AND DOUBLE FLUORIDES OF ALUMINUM[1]

By Martin Tosterud

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## Introduction

A review of the literature[2] on the hydrated fluorides of aluminum and of the double fluorides reveals the fact that the composition as recorded is uncertain.

## Experimental Part

**Preparation of $Al_2F_6.18H_2O$.**—A solution of aluminum fluoride was prepared by the addition of alumina in excess of 10% to a solution containing 14% of hydrofluoric acid in a Bakelite beaker. The solution was stirred until it reacted neutral to methyl orange. It was then cooled as quickly as possible and filtered by means of suction.

When such a solution is quickly cooled to a temperature of about 0° a crop of finely divided crystals is formed. These crystals are very unstable at room temperature. The growing of larger crystals which could be more conveniently handled was accomplished by chilling a solution of aluminum fluoride to 15–20°, inoculating with crystals and allowing to cool further. In this manner some large crystals grew in the container. When one of the larger crystals was tied to a string lowered into a solution of aluminum fluoride that had been previously cooled to 15–20°, and the whole then placed in an ice box for several hours, many large crystals adhered to the string. The crystals were purified by repeated crystallization from distilled water. The large crystals were dried and easily prepared for chemical analysis.

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[1] Part of a thesis submitted at the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Mazzuchelli, *Atti accad. Lincei*, **16**, 775 (1907). Baud, *Ann. chim. phys.*, **1**, 8 (1904).

**Determination of Water in $Al_2F_6.18H_2O$.**—Since ignition decomposes the hydrated salt, liberating hydrofluoric acid, as well as water, the following method was adopted. The crystals which had been grown on a string were crushed off between filter papers and dried by means of alcohol and ether which had been previously cooled to 0°. As soon as the ether had evaporated, the crystals were quickly transferred to a weighed platinum crucible, covered and weighed. Part of the water was obtained by drying the crystals over phosphorus pentoxide. The remaining water was determined as follows. About 0.25 g. of the salt which had been dried over phosphorus pentoxide was intimately mixed with twenty times its weight of lead oxide which had previously been ignited at 550° for 12 hours. The charge was transferred to a porcelain boat which had previously been ignited. The boat and contents were placed in a Pyrex combustion tube and heated to redness in a current of air that had been dried by passage through a long tube containing soda lime and through two wash bottles containing sulfuric acid. The water was collected in a U-tube containing glass beads and concd. sulfuric acid. When the U-tube gave a constant weight, the determination was considered complete. The weight of the water lost over phosphorus pentoxide and by the combustion method gave the total amount of water in the original crystals. A blank determination gave a small weight of water which was deducted. The maximum deviation of any individual determination from the calculated amount was $\pm 0.13\%$. The average of 16 determinations was 65.91% of water, as compared with 65.87%; calculated for $Al_2F_6.18H_2O$.

**Determination of Aluminum in $Al_2F_6.18H_2O$.**—The crystals of aluminum fluoride were dried with alcohol and ether which had been cooled to 0°. About 0.5 g. of the salt was transferred to a weighed platinum crucible, covered and weighed. Part of the water was removed by heating the contents to a temperature of about 100°. The sample was mixed in a platinum crucible with eight times its weight of sodium bisulfate and fused. When the evolution of sulfur trioxide fumes had subsided, the charge was cooled. The mass was then treated with a few drops of sulfuric acid and reheated in order to drive off the last trace of hydrogen fluoride. The charge was cooled and dissolved in water. About 15 g. of ammonium chloride was added to the solution and the aluminum determined in the usual way. The maximum deviation of any individual determination from the calculated amount was $\pm .08\%$. The average of fourteen determinations gave 10.94% of aluminum as compared with 10.97% calculated for $Al_2F_6.18H_2O$.

The analyses show that the composition of the crystals is $Al_2F_6.18H_2O$ and not $Al_2F_6.17H_2O$ as claimed by Mazzuchelli.[2]

**The Effect of Heating $Al_2F_6.18H_2O$ in a Closed System.**—Crystals of the hydrated aluminum fluoride were placed in a platinum crucible of about 15cc. capacity. The crucible was covered and lowered into a Morey pressure bomb. Some water was placed on the outside of the crucible in order to insure the presence of the liquid phase. The bomb was closed and placed in an electric oven which was automatically regulated and heated at various temperatures for different time intervals. The bomb was removed from the oven and allowed to cool at room temperature. The salt was removed and washed with a small amount of distilled water and finally dried at 105°. The water and alumina were determined as previously mentioned. The longer the heating at a given temperature the more complete was the dehydration. The analysis of the product heated for 170 hours is given in Table I.

TABLE I

ANALYSIS OF HEATED ALUMINUM FLUORIDE

| Temp., °C. | % $H_2O$ found | % Al found Dry basis | Temp., °C. | % $H_2O$ found | % Al found Dry basis |
|---|---|---|---|---|---|
| 110 | 38.34 | 32.10 | 140 | 6.56 | 32.00 |
| 115 | 33.06 | 32.04 | 150 | 5.25 | 32.15 |
| 120 | 22.91 | 32.06 | 160 | 3.36 | 32.12 |
| 125 | 11.91 | 32.18 | 185 | 2.09 | 32.09 |
| 135 | 9.58 | 32.10 | 215 | 2.07 | 32.08 |
| | | | | Calcd. | 32.14 |

Chemical analysis failed to indicate the formation of any definite hydrate at elevated temperatures. The form $Al_2F_6.18H_2O$ decomposes at room temperature into another hydrate which has approximately the composition[2] $Al_2F_6.7H_2O$. This latter phase, according to analysis, seems to be stable above 100°.

Mr. C. O. Swanson, of the Geology Department of the University of Wisconsin, made several X-ray photographs of the salt heated at various temperatures. The X-ray spectra of the salt heated at 115° and 120° are the same. The salt heated at 125° and up to 320° has the same spectrum, but one that is different from the spectrum of the salt heated at 115° and 120°. X-ray photographs may, therefore, be used in a qualitative way in discovering transitions. The X-ray photograph is shown in Fig. 1.

**The Preparation of the Double Potassium Salt, $4KF.Al_2F_6$.**—Baud[2] claims the preparation of a gelatinous hydrated potassium cryolite of the composition $Al_2F_6.6KF.7H_2O$. An attempt was made to repeat the work of Baud. For this purpose a 1/6 *M* solution of aluminum fluoride was prepared from recrystallized $Al_2F_6.18H_2O$ (82.048 g.). The potassium fluoride was prepared by treating recrystallized potassium bicarbonate with an excess of hydrogen fluoride. The salt was fused in a platinum crucible in order to drive off any free acid. A molar solution was prepared from this salt.

In preparing the potassium cryolite hydrate 1 molecular equivalent of $Al_2F_6.18H_2O$ (82.048 grams) was added to 6 molecular equivalents of potassium fluoride. The gelatinous precipitate with the supernatant liquid was heated in a platinum crucible to about 270° in the Morey pressure bomb. Upon cooling the system to room temperature it was found that the gelatinous precipitate had been transformed into an anhydrous crystalline product. Two types of crystals were present. Some were needle-like and others plate-like in appearance.

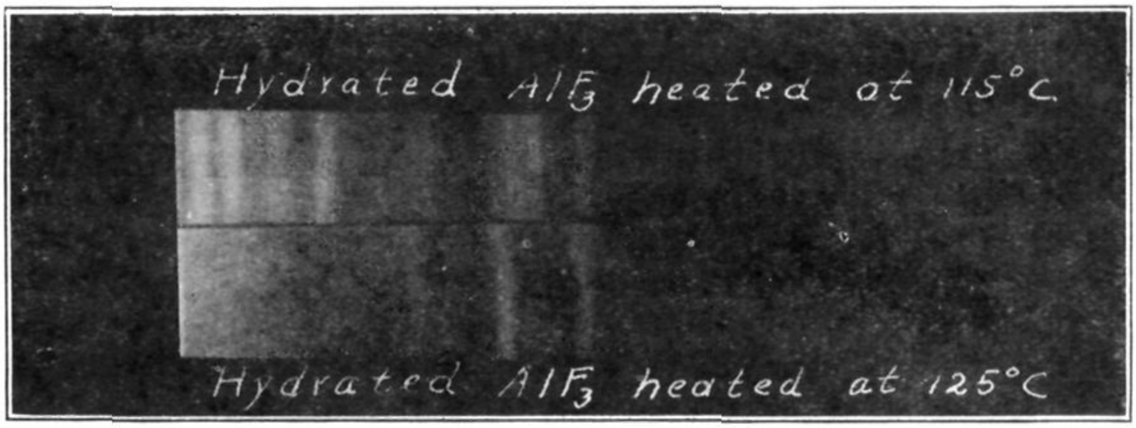

Fig. 1.

Professor A. N. Winchell of the Department of Geology of the University of Wisconsin was kind enough to examine the optical properties of the two types of crystals. His observations are given below.

"Fibers or needles are orthorhombic with small optic angle (2 v. = 40 est.) of negative sign and negative elongation; twinned on a fusion face; parallel extinction. All indices below 1.445 and above 1.34. Birefringence or $Ng - Np = 0.002 - 0.01$. Plate-like crystals are monoclinic with small optic angle (2 v. = 40 est.) of positive sign. Extinction reaches at least 8 on cleavage. All indices below 1.445 and above 1.34. Birefringence similar to preceding."

*Anal.* Needle-like crystals. Calcd. for $4KF.Al_2F_6$: Al, 13.49; K, 39.07. Found: Al, 13.53, 13.62, 13.50, 13.44; K, 38.84, 39.03.

Plate-like crystals. Found: Al, 13.58, 13.53, 13.42, 13.52; K, 39.07, 38.95, 38.86, 38.95.

The chemical analyses show that the formula of the compound is $4KF.Al_2F_6$ and not $6KF.Al_2F_6$ as indicated by Baud.

**The Preparation of $4RbF.Al_2F_6$.**—The rubidium fluoride was prepared by neutralizing rubidium carbonate with an excess of hydrofluoric acid. The salt was fused in a platinum crucible in order to drive off any free acid. The double salt was prepared by adding one molecular equivalent of $Al_2F_6.18H_2O$ (82.048 g.) to 6 molecular equivalents of rubidium fluoride. The resulting solution and gelatinous precipitate were placed in a platinum crucible and heated in a Morey bomb to about 270°. Upon cooling the system a crystalline product was obtained. The crystals were similar in appearance to the orthorhombic crystals of potassium-aluminum fluoride.

*Anal.* Calcd. for $4Rb.Al_2F_6$: Al, 9.22; Rb, 58.34. Found: Al, 9.21, 9.37; Rb, 58.33, 58.12.

It will be observed that this compound is analogous to the potassium salt, $4KF.Al_2F_6$.

**The Study of the System Sodium Fluoride-Aluminum Fluoride.**—Six moles of sodium fluoride were added to 1 mole of $Al_2F_6.18H_2O$. When the gelatinous product was subjected to a temperature even as high as 400°, there was scarcely any crystallization. Small crystals adhered to the sides of the platinum crucible, but they were not obtained in sufficient quantity for chemical analysis.

**The Study of the System Alkali Fluorides—Aluminum Fluoride by Means of Electrical Conductance.**—The conductivity determinations were made by means of the Kohlrausch method. The modified Leeds and Northrup Wheatstone bridge and telephone were used. The conductivity water had a specific conductance of $3.14 \times 10^{-6}$ ohms. A certain quantity of the aluminum fluoride solution of known concentration was measured into the conductivity cell. The cell and its contents were placed in a thermostat which was held at 25°. When the solution had attained the temperature of the bath, the resistance of the solution was taken. The resistance was then taken upon separate additions of potassium fluoride, rubidium fluoride, ammonium fluoride and sodium fluoride, respectively. The system aluminum fluoride-potassium fluoride gave a maximum resistance when 4 moles of potassium fluoride were added to 1 mole of $Al_2F_6$. The system aluminum fluoride-rubidium fluoride gave also a maximum resistance when 4 moles of rubidium fluoride were added to 1 mole of $Al_2F_6$. These ratios are in agreement with the chemical analyses of these salts. The system aluminum fluoride-ammonium fluoride gave a maximum resistance when 4 moles of ammonium fluoride were added to 1 mole of $Al_2F_6$. The system aluminum fluoride-sodium fluoride gave a maximum resistance when 5 moles of NaF were added to 1 mole of $Al_2F_6$. The compounds ammonium aluminum fluoride and sodium aluminum fluoride have not been verified by chemical analysis.

Acknowledgment is hereby tendered to Professor Victor Lenher for his guidance and helpful suggestions throughout this work.

## Summary

1. Hydrated aluminum fluoride of the composition $Al_2F_6.18H_2O$ has been prepared from aluminum hydrate and aqueous hydrofluoric acid.

2. The preparation of anhydrous aluminum fluoride by subjecting crystals of $Al_2F_6.18H_2O$ or a neutral solution of aluminum fluoride to high temperatures has been accomplished.

3. The compounds $4KF.Al_2F_6$ and $4RbF.Al_2F_6$ have been prepared in crystalline form by subjecting the gelatinous precipitate to high temperatures in a closed system.

ARNOLD, PENNSYLVANIA