

PREPARATION OF HEXAFLUOROALUMINIC ACID AND SOME OF ITS SALTS*

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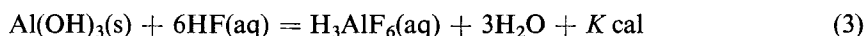
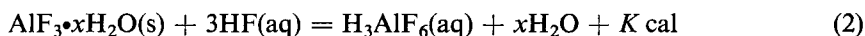
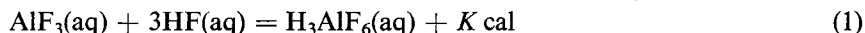
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SUMMARY

A highly acidic solution of hexafluoroaluminic acid may be obtained by dissolving alumina in hydrofluoric acid and its concentration determined either by precipitation of Na_3AlF_6 or by titration with alkali. The copper, silver, zinc and cadmium salts of this acid have been prepared. Dilute solutions of the acid (up to 2 N) are stable at room temperature over long periods: more concentrated solutions decompose with precipitation of $\beta\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$, as shown by chemical, thermogravimetric and X-ray analysis.

INTRODUCTION

Tetrafluoroboric acid and hexafluorosilicic acid are known only as aqueous solutions which have been investigated in detail. In contrast, hexafluoroaluminic acid, H_3AlF_6 , was almost unknown until recently. The possibility of preparing this acid *via* the reaction depicted below was mentioned by Petersen in 1890¹ and by Baud in 1904², but the conditions for its existence were not defined.



In 1968, Tananaev and his co-workers investigated the system $\text{AlF}_3\text{-HF-H}_2\text{O}$ by NMR spectroscopy and found solid phases to which they assigned the formulae $\text{H}_3\text{AlF}_6 \cdot 3\text{H}_2\text{O}$ and $\text{H}_3\text{AlF}_6 \cdot 6\text{H}_2\text{O}$ ³. Later work by Kalach *et al.*⁴, also based on the NMR method, likewise produced evidence for the formation of hexafluoro-

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aluminic acid in this system. In neither case, however, was it studied chemically. The experiments described in this paper show that the acid is capable of existence in aqueous solution and that its solutions may be used to prepare hitherto unknown salts.

EXPERIMENTAL

In preliminary experiments it was found that crystalline $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ did not dissolve in a 20% solution of hydrofluoric acid even on boiling [equation (2)]. Solid alumina, however, dissolved readily in either dilute or concentrated hydrofluoric acid [equation (3)] and our investigation was based on this reaction. Stoichiometric quantities of either pure $\text{Al}(\text{OH})_3$ or material of technical grade were used with acid concentrations up to 80%, the reaction being carried out in plastic vessels which were cooled externally. Clear solutions of $\text{pH} \leq 1$ were obtained, from which the salts Na_3AlF_6 , $\text{Ca}_3(\text{AlF}_6)_2 \cdot 3\text{H}_2\text{O}$, $\text{Sr}_3(\text{AlF}_6)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Ba}_3(\text{AlF}_6)_2 \cdot \text{H}_2\text{O}$ were precipitated by addition of the appropriate cations. The last three of these salts have been described by Nielsen⁵. It was concluded, therefore, that the solutions contained hexafluoroaluminic acid. The concentration of free acid was determined either by titration with a standard base using methyl red as an indicator or by precipitation of Na_3AlF_6 and weighing the latter. The results agreed, although the precipitate of Na_3AlF_6 was gelatinous and difficult to filter. Solutions of the free acid with concentrations in the range 0.1–15 *N* were prepared, but on attempting to dissolve alumina in 80% HF to obtain stronger solutions a white precipitate appeared. Table 1 shows the results of a series of experiments on the stability of aqueous solutions of H_3AlF_6 of different concentration at room temperature.

Dilute solutions (up to 2 *N*) were shown by analysis to be unchanged for 12 months at 22°. At higher concentrations the stability decreased progressively

TABLE 1

CONDITIONS OF SYNTHESIS AND STABILITY OF SOLUTIONS OF H_3AlF_6
AT ROOM TEMPERATURE

Synth. No.	Concentration of HF solution (%)	Alumina (techn.) or $\text{Al}(\text{OH})_3$ (p.a.)	Concentration of H_3AlF_6 solutions (<i>N</i>)	Stability of H_3AlF_6 solutions
1	20 ^a	$\text{Al}(\text{OH})_3$	2	1 year
2	25 ^a	alumina	2	1 year
3	40 ^a	$\text{Al}(\text{OH})_3$	3	7 days
4	40 ^a	alumina	8.84	20 h
5	50 ^b	alumina	12.5	12 h
6	60 ^b	alumina	15	8 h
7	80 ^b	alumina	(18.8)	0 h

^a p.a.

^b Techn.

and at concentrations of 9–15 *N* a white precipitate appeared within a few hours. The precipitate consisted of thin needle-like crystals which became slightly yellow in colour after 10 days recrystallisation at 105°. The precipitate was identified as $\beta\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$ (Analysis: Found: Al, 19.6; F, 39.7; H_2O , 38.9%. $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ requires Al, 19.58; F, 41.3; H_2O , 39.15%). Thermogravimetric analysis with a Perkin–Elmer TGS-1 instrument with a scan rate of $16^\circ \text{ min}^{-1}$, sample weights of about 2 mg in an atmosphere of nitrogen, gave a curve almost identical with that for an authentic specimen of $\beta\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$ (Fig. 1).

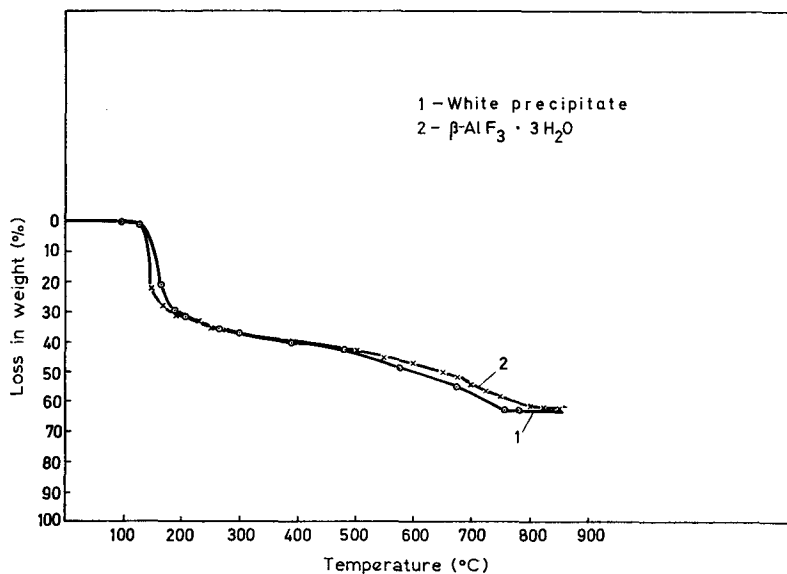
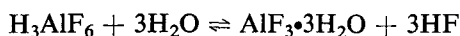


Fig. 1. Thermogravimetric curves of the white precipitate and of $\beta\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$.

A series of Debye diagrams was obtained using specimens prepared by the direct decomposition of aqueous H_3AlF_6 and also after recrystallisation of the product. In both cases the Debye diagrams exhibited the same patterns although differing in the intensities of some reflections. This may indicate the presence of two forms of the same crystalline compound. These results are in agreement with those reported for $\beta\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$ by Cowley and Scott⁶ and by Bulgakov and Antipina⁷. In some samples which had not been recrystallised small amounts of compounds of the type $16\text{AlF}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ and $16\text{AlF}_2(\text{OH}) \cdot 6\text{H}_2\text{O}$ as described by Bulgakov and Antipina⁷ were observed. These results, which are summarised in Table 2, confirm that the decomposition of the aqueous acid may be represented by the equation:



The increased amount of fluoride ions observed after isolation of the white precipitate confirms the accuracy of this equation.

TABLE 2
DIFFRACTION PATTERNS OF THE COMPOUNDS β -AlF₃•3H₂O, 16AlF(OH)₂•6H₂O AND 16AlF₂(OH)•6H₂O

No.	Product before recrystallisation		Product after recrystallisation		AlF ₃ •3H ₂ O ^a		AlF ₃ •3.5H ₂ O ^b		16AlF(OH) ₂ •6H ₂ O and 16AlF ₂ (OH)•6H ₂ O ^b	
	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n
1	10	5.47	10	5.47	10	5.47	10	5.50	10	5.70
2	9	3.83	5.3	3.38	5.6	3.86	5	3.86	—	—
3	0.4	3.63	0.23	3.63	1.7	3.66	0.6	3.63	—	—
4	1	3.30	4	3.30	5.2	3.29	5	3.28	—	(3.48)
5	0.9	3.02	2	3.02	3.5	3.01	3	3.03	4.8	2.98
6	5.8	2.71	4.3	2.71	2.7	2.72	1.6	2.73	2.2	2.84
7	0.9	2.64	3.3	2.64	2.5	2.64	—	—	—	—
8	1	2.50	4	2.50	2.7	2.50	—	—	—	—
9	9	2.43	8	2.43	5.8	2.43	4	2.44	0.6	2.46
10	0.4	2.18	1	2.18	1.0	2.18	0.2	2.18	0.6	2.26
11	0.3	2.09	0.5	2.09	0.4	2.08	0.2	2.09	—	—
12	1.2	2.02	3.3	2.02	2.3	2.02	1.6	2.03	—	—
13	2.8	1.93	2.3	1.93	1.5	1.92	0.6	1.93	—	2.01
14	0.8	1.84	2	1.84	1.5	1.83	0.4	1.84	2	1.83
15	0.5	1.77	5.7	1.77	4.4	1.77	4	1.77	—	—
16	8	1.72	7.6	1.72	5.6	1.72	5	1.72	2.4	1.74
17	0.4	1.66	1.1	1.66	1.2	1.66	0.4	1.66	—	1.66
18	0.2	1.62	0.3	1.62	—	—	0.4	1.61	—	—
19	0.2	1.56	0.6	1.56	—	—	0.2	1.56	0.6	1.55
20	0.8	1.51	1	1.51	—	—	0.2	1.51	0.9	1.50
21	—	—	—	—	—	—	—	—	0.9	1.48
22	—	—	—	—	—	—	—	—	0.2	1.42
23	0.3	1.39	0.7	1.39	—	—	1	1.39	1.1	1.38
24	0.3	1.33	0.3	1.33	—	—	—	—	—	—
25	0.3	1.32	0.2	1.32	—	—	—	—	—	—

^a According to Cowley and Scott⁶.

^b According to Bulgakov and Antipina⁷.

TABLE 3
CHEMICAL ANALYSES OF FLUOROALUMINATES

	Calculated (%)						Found (%)							
	Al	F	H ₂ O	Ag	Cu	Zn	Cd	Al	F	H ₂ O	Ag	Cu	Zn	Cd
Ag ₃ AlF ₆ •3H ₂ O	5.25	21.95	10.45	62.35	—	—	—	5.72	21.83	10.26	61.99	—	—	—
Cu ₃ (AlF ₆) ₂ •12H ₂ O	7.84	33.11	31.36	—	27.69	—	—	8.30	33.08	31.36	—	27.26	—	—
Zn ₃ (AlF ₆) ₂ •18H ₂ O	6.73	28.42	40.39	—	—	24.46	—	7.30	28.20	40.15	—	—	23.73	—
Cd ₃ (AlF ₆) ₂ •12H ₂ O	6.47	27.30	25.86	—	—	—	40.37	6.73	27.25	26.60	—	—	—	40.19

As is to be expected, solutions of hexafluoroaluminic acid attack glass. Aluminium and cadmium dissolve readily in cold dilute solutions, zinc rather slowly while copper remained unchanged for several days. The cadmium salt was prepared by this method, while copper and zinc salts were obtained by reaction of 2 *N* or 3 *N* solutions of the acid with concentrated solutions of the acetates of these two metals. A silver salt was similarly obtained by dissolving Ag₂O in the acid. All of these salts were isolated from their clear solutions by slow evaporation at room temperature in a stream of air. The copper salt was sky-blue in colour the others being white, though the silver salt darkened on exposure to light. All the salts were first dried in a vacuum dessicator over concentrated H₂SO₄ or P₂O₅ and then analysed chemically and thermogravimetrically. The results of the chemical analyses are given in Table 3.

Thermogravimetric analyses showed that all the salts lose water below 100°, this process being complete at 90° for the silver salt but requiring temperatures of 300–400° for the remainder. The silver and cadmium salts were readily soluble in cold water. Copper and zinc salts, however, were only sparingly soluble in cold water but were more soluble in hot water. All these salts are soluble in dilute sulphuric acid.

The above salts are the only metallic hexafluoroaluminates prepared to date apart from those of the alkali and alkaline earth metals, ammonium and thallium prepared earlier and the hydrazine hexafluoroaluminates prepared recently by Šiftar and Bukovec⁸ from aluminium fluoride and hydrazinum fluoride.

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