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HIGH TEMPERATURE CRYSTALLIZATION OF ALUMINUM FLUORIDE.
COURSE, HYDROLYSIS, SOLID PHASES.

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SUMMARY

A study for AlF_3 crystallization from water solution was performed in the temperature range 100 to 200°C.

Four solid phases were found to be precipitated, $AlF_3 \cdot 3H_2O$ (up to ca. 120°C), cubic α - $AlF_3 \cdot H_2O$ (decomposition of $AlF_3 \cdot 3H_2O$ in suspension), hexagonal β - $AlF_3 \cdot H_2O$ (direct from solution) and the hydroxyfluoride $Al(OH,F)_3 \cdot H_2O$ with an F/Al ratio of ca. 2.5 (hydrolysis of AlF_3). The extent of hydrolysis was established as a function of the initial AlF_3 concentration.

X-ray diffraction and thermogravimetric data for the monohydrates were given and differences between the two indicated.

INTRODUCTION

A particular feature of the AlF_3 crystallization process is that, as far as the stable sparingly soluble $AlF_3 \cdot 3H_2O$ is concerned, it requires prolonged heating of supersaturated solutions, preferably near to boiling temperature, instead of cooling, as is usually the case in other typical processes of this kind. This phenomenon is considered as substantially depending on irreversible intramolecular rearrangement of AlF_n^{3-n} ($n=1-6$) hydrate complexes into which AlF_3 molecules are dissociated, especially into the $[AlF_2 \cdot 4H_2O]^+$ and $[AlF_4 \cdot 2H_2O]^-$ ions, or in progressive breakdown of higher AlF_3 hydrates to $AlF_3 \cdot 3H_2O$ which precipitates from the solution [1-3].

Cooling the AlF_3 solutions provides $AlF_3 \cdot 9H_2O$ (<8°C), $AlF_3 \cdot 5.5H_2O$ or $AlF_3 \cdot 3.5H_2O$ (e.g. by 'salting out' with

ethanol at ambient temperature), all of which are unstable and progressively transform to the $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ [2, 4].

$\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$ was reported by Yatlov and Pinaevskaya [4] to exist in two unstable forms differing in their solubilities and refractive indexes. Similarly, Ehret and Frere [1] consider a dimorphism in $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ (α and β) but later findings of Schmidt [2] suggest that α - $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ is virtually identical with well-soluble $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$. (For X-ray patterns see Fig.9, no.1 and 4).

Apart from the above mentioned AlF_3 -hydrates, mono- and hemihydrate are known as intermediates in the dry calcination of $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$ and $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$, respectively, both having the crystal structure of the anhydrous rhomboedral α - AlF_3 [2]. As a new crystalline phase, the cubic monohydrate $\text{AlF}_3 \cdot \text{H}_2\text{O}$ was discovered by Chandross [5] in a precipitate formed in an industrial column for HF gas scrubbing with AlCl_3 -HCl-solution, but several attempts made by this author to duplicate the synthesis on a laboratory scale all failed.

In the anhydrous state aluminum fluoride is known to exist in three forms: the most stable α (rhomboedral) [6], β (hexagonal) [7] and γ (tetragonal) [8].

Solutions of AlF_3 undergo slight hydrolysis on boiling, but no hydroxyfluoride has hitherto been obtained in this way. There were expectations, however, that hydrolysis at 150-200°C would produce basic fluorides in greater amounts [9]. Aluminum basic fluoride has however been obtained in other ways [9-11] and well characterized by Cowley and Scott [9].

In the last few years several patents appeared in various countries concerning the AlF_3 crystallization process carried out at elevated temperatures under autoclave conditions [12-15], all indicating that lower-hydrated aluminum fluorides are precipitated at temperatures in excess of ca. 120°C. These have compositions between the mono- and hemihydrate [12]. Apart from the information that β - AlF_3 is formed [14] under these conditions, there are no reports, as yet, on the physicochemistry of AlF_3 solutions at temperatures above 100°C or on the nature of the solids precipitated or the extent of AlF_3 hydrolysis.

The purpose of this work was to report some investigations made in this field.

EXPERIMENTAL

Crystallization of aluminum fluoride out of its supersaturated solutions was examined in the temperature range 100-200°C with autogenous pressures of 0-20 at. For this purpose AlF_3 -solutions were obtained by reaction of H_2SiF_6 with $\text{Al}(\text{OH})_3$ at 80-100°C, after which silica was filtered off with suction. They were of concentrations between 25 and 300 g/l and of pH ca. 4.

Most experiments were run in a steel autoclave (capacity 1 l) with external electric heating. It was equipped with a manometer, an anchor stirrer (45 rpm) and a needle valve for sampling and discharging. The internal autoclave pressure served to expel the slurry. A freshly prepared solution of AlF_3 of a given strength at a temperature of about 80°C was brought in the autoclave to boiling within 10-15 min and then further heated with stirring. The heating rate gave a pressure increase of 0.1-0.15 at/min, which enabled steam pressures of 2, 3, 5 at to be attained within 15-25, 25-40 and 40-60 min, respectively. With such a heating rate the overall crystallization process was complete before a pressure of 10 at could be approached and was nearly complete at about 7 at. Some tests were performed on a pilot plant involving a stirred autoclave with carbon lining, and heated by direct injection of live steam. It enabled experiments to be carried out in acidic media.

The course of the crystallization process was followed by taking samples of the slurry at certain intervals and determining the AlF_3 content by density measurements of the supernatant solution at 20°C, using an AlF_3 concentration versus density calibration curve. The relevant data for this curve are given in Table 1.

TABLE 1

Density of AlF_3 solutions at ca. 20°C

d., g/cm ³	1.020	1.060	1.100	1.140	1.180	1.220
AlF_3 , g/l	22.0	63.0	107.0	151.0	197.0	243.0

After drying at ca. 100°C residues were analyzed for Al and F, the water content being obtained by difference

(100 - % Al x 3.11). Al was determined by the EDTA method and fluorine by the alizarine method after distillation. The precipitates were characterized as to their structure and thermal behavior by the X-ray and thermogravimetric methods. X-ray diffraction patterns were taken using an MUR analyzer (GDR), and derivatograms on a MOM (Budapest) device. Granulation was determined microscopically, pH values being measured on a pH-meter with a glass electrode.

RESULTS AND DISCUSSION

Course

The course of AlF_3 crystallization was investigated under iso- and polythermic conditions in the range 100-150°C with continuous stirring. Isothermic conditions were possible only at comparatively low temperatures, basically not exceeding ca. 120°C and in the absence of seed. At higher temperatures, as for example at ca. 130°C, crystallization was far advanced before this temperature could be attained. Inasmuch as the AlF_3 crystallization process is strongly affected by numerous variables such as the heating rate and temperature distribution, the solute concentration, pH, time of allowing the solution to stand before using etc., all experiments were carried out, as far as possible, under the same conditions, to make them comparable.

The effect of temperature in the range 100-150°C on the course of AlF_3 -crystallization using solutions of 150 g/l, pH ~ 4, is illustrated in Figure 1 by (poly)isotherms taken at (°C/at): 102/0.5, 108/1.0, 122/2.0, 132/3.0 and 144/5.0. As is seen, increase in temperature results in shortening of the induction periods and increase in the crystallization rate as measured by the slopes of the curves. Furthermore, there is a decrease in the pH value (Fig. 2, curve 1) in approaching the process temperature. After that, when the temperature is kept constant and the crystallization of AlF_3 is continued, pH increases progressively to the final value, this being a characteristic one for the equilibrium state in solution after the crystallization. The equilibrium pH values are

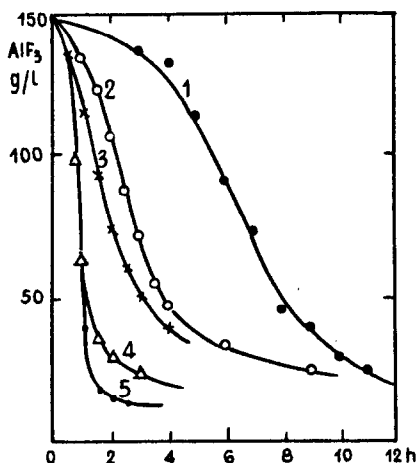


Fig. 1. The effect of temp. on the course of AlF_3 crystn. value in AlF_3 solns.: 1 - 102/0.5, 2 - 108/1.0, 3 - 122/2.0, 4 - 132/3.0, 5 - 144/5.0 ($^{\circ}\text{C}/\text{at}$).

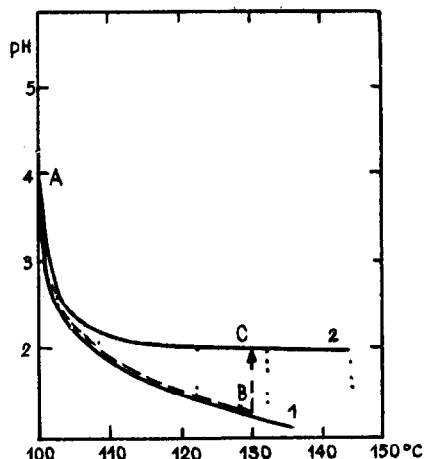


Fig. 2. The effect of temp. on pH value in AlF_3 solns.: 1 - 150 g/l, 2 - 20 g/l. Dotted line: direction of pH changes during the crystn. (example).

given by curve 2. The way in which pH varies during the process is exemplified by the dotted line ABC.

From chemical and X-ray analysis of the resultant precipitates (Table 2) at 102 and 108 $^{\circ}\text{C}$, $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ is the final crystallization product, whereas at 122 $^{\circ}\text{C}$ and above, lower-hydrated phases are formed which approximate to monohydrate, the water content varying from 1.0 to 0.9 mole per mole AlF_3 when progressing from 122 to 144 $^{\circ}\text{C}$. All the crystalline phases are 2-3% deficient in F content, regardless of temperature. These

TABLE 2

The effect of temperature on chemical and phase composition of precipitates from AlF_3 solution of 150 g/l

Sample No	at/ $^{\circ}\text{C}$	Chemical composition weight %		$\frac{[\text{F}]}{[\text{Al}]}$	$\frac{[\text{H}_2\text{O}]}{[\text{Al}]}$	Solid phase
		Al	F			
1	0.5/102	19.9	40.9	2.92	3.0	$\text{AlF}_3 \cdot 3\text{H}_2\text{O}$
2	1/108	20.4	.	.	3.0	
3	2/122	26.5	54.4	2.92	1.0	$\text{AlF}_3 \cdot \text{H}_2\text{O} +$
4	3/132	26.8	55.3	2.93	0.93	
5	5/144	27.1	.	.	0.87	$\text{Al}(\text{OH}, \text{F})_3 \cdot \text{H}_2\text{O}$

precipitates were identified as binary systems composed primarily of β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ with less than 10% mole of basic fluoride $\text{Al}(\text{OH},\text{F})_3 \cdot \text{H}_2\text{O}$, and will be described in detail later.

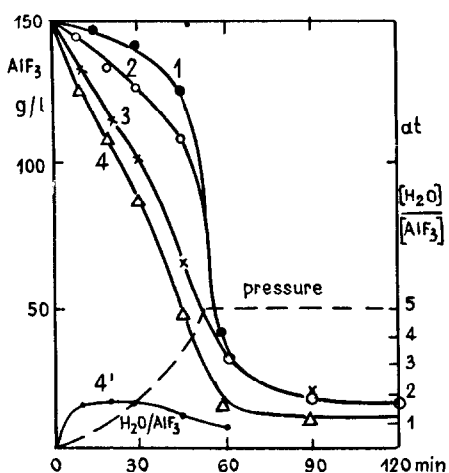
Experimental data given in Table 3 confirm the relation between the crystal water content in the monohydrate phase and the crystallization temperature. Increase from 132°C (3 at) up to 200°C (22 at) resulted in decrease in water content from 1.2 to 0.6 mole per mole of AlF_3 .

TABLE 3

The effect of temperature on crystal water content in aluminum fluoride precipitates

Time min	Pressure/ temp. at/ $^\circ\text{C}$	AlF_3 concn. g/l	Chemical composition weight %		$[\text{H}_2\text{O}]$
			Al	F	$[\text{Al}]$
0	0/100	150	-	-	
50	3/132	84	25.7	51.8	1.17
63	5/144	30	26.7	54.0	0.96
85	10	18	27.3	55.3	0.83
105	15	18	27.6	55.5	0.76
125	20	18	28.1	56.6	0.67
140	22/200	18	28.3	58.4	0.59

The effect of seed crystals of size $3\text{-}5\ \mu\text{m}$, used at 10, 50 and 100 g/l, on the course of the crystallization process was exemplified on AlF_3 solution 150 g/l, heated up to 144°C



(5 at). From the shape of particular curves (Figure 3), increasing amounts of seeding reduce the importance of nucleation step. The crystal growth step becomes more significant,

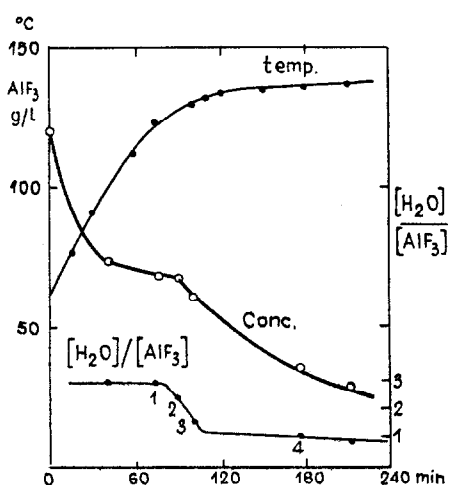
Fig.3. The effect of β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ seed crystals ($3\text{-}5\ \mu\text{m}$) on the course of AlF_3 crystn. 1 - without seed, 2 - 10 g/l, 3 - 50 g/l, 4 - 100 g/l 4' - water content in ppt. corresp. to the curve 4. Final temp. 144°C (5 at).

the rate of the latter being increasingly controlled by the available surface of the added crystals. As a result of seeding the solution, the polycrystalline product increases in size to 60-80 μm . It is notable that crystallization curves exhibit deflections, indicating an acceleration of the process after passing a temperature of about 125°C (2.2 at).

Examination of the resulting solids taken along curve 4 indicates that the trihydrate $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ is generated initially from the nutrient solution and then yields (together with 0.8-hydrate seed crystals) a mixture with an average composition of up to $\text{AlF}_3 \cdot 1.8\text{H}_2\text{O}$ after 20 min. As crystallization proceeds with continuous increase in temperature, a rapid drop of water content follows to give ultimately solids with $\text{H}_2\text{O}/\text{Al} = 0.9$. Such behavior is evidently associated with thermal decomposition of the AlF_3 -trihydrate phase in suspension.

X-ray patterns of such solids show the presence of a third phase, in addition to $\beta\text{-AlF}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}(\text{OH},\text{F})_3 \cdot \text{H}_2\text{O}$. It is readily noticeable by examining the line of the β -phase with $d=3.64$ which increased in intensity due to overlapping with a line of this new phase. It was found that the proportion of this new phase became greater as seed crystals were increasingly employed. The same was observed for AlF_3 solutions with high strength, e.g., of 300 g/l, which are of decreased stability.

More persuasive evidence was provided in an additional experiment conducted at a comparatively low rate of increase



of temperature. The starting AlF_3 solution was acidic ($\text{H}_2\text{SiF}_6 \sim 8 \text{ g/l}$, pH 1.8) and was heated by injection of live steam into the stirred vessel. Under such conditions a great deal of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ crystallized

Fig. 4. The effect of temp. on the course of AlF_3 crystn. from acidic soln. (H_2SiF_6 8 g/l, pH 1.8) and on the compn. of the products.

from solution before a temperature of 100°C was attained (Figure 4). Initially this process was rapid but was considerable slowed down on approaching a temperature of ca. 125°C, only to accelerate instantly after passing this point. The sudden alteration in the process rate was attended by rapid decrease in the hydration of the precipitate which changed from the composition $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ at 125°C to the monohydrate at 135°C. In the conversion process, as shown by the X-ray method, $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ goes over to a monohydrate phase other than hexagonal $\beta\text{-AlF}_3 \cdot \text{H}_2\text{O}$, viz., to cubic $\text{AlF}_3 \cdot \text{H}_2\text{O}$ (Fig. 9, no. 1 and 2) which was recognized as identical with that described by Chandross [5]. In this work it was referred to as the

α -form, because of its relationship to the well-known anhydrous rhomboedral $\alpha\text{-AlF}_3$.

The effect of initial concentration of AlF_3 in the range 25-300 g/l on the course of crystallization for comparable rates of increase of temperature from 100 to 144°C (0-5 at) and with continuous stirring is illustrated by the curves in Figure 5. Chemical and phase compositions of the products obtained are summarized in Table 4. In all cases the duration of the whole process was about the same (ca. 90 min.), as well as the final concentration of AlF_3 (15-20 g/l).

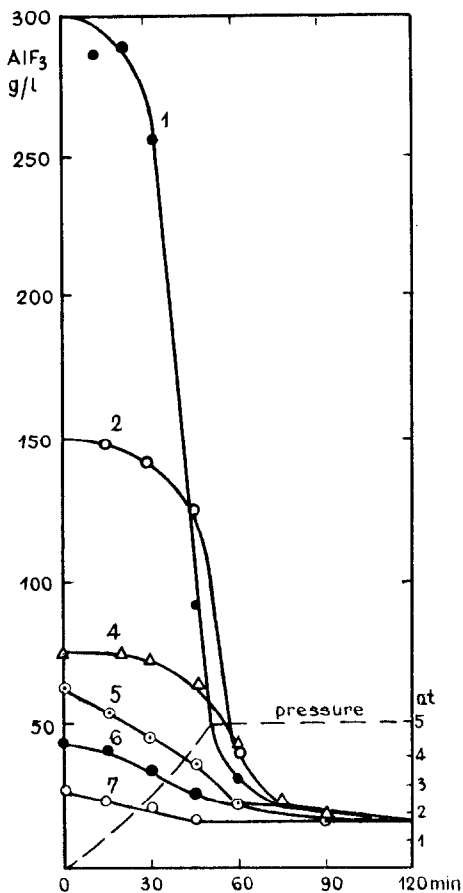


Fig. 5. The course of AlF_3 crystn. for different initial solute content. Final temp. 144°C/5 at. Numeration as in Table 4.

TABLE 4

The effect of initial concentration of AlF_3 on chemical and phase composition of solids after crystallization

Sample No	Initial AlF_3 concn. g/l	Chemical composition, wt. %		[F]	[H_2O]	Phase composition, %	
		Al	F	[Al]	[Al]	$\text{AlF}_3 \cdot \text{H}_2\text{O}$	$\text{Al}(\text{OH}, \text{F})_3 \cdot \text{H}_2\text{O}$
1	300	26.45	54.8	2.94	0.93	94	6
2	150	26.90	55.9	2.95	0.90	92	8
3	100	27.50	56.80	2.93	0.92	90	10
4	75	27.00	54.30	2.86	0.89	74	26
5	60	27.20	53.25	2.77	0.85	71	29
6	42	27.73	50.45	2.60	0.75	27	73
7	25	26.32	46.42	2.50	1.04	0	100

From the shapes of the curves it is seen that those at higher concentrations (1-4), in contrast to those at lower concentrations (5-7), have more pronounced boundaries between the nucleation and crystal growth steps. This suggests that different mechanisms are involved in the precipitation of solid phases. Chemical analysis shows (Table 4) that there is a drop in the F/Al ratio from 2.9 to 2.5 when passing from 300 g/l to 25 g/l, the ratio of crystalline water to Al remaining at a constant value of 0.9-1.0.

X-ray diffraction patterns reveal two phases, that of β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ and that of the basic fluoride, $\text{Al}(\text{OH}, \text{F})_3 \cdot \text{H}_2\text{O}$, the latter contributing increasingly to solids precipitating from AlF_3 solutions of lower concentration, especially below 100 g/l. The precipitate derived from a solution of AlF_3 , 25 g/l, appeared to be the basic fluoride with a chemical composition $\text{Al}(\text{OH})_{0.5}\text{F}_{2.5} \cdot \text{H}_2\text{O}$ and is identical with the cubic phase $16\text{Al}(\text{OH}, \text{F})_3 \cdot 6\text{H}_2\text{O}$ described earlier by Cowley and Scott [9], for compositions with an F/Al ratio varying from 1 to 2. Whether the F/Al ratio increase to 2.5 is attributable to HF adsorption or to extended substitution OH^- by F^- ions was not ascertained in this work and further examination is required.

The wide range of existence of the basic fluoride phase with respect to F/Al ratios from 1.0 to probable 2.5 and uncertainty as to the precise composition of β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ make it impossible to estimate the proportions of these two

constituents in their mixtures on the basis of the chemical analysis only, as given in Table 4. It may be, however, done by the aid of the X-ray method, on the basis of the relationship between the content of one of the two components and the height ratio of suitable lines. To obtain the calibration curve, the most intense peaks for β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ ($d=6.3 \text{ \AA}$, 7°) and for $\text{Al}(\text{OH},\text{F})_3 \cdot \text{H}_2\text{O}$ ($d=5.7 \text{ \AA}$, 7.75°) were utilized in known mixtures of both pure components. Based on this curve the phase composition of solids for various initial concentrations was estimated (Table 4) and compared in Figure 7 with theoretical curve (see next section). As is seen, the proportion of basic fluoride admixed with $\text{AlF}_3 \cdot \text{H}_2\text{O}$ amounts to several percent in the AlF_3 concentration range between 300 and 100 g/l, and increases rapidly for AlF_3 concentrations below 100 g/l. It is 100% at 25 g/l.

Hydrolysis of aluminum fluoride

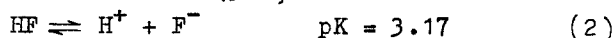
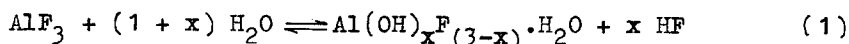
The presence of Al hydroxyfluoride among the other crystallization products shows that AlF_3 suffers hydrolysis at elevated temperatures under autoclave conditions. So, decrease in the pH values from ca. 4 to 1.3 is observed when AlF_3 solutions of 150 g/l are heated from 100 to 130°C (curve 1, Fig. 2). Observations made with variable time of the crystallization process indicated that at a given temperature the pH increases when the AlF_3 concentration decreases, passing from a value lying on the lower curve 1 to the corresponding value on the higher curve 2. Thus variations in pH during the crystallization process from AlF_3 150 g/l to 20 g/l at different temperatures between $100\text{--}150^\circ\text{C}$ proceed in an area enclosed by the two lines mentioned, for example along the line ABC.

One can infer from these facts that aluminum hydroxyfluoride should be formed basically in the same quantities along with different amounts of β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$, depending on the initial solute concentration. It does not apply obviously to AlF_3 solutions that are previously acidified to prevent hydrolysis.

In order to quantify the hydrolysis, an expression was derived for the degree of AlF_3 hydrolysis, α_{H} , which enables the proportion of basic fluoride in admixture with β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$

to be calculated in relation to the initial solute content, C_{AlF_3} , the degree of its dissociation, x , and the final pH value.

Assuming that hydrolysis follows equation:



α_h may be expressed by

$$\alpha_h = \frac{1}{x} \frac{C_{\text{HF tot.}}}{C_{\text{AlF}_3}} \quad (3)$$

Since $C_{\text{HF tot.}}$ is related to pH by the equation:

$$\alpha_{\text{dis.}} = \frac{C_{\text{H}^+}}{C_{\text{HF equil.}} + C_{\text{H}^+}} = \frac{1}{1 + 10^{\text{pK} - \text{pH}}} \quad (4)$$

hence:

$$C_{\text{HF tot.}} = C_{\text{HF equil.}} + C_{\text{H}^+} = C_{\text{H}^+} (1 + 10^{3.17 - \text{pH}})$$

$$C_{\text{HF tot.}} = 10^{-\text{pH}} + 10^{3.17 - 2 \text{pH}} \quad (5)$$

The degree of AlF_3 hydrolysis is thus given by:

$$\alpha_h = \frac{1}{x} \frac{1}{C_{\text{AlF}_3}} \cdot (10^{-\text{pH}} + 10^{3.17 - 2 \text{pH}}) \cdot 100, \text{ in } \% \quad (6)$$

The relation given by the expression (5), plotted in Figure 6, may be of significance for estimation x-values by comparison of an actual concentration of AlF_3 with that of HF, due to hydrolysis, and defined by the pH of the solution concerned.

For example, lowering the pH from an initial value of 4 in AlF_3 solution with 150 g/l (1.8 M) to 1.3 ($C_{\text{HF}} \sim 4 \text{ M}$) when the temperature is raised to ca. 132°C , indicates that AlF_3 undergoes hydrolysis to an

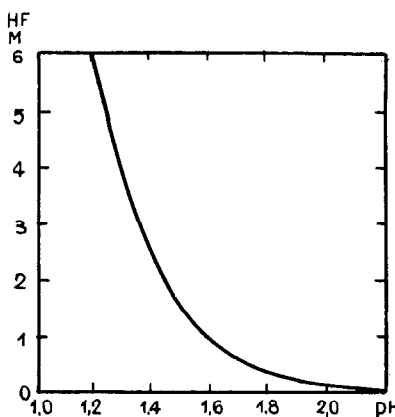


Fig. 6. HF concn.(M) versus pH plot according to the equation $C_{\text{HF}} = 10^{-\text{pH}} + 10^{3.17 - 2 \text{pH}}$

extent corresponding to the formation of hydroxyfluoride with an F/Al ratio as low as 1. However, subsequent increase in the pH value observed at a constant process temperature as the concentration of AlF_3 decreases, due to the crystallization, might be brought about by the formation of hydroxyfluoride with higher F/Al values. These considerations may be confirmed by studying the function $\alpha_h = f(C_{\text{AlF}_3})$, given by equation (6). It is inversely proportional to the AlF_3 concentration and is graphically illustrated by a hyperbole in Figure 7 for $\text{pH} = 2.1$ and $x = 0.5$ ($\text{F/Al} = 2.5$). There is seen to be a reasonable consistency between this theoretical graph and the experimental data (points 1-7). The line B for F/Al ratios (from Table 4) against compositions of the system $\beta\text{-AlF}_3 \cdot \text{H}_2\text{O} - \text{Al}(\text{OH},\text{F})_3 \cdot \text{H}_2\text{O}$ is also consistent with the assumption that the hydroxyfluoride enters the mixtures when $\text{F/Al} = 2.5$, whereas the β -phase does so when $\text{F/Al} \approx 2.95$.

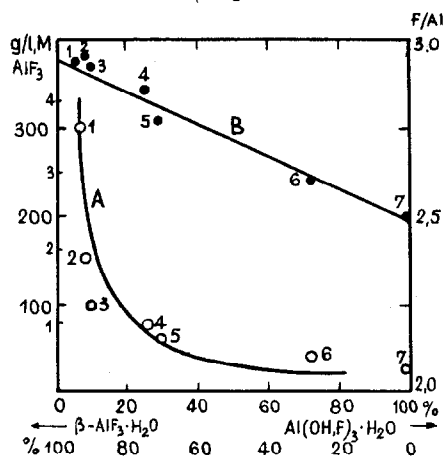


Fig. 7. Compn. of the system $\text{Al}(\text{OH},\text{F})_3 \cdot \text{H}_2\text{O} - \beta\text{-AlF}_3 \cdot \text{H}_2\text{O}$ crystd. in relation to the initial concn. of AlF_3 .

A - degree of AlF_3 hydrolysis for $\text{pH} = 2.1$ and $\text{F/Al} = 2.5$ ($x=1$) from equation (6).
 B - av. F/Al values in mixts.
 Points 1-7 - exptl. data (see Table 4).

X-ray and thermal investigations

$\text{Al}(\text{OH})_{0.5}\text{F}_{2.5} \cdot \text{H}_2\text{O}$

The interplanar distances and intensities of basic fluoride with $\text{F/Al} = 2.50$, as compared with those given by Cowley and Scott for $\text{F/Al} = 1.65$, are given in Table 5. Calculations made for the line with the assignment 222 give a value of 9.85 \AA for the lattice constant, which after heating to 500°C , undergoes reduction to 9.77 . Analogous values given by Cowley and

TABLE 5
The interplanar distances and intensities of X-ray diffraction lines for various aluminium fluoride monohydrates

16Al(OH) ₂ ·1.35F ₂ ·1.65·6H ₂ O ^a 1500°C		Al(OH) _{0.5} F _{2.5} ·2.5H ₂ O ^b 500°C		β-AlF ₃ ^c		β-AlF ₃ ·H ₂ O ^d 600°C		AlF ₃ ·H ₂ O ^e		α-AlF ₃ ·H ₂ O ^f			
hkl	d	I	I ^h	d	I	hkl	d	I ^h	hkl	d ⁱ	I	d	I ^h
111	5.70	460	320	5.70	350	100	6.002	st	100	3.55	100	3.64	100
220	3.44	26	26	3.44	26	002	3.563	st	110	2.51	0		
311	2.979	220	100	2.92	108	110	3.465	st	111	2.05	13	2.09	16
222	2.841	100	100	2.83	100	102	3.063	st	200	1.78	37	1.81	56
400	2.460	26	9	2.45	26	200	3.001	st	210	1.59	28	1.62	45
331	2.258	21	8	2.27	24	111	2.484	st	211	1.45	1	1.48	3
422	2.009	44	74	1.99	68	202	2.295	w	220	1.26	13	1.28	24
333	1.893	92	80	1.88	110	210	2.266	w	221				
440	1.737	110	71	1.73	108	103	2.209	w	300	1.23	9	1.20	16
531	1.661	33	37	1.65	30	211	2.161	w	222	1.02	4	1.04	6
620	1.553	26	17	1.54	24	49	300	m	320	0.98	3		
535	1.498	40	26	1.49	40	212	1.914	m	321	0.89	1		
622	1.480	42	32	1.45	42	32	0.782	mst	400	0.89	2		
444	1.417	9	7	1.42	10	220	1.732	mst	410	0.86	7		
711	1.375	51	41	1.36	52	104	1.708	mw	410				
731	1.277	45	30	1.27	35	310	1.665	m	330	0.84	2		
553	1.227	13	12	1.22	12	114	1.585	m	420	0.79	8		
800	1.201	12	12	1.20	11	222	1.558	m	421	0.77	11		
733	1.201	12	12	1.20	11	400	1.500	m					
822	1.158	31	28	1.14	24	320	1.377	m					
660	1.127	17	11	1.10	11	304	1.330	w					
840	1.099	14	12	1.08	11	410	1.310	w					
911	1.079	10	12	1.07	12	322	1.284	w					
733	1.079	10	12	1.07	6	224	1.242	w					
684	1.047	9	6	1.04	5	314	1.216	w					
551	1.031	20	12	1.01	11	500	1.200	w					
						006	1.188	w					
						404	1.148	w					
						420	1.134	w					

^a Cowley and Scott [9]; cubic, $a=9.83$ Å, $d_{\text{det.}}=2.25$ g/cm³

^b from hydrolysis of AlF₃ soln. at ca. 140°C; cubic, $a=9.85$ Å, dehydrated at 500°C; $a=9.77$ Å

^c Christoph and Tenfer [7]; hexagonal, $a=6.93$ Å, $c=7.125$ Å, $d_{\text{calcd.}}=2.815$ g/cm³

^d crystall. out of AlF₃ soln. at ca. 140°C; hexagonal, $a=7.29$ Å, $c=7.36$ Å, $d_{\text{det.}}=2.45$ g/cm³;

^e dehydrated at 600°C; $a=7.20$ Å, $c=7.26$ Å.

^f Chandross [5]; cubic, $a=3.610$ Å, $d_{\text{det.}}=2.45$ g/cm³

^g from AlF₃·3H₂O crystals suspended in acidic AlF₃ soln., at ca. 140°C; cubic, $a=3.61$ Å, $d_{\text{det.}}=2.27$ g/cm³

^h from height of lines; h from area;
ⁱ recalcd. from assignments hkl given
by Chandross [5] using the expression
 $\sin^2 \theta = (h^2 + k^2 + l^2) \frac{\lambda^2}{4a^2}$
v - very, w - weak, m - medium,
st - strong

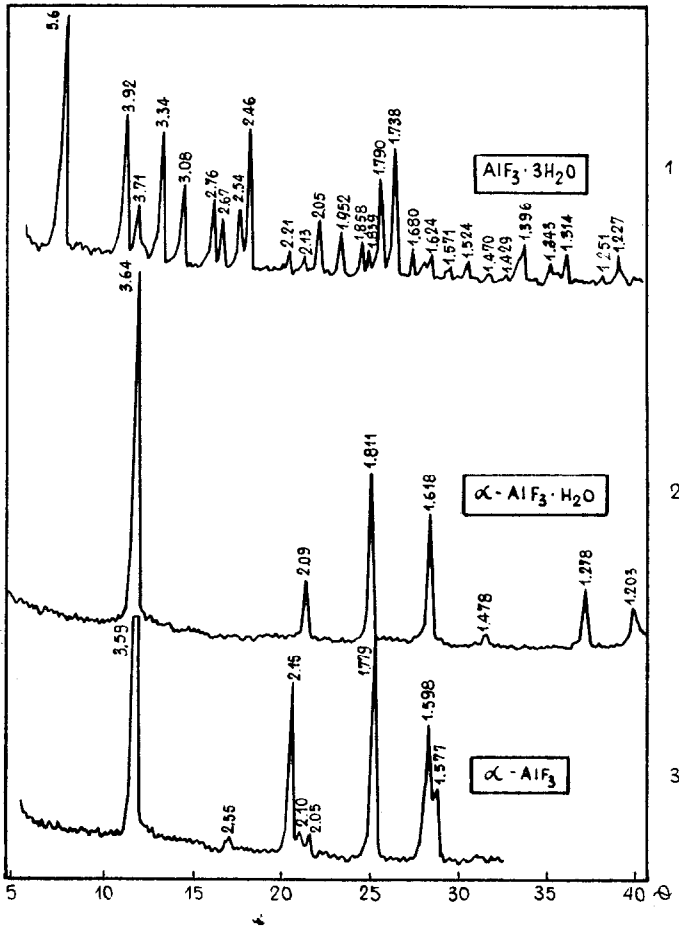
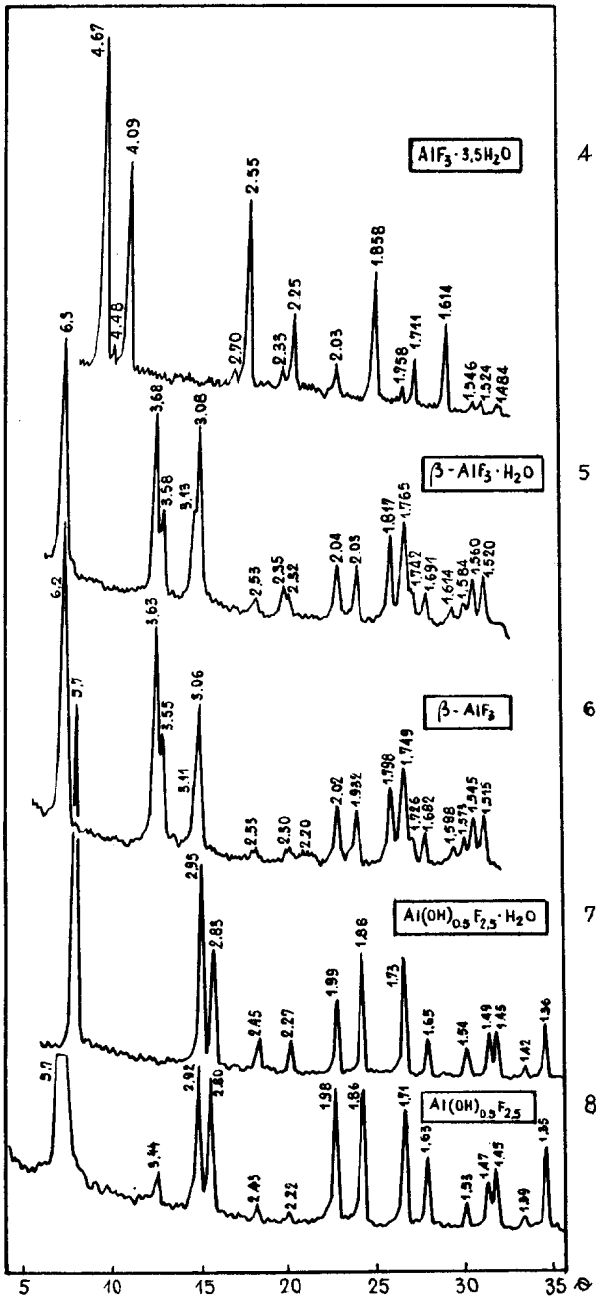


Fig. 9. X-ray diffraction patterns of various aluminum fluorides.



Scott for the compound with $F/Al = 1.96$ are 9.77 and 9.63 Å, respectively. Greater contraction of the lattice in this case may be accounted for by the difference between the volumes of F^- and OH^- ions as well as by thermal decomposition of the latter to lose H_2O molecules. Apart from that, variation in intensity distribution of lines, especially those with assignments 111, 422 and 333 are observed in both cases (Table 5; Figure 9, nos. 7 and 8).

Thermogravimetric analysis (Fig. 8a) reveals two exothermic peaks at 360 and 550°C, the latter being the result of decomposition to give a mixture of $\alpha-AlF_3 + Al_2O_3$. The weight loss at 600°C being ~21% is in good correspondence with the theoretical value (22.3%). For comparison, the weight loss for $Al(OH)F_2 \cdot H_2O$ amounts to 27% theoretically. The heat evolution at 360°C is difficult to rationalize. It is notable that it is accompanied by a comparatively great loss in weight. If the compound supposed to be $Al(OH)_{0.5}F_{2.5} \cdot H_2O$ had actually been $Al(OH)F_2 \cdot 0.5HF \cdot 0.5H_2O$, thus retaining some HF physically, it would react with OH at higher temperature to substitute it, with liberation of one water molecule. This would agree with the weight loss of ca. 12% at 360°C which might be the sum of the reaction water (9%) and the water evolved earlier at 150°C (3%).

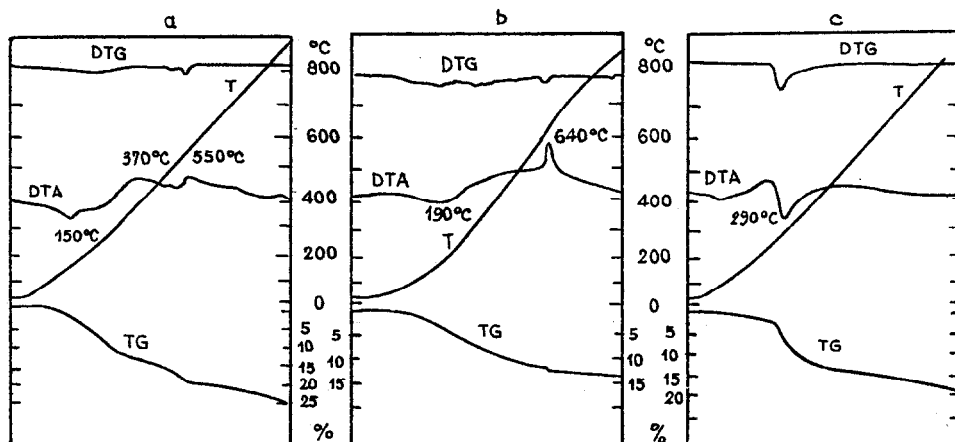


Fig. 8. Thermograms of a) $Al(OH)_{0.5}F_{2.5} \cdot H_2O$, b) $\beta-AlF_3 \cdot H_2O$ and c) $\alpha-AlF_3 \cdot H_2O$.

β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ phase

Attempts to obtain β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ in its pure form encountered difficulties due to hydrolysis, which leads to partial precipitation of basic fluoride, even when the AlF_3 content is as high as 300 g/l. Only once was it possible to crystallize pure β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ out of solution; all further attempts failed. They succeeded, however, in two cases: when AlF_3 solution (150 g/l) before crystallization was artificially contaminated by minor amounts of NaF (~ 1 g/l) or NaH_2PO_4 , or when a suspension of $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$ crystals in acetone was heated in an autoclave up to 150°C (Fig. 9, nos. 4 and 5).

The structure of β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ bears a striking resemblance to that of hexagonal anhydrous β - AlF_3 which was discovered by Christoph and Tenfer [7] on thermal dehydrating of α - $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ (identical with $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$) crystals at 150 - 450°C , although unit cell dimensions are slightly higher. The similarity is evident from a comparison of the interplanar distances and intensities of particular lines (Table 5). Calculations made by using d -values for lines with assignments (100) and (002) gave for the monohydrate $a = 7.29$ and $c = 7.36$ Å, which after calcination at 600°C dropped to 7.20 and 7.26, respectively. Thermogravimetric observations coupled with X-ray results show that increase of temperature up to 600°C failed to change the basic crystal structure despite the fact that all the crystal water was removed. There were only variations in the relative intensities, as well as in d -values, indicating a contraction of the crystal lattice (Fig. 9, nos. 5 and 6). It seems therefore reasonable to assume that at least some of the crystal water is combined in the lattice structure, the remainder being absorbed physically or occupying the interoctahedra spaces.

The DTA curve reveals primarily two peaks (Fig. 8b). The sharp exothermic one at 640°C is concerned with the phase transition from hexagonal β - to rhomboedral α - AlF_3 . The weak endothermic peak at 180°C , accompanied by 3.5% weight loss (in comparison to the total weight loss of 13% corresponding to the formula $\text{AlF}_3 \cdot 0.7\text{H}_2\text{O}$) might be due to hydrate water to form $\text{AlF}_3 \cdot 0.2\text{H}_2\text{O}$, the remaining $0.5\text{H}_2\text{O}$ as crystal water occupying free spaces in the lattice. One can see an analogy with the

basic aluminum fluoride where of the total water content involved, corresponding approximately to monohydrate, merely a small part of it contributes to the lattice structure, according to the formula $\text{Al}(\text{OH},\text{F})_3 \cdot 0.375\text{H}_2\text{O}$ [9].

α - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ phase

As to its chemical composition, the α -monohydrate is undistinguishable from the β -form. The two are deficient in their F and H_2O contents and correspond closely to the formula $\text{AlF}_{2.95} \cdot 0.9\text{H}_2\text{O}$. They differ however in respect to their structures and thermal behavior.

The α - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ phase was obtained in an X-ray pure state in the crystallization process at $>125^\circ\text{C}$, using acidic AlF_3 solutions, e.g., with the initial composition AlF_3 60 g/l and H_2SiF_6 8 g/l, with suspended $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ crystals in them. The X-ray pattern and diffraction data are shown in Figure 9 no.2 and Table 5 in comparison with those calculated from assignments given earlier by Chandross for cubic monohydrate and obtained in another way [5]. The lattice constant is in both cases the same, amounting to $a = 3.610 \text{ \AA}$.

Thermogravimetric analysis shows an endothermic effect with a maximum rate at 290°C which is associated with dehydration of α -monohydrate and the aforementioned phase transition (Fig. 8c). Thermal dehydration of cubic α - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ results in minor but essential changes in X-ray patterns associated with the conversion into anhydrous rhomboedral α - AlF_3 (comp. nos. 2 and 3 in Fig. 9). Successive steps of this process, showing the coexistence of the two phases, were observed in the temperature range between 250 and 350°C .

CONCLUSIONS

Experiments carried out in this work may be summarized as follows:

Precipitation of aluminum fluoride from water solutions in the temperature range 100 - 150°C exhibits a series of characteristic features differing from known processes carried out at temperatures not exceeding 100°C .

In the course of the crystallization as represented by a descending lines of AlF_3 concentration (Fig. 1), no special features in isothermic runs were observed, but only the regular increase in the process rate with temperature. However, in polythermic processes proceeding at low rates of temperature increase, as well as in the presence of seeding crystals and a free acid, there may be characteristic inflections in the bulk crystallization curves between 125 and 130°C. They reflect the phase transition from $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ initially formed to cubic $\alpha\text{-AlF}_3 \cdot \text{H}_2\text{O}$.

Whereas at temperatures below 100°C the sole stable phase crystallizing out of solution is $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$, in the range 100-150°C one can meet three additional phases, involving two monohydrate fluorides: $\beta\text{-AlF}_3 \cdot \text{H}_2\text{O}$ and $\alpha\text{-AlF}_3 \cdot \text{H}_2\text{O}$ and the hydroxyfluoride $\text{Al}(\text{OH},\text{F})_3 \cdot \text{H}_2\text{O}$, where F/Al ratio may reach value of 2.5, the latter phase being a hydrolysis product of AlF_3 in solution.

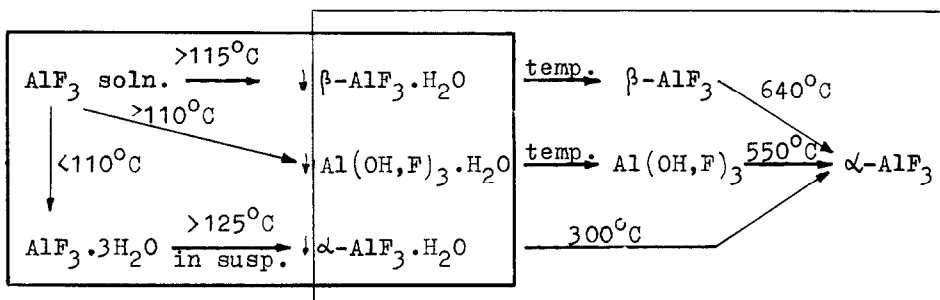
Depending on the variables employed, such as initial concentration of AlF_3 , rate of temperature increase, presence or otherwise of seeding crystals and free acid, the solids precipitated may form mono-, binary or tertiary systems of aluminum fluorides.

X-ray pure basic aluminum fluoride precipitates from AlF_3 solution with a low supersaturation. It possesses the composition $\text{Al}(\text{OH})_{0.5}\text{F}_{2.5} \cdot \text{H}_2\text{O}$ and the same structure as the well known phase described by Cowley and Scott [9] for solids having F/Al ratio between 1 and 2. On heating it decomposes at 550°C.

The hexagonal $\beta\text{-AlF}_3 \cdot \text{H}_2\text{O}$ arises directly from supersaturated AlF_3 -solution at $> 115^\circ\text{C}$, usually along with the basic fluoride, or may be formed by thermal dehydration of $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$ crystals suspended in acetone. This β -phase was found to lose crystal water without essential change of its hexagonal structure and to undergo a transition at 640°C into rhomboedral $\alpha\text{-AlF}_3$. The β -monohydrate structure was recognized as identical with that described previously by Christoph and Tenfer [7] which was obtained by these authors by air dehydrating $\alpha\text{-AlF}_3 \cdot 3\text{H}_2\text{O}$ crystals (identical with the above mentioned $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$) between 150 and 450°C.

The cubic α - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ phase is formed as the thermal decomposition product of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ crystals in a rather acidic suspension, at $>125^\circ\text{C}$. It may also be accompanied by β - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}(\text{OH},\text{F})_3 \cdot \text{H}_2\text{O}$ unless the AlF_3 solution had been previously acidified. On heating, α - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ undergoes dehydration above 250°C and turns simultaneously into anhydrous rhomboedral α - AlF_3 . The α - $\text{AlF}_3 \cdot \text{H}_2\text{O}$ was recognized as identical with the solid phase discovered by Chandross [5] which was fortuitously formed in the reaction of gaseous HF with AlCl_3 -HCl solution in an industrial scrubber. Conditions for its preparation have not been however established.

Processes going in AlF_3 solutions, when kept in an autoclave under continuous stirring at elevated temperatures and, further, on thermal dehydrating the solids precipitated, may be summarized as follows:



on heating the solution on air heating the solids

It seems that the results presented in this paper may explain why Chandross was unsuccessful in his efforts to obtain cubic $\text{AlF}_3 \cdot \text{H}_2\text{O}$. Furthermore, it is likely that under suitably selected conditions it should be possible to obtain this cubic phase also by air dehydration of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$.

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