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THE REACTION OF ALUMINUM FLUORIDE SOLUTION WITH CRYOLITE

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SUMMARY

The title reaction was investigated kinetically and the products obtained were analyzed and examined by physicochemical methods. The reaction was found to result in the formation of $NaAlF_4.H_2O$ and its solid solutions with aluminum fluoride with compositions down to $Na_{0.5}AlF_{3.5}.1.3H_2O$, except in the presence of chiolite seed crystals, which cause the reaction to give it as the final product.

It was suggested that the solid solution are brought about by coprecipitation of approximately monohydrated hexagonal β-AlF_3 direct from solution, both compounds being presumably isostructural each other.

Differences in the infrared spectra of Na_3AlF_6, $Na_5Al_3F_{14}$ and $NaAlF_4.H_2O$ were indicated.

Homogenous mixtures of Na_3AlF_6 and $NaAlF_4.H_2O$ are found to react exothermally at 350°C to give $Na_5Al_3F_{14}$, while $NaAlF_4.H_2O$ alone decomposes into $Na_5Al_3F_{14}$ and AlF_3.

INTRODUCTION

In the previous paper [1] dealing with reactions involved in the AlF_3-NaF-H_2O system, it was found that cryolite first formed may be further converted with excess AlF_3 solution to chiolite or $NaAlF_4.H_2O$, depending on the conditions used. Chiolite resulted particularly when its seed crystals were present, while sodium tetrafluoroaluminate arose readily at temperatures above ca. 80°C. There were also some indications that the $NaAlF_4.H_2O$ phase might form solid solutions with aluminum fluoride.

The title reaction has not hitherto been the subject of an investigation and, prior to this work, only the reaction between cryolite and anhydrous aluminum fluoride in the solid state has been reported to provide chiolite only, at ca. 680°C [2].

The purpose of the present work was to study in more detail the reactions involved in the system $AlF_3-Na_3AlF_6-H_2O$ under a variety of conditions, as well as to characterize the products obtained.

EXPERIMENTAL

In experiments were used:

a) aluminum fluoride solution (150 g/l, pH ~ 4) prepared by reaction of H_2SiF_6 1 M with $Al(OH)_3$; prior to use it was diluted to an appropriate concentration;

b) synthetic cryolite of commercial grade. Analysis: Na, 31.2%; Al, 13.3%; F, 52.4%; H_2O, 2.7% (ignition loss at 500°C); molar ratio NaF/AlF_3 = 2.75;

c) synthetic chiolite of commercial grade. Analysis: Na, 24.2%; Al, 17.7%; F, 57.0%; Na/Al = 1.6.

All experiments were carried out using a 1 liter three-necked flask equipped with a thermometer, reflux condenser and a stirrer. An aluminum fluoride solution of a given concentration was warmed to an appropriate temperature in the range 60-95°C, and then treated with the calculated amount of synthetic cryolite to give a suspension with the desired NaF/AlF_3 ratio, varying from 0.25 to 2.24. The reaction mixture was then stirred at a constant temperature. After the reaction was complete, the resultant solids were filtered, dried, analysed and examined by physicochemical methods. The reaction course was followed by density measurement of aluminum fluoride solution samples taken at intervals.

Solid samples were analysed for sodium content using a flame photometer, aluminum by the EDTA method and fluorine by the distillation method.

X-ray diffraction patterns were taken using a MUR-61 analyzer with Cu radiation and an Ni filter. Thermogravimetric analyses were done on a MOM Budapest type OD 102

Derivatograph at a heating rate of 9°/min and with Al_2O_3 as the reference material. Infrared spectra were measured on a C.Zeiss Jena UR-10 spectrophotometer.

RESULTS

The interaction between aluminum fluoride solution and cryolite was studied both in terms of its kinetics(but rather qualitatively) and of the nature of resulting crystal phases. In the first series of runs aluminum fluoride solution of 20-25 g/l, pH ~ 6 or 2.3, and cryolite in the molar proportion of 1:2 ($NaF/AlF_3 = 2$) were employed. Runs were carried out at various temperatures in the range 60-95°C, in part using $Na_5Al_3F_{14}$ or $NaAlF_4.H_2O$ as nucleating agents in quantities of 20 g/l. The solute concentration curves against time are shown in Figure 1.

Experiments in the second group were performed at a constant temperature of 95°C for 2 hr, using aluminum fluoride solution primarily of 21 g/l, pH ~ 3 (slightly extending into the metastable region to be over about 18 g/l when approached from supersaturated solution on heating for several hours), and such quantities of cryolite that the stoichiometry of the reactants, as expressed by the molar ratio NaF/AlF_3, was 2.24, 1.94, 1.76, 1.44, 1.03, 0.47 and 0.24. For comparison, runs at approximately the last value were also made using more concentrated solutions, containing AlF_3 42 and 71 g/l. It was to be expected that higher concentrations would, in the case of solid solutions, yield a sodium tetrafluoroaluminate phase with a lower proportion of NaF in relation to AlF_3. Despite supersaturation, the possible contamination of the reaction product by β-$AlF_3.3H_2O$ could be neglected, for its crystallization rate out of solution is, under the conditions used, (low concentration, the lack of seed) much slower than that of the reaction.

The course of the reaction between Na_3AlF_6 and AlF_3 solution for various stoichiometries is illustrated in Figure 2 by solute concentration curves versus time, taken at 95°C. Analytical results and calculated phase composition of the solids obtained, including the unreacted cryolite in some cases, are shown in Table 1. X-ray diffraction patterns of the residues, having molar ratios NaF/AlF_3 2.75, 2.0, 1.54, 1.10, 0.70 and 0.54 are summarized in Figure 3. In order to ascertain how they behave on heating, some of the samples (NaF/AlF_3 = 2.75, 2.0, 1.54 and 1.1) were examined thermogravimetrically (Figure 5).

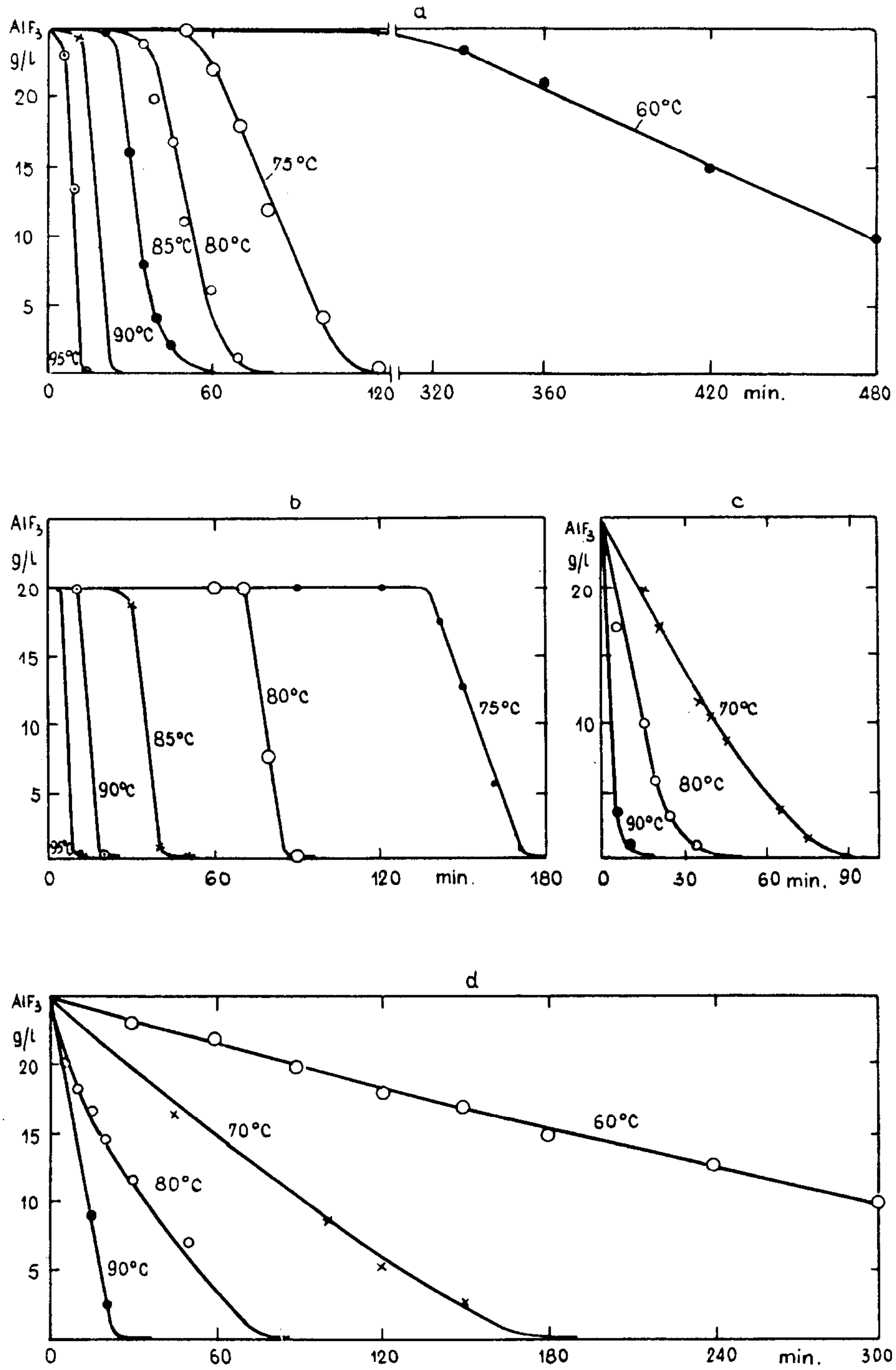
DISCUSSION

Kinetics and composition

The course of the reaction between AlF_3 solution and cryolite at a 1:2 mole ratio (NaF/AlF_3 = 2) was found to depend on the conditions employed, involving temperature, pH, and the nature and quantity of seeding material. The reaction proved to be essentially zero at lower temperatures, proceeding with increasing rate as the temperature was raised.

In absence of seeding (Figs. 1a and 1b), the reaction isotherms of AlF_3 concentration resemble in their shape a typical crystallization process involving an initial nucleation stage, during which the solute content remains at a constant level, and a subsequent crystal growth stage resulting in a rapid drop of this content. Nucleation periods became greater with decreasing temperature, extending at pH 2.3 from 10 minutes at 90°C to about 5 hours at 60°C (Fig. 1a). AlF_3 solutions with an increased pH value to 6 gave rise to the induction period at all temperatures under study (compare corresponding isotherms in Figs. 1a and 1b). It seems likely that the observed facts can be explained in terms of equilibria between AlF_6^{3-} and AlF_4^- species and of a nuclei formation rate, followed by growth to yield eventually the reaction product.

Fig. 1. Isotherms of AlF_3 concentration during the reaction with Na_3AlF_6 at 1:2 molar ratio (NaF/AlF_3 = 2) over the range 60 – 95°C.
Initial conditions: a) AlF_3 25 g/l, pH 2.3; b) AlF_3 20 g/l, pH ~ 6; c) AlF_3 25 g/l, pH ~ 6, $Na_5Al_3F_{14}$ seed 20 g/l; d) AlF_3 25 g/l, pH ~ 6, $NaAlF_4.H_2O$ seed 20 g/l.


a
AlF₃
g/l
20
15
10
5
0
60
120
320
360
420
min.
480
95°C
90°C
85°C
80°C
75°C
60°C
b
AlF₃
g/l
20
15
10
5
0
60
120
min.
180
95°C
90°C
85°C
80°C
75°C
c
AlF₃
g/l
20
10
0
30
60 min.
90
90°C
80°C
70°C
d
AlF₃
g/l
20
15
10
5
0
60
120
180
240
min.
300
90°C
80°C
70°C
60°C

X-ray analysis showed in all cases the formation of $NaAlF_4 \cdot H_2O$ as the sole product, along with unreacted cryolite when it was used in excess over that required by the equation:

$$2\ AlF_3 + Na_3AlF_6 + 3\ H_2O \longrightarrow 3\ NaAlF_4 \cdot H_2O \qquad (1)$$

The reaction takes an entirely different course with time when carried out in the presence of adequate amounts of chiolite or $NaAlF_4 \cdot H_2O$ crystals. All the isotherms are then devoid of their initial horizontal branches and from the very beginning, consist of descending lines only, being however less sloped than those obtained in absence of any seed. This is so because the whole process is primarily controlled by the crystal growth process which is going on the surface of seed material employed. Again, comparison of the corresponding lines in Figs. 1c and 1d indicates that the process is quicker when the seed is $NaAlF_4 \cdot H_2O$ rather than $Na_5Al_3F_{14}$, despite the same quantities (20 g/l) of either substance being used. X-ray analysis makes this difference partially clear, for in the first case reaction (1) occurs, whereas in the second it follows the equation:

$$5\ Na_3AlF_6 + 4\ AlF_3 \xrightarrow{\text{chiolite seed}} 3\ Na_5Al_3F_{14} \qquad (2)$$

The formation of chiolite,which proceeds more slowly and requires seed crystals, seems to be less favorable than that of $NaAlF_4 \cdot H_2O$.

Results of the experiments carried out at a constant temperature of 95°C using AlF_3 solutions and cryolite with NaF/AlF_3 molar ratios over the range 0.24-2.24 are shown in Figure 2 and in Table 1.

From the plots of Figure 2 it is seen that the reaction was essentially complete in 20 minutes and the remaining AlF_3 solutions, even though supersaturated in two cases (No 8 and 9) turned out to be quite stable during further stirring and heating for 90 minutes. This might be taken as evidence that the solid reaction products were not contaminated by $AlF_3 \cdot 3H_2O$ crystals. When molar ratios of NaF/AlF_3 in the reactants exceeded 1:1, the AlF_3 concentration dropped rapidly to a small value of below 1 g/l, resulting from the solubility of the product obtained.

TABLE 1

The chemical and X-ray analyses of solids obtained in the reaction of aluminum fluoride solutions with cryolite at 95°C

Sample Nr.	Suspension before the reaction AlF_3 g/l	Na_3AlF_6 g/l	$\frac{[NaF]}{[AlF_3]}$	Chemical analysis, weight % Na	Al	F	H_2O^a	Empirical formulae $\frac{[Na]}{[Al]}$	$\frac{[F]}{[Al]}$	$\frac{[H_2O]}{[Al]}$	Phase composition, mole %	
1	2	3	4	5	6	7	8	9	10	11	12	
0	0	-	2.75	31.2	13.3	52.4	2.7	2.75	5.60	0.28	0 I + 100 II	two-phase systems
1	21	224.2	2.24	27.8	14.4	53.2	4.0	2.27	5.25	0.42	28 I + 72 II	
2	21	123.5	1.94	26.1	15.1	52.5	5.2	2.03	4.89	0.52	41 I + 59 II	
3	21	90.0	1.76	24.8	15.7	53.3	6.3	1.85	4.76	0.60	52 I + 48 II	
4	21	56.2	1.44	22.0	16.7	52.1	8.5	1.54	4.44	0.76	69 I + 31 II	
5	21	32.8	1.03	17.5	18.5	52.2	11.0	1.10	4.00	0.90	92 I + 8 II	
6	21	10.5	0.47	13.7	19.2	51.0	14.5	0.81	3.74	1.15	81 I + 19 III1	one-phase systems
7	21	4.8	0.24	11.7	19.3	50.0	16.3	0.70	3.68	1.27	70 I + 30 III1	
8	42	10.5	0.26	9.5	20.6	.	17.1	0.54	3.54	1.24	54 I + 46 III2	
9	71	20.0	0.28	8.0	21.3	.	17.3	0.44	3.44	1.22	44 I + 54 III3	
10[b]	21	10.5	0.47	10.4	22.3	.	12.0	0.55	.	0.81	55 I + 45 III4	

[a] ignition losses at 500°C after 2 h.
[b] in autoclave at ca. 140°C under autogenous pressure (ca. 5 at.)

I - $NaAlF_4.H_2O$, II - Na_3AlF_6

III1 - $AlF_3.1.9H_2O$, III2 - $AlF_3.1.5H_2O$, III3 - $AlF_3.1.4H_2O$, III4 - $AlF_3.0.6H_2O$.

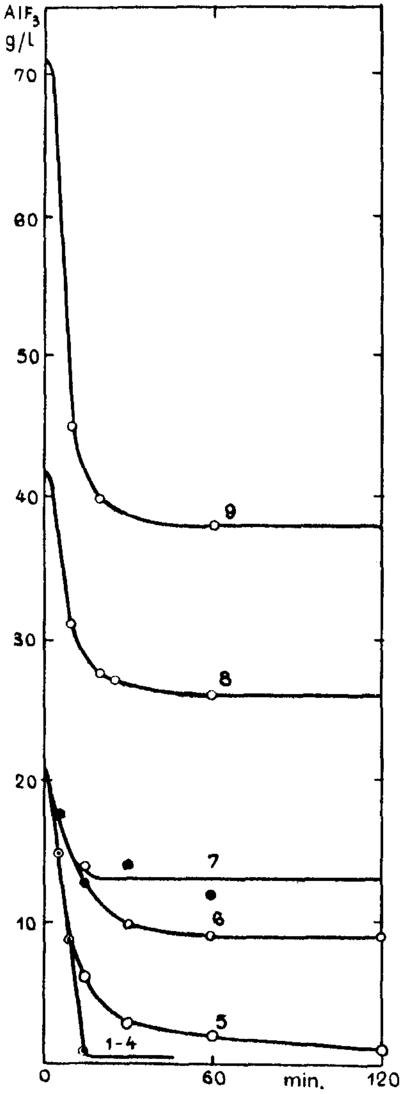


Fig. 2. Isotherms of AlF$_3$ concentration during the reaction with Na$_3$AlF$_6$ at 95°C, for different proportions of reactants.

NaF/AlF$_3$ molar ratio: 1) 2.24; 2) 1.94; 3) 1.76; 4) 1.44; 5) 1.03; 6) 0.47; 7) 0.24; 8) 0.26; 9) 0.28. Numeration as in Table 1.

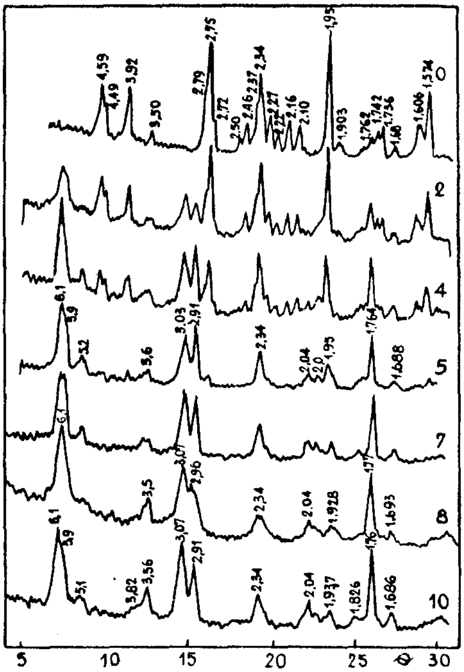


Fig. 3 (top) . X-ray diffraction patterns of Na$_3$AlF$_6$ (0) and reaction products of it with AlF$_3$ solution at 95°C.

NaF/AlF$_3$ molar ratio: 2) 2.0; 4) 1.54; 5) 1.1; 7) 0.70; 8) 0.54; 10) 0.55 (at 140°C). Numeration as in Table 1.

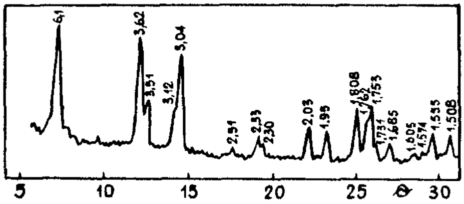


Fig. 4 bottom . X-ray diffraction pattern of β-AlF$_3$.H$_2$O.

Decrease in the molar proportion of NaF/AlF_3 in the reaction suspension to below 1:1 did not result in a proportional decrease in the precipitate obtained. The AlF_3 reacted only partially, although to a greater extent than would be expected from the stoichiometry of equation (1).

Chemical analysis shows (Table 1) that NaF/AlF_3 ratios in the reactants are in reasonable agreement with those of the products, as far as the composition range intermediate between cryolite and $NaAlF_4.H_2O$ is concerned (samples 1-5). When going to NaF/AlF_3 values less than 1 (samples 6-9), inconsistencies are found and there is unreacted AlF_3 left in solution. The solids obtained are then characterized by NaF/AlF_3 molar ratios down to 0.5, depending on the initial composition of suspension used. From comparison of runs 7-9 for a value of about 0.25, the higher the initial AlF_3 concentration the smaller is the NaF/AlF_3 molar ratio in the product. Whereas an AlF_3 solution with 21 g/l gave rise to to the formation of a solid with $NaF/AlF_3 = 0.70$, one with 42 g/l yielded a product of 0.54 and that of 71 g/l resulted in 0.44. These facts lead to the conclusion that an equilibrium exists between AlF_3 in solution and the solid phase with a lower NaF/AlF_3 molar ratio in relation to the composition of $NaAlF_4.H_2O$:

$$NaAlF_4.H_2O + x\ AlF_3 + y\ H_2O \rightleftharpoons NaAl_{(1+x)}F_{(4+3x)}.(1+y)H_2O \quad (3)$$

where: $0 < x < 1$, $0 < y < 0.3$.

The increase in the content of AlF_3, as the NaF/AlF_3 ratio decreases is illustrated by the considerable increase in water content of samples, from 2.5% in the cryolite used to 17.3% in the product with Na/Al = 0.44.

X-ray patterns of the subsequent reaction products (Figure 3) reveal a progressive and gradual disappearance of the cryolite phase in favour of a new phase which was identified previously [1] as being $NaAlF_4.H_2O$. In the almost pure state it is seen for solid of Na/Al = 1.1 (sample 5) along with the X-ray traces of cryolite. This new phase retains its crystal structure over a considerable range of NaF/AlF_3 ratios from 1.0 to 0.5, as reflected in the relative intensities of diffraction lines.

On the assumption that the solids with NaF/AlF_3 between 1 and 3 (samples 1-5) consist of cryolite and $NaAlF_4.H_2O$, the proportion y (mole %) of the former can be calculated from the following formula:

$$y = \frac{m - b}{a - b} \cdot 100 = \frac{m - 1}{1.75} \cdot 100$$

where a = 2.75, b = 1 and m - values mean NaF/AlF_3 molar ratios of the cryolite used in the experiments, in $NaAlF_4.H_2O$ and in the product obtained, respectively. The calculated compositions of solids (col.12, Table 1) are in good agreement with the experimental data given in col. 9-11.

This method of calculation failed entirely for solids with NaF/AlF_3 less than 1 (samples 6-10) when trying to consider them as mixtures of $NaAlF_4.H_2O$ with $AlF_3.3H_2O$. It shows that when dividing the respective constituents, according to the empirical formulae (col. 9-11) between these two compounds, the total water content is sufficient, but only to form $NaAlF_4.H_2O$ and aluminum fluoride hydrates between $AlF_3.1.9H_2O$ and $AlF_3.1.5H_2O$. It should be assumed that such hydrates, as derived direct from solution, are structurally related to hexagonal β-AlF_3 (being a derivative of soluble α-$AlF_3.3H_2O$) rather than to insoluble β-$AlF_3.3H_2O$. The additional fact that β-AlF_3 is, in turn, probably isostructural with $NaAlF_4.H_2O$ would make it clear why aluminum fluoride could not be detected by the X-ray method in sodium fluoroaluminates with NaF/AlF_3 molar ratio less than 1. I have found that β-AlF_3 which was detected by Christoph and Tenfer [3] as a dehydration product of α-$AlF_3.3H_2O$, can also occur in a hydrated form ranging from nil to ca. one water molecule per mole of AlF_3 without any essential change in its crystal structure.

It is notable that in samples 6 and 7, with molar ratio 0.8 and 0.7, which are obtained from diluted AlF_3 solutions, the total of ($Na + H_2O$) remain at a constant value of 2. This would imply the ability of NaF molecules to be substituted by H_2O in the lattice of $NaAlF_4.H_2O$, as in the case of cryolite [4]. However, such an interpretation does not apply to the other samples (8 and 9), where about 0.5 mole NaF is replaced by 0.2-0.3 mole H_2O only. It is necessary to assume that co-precipitation or incorporation of hydrated β-$AlF_3.xH_2O$ also takes place. A compound of average composition $Na_{0.5}AlF_{3.5}.1.2H_2O$ (sample 8 and 9) may be formed by 0.4 mole of $AlF_3.H_2O$ with 1 mole of $Na_{0.7}AlF_{3.7}.1.3H_2O$ or $AlF_3.1.4H_2O$ with $NaAlF_4.H_2O$.

The structural relationship between the $NaAlF_4.H_2O$ phase and hexagonal β-$AlF_3.H_2O$ is apparent from Figure 3 and 4 from a comparison of their diffraction patterns and interplanar distances.

Other evidence is provided by experiments carried out in a steel autoclave at ~ 140°C and ~ 5 at., under which conditions, as stated, crystallization of β-$AlF_3.0.8H_2O$ out of supersaturated AlF_3 solutions is favoured. A suspension of cryolite in AlF_3 solution of 21 g/l at a NaF/AlF_3 molar ratio of 0.47 gave a product with basically the same composition and diffraction pattern as that of one prepared at the lower temperature of 95°C, but from more concentrated AlF_3 solution (42 g/l) used in a higher excess (NaF/AlF_3 = 0.26; sample 8). The high-temperature product showed, however, a minor content of crystal water as expressed by the formula $Na_{0.55}AlF_{3.55}.0.8H_2O$ (sample 10), which corresponds nearly to an equimolar mixture of $NaAlF_4.0.8H_2O$ and $AlF_3.0.8H_2O$. One can infer from this that temperature plays the role of a "driving force" in yielding solid solutions of aluminum fluoride in $NaAlF_4.H_2O$ according to equation (3), just as the AlF_3 concentration does. It may be explained by taking into account the fact that complex ions such as $[AlF_2.4H_2O]^+$ and $[AlF_4.2H_2O]^-$, which predominate in AlF_3 solutions [5], may lose their hydration water partially on heating thus allowing β-$AlF_3.H_2O$ to be precipitated out of solution along with $NaAlF_4.H_2O$ to form an integral part of its space net.

Thermograms

In order to learn how the various products obtained behave on heating, a thermogravimetric study has been made using samples of cryolite and its mixtures with $NaAlF_4.H_2O$ at different molar ratios. The derivatogram of pure cryolite (Fig. 4a) reveal on the TG-curve a total mass decrement of 2.7% and on the DTA curve an endothermic peak at 570°C, corresponding to the reversible phase transition from monoclinic to cubic cryolite. The weak effect observed at ca. 300°C is probably due to admixture of hydrargilite.

Derivatograms of the other samples, which are homogenous mixtures of Na_3AlF_6 and $NaAlF_4.H_2O$ with compositions defined by NaF/AlF_3 molar ratios 2.0; 1.54 and 1.1 are slightly more complicated. Upon increasing the temperature, all the TG curves exhibit up to ca. 320°C rapid weight loss corresponding essentially to the total water content. It is attended by endothermic peaks on the DTA curves at 270°C and by minima points on the DTG curves. Further weight losses on increasing the temperature up to 900°C are comparatively low. The DTA thermograms indicate a remarkable exothermic effect at 330-350°C, especially for the sample with molar ratio of 1.54, which is formally close to that of chiolite. The X-ray patterns taken in the vicinity of 350°C indicate that this effect is ascribable to the reaction:

$$Na_3AlF_6 + 2\ NaAlF_4.H_2O \longrightarrow Na_5Al_3F_{14} + 2\ H_2O \qquad (4)$$

or:

$$5\ NaAlF_4.H_2O \longrightarrow Na_5Al_3F_{14} + 2\ AlF_3 + 5\ H_2O \qquad (5)$$

The thermal transition proceeds predominantly between 300 and 400°C, extending up to 500°C, or even up to 600°C in the case of reaction (5), indicating that cryolite facilitates thermal decomposition of $NaAlF_4.H_2O$. There were no indications of an intermediate anhydrous $NaAlF_4$ which, according to Howard [6], is stable up to 470°C.

Upon increasing the temperature from 300 to 600°C, the proportion of $NaAlF_4.H_2O$ decreases progressively, while those of chiolite and aluminum fluoride increase. The endothermic effect observed at 740°C for samples 2 and 4 is characteristic for the peritectic of chiolite, whereas that at 695°C (samples 4 and 5) is associated with the binary eutectic point between $Na_5Al_3F_{14}$ and $NaAlF_4$, the latter being formed in the reaction between chiolite and aluminum fluoride at 680°C [7].

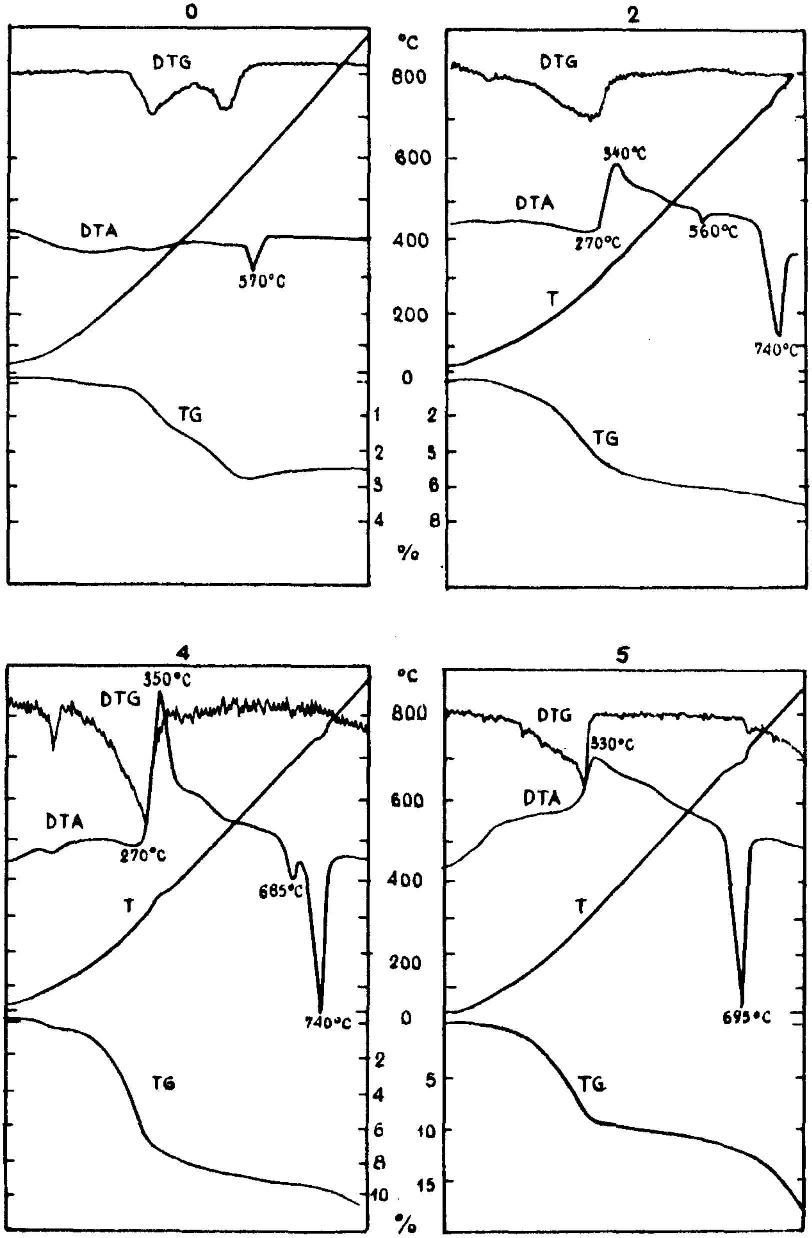


Fig. 5. Thermograms of Na_3AlF_6 (0) and reaction products of it with AlF_3 solution at 95°C (homogenous mixtures of Na_3AlF_6 with $NaAlF_4.H_2O$).

NaF/AlF_3 molar ratio: 0) 2.75; 2) 2.0; 4) 1.54; 5)1.1. Numeration as in Table 1.

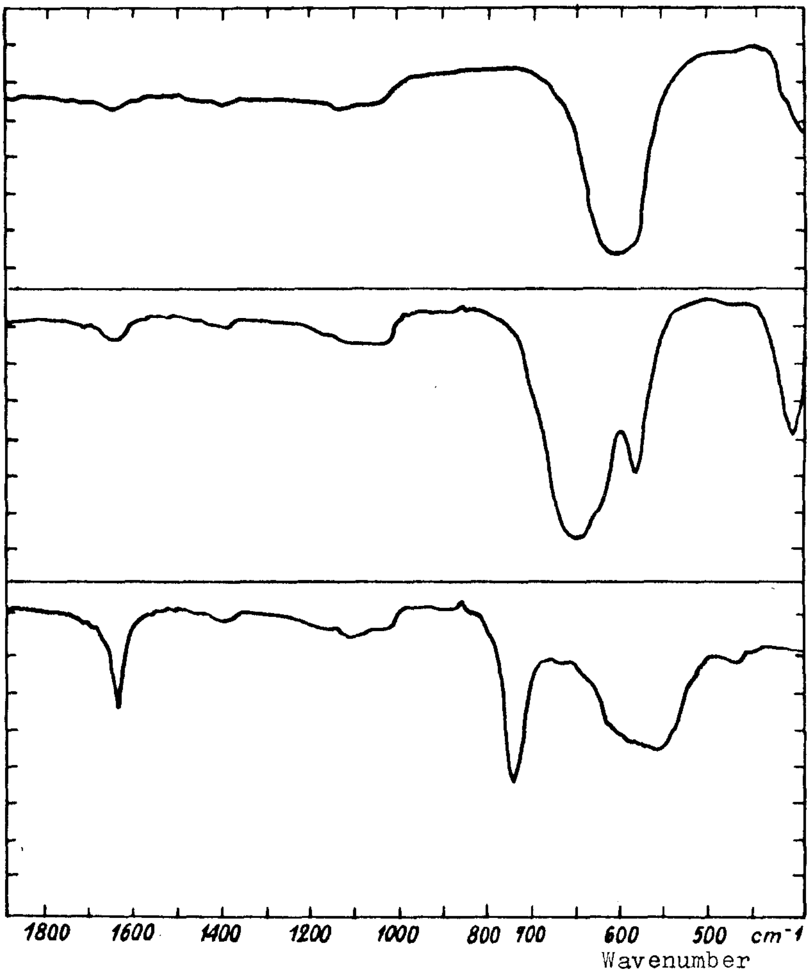


Fig. 6. Infrared spectra of (top) Na_3AlF_6, (middle) $Na_5Al_3F_{14}$ and (bottom) $NaAlF_4.H_2O$.

Infrared spectra

The infrared absorption spectra reveal distinct differences between cryolite, chiolite and $NaAlF_4.H_2O$, especially in the wavenumber region between 500 and 800 cm^{-1}, where deformational vibrations are represented by main absorptions [8]. In Na_3AlF_6, the main absorption occurs at ca. 600 cm^{-1}, whereas in chiolite it is split into two frequencies, at 580 cm^{-1} and 650 cm^{-1}.

The spectrum of $NaAlF_4.H_2O$ presents a broad band with a maximum at 565 cm^{-1} and a very sharp peak at 750 cm^{-1}. In addition, it possess another well defined absorption maximum at 1640 cm^{-1}, which is a characteristic feature for water molecules [9]. There exists a great similarity of the spectra of $NaAlF_4.H_2O$ and $Na_{0.5}AlF_{3.5}.1.3H_2O$ reflecting their isostructural nature.

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