has been a transition from one solid phase to another and they permit the following conclusions to be drawn: the seven-day old material is a mixture of two substances but contains one of them in a relatively large amount (we have called this metastable or α-$AlF_3 \cdot 3H_2O$); that with time the substance present in small quantity (β) increases at the expense of the other; and finally, at the end of one year, a single substance, stable, or β-$AlF_3 \cdot 3H_2O$, remains. This transformation in the solid state occurs independent of contact with a solution although it is more rapid when the liquid phase is present.

In the table the composition is shown as the trihydrate although the salts for which the diffraction effects are given showed a salt to water ratio of nearly 1:3.5 before irradiation. This probably diminished slightly during the exposure to X-radiation (see dehydration studies). Other samples of hydrated aluminum fluoride having a salt to water ratio of 1:2.86 (Eimer and Amend) and 1:3.06 (authors, Method A, aged 1 year in closed bottle) gave diffraction patterns identical with those here shown for the aged salt and that prepared at 100°.

An examination of Hanawalt's tables[10] reveals an almost exact correspondence in diffraction pattern between what is listed there as $CrF_3 \cdot 4H_2O$ and what we have called α-$AlF_3 \cdot 3H_2O$. This caused us to examine the possibility that the latter might actually be a tetrahydrate. If such were the case, and it were metastable with respect to the trihydrate at 25°, the solubility and diffraction phenomena above reported could be understood. The fact that a structural change, as shown by solubility and diffraction measurements, takes place while aging the salt in a closed vessel has convinced us, however, that the transformation is not that from a higher to a lower hydrate. An extension of this reasoning leads to the deduction that the substance listed as $CrF_3 \cdot 4H_2O$ by Hanawalt may well have been the trihydrate, particularly since Yatlov, Polyakova and Podtymchenko[14] report that the latter is the stable form at 25°.

Summary

1. Solubility determinations indicate the existence of a metastable (α) and a stable (β) form of aluminum fluoride trihydrate.

2. Conditions are given for the preparation of the two forms and for the conversion $\alpha \rightarrow \beta$. This change is irreversible and, at 25°, requires about nine months when the salt is in contact with solution. When dry, more than two years are required. The change is completed in a few hours if the salt is digested on the steam-bath.

3. Dehydration studies lead to the conclusion that, at 25°, β-$AlF_3 \cdot 3H_2O$ will be stable over the range of water vapor pressures (7–20 mm.) ordinarily encountered in air. These studies also show that it is difficult to attain the exact stoichiometric water content in the crystals since a slight excess of water is tenaciously retained.

4. X-Ray diffraction data confirm the existence of two different crystalline forms of the trihydrate. The α or metastable form is isomorphous with what is called $CrF_3 \cdot 4H_2O$ in Hanawalt's tables.

5. The solubility of aluminum fluoride in water at 25° has been found to be 0.41 weight per cent.

[14] Yatlov, Polyakova and Podtymchenko, *J. Chem. Ind.* (U. S. S. R.), **14**, 935 (1937).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Ternary Systems Involving Water and Aluminum Fluoride with Aluminum Nitrate, Sulfate or Chloride[1]

BY W. F. EHRET AND F. J. FRERE

Information in the literature on aqueous ternary systems involving fluorides is very sparse. While several double salts of aluminum fluoride and the fluorides of the divalent metals have been reported, none of them were investigated from the standpoint of the phase rule. Two ternary systems that have come to our attention are: AlF_3–NH_4F–H_2O at 25° by Novoselova,[2] and AlF_3–HF–H_2O at 25° by Tananaev.[3] In 1889, Grabau,[4] while investigating the action of aqueous solutions of aluminum sulfate on calcium fluoride, reported the formation of an aluminum fluosulfate of the formula $Al_2(SO_4)F_4$. It is not entirely clear upon what he based his conclusions, because the data given are too meager to establish definitely the existence of such a salt. Inasmuch as he stated that one mole of aluminum sulfate dissolved two moles of calcium fluoride, it seems quite probable that it was upon this fact alone that a salt of the above composition was assumed to be obtained. The dodecahydrate of the same compound is again mentioned by Nikolaev.[5] Weinland and Köppen[6] found that aluminum fluoride combined with

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[1] Abstracted from a thesis submitted by Francis J. Frere to the Graduate School of New York University in partial fulfillment of the requirements for the degree of doctor of philosophy.

[2] Novoselova, *J. Gen. Chem.* (U. S. S. R.), **10**, 1547 (1940).

[3] Tananaev, *ibid.*, **8**, 1120 (1938).

[4] Grabau, *Jahresbericht Fortschritte der Chemie*, 2609 (1889); see also Gmelin-Kraut, "Handbuch der anorganischen Chemie," **2**, No. 2, 621 (1909).

[5] Nikolaev, *J. Chem. Ind.* (U. S. S. R.), **14**, 1087 (1937).

[6] Weinland and Köppen, *Z. anorg. Chem.*, **22**, 266 (1900).

cupric fluoride to form two double salts: $AlF_3 \cdot 2CuF_2 \cdot 11H_2O$ and $2AlF_3 \cdot 3CuF_2 \cdot 18H_2O$. When much acid was present, $CuF_2 \cdot AlF_3 \cdot HF \cdot 8H_2O$ was formed. These authors[7] also prepared $AlF_3 \cdot ZnF_2 \cdot 7H_2O$ by mixing aluminum fluoride and zinc fluoride in dilute hydrofluoric acid and evaporating over lime. Heptahydrated ferrous, nickel, and cobalt pentafluoaluminates were obtained in a similar way. Ephraim and Barteczko[8] prepared $3TlF \cdot 3AlF_3$ by the action of thallous fluoride in hydrofluoric acid upon aluminum hydroxide. Aside from these reports, reference can be found only to the fluoaluminates of the cryolite type, some of which have been rather exhaustively studied in the fused state.

As far as can be ascertained, the present is the first attempt at a systematic study of aqueous ternary systems involving aluminum fluoride and another salt of aluminum, and for this reason it is felt that the systems herein reported will be of particular interest.

Experimental Methods

Solubility Measurements.—These were made by chemical analysis of the solutions that had come to equilibrium with their respective solid phases. Equilibration was achieved in Pyrex bottles covered with "Celon" cellulose seals and rotated in a water thermostat at 25.0 ± 0.02°. At intervals of one to two months the bottles were removed from the rotating device and allowed to stand in the bath until the solid had settled out. Solid was removed by filtering through a sintered glass crucible enclosed in a device held below the surface of the bath. The samples, both solution and solid, were transferred to weighing bottles and reserved for analysis. The compositions of the solid phases in equilibrium with the several solutions was determined by the familiar wet residue method of Schreinemakers[9] coupled with the method of algebraic extrapolation suggested by Hill and Ricci.[10]

The solutions used for the aluminum fluoride branches of the solubility curves were prepared by mixing appropriate amounts of each salt and water to give the desired concentration. Two solutions in each ternary system were prepared from α-aluminum fluoride (metastable).[11] The concentrations in the latter solutions extended several per cent. into the metastable region and they were quite persistent over long periods of time. The time required for them to reach equilibrium depended very largely upon the particular additional ion present and upon its concentration. In general, it was found that in solutions containing aluminum nitrate, in concentrations up to 20%, about four months, and in solutions containing aluminum chloride of the same concentration, about six months were required for equilibrium to be established. For all added salt concentrations in excess of 20%, the time required to establish equilibrium when β-aluminum fluoride (the stable form at 25°) was used was about the same as that required for α-aluminum fluoride. At added salt concentrations of 15% or less, equilibrium was attained in four to six weeks when the stable form was used. Solutions to which aluminum sulfate had been added showed the greatest tendency to remain metastable, the time required for attaining equilibrium being rather appreciably longer than that required for solutions containing aluminum chloride or nitrate of the same concentration. One solution containing approximately 10% added aluminum sulfate required about twelve months to reach equilibrium.

For the other branches of the solubility curves, the solutions were generally prepared by adding an appropriate amount of a solution corresponding to the invariant point to a solution containing crystals of each respective salt. In some cases the solutions were prepared as mentioned in the previous paragraph, this being particularly true for the invariant point mixtures.

Criterion for Equilibrium.—Equilibrium was assumed to be established when the change in concentration of the solutions between successive analyses, which were made at intervals of one to two months, did not exceed two parts per thousand. In a number of cases equilibrium was approached both from undersaturation and supersaturation. In general, the solutions on the double salt branches of the curves were saturated at a temperature several degrees above 25° and then allowed to come to equilibrium at 25°. A small amount of water was then added and the solutions were again allowed to come to equilibrium. In the case of the solutions in which the solid phases were the simple hydrated salts, equilibrium was first approached from undersaturation. The solutions were then warmed to a temperature several degrees above 25° and again allowed to come to equilibrium at the latter temperature. On the aluminum fluoride branches of the curves, equilibrium could not be approached from supersaturation when β-aluminum fluoride was used, unless the temperature was elevated considerably for a relatively long period of time. This is because the solubility of β-aluminum fluoride changes very little for a 5–10° rise in temperature.

Analytical Methods

In a three-component system, such as here studied, in which the cation is common to both salts, it is only necessary to know its concentration and that of one of the anions in order to calculate the concentration of both salts. While the determination of fluoride in mixtures containing chloride or nitrate may be accomplished with a satisfactory degree of accuracy, the method, at best, is quite tedious and is not entirely free of uncertainties. This is particularly true when the ions concerned are present in rather high concentration. For this reason, in the systems in which these ions were involved, the concentrations of aluminum, chloride and nitrate were determined and the fluoride ion concentration taken by difference. The determination of sulfate in fluorine bearing materials can only be accomplished with great difficulty and with a low degree of precision. Considerable work was done in an attempt to develop a satisfactory method, but with only partial success. Therefore, in this system, the concentrations of the aluminum and the fluoride ions were determined and the sulfate taken by difference.

Aluminum was determined by precipitating with 8-hydroxyquinoline and weighing as the oxime salt after drying at 130 to 140°. Chlorine was determined gravimetrically by precipitating with silver nitrate according to standard procedure. Nitrogen was determined according to Devarda's method. This is based upon the reduction of nitrates by Devarda's alloy in alkaline solution. Fluorine was determined according to the method of Willard and Winter[12] as modified by Rowley and Churchill.[13]

All analytical results used in constructing the ternary diagrams were the averages of at least three, and in many cases of five, determinations giving an accuracy and precision of from 0.1 to 0.2%.

Materials

Aluminum Sulfate.—A C. P. grade of salt was recrystallized from distilled water. The salt was air dried.

Aluminum Nitrate.—A C. P. grade of salt was recrystallized from distilled water. The salt was dried in a desiccator over sulfuric acid.

Aluminum Chloride.—A C. P. grade of salt was dissolved in distilled water to give a saturated solution and the aluminum chloride was precipitated by saturating the solu-

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(7) Weinland and Köppen, *Z. anorg. Chem.*, **22**, 273 (1900)

(8) Ephraim and Barteczko, *ibid.*, **61**, 243 (1909).

(9) Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).

(10) Hill and Ricci, THIS JOURNAL, **53**, 4306 (1931).

(11) Ehret and Frere, *ibid.*, **67**, 64 (1945).

(12) Willard and Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

(13) Rowley and Churchill, *ibid.*, **9**, 551 (1937).

tion with hydrogen chloride gas. The salt was air dried on porous plates. Analysis showed that this, as well as the foregoing salts, contained less than 0.03% of total impurities. The ratio of cation to anion in each salt was 1 : 3.00 ± 0.01.

Hydrofluoric Acid.—A special grade of "Baker's Analyzed" acid was used. Baker's analysis showed that the acid contained not more than 0.06% of total impurities.

Aluminum Metal.—The aluminum metal was generously supplied by Dr. Francis C. Frary of the Aluminum Company of America. The purity of the metal was 99.98%.

Aluminum Fluoride.—This salt was prepared as described by Ehret and Frere.[11]

Experimental Results

The System: $Al(NO_3)_3$–AlF_3–H_2O.—Table I shows the results which are plotted in Fig. 1.

TABLE I

THE TERNARY SYSTEM: $Al(NO_3)_3$–AlF_3–H_2O AT 25°

Weight per cent. Solution $Al(NO_3)_3$	Solution AlF_3	Wet residue $Al(NO_3)_3$	Wet residue AlF_3	Solid phase
39.43	..	...	...	$Al(NO_3)_3 \cdot 9H_2O$
38.83	1.17	55.58	0.03	$Al(NO_3)_3 \cdot 9H_2O$
38.53	2.65	54.77	0.31	$Al(NO_3)_3 \cdot 9H_2O$
38.33	3.95	52.13	0.99	$Al(NO_3)_3 \cdot 9H_2O$
37.92	5.17	51.02	1.58	$Al(NO_3)_3 \cdot 9H_2O$
37.92	5.35	45.78	4.37	$Al(NO_3)_3 \cdot 9H_2O$ + $AlF_3 \cdot 3H_2O$
37.88	5.41	37.28	16.55	
31.05	5.29	12.72	37.96	$AlF_3 \cdot 3H_2O$
24.47	5.20	9.62	38.94	$AlF_3 \cdot 3H_2O$
19.46	5.09	7.39	39.36	$AlF_3 \cdot 3H_2O$
15.20	4.51	6.07	38.34	$AlF_3 \cdot 3H_2O$
10.79	3.99	4.77	36.02	$AlF_3 \cdot 3H_2O$
5.78	2.78	2.18	38.96	$AlF_3 \cdot 3H_2O$
...	0.41	...	...	$AlF_3 \cdot 3H_2O$

The solubility curve consists of two branches. The stable solid phases are $Al(NO_3)_3 \cdot 9H_2O$ and $AlF_3 \cdot 3H_2O$. No evidence was found for the existence of either a double salt or solid solution. The tie-lines for aluminum nitrate converge sharply at 56.83 ± 0.03% of $Al(NO_3)_3$, with a maximum deviation of 0.05%, as compared to 56.82% calculated for $Al(NO_3) \cdot 9H_2O$. As for the aluminum fluoride, the extrapolation of the tie-lines establishes very clearly the degree of hydration of this salt. In this system, and in the two following, the lines converge on the average to 60.93 ± 0.12 as compared to 60.83% AlF_3, calculated for the trihydrate.

The System: $Al_2(SO_4)_3$–AlF_3–H_2O.—Table II shows the results which are plotted in Fig. 2.

TABLE II

THE TERNARY SYSTEM: $Al_2(SO_4)_3$–AlF_3–H_2O at 25°

Weight per cent. Solution $Al_2(SO_4)_3$	Solution AlF_3	Wet residue $Al_2(SO_4)_3$	Wet residue AlF_3	Solid phase
28.22	..	...	...	$Al_2(SO_4)_3 \cdot 17H_2O$
28.46	0.68	41.25	0.33	$Al_2(SO_4)_3 \cdot 17H_2O$ + $Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$
28.59	0.80	44.10	4.64	
28.63	0.80	43.70	2.31	$Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$
26.61	1.18	40.98	8.12	$Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$
24.85	1.47	37.25	6.84	$Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$
22.55	1.93	37.86	7.79	$Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$
20.07	3.05	35.44	7.82	$Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$
18.95	3.75	34.80	8.13	$Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$
17.82	4.60	31.48	7.88	$Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$
17.45	5.33	31.68	8.38	$Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$
17.12	5.97	15.46	20.77	$Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$ + $AlF_3 \cdot 3H_2O$
17.08	5.98	33.62	11.82	
14.97	5.51	5.64	39.57	$AlF_3 \cdot 3H_2O$
10.00	4.46	3.66	40.31	$AlF_3 \cdot 3H_2O$
6.18	3.43	2.25	38.55	$AlF_3 \cdot 3H_2O$
...	0.41	...	...	$AlF_3 \cdot 3H_2O$

The solubility curve consists of three branches. The stable solid phases are the two simple salts $Al_2(SO_4)_3 \cdot 17H_2O$ and $AlF_3 \cdot 3H_2O$, and the double salt $Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$. The tie-lines for the double salt converge sharply at 12.07 ± 0.02% of AlF_3, with a maximum deviation of 0.06%, and at 49.16 ± 0.06% of $Al_2(SO_4)_3$, with a maximum deviation of 0.14%; calculated for $Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$, 12.06% AlF_3, 49.13% $Al_2(SO_4)_3$.

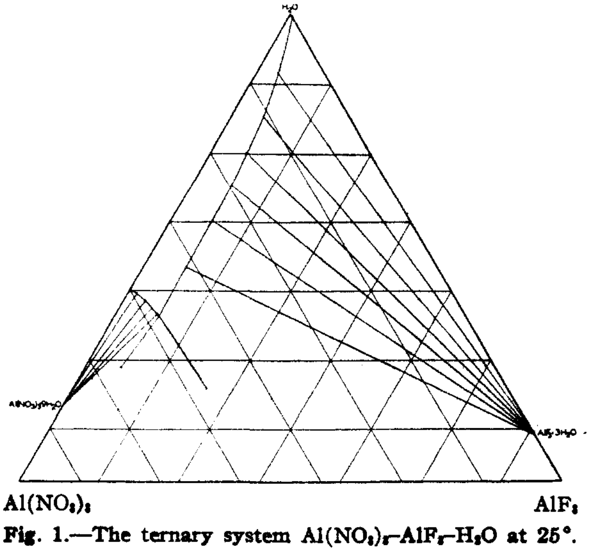

Fig. 1.—The ternary system $Al(NO_3)_3$–AlF_3–H_2O at 25°.

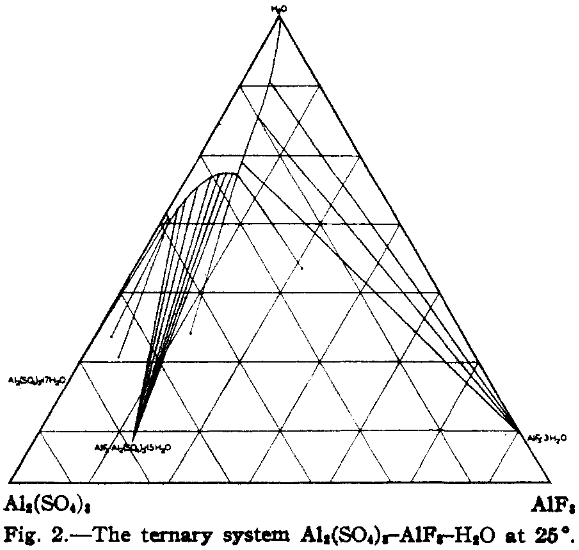

Fig. 2.—The ternary system $Al_2(SO_4)_3$–AlF_3–H_2O at 25°.

The tie-line for the simple sulfate extrapolates to 52.96 as compared to 52.81% $Al_2(SO_4)_3$, calculated for $Al_2(SO_4)_3 \cdot 17H_2O$. Smith[14] has recently come to the same conclusion in regard to the composition of this hydrate.

Dehydration by the method described for AlF_3,[11] showed that the double salt is stable over a wide range of aqueous vapor pressures at 25°. The salt gave the correct content of Al_2O_3 (21.98, 21.96, 21.98, as compared with the theoretical 21.96%) after three to six weeks of such dehydration.

The System: $AlCl_3$–AlF_3–H_2O.—Table III shows the results which are plotted in Fig. 3. The solubility curve again consists of three branches. The stable solid phases are the two simple salts $AlCl_3 \cdot 6H_2O$ and $AlF_3 \cdot 3H_2O$, and the double salt $AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$. The tie-lines for the double salt converge sharply at 5.84 ± 0.03% of AlF_3, with a maximum deviation of 0.05%, and at 46.48 ± 0.03% of $AlCl_3$, with a maximum deviation of 0.05%; calculated for $AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$, 5.85% AlF_3, 46.45% $AlCl_3$. The extrapolated tie-lines for aluminum chloride converge at 55.14 ± 0.13%, with a maximum deviation of 0.13%, as compared to 55.22% $AlCl_3$ calculated for $AlCl_3 \cdot 6H_2O$.

TABLE III

THE TERNARY SYSTEM: $AlCl_3$–AlF_3–H_2O AT 25°

Weight per cent.				
Solution		Wet residue		
$AlCl_3$	AlF_3	$AlCl_3$	AlF_3	Solid phase
31.10	..	...	...	$AlCl_3 \cdot 6H_2O$
30.48	1.50	48.50	0.40	$AlCl_3 \cdot 6H_2O$
30.37	2.64	47.63	0.94	$AlCl_3 \cdot 6H_2O$ +
30.21	3.46	42.11	4.00	$AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$
30.22	3.46	43.69	3.33	$AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$
29.81	4.37	38.44	5.14	$AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$
29.47	4.93	40.12	5.49	$AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$
28.89	5.62	39.66	5.77	$AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$
28.78	6.03	40.84	5.91	$AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$
28.72	6.46	39.70	6.05	$AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$
28.58	6.90	38.73	6.28	$AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$
28.47	6.97	29.40	17.76	$AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$
28.45	7.01	16.82	29.74	+ $AlF_3 \cdot 3H_2O$
24.07	6.30	9.59	39.05	$AlF_3 \cdot 3H_2O$
21.04	5.96	8.11	39.52	$AlF_3 \cdot 3H_2O$
14.33	5.52	5.72	38.91	$AlF_3 \cdot 3H_2O$
10.68	4.93	4.26	38.04	$AlF_3 \cdot 3H_2O$
5.50	3.56	1.79	41.70	$AlF_3 \cdot 3H_2O$
...	0.41	...	...	$AlF_3 \cdot 3H_2O$

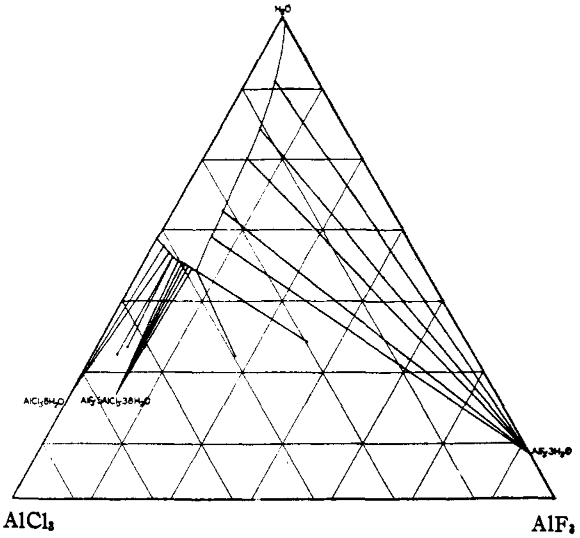

Fig. 3.—The ternary system $AlCl_3$–AlF_3–H_2O at 25°.

The moist, finely-divided double salt was placed in a desiccator over a saturated solution of zinc chloride which was in contact with excess of the latter. The vapor pressure of this solution at 25° is about 2.1 mm. Analysis of the salt showed progressive dehydration. After two weeks, alumina determinations showed little if any further change in composition. At the end of four weeks the alumina value was 21.30%, while the theoretical required of $AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$ is 21.31%. The salt is deliquescent over a saturated solution of calcium chloride (see ref. (11)). These results show that the double salt is stable over a rather narrow range of aqueous vapor pressures at 25°.

Acknowledgment.—The authors wish to take this opportunity to thank Professor John E. Ricci for valuable suggestions in connection with certain phases of the work.

Summary

The isotherms for the systems $Al_2(SO_4)_3$–AlF_3–H_2O, $AlCl_3$–AlF_3–H_2O and $Al(NO_3)_3$–AlF_3–H_2O have been determined at 25°. In the system $Al(NO_3)_3$–AlF_3–H_2O no evidence was found for the existence of either a double salt or solid solution. In the system $Al_2(SO_4)_3$–AlF_3–H_2O a double salt of the formula $Al_2(SO_4)_3 \cdot AlF_3 \cdot 15H_2O$ has been shown to exist. It is congruently soluble. In the system $AlCl_3$–AlF_3–H_2O a double salt of the formula $AlF_3 \cdot 5AlCl_3 \cdot 38H_2O$ exists. It, too, is congruently soluble.

Attention is drawn to the influence which the more soluble, metastable α-aluminum fluoride has upon solubility determinations in these ternary systems.

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[14] Smith, THIS JOURNAL, 64, 41 (1942).