sorption alone. In the case of poisoned copper Row 4 of Table II also measures solution, for here a total sorption of Row 3 represents the sum of adsorption plus the low-pressure increase plus solution, if any; Row 2 here represents adsorption plus low-pressure increase. The further check on the extent of solution, Row 8 of Table II, might have been complicated by the low-pressure increase in adsorption occurring while the sorbent was at 0°. Had the calculations of Row 8 for poisoned copper yielded results much higher than those of Row 4, such would have pointed to a retention of the 0° low-pressure increase under −78.5° conditions. However, since Row 8 yields volumes for solution which, with one exception, closely check the values of Row 4, the conclusion is justified that the 0° low-pressure increase in adsorption is given up when the temperature is lowered to −78.5°, the activated adsorption at this lower temperature resuming its normal value.

TABLE II

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF HYDROGEN BY 80 G. OF MASSIVE COPPER POISONED WITH 0.039 ML. OF CARBON MONOXIDE

(1) Gas taken up at −78.5°	Press.	51.2	267.8	466.6
	Vol.	1.77	2.36	2.49
(2) Initial values after warming to 0°	Press.	78.5	392.9	653.9
	Vol.	1.38	1.72	1.80
(3) Total sorption at 0° at pressures given in (2)		1.35	1.80	1.86
(4) Differences of (2) and (3)		−0.03	0.08	0.06
(5) Final values reached at 0°	Press.	78.5	392.3	652.9
	Vol.	1.38	1.75	1.85
(6) After cooling to −78.5°	Press.	51.4	276.5	466.1
	Vol.	1.76	2.38	2.52
(7) Direct values at −78.5° at pressures given in (6)		1.77	2.36	2.49
(8) Differences of (6) and (7)		−0.01	0.02	0.03

To secure the points for Curve 3, the activated adsorption, with data from poisoned copper, it is, of course, necessary to take the difference between the sorption given by the isotherm (Curve II) and the solution plus low-pressure increase, and not simply, as in the case of pure copper, the difference between the isotherm (Curve 2) and solution alone. For the sorbent of this study the value of 0.25 ml. was taken as the low-pressure increase since 0.25 ml. is seen from Fig. 1 to be the volume at most pressures, including zero pressure, by which Curves II and 3 differ, Curve 3 having already been established from runs with the unpoisoned copper.

In the present investigation, by obtaining Curve 3 in addition to Curve II, the first experimental evidence is secured for the parallel nature of Curves X and Y of Fig. 6 of an earlier study.[2] In the latter figure Curve Z corresponds to Curve 2 of the present work.

The rate of attaining equilibrium for hydrogen on pure copper was rather slow, resulting only after four or five hours. Both for 0 and for −78.5° there is some evidence of hysteresis as seen in Curves 1 and 2 (full black symbols). At low pressures however no pressure change was noted after a half hour. Equilibrium resulted more quickly on the poisoned copper, due to the almost total absence of solution, 90 to 150 minutes being sufficient.

Summary

The sorption of hydrogen with temperature variation on pure massive copper has been determined and compared with that of hydrogen on the same copper poisoned with a small quantity of carbon monoxide. The effect of the poison is to prevent largely the solution of hydrogen in copper.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Dimorphism in Aluminum Fluoride Trihydrate[1]

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

In connection with our study of ternary systems involving aluminum fluoride, a report of which appears elsewhere,[2] it became necessary to investigate the structure, the extent of hydration, and the solubility of the stable form of aluminum fluoride at 25°. This necessity arose out of conflicting statements about this salt in the literature and, further, out of slow changes with time which we noticed in the solubility and other properties of the salt as usually prepared. One is led to believe from the statements found in the literature that aluminum fluoride exists in a soluble and an insoluble form, the soluble form being prepared at low temperature. The latter is said not to undergo any change with time, providing there is no appreciable rise in temperature.

According to Baud[3] and Mazzucchelli,[4] when two volumes of 95% alcohol are added to a neutral solution of alumina in hydrofluoric acid, a crystalline precipitate of $AlF_3 \cdot 3.5H_2O$ is obtained. Baud states that the salt precipitates first in the form of an oil which, upon standing, crystallizes. The above authors state that another form of hemiheptahydrated aluminum fluoride, almost

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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) Ehret and Frere, THIS JOURNAL, **67**, 68 (1945).

(3) Baud, *Ann. chim. phys.*, (8) **1**, 60 (1904).

(4) Mazzucchelli, *Atti Accad. Lincei*, (5), **16**, 775 (1907).

insoluble in water, is prepared by evaporating, at 100°, a solution of alumina in hydrofluoric acid. Mazzucchelli points out that there also exists a soluble and insoluble trihydrated aluminum fluoride. The soluble form is prepared by allowing a concentrated solution to stand at ordinary temperature; after some time the salt is deposited as a gelatinous, transparent precipitate. After being allowed to stand, it eventually becomes rubber-like and opaque, and upon drying goes irreversibly to the insoluble form. This Mazzucchelli describes as the stable form in air and the one eventually formed by all other hydrates in contact with water at ordinary temperature. Few reports on solubility determinations for aluminum fluoride appear in the literature. Novoselova[5] reports the solubility at 25° as 0.55%. Carter[6] and Nikolaev, Ivanov and Koltypin[7] give similar values.

Additional data on the composition of the hydrate stable at 25° are obtained from Yatlov and Zelyanskaya[8] who measured the vapor pressures over aluminum fluoride containing various amounts of water of hydration and found the hydrates $AlF_3 \cdot 9H_2O$ ("stable up to 20°"), $AlF_3 \cdot 3H_2O$, and $AlF_3 \cdot 0.5H_2O$. Novoselova[5] and Tananaev[9] report $AlF_3 \cdot 3H_2O$ as the stable solid phase in contact with saturated aqueous solutions at 25°. Nikolaev, Ivanov and Koltypin,[7] however, conclude that $AlF_3 \cdot 2.5H_2O$ is the correct formula. Hanawalt[10] and others have accepted the formula $AlF_3 \cdot 3.5H_2O$.

Crystal diffraction data on aluminum fluoride and its hydrates[10,11] throw no light on the question of the existence of polymorphic modifications of these substances. Tosterud[12] reproduced diffraction patterns showing that hydrated aluminum fluoride heated to between 115–120° had a different crystal structure from that heated to between 125–320°. From the reproductions it is not possible to tell whether these diffraction effects correspond to those obtained by the present authors for the salt produced at lower temperatures.

Experimental Methods

Solubility Measurements.—Aluminum fluoride which had been variously prepared and aged was added in excess to distilled water in glass-stoppered "Pyrex" bottles. These were covered with "Celon" cellulose caps waxed in place. Equilibration of salt and solution was brought about by rotating the bottles in a water-bath at 25.0 ± 0.02°. Samples were removed at intervals for analysis by drawing a portion of liquid through a filter fitted over the end of a pipet. These samples were transferred to glass-stoppered weighing bottles and the aluminum concentration was used as a measure of the solubility. The analytical method for aluminum was that using 8-hydroxyquinoline and weighing as the oxime salt after drying at 130–140°.

Diffraction Analysis.—The X-ray diffraction patterns were obtained with Cu Kα radiation using a General Electric XRD powder camera of 14.32 cm. diameter. Intensities of the diffraction lines were measured with a microphotometer. The values for each pattern were expressed relative to the most intense line which was taken as unity.

Materials

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

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

Aluminum Fluoride.—Two methods were used for the preparation of this salt. For convenience they are designated A and B.

Method A.—The aluminum sheets were cut into small strips and were added a few pieces at a time to an approximately 15% solution of hydrofluoric acid contained in a platinum dish. The temperature was kept below 25° by immersing the dish in a pan of ice water. After several hours, when practically all of the acid had been used up and the rate of solution had become extremely slow, the solution was filtered through a hard rubber funnel into a hard rubber beaker in order to remove the small particles of undissolved metal. A sheet of aluminum was suspended in the solution and the beaker placed in an ice chest. In general, crystallization was complete after one day.

The supernatant liquor was poured off, the crystals were washed several times by decantation with small portions of cold water, and finally were transferred to a Büchner funnel and washed several times more with small portions of cold water. The salt was allowed to air dry.

Method B.—The aluminum was added in small pieces to an approximately 15% solution of hydrofluoric acid contained in a platinum dish. After most of the metal had dissolved and the reaction had subsided, the temperature was gradually raised to about 100°. The solution was evaporated at this temperature until crystallization occurred. It was then allowed to cool to room temperature and the crystals filtered, washed, and dried as described in Method A.

Analysis showed that aluminum fluoride prepared by either method contained less than 0.02% of total impurities. The ratio of aluminum to fluorine was 1:3.00 ± 0.01. The latter element was determined by the method of Willard and Winter.[12a]

Results

The results of the solubility determinations are given in Table I. The first column gives the time in days during which the salt and solution were rotated in the thermostat before a sample of the solution was taken for analysis. The headings of the other columns indicate the mode of preparation and the treatment of the aluminum fluoride before it was added to the water in the bottles used to determine the solubility.

It is evident from these data that the equilibrium value for the solubility of aluminum fluoride is independent of the manner in which it is prepared. It is also clear that the initial "solubility" of the salt depends both upon its age and upon the temperature at which it was prepared. Aluminum fluoride prepared by Method A apparently contains a metastable form of higher

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(5) Novoselova, *J. Gen. Chem.* (U. S. S. R.), **10**, 1547 (1940).

(6) Carter, *Ind. Eng. Chem.*, **20**, 1195 (1928).

(7) Nikolaev, Ivanov and Koltypin, *J. Applied Chem.* (U. S. S. R.), **9**, 1183 (1936).

(8) Yatlov and Zelyanskaya, *J. Gen. Chem.* (U. S. S. R.), **7**, 1787 (1937).

(9) Tananaev, *ibid.*, **8**, 1120 (1938).

(10) Hanawalt, *Ind. Eng. Chem., Anal. Ed.*, **10**, 473 (1938).

(11) Ketelaar, *Z. Krist.*, **85**, 119 (1933).

(12) Tosterud, THIS JOURNAL, **48**, 1 (1926).

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

TABLE I

SOLUBILITY OF ALUMINUM FLUORIDE IN WATER AT 25° IN PER CENT. BY WEIGHT

Time, days	Crystallized below 25° (method A) aged one day	Crystallized below 25° (method A) aged two years	Crystallized at 100° (method B) aged seven days	Crystallized at 100° (method B) digested 8 hours on steam-bath, aged one day
1	4.23	0.48	0.48	0.36
2	3.34	.51	.52	.40
3	2.77	.51	.53	.41
5	1.89	.49	.50	.41
15	0.84	.46	.47	.41
40	.63	.45	.44	.41
80	.56	.44	.43	.41
140	.51	.43	.41	
190	.45	.41	.41	
240	.42	.41	.41	
270	.41	.41		

solubility (Column 2) than the stable form. The forms have been called for convenience the α and the β, respectively. After some nine months in contact with solution the transformation from α to β is complete and the concentration of the solution becomes constant. If the salt prepared by Method A is aged two years before its solubility is tested there is evidence of some of the α-form remaining (Column 3). It apparently dissolves faster than it is transformed, for it takes over six months for the concentration of the solution to drop to that for the stable form. Column 4 indicates that aluminum fluoride prepared by Method B contains relatively little of the α-form, yet almost five months elapsed before the solution came to equilibrium with the solid phase. From Column 5 it is clear that Method B, coupled with an eight-hour digestion of the crystals on the steam-bath, yields almost solely the stable or β-aluminum fluoride. The solubility of this substance in water at 25° is evidently 0.41 per cent. by weight. Higher solubilities reported by others must be attributed to lack of equilibrium.

After equilibrium had been established fresh water was added to the salt which had been aged two years. At the end of three days the solubility amounted to 0.41%. The water was again renewed and at the end of the second three-day period the solubility was still 0.41%. The remaining salt was completely soluble in an amount of water judged to be in accord with the above solubility. The ratio of aluminum to fluorine, both in the saturated solution at equilibrium and in the salt, was 1:3.00 ± 0.01. This indicates the absence of appreciable amounts of insoluble hydrolytic products. No evidence was found to indicate that these solutions attacked glass even though the *p*H of the saturated solution was 3.33. The sample bottles after being in continuous use for more than three years showed no signs of being etched. Examination of a solution and solid, which were in contact with glass for about one year, showed the absence of silica. The latter was determined according to the method of Schrenk and Ode.[13] The sample used for analysis was of such size that 0.01% of silica could be readily determined.

Attention was drawn above to conflicting statements in the literature in regard to the extent of hydration of the form of aluminum fluoride stable at 25° in contact with solution. An attempt to obtain direct information on this question by centrifuging out the solid phase failed because the mother liquor could not be removed to a sufficient degree. Conclusive evidence that the trihydrate is stable in contact with saturated solution at 25° was however obtained from the study of ternary systems involving aluminum fluoride, water and another aluminum salt.[2]

In order to ascertain whether the trihydrate was also stable in contact with the aqueous vapor pressures found in ordinary atmospheres a dehydration study was carried out under controlled conditions. Finely divided salt was prepared according to Method B and, while still moist, was placed in Petri dishes in desiccators over saturated solutions of potassium chloride, sodium bromide, and calcium chloride containing excess of these salts. The vapor pressures of these solutions at 25° are 20.2, 13.5 and 6.9 mm., respectively. The desiccators were stored in a room whose temperature remained within a few degrees of 25. Analysis of the salt showed progressive dehydration. After three weeks, during which the salt was stirred each day, alumina determinations showed little further change in composition. At the end of seven weeks the alumina values were 36.11, 36.23 and 36.34%, respectively. This is considerably higher than that required of $AlF_3\cdot 3.5H_2O$ (34.67%) and somewhat lower than that required of $AlF_3\cdot 3H_2O$ (36.93%). The "degrees of hydration" corresponding to these values are $AlF_3\cdot 3.18H_2O$, $AlF_3\cdot 3.15H_2O$, and $AlF_3\cdot 3.13H_2O$, respectively. This result may be interpreted as meaning that the process of removing water from moist aluminum fluoride crystals is extremely slow in its final stages, and that a considerable length of time is required for the establishment of equilibrium in relatively dry surroundings. It is apparent that under the above-stated conditions of constant aqueous vapor pressure, the questionable hemiheptahydrate of aluminum fluoride is incapable of existing. The experiments also indicate that the trihydrate when prepared pure will be stable in contact with air at 25°, over a wide range of humidity.

Since the solubility measurements (Table I) clearly indicate that hydrated aluminum fluoride exists in two modifications, an X-ray diffraction analysis was made for the purpose of obtaining information on whether the more soluble form undergoes a change in structure when it passes to the less soluble.

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(13) Schrenk and Ode, *Ind. Eng. Chem., Anal. Ed.*, **1**, 201 (1929).

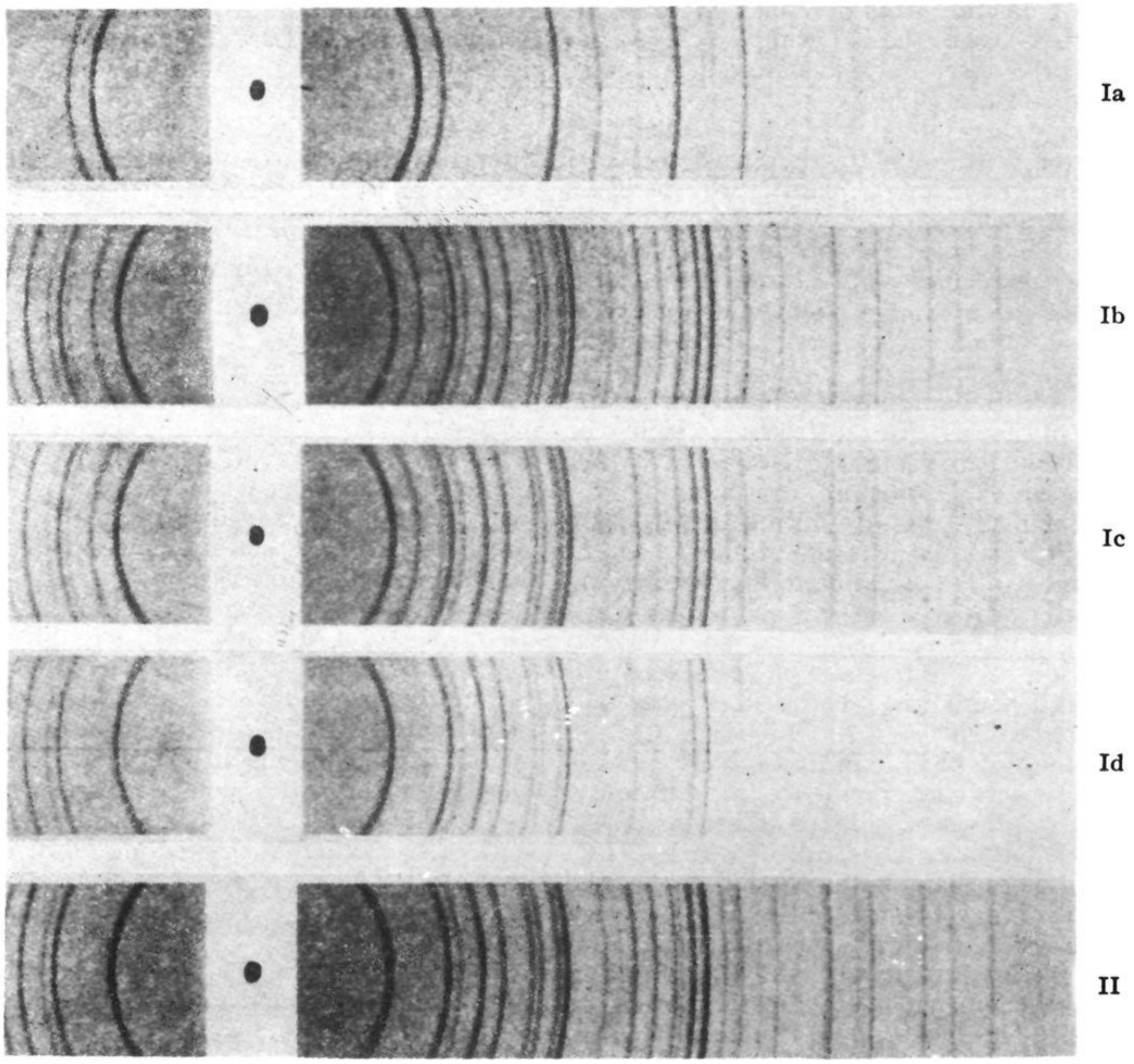

Fig. 1.—Diffraction patterns of $AlF_3·3H_2O$, crystallized: Ia, below 25°, 7 days old; Ib, below 25°, 39 days old; Ic, below 25°, 102 days old; Id, below 25°, 1 year old; II, at 100°, 7 days old.

Aluminum fluoride from two sources was used, namely, that prepared at 100° (Method B) and that prepared below 25° (Method A), as previously described. The initial diffraction patterns were made at the end of one week. At intervals of thirty-nine days, one hundred and two days, and one year, diffraction patterns were made of the salt prepared below 25°. Only one pattern was made of the salt prepared at 100°. It was identical with the pattern for the salt prepared below 25° and allowed to age one year (Fig. 1). This complete identity is consistent with the fact that the two samples of salt possessed the same solubility. The interplanar distances *d* in Å. units and relative intensity values *I* (Table II) for these two samples of salt agree very well with Hanawalt's[10] data for the "hemiheptahydrate." The results of the present investigation indicate that this is the stable or β-form of the trihydrate.

An analysis of the diffraction data for the seven-day old salt prepared below 25°, the partially aged salts, and the one-year old salt (Fig. 1) shows that some of the lines decrease in intensity with time while others increase, and that during the same period, new lines appear while others disappear. No shift in the position of the lines is noticed. It is also apparent that the greatest change takes place during the first thirty-nine days; during this time all of the lines common to the aged salt have appeared and only three lines common to the seven-day old salt remain. The diffraction patterns indicate clearly that there

TABLE II

X-RAY DIFFRACTION DATA FOR β-$AlF_3·3H_2O$

d	*I*	*d*	*I*
5.47	1.00	2.18	0.10
3.86	0.56	2.08	.04
3.66	.17	2.02	.23
3.29	.52	1.92	.15
3.01	.35	1.83	.15
2.72	.27	1.77	.44
2.64	.25	1.72	.56
2.50	.27	1.66	.12
2.43	.58		

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).

NEW YORK, N. Y. RECEIVED JUNE 26, 1944

[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).